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FULL PAPER

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Rh(I) complexes with new C_2-symmetric chiral diphosphoramidite ligands: Catalytic activity for asymmetric hydrogenation of olefins

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The design and synthesis of three new C_2-symmetric chiral diphosphoramidite ligands starting from simple and cheap building blocks have been developed. Rhodium(I) cationic complexes bearing these chelate ligands have been prepared and applied in asymmetric hydrogenation of model olefins. A rhodium complex with a diphosphoramidite containing a chiral diamine configurationally stable and two fluxional chiral biphenyl units gave higher enantioselectivity with increasing hydrogen pressure (87% ee) in the hydrogenation of dimethyl itaconate.

KEYWORDS
asymmetric hydrogenation, C_2-symmetric ligand, chiral rhodium complexes, diphosphoramidite

1 | INTRODUCTION

The development of a really worthwhile catalytic system for asymmetric synthesis is still a challenge for the chemical community. Presently, most efficient enantioselective catalysts are chiral ligand modified transition metal complexes. Therefore, the chiral environment generated by the enantiopure ligand coordinated to the metal is a crucial element in determining the outcome of the process.

Although significant enantiomeric excesses were achieved with chiral metal complexes, the cost and availability of the ligands remain critical factors for larger scale applications.[1] Industrial demand for economical and modular chiral ligands have given rise to the development of rationally designed syntheses of chiral ligands derived from a simple and inexpensive enantiopure source. In this context, over the last years phosphoramidites have arisen as cheap and easily available chiral ligands for asymmetric catalysis.[2]

Among catalytic asymmetric reactions, the hydrogenation of C=C bond catalyzed by chiral ligand modified transition metal complexes is an important and efficient tool for the organic synthesis[3,4] and fine chemical production.[5]

Several monodentate phosphoramidites as MonoPhos, SiPhos, DpenPhos, PipPhos, Morphos, PegPhos[6,7] as well as bidentate phosphine-phosphoramidites[8,9] have been applied in the rhodium catalyzed asymmetric hydrogenation of functionalized olefins with outstanding results. Although, diphosphoramidites are readily obtainable from inexpensive achiral/chiral diamines, only a few of them have been evaluated in the asymmetric hydrogenation.[10,2]

Some years ago, we reported a family of C_2-symmetric bidentate diphosphoramidite ligands containing the inexpensive chiral source (1*R*,2*R*)-diaminocyclohexane as the backbone and two biaryl units (Figure 1). We tested these P,P ligands in transition metal catalyzed asymmetric reactions such as conjugate addition,[11] hydrosilylation,[12] Diels-Alder[13] and hydrogenation.[14]

Interestingly, we observed an uncommon positive H_2 pressure effect on the stereoselectivity in the Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate using the diphosphoramidite (R,R,S_aS_a)-**L2** which contains two (*S*)-BINOL (1,1′-binaphthalene-2,2′-diol) moieties.

We also note that rhodium catalyst bearing the diphosphoramidite ligand **L3** in which each BINOL-unit was replaced by a fluxional axially chiral 2,2′-biphenol containing sterically demanding ortho *tert*-butyl groups, showed very low activity as well as poor asymmetric induction in the same reaction.

The results achieved with diphosphoramidites **L1**-**L3** prompt us to develop a series of new readily accessible diastereomeric C_2-symmetric diphosphoramidite ligands.

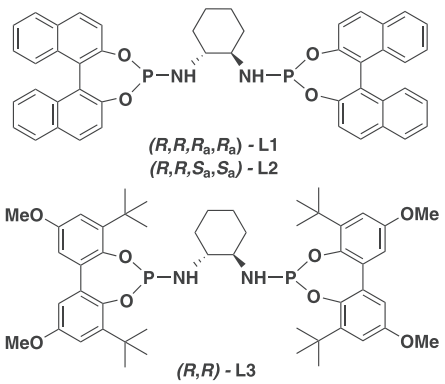


FIGURE 1 C_2-symmetric chiral diphosphoramidite ligands **L1-L3**

The new chiral ligands **L4-L6** (Figure 2) were designed either by changing the biaryl group in the two P/O heterocycles of (1*R*,2*R*)-diaminocyclohexane unit or by replacing the chiral backbone with an achiral one. Moreover, the diphosphoramidite **L4** was planned with the aim to assess the steric hindrance influence of the ortho substituents in 2,2′-biphenol moieties on catalyst performance.

In this work, we report on C_2-diphosphoramidite ligands **L4-L6** and their corresponding 1,5-cyclooctadiene rhodium(I) cationic complexes. We also describe the catalytic activity of these new chiral diphosphoramidite rhodium complexes in the asymmetric hydrogenation of model olefins.

2 | EXPERIMENTAL

2.1 | Materials and methods

All reactions were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were purchased in crown cap anhydrous bottles. Unless otherwise indicated, all materials were commercially available and were used without further purification. (1*R*,2*R*)-diaminocyclohexane was treated with NaOH pellets for 3 days prior to use.

The nuclear magnetic resonance spectra were recorded with a Bruker AMX R-300 and with a Varian 500 MHz spectrometer equipped with a pulsed field gradient probe. The values of chemical shifts (δ) for ^{1}H spectra and $^{13}C\{^{1}H\}$ NMR are measured relative to the solvent peak and are reported in ppm in reference to the value for the tetramethylsilane (TMS δ = 0 ppm). The chemical shifts for the $^{31}P\{^{1}H\}$ NMR spectra were measured using aqueous H_3PO_4 (85% D_2O) as an external reference (δ = 0 ppm). For *phase-sensitive* methods (TPPI) ^{1}H-2D-NOESY and ^{13}C–^{1}H-correlation (adiabatic HSBC) have been employed to standard pulse sequences. In addition, experiments they were performed two-dimensional ^{1}H-^{1}H gCOSY, ^{1}H-^{1}H gTOCSY, ^{1}H-^{13}C gHSQC, ^{1}H-^{13}C gHMBC using a *broad-band* with Z-Gradient Probe BBI 1H–BBZ-GRD Z8421 300 MHz 5mm. The evolution of mating long-range ^{1}H-^{13}C HMBC experiment has been set at 80 ms and a mixing time for the experiment ^{1}H-^{1}H NOESY of 80 ms.

Hydrogenation experiments were performed in a 100 ml stainless steel autoclave equipped with glass reaction vessel. Conversion was determined by ^{1}H NMR and GC coupled to a mass spectrometer GCMS-QP 5000 Shimadzu. Enantioselectivity was measured by 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 chromatographic column; Chirasil-Val was used for determination of hydrogenated products methyl 2-(acetylamino) propanoate and methyl 2-(acetylamino)-3-phenylpropanoate. Enantiomeric excess values were confirmed by a Shimadzu HPLC LC8A with a 5u Lux Cellulose-1 250 x 4.6 mm Phenomenex column (Substrate **11**, UV λ 250 nm, Hexane/Isopropanol 95/5, 25 °C; Substrate **9** and **12**, UV λ 215 nm, Hexane/Isopropanol 98/2, 25 °C). The absolute configurations of the materials were determined by comparison with reported data.[15,16] Optical rotations were measured on a Jasco P-1010 polarimeter at 25 °C. Elemental analyses were performed by Redox Srl, Monza, Milan.

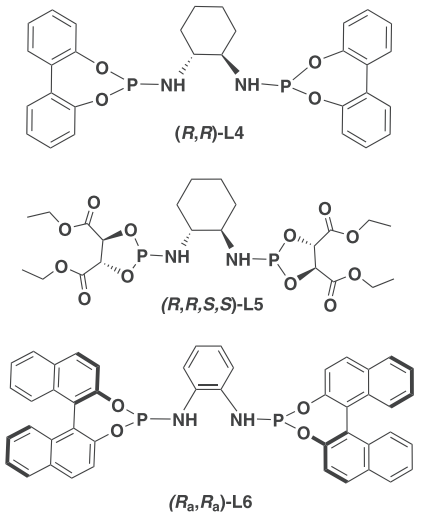


FIGURE 2 C_2-symmetric chiral diphosphoramidite ligands **L4-L6**

2.2 | Preparation of 2-Chloro-(4*S*,5*S*)-dicarboethoxy-1,3,2-dioxaphospholane 3

1-methyl-2-pyrrolidone (43 mg, 0.44 mmol) was added to a stirred mixture of diethyl (2*S*,3*S*)-tartrate (907 mg, 4.4 mmol) and PCl_3 (9.06 g, 66 mmol) at room temperature. Upon addition, a rapid evolution of HCl bubbles was observed which were removed by a slow flow of argon. After 5 min., the bulk of excess PCl_3 was removed under reduced pressure and then the final traces were removed by azeotropic distillation with

toluene (10 ml). The product was obtained as a colourless oil, which was used without further purification. For spectral data see ref.[17]

2.3 | General procedure for the preparation of diphosphoramidites L4-L5

A solution of (1*R*,2*R*)-diaminocyclohexane (2.2 mmol) and Et_3N (8.8 mmol) in 10 ml of toluene was added dropwise to a stirred solution of the appropriate phosphorochloridite (4.4 mmol) at 0 °C. The mixture was stirred overnight at room temperature and Et_3N·HCl precipitate was removed by filtration. The solvent was evaporated under reduced pressure to give the crude product which was washed with hexane (3x5 ml). The resulting pale yellow solid was purified by extraction in toluene and recrystallization from toluene/hexane.

2.4 | (1*R*,2*R*)-N^1,N^2-bis(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)cyclohexane-1,2-diamine L4

White powder (0.894 g, yield 75%). Mp 120–127 °C. $[\alpha]_D^{21}$ = + 12.2 (c 1.0 THF). $^{31}P\{^1H\}$ NMR (122 MHz, Benzene-d_6) δ 152.40.^1H NMR (300 MHz, Benzene-d_6) δ 7.46 (d, $^3J_{HH}$ = 7.9 Hz, $H_{Ar\text{-}ortho}$, 4H), 7.30 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.8 Hz, H_{Ar}, 4H), 7.08 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.8 Hz, H_{Ar}, 4H), 6.99 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.4 Hz, H_{Ar}, 4H), 3.06 (s, N*H*, 1H), 3.03 (s, N*H*, 1H), 2.53 (m, *C$H_{cyclohex}$, 1H), 2.48 (m, *C$H_{cyclohex}$, 1H), 1.88 (m, $H_{cyclohex}$, 1H), 1.76 (m, $H_{cyclohex}$, 1H), 1.33 (m, $H_{cyclohex}$, 1H), 1.28 (m, $H_{cyclohex}$, 1H), 0.85 (m, $H_{cyclohex}$, 1H), 0.79 (m, $H_{cyclohex}$, 1H), 0.76 (m, $H_{cyclohex}$, 1H), 0.70 (m, $H_{cyclohex}$, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, Benzene-d_6) δ 151.40 (d, $^2J_{CP}$ = 31.2 Hz, $C_{Ar(q)}$, 2C), 150.98 (d, $^2J_{CP}$ = 31.2 Hz, $C_{Ar(q)}$, 2C), 132,50 (d, $^3J_{CP}$ = 10.0, Hz, $C_{Ar(q)}$, 2C), 132,36 (d, $^3J_{CP}$ = 10.0, Hz, $C_{Ar(q)}$, 2C), 130.02 (s, C_{Ar}, 2C), 129.28 (s, C_{Ar}, 2C), 124.90 (s, C_{Ar}, 2C), 124.83 (s, C_{Ar}, 2C), 122.80 (s, $C_{Ar\text{-}ortho}$, 4C), 56.89 (d, $^3J_{CP}$ = 3.9 Hz, *$C_{cyclohex}$, 1C), 56.61 (d, $^3J_{CP}$ = 3.8 Hz, *$C_{cyclohex}$,1C), 36.21 (s, $C_{cyclohex}$, 1C), 36.16 (s, $C_{cyclohex}$, 1C), 25.25 (s, $C_{cyclohex}$, 2C). Anal. Calcd. for $C_{30}H_{28}N_2O_4P_2$: C, 66.42; H, 5.20; N, 5.16. Found: C, 66.71; H, 5.15; N, 5.29.

2.5 | Tetraethyl 2,2′-(((1*R*,2*R*)-cyclohexane-1,2-diyl)bis-(azanediyl))(4S,4′S,5S,5′S)-bis(1,3,2-dioxaphospholane-4,5-dicarboxylate) L5

Colorless solid. (0.833 g, yield 65%). Mp 69–73 °C. $[\alpha]_D^{21}$ = + 10.3 (c 1.2 THF). $^{31}P\{^1H\}$ NMR (122 MHz, Benzene-d_6) δ 149.95. ^1H NMR (300 MHz, Benzene-d_6) δ 4.83 (m, C*H*, 4H), 3.87 (m, CH_2, 8H), 2.72 (m, N*H*, 2H), 2.46 (m, *C$H_{cyclohex}$, 2H), 1.94 (m, C$H_{cyclohex}$, 4H), 1.34 (m, C$H_{cyclohex}$, 4H), 0.95 (m, CH_3, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, Benzene-d_6) δ 171.23 (s, $C_{C=O(q)}$, 4C), 74.63 (s, $C_{Ar(q)}$, 4C), 62.14 (s, *$C_{cyclohex}$, 2C), 58.76 (s, CH_2, 4C), 35.22 (s, $C_{cyclohex}$, 2C), 24.51 (s, CH_3, 4C), 14.34 (s, $C_{cyclohex}$, 2C). Anal. Calcd. for $C_{22}H_{36}N_2O_{12}P_2$: C, 45.37; H, 6.23; N, 4.81. Found: C, 45.53; H, 6.30; N, 4.67.

2.6 | N^1,N^2-Bis((11b*R*)-dinaphtho[2,1-d:1′,2′-f][1,3,2]-dioxaphosphepin-4-yl)benzene-1,2-diamine L6

A solution of (*R*,*R*)-BINOL-phosphorochloridite[18] **5** (1,82 g, 5.20 mmol) in toluene (10 ml) was added dropwise to a stirred solution of o-phenylenediamine **4** (0.281 g, 2.60 mmol), Et_3N (1.32 g, 13 mmol) and DMAP (0.012 g, 0.1 mmol) in toluene (25 ml) at 0 °C. The reaction mixture was stirred for 12 h at room temperature and then Et_3N·HCl precipitate was removed by filtration. The filtrate was subsequently concentrated to a volume of 5 mL and upon addition of 25 ml di hexane a white solid was deposited. This solid was filtered off, washed with pentane and dried under reduced pressure. White powder. (1.63 g, yield 85%). Mp 134–137 °C. $[\alpha]_D^{21}$ = + 104 (c 0.75 $CHCl_3$). $^{31}P\{^1H\}$ NMR (122 MHz, Benzene-d_6) δ 145.23. ^1H NMR (300 MHz, Benzene-d_6) δ 7.62 (d, $^3J_{HH}$ = 8.0 Hz, H_{Ar}, 2H), 7.58 (d, $^3J_{HH}$ = 8.8 Hz, H_{Ar}, 2H), 7.52 (m, H_{Ar}, 2H), 7.44 (d, $^3J_{HH}$ = 8.4 Hz, H_{Ar}, 2H), 7.38 (d, $^3J_{HH}$ = 9.2 Hz, H_{Ar}, 2H), 7.34 (d, $^3J_{HH}$ = 9.0 Hz, H_{Ar}, 2H), 7.29 (d, $^3J_{HH}$ = 8.9 Hz, $H_{Ar\text{-}ortho}$, 2H), 7.22 (d, $^3J_{HH}$ = 8.3 Hz, $H_{Ar\text{-}Ph}$, 4H), 7.09 (m, $H_{Ar\text{-}ortho}$, 4H), 7.00 (d, $^3J_{HH}$ = 6.9 Hz, H_{Ar}, 2H), 6.90 (d, $^3J_{HH}$ = 8.7 Hz, $H_{Ar\text{-}Ph}$, 2H), 6.84 (m, H_{Ar}, 2H), 2.11 (s, N*H*, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, Benzene-d_6) δ 153.49 (s, $C_{Ar(q)}$, 4C), 148.41(s, $C_{Ar\text{-}Ph(q)}$, 2C), 134.27 (s, $C_{Ar(q)}$, 4C), 133.34 (s, $C_{Ar(q)}$, 4C), 131.38 (s, C_{Ar}, 2C), 130.51 (s, C_{Ar}, 2C), 130.02 (s, $C_{Ar\text{-}Ph}$, 2C), 128.66 (s, C_{Ar}, 4C), 127.63 (s, C_{Ar}, 2C), 127.45 (s, $C_{Ar(q)}$, 4C), 126.73 (s, C_{Ar}, 2C), 126.49 (s, C_{Ar}, 2C), 125.39 (s, C_{Ar}, 2C), 125.15 (s, $C_{Ar(q)}$, 2C), 124.81 (s, C_{Ar}, 2C), 124.06 (s, $C_{Ar\text{-}ortho}$, 2C), 122.55 (s, $C_{Ar\text{-}Ph}$, 2C), 118.26 (s, $C_{Ar\text{-}ortho}$, 2C). Anal. Calc. for $C_{46}H_{30}N_2O_4P_2$: C, 75.00; H, 4.10; N, 3.80. Found: C, 75.38; H, 4.18; N, 3.72.

2.7 | Synthesis of [Rh(COD)(P,P)]BF_4 complexes 6–8

Diphosphoramidite ligand (0.11 mmol) was added to a solution of [Rh(COD)$_2$]BF_4 (0.099 mmol, 40 mg) in CH_2Cl_2 (4 ml). The reaction mixture was then stirred for 15 min. at room temperature. The solution was subsequently reduced

to ~2 ml and by addition of hexane, a powder was obtained. It was collected, washed with hexane and dried.

2.8 | [Rh(cod)(L4)]BF_4 6

Yellow powder. (0.0784 g, yield 91%) $^{31}P\{^1H\}$ NMR (122 MHz, Chloroform-*d*) δ 136.60 (d, J_{RhP} = 233.5 Hz).^1H NMR (300 MHz, Chloroform-*d*) δ 7.53 (m, H_{Ar}, 4H), 7.48 (m, H_{Ar}, 4H), 7.37 (m, H_{Ar}, 4H), 7.35 (m, $H_{Ar\text{-}ortho}$, 4H), 5.76 (s, H_{cod}, 2H), 5.34 (s, H_{cod}, 2H), 4.06 (s, N*H*, 2H), 3.71 (m, *C$H_{cyclohex}$,2H), 2.49 (m, H_{cod}, 2H), 2.36 (m, H_{cod}, 2H), 2.27 (m, H_{cod}, 2H), 2.20 (m, $H_{cyclohex}$, 2H), 2.10 (m, H_{cod}, 2H), 1.84 (m, $H_{cyclohex}$, 2H), 1.53 (m, $H_{cyclohex}$, 2H), 1.39 (m, $H_{cyclohex}$, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, Chloroform-*d*) δ 152.67 (s, $C_{Ar(q)}$, 4C), 148.28 (s, $C_{Ar(q)}$, 4C), 129.66 (s, C_{Ar}, 4C), 129.31 (s, C_{Ar}, 4C), 126.01 (s, C_{Ar}, 4C), 121.82 (s, $C_{Ar\text{-}ortho}$, 4C), 106.09 (s, C_{cod}, 4C), 58.34 (s, *$C_{cyclohex}$, 2C), 35.01 (s, $C_{cyclohex}$, 2C), 30.44 (s, C_{cod}, 2C), 29.27 (s, C_{cod}, 2C), 24.51 (s, $C_{cyclohex}$, 2C). Anal. Calcd. for $C_{40}H_{46}BF_4N_2O_4P_2Rh$: C, 55.19; H, 5.33; N, 3.22. Found: C, 55.48; H, 5.27; N, 3.16.

2.9 | [Rh(cod)(L5)]BF_4 7

Yellow powder. (0.0767 g, yield 89%). $^{31}P\{^1H\}$ NMR (122 MHz, Methylene Chloride-d_2) δ 144.64 (d, J_{RhP} = 226.8 Hz).^1H NMR (300 MHz, Methylene Chloride-d_2) δ 6.05 (m, H_{cod}, 2H), 5.58 (m, H_{cod}, 2H), 4.97 (m, C*H*, 4H), 4.54 (s, N*H*, 2H), 4.32 (m, CH_2 + *$CH_{cyclohex}$, 10H), 2.67 (m, H_{cod}, 2H), 2.64 (m, H_{cod}, 2H), 2.47 (m, H_{cod}, 2H), 2.38 (m, H_{cod}, 2H), 1.83 (m, C$H_{cyclohex}$, 4H), 1.35 (m, CH_3 + C$H_{cyclohex}$, 16H).$^{13}C\{^1H\}$ NMR (75 MHz, Methylene Chloride-d_2) δ 172.18 (s, $C_{C=O(q)}$, 4C), 107.00 (s, C_{cod}, 2C), 106.87 (s, C_{cod}, 2C), 77.29 (s, $C_{Ar(q)}$, 4C), 63.64 (s, *$C_{cyclohex}$, 2C), 62.96 (s, CH_2, 4C), 31.11 (s, C_{cod}, 2C), 30.61 (s, C_{cod}, 2C), 24.62 (s, $C_{cyclohex}$, 2C), 14.44 (s, CH_3, 4C), 9.19 (s, $C_{cyclohex}$, 2C). Anal. Calcd. for $C_{33}H_{56}BF_4N_2O_{12}P_2Rh$: C, 42.87; H, 6.11; N, 3.03. Found: C, 43.54; H, 6.22; N, 2.92.

2.10 | [Rh(cod)(L6)]BF_4 8

Red-brown powder. (0.0980 g, yield 93%). $^{31}P\{^1H\}$ NMR (122 MHz, Chloroform-*d*) δ 128.04 (d, J_{RhP} = 260.4 Hz). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, $^3J_{HH}$ = 9.0 Hz, H_{Ar}, 2H), 8.11 (d, $^3J_{HH}$ = 8.9 Hz, H_{Ar}, 2H), 7.98 (d, $^3J_{HH}$ = 8.9 Hz, $H_{Ar\text{-}Ph}$, 2H), 7.96 (d, $^3J_{HH}$ = 8.4 Hz, H_{Ar}, 2H), 7.93 (d, $^3J_{HH}$ = 8.4 Hz, H_{Ar}, 2H), 7.85 (d, $^3J_{HH}$ = 8.9 Hz, $H_{Ar\text{-}ortho}$, 2H), 7.64 (d, $^3J_{HH}$ = 9.0 Hz, $H_{Ar\text{-}ortho}$, 2H), 7.44 (m, H_{Ar}, 2H), 7.34 (m, H_{Ar}, 2H), 7.23 (m, H_{Ar}, 2H), 7.15 (d, $^3J_{HH}$ = 8.5 Hz, H_{Ar}, 2H), 7.03 (m, H_{Ar}, 2H), 6.90 (d, $^3J_{HH}$ = 8.6 Hz, H_{Ar}, 2H), 6.72 (d, $^3J_{HH}$ = 8.9 Hz, $H_{Ar\text{-}Ph}$, 2H), 5.84 (m, H_{cod}, 2H), 4.46 (m, H_{cod}, 2H), 3.05 (m, N*H*, 2H), 2.22 (m, H_{cod}, 4H), 2.04 (m, H_{cod}, 2H), 1.72 (m, H_{cod}, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 147.40 (s, $C_{Ar(q)}$, 2C), 146.99 (s, $C_{Ar(q)}$, 2C), 145.55 (s, $C_{Ar\text{-}Ph(q)}$, 2C), 134.13 (s, $C_{Ar(q)}$, 4C), 132.33 (s, $C_{Ar(q)}$, 2C), 132.30 (s, $C_{Ar(q)}$, 2C), 132.05 (s, C_{Ar}, 2C), 131.93 (s, $C_{Ar(q)}$, 2C), 131.60 (s, $C_{Ar(q)}$, 2C), 131.52 (s, C_{Ar}, 2C), 131.27 (s, $C_{Ar\text{-}Ph}$, 2C), 128.77 (s, C_{Ar}, 2C), 128.55 (s, C_{Ar}, 2C), 127.39 (s, C_{Ar}, 2C), 127.14 (s, C_{Ar}, 2C), 127.07 (s, C_{Ar}, 2C), 126.84 (s, C_{Ar}, 2C), 126.10 (s, C_{Ar}, 2C), 126.05 (s, C_{Ar}, 2C), 120.72 (s, $C_{Ar\text{-}ortho}$, 2C), 120.27 (s, $C_{Ar\text{-}Ph}$ + $C_{Ar\text{-}ortho}$, 4C), 111.49 (m, C_{cod}, 2C), 106.66 (m, C_{cod}, 2C), 30.06 (s, C_{cod}, 2C), 29.72 (s, C_{cod}, 2C). Anal. Calcd. for $C_{56}H_{48}BF_4N_2O_4P_2Rh$: C, 63.18; H, 4.54; N, 2.63. Found: C, 63.54; H, 4.62; N, 2.75.

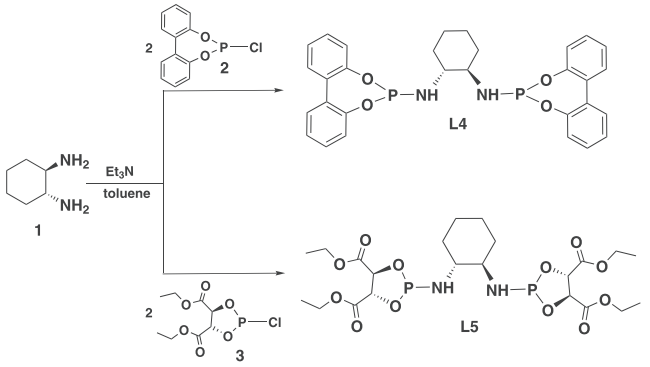
2.11 | General procedure for the Rh(I)-catalyzed asymmetric hydrogenation

[Rh(cod)(P,P)]BF_4 **6–8**, (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 ^1H NMR, GC and HPLC.

3 | RESULTS AND DISCUSSION

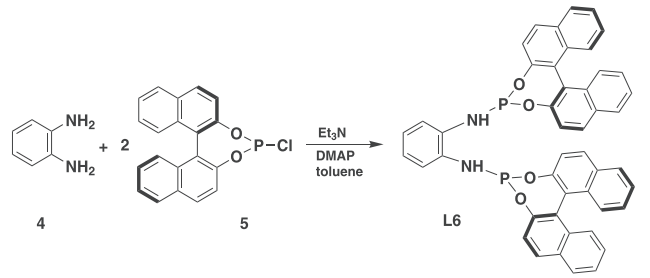
The chiral diphosphoramidite ligands **L4-L5** were synthesized by reaction of (1*R*,2*R*)-diaminocyclohexane **1** with two equivalents of phosphorochloridites **2** and **3** respectively, using triethylamine as base (Scheme 1). The compounds **2** and **3** were prepared, in a short time and in high yields, by treatment of 1,1′-biphenyl-2,2′-diol and diethyl (2*S*,3*S*)-tartrate with PCl_3 without solvent and in the presence of a catalytic amount of 1-methyl-2-pyrrolidone. This protocol was previously applied by us[18] and others[19] for preparing diarylphosphorochloridites but, to our knowledge, never applied to the synthesis of alkylphosphorochloridites.[17,20]

Ligands **L4-L5** are quite stable in a dry and inert atmosphere as solids but in common organic solvents they decompose slowly giving an insoluble white powder. The multinuclear NMR spectra are in agreement with the proposed structures. In particular, the two equivalent phosphorus atoms appear as a singlet in the $^{31}P\{^1H\}$ NMR spectra of **L4** (δ 152.42) and **L5** (δ 149.95) ligands. The ^1H NMR spectrum exhibits all estimated signals relative to the two ligands, such as two NH protons, two 1,2-(*R*,*R*) methynic chiral protons relative to the cyclohexane ring and all remaining expected aliphatic and aromatic protons.



SCHEME 1 Synthesis of ligands **L4-L5**

The chiral diphosphoramidite **L6** having the 1,2 diaminobenzene fragment as the achiral backbone, was prepared by reaction of *o*-phenylenediamine **4** with (*R*)-BINOL-phosphorochloridite **5** in the presence of an excess of NEt_3 and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) (Scheme 2). The white solid obtained is stable for a long time under argon. The $^{31}P\{^1H\}$ NMR spectrum of **L6**, show a sharp singlet at 145.23 ppm for the two phosphorus atoms. In the aromatic region of the ^1H NMR spectrum, there are many buried peaks, that have needed COSY and C,H bidimensional correlation spectra for their completely assignment (See Experimental part).



SCHEME 2 Synthesis of ligand **L6**

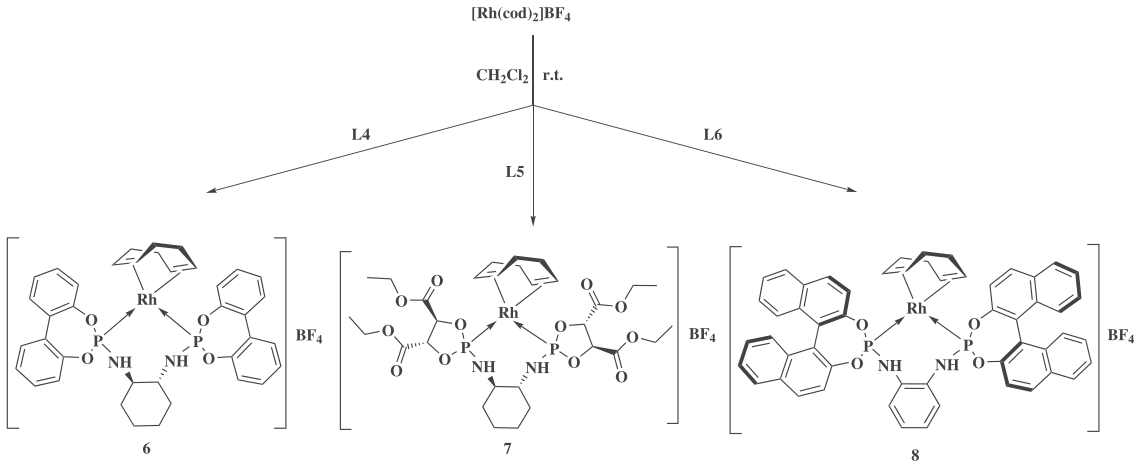
The chiral rhodium(I) complexes $[Rh(cod)(P,P)]BF_4$ (cod = 1,5-cyclooctadiene) **6–8** containing the bidentate ligands **L4-L6** chelated to the metal center were synthesized by reaction of $[Rh(cod)_2]BF_4$ with a slight excess of the corresponding P,P ligand in dichloromethane solution. Compounds [Rh(cod)(**L4**)]BF_4 **6** and [Rh(cod)(**L5**)]BF_4 **7** were isolated as fairly stable yellow solids under a dry argon atmosphere. Instead, the complex [Rh(cod)(**L6**)]BF_4 **8** is a red-brown solid stable in inert atmosphere (Scheme 3).

All proton and carbon resonances belonging to **6** and **7** complexes were assigned through mono- and bi-dimensional NMR spectroscopy (2D–gCOSY, ^1H-^{31}P gHMBC, ^1H-^{13}C gHSQC and ^1H-^{13}C gHMBC experiments). In the $^{31}P\{^1H\}$ NMR spectra, compound [Rh(cod)(**L4**)]BF_4 **6** shows a doublet at 136.60 ppm with a coupling constant $^1J_{RhP}$ value of 233 Hz while the [Rh(cod)(**L5**)]BF_4 **7** exhibits a doublet at 144.64 ppm ($^1J_{RhP}$ value of 227 Hz), in agreement with already reported values for similar mononuclear complexes of rhodium with a cis arrangement of the two phosphorus atoms.[12]

The ^1H NMR spectra for the two complexes **6** and **7** exhibit all expected signals relative to the **L4-L5** and cyclooctadiene ligands chelated to the rhodium center.

In particular, for the complex **6**, the ^{31}P,^1H–HMBC correlation map allowed us to assign the broad signal at 4.06 ppm relative to the two NH protons and at 3.71 ppm to the two (1*R*,2*R*) chiral methinic protons of the cyclohexane ring. The coordination of cod ligand was confirmed by the presence of two broad signal at 5.76 and 5.34 ppm relative to alkene double bond hydrogens.

In the same way, we have assigned the hydrogen ligands of complex **7**. The ^1H NMR spectrum shows widened signals so it was indispensable study the compound by 2D NMR spectroscopy; we assigned the shift of the methinic protons of fragment (1*R*,2*R*)-diaminocyclohexane at 4.32 ppm while the hydrogen atoms of the NH group are moved (broad



SCHEME 3 Synthesis of cationic diphosphoramidite rhodium(I) complexes **6–8** (Rh/L 1:1.1)

singlet at 4.54 ppm) in lower field compared to the free ligand. The aliphatic protons of tartrate fragment are very broad; indeed, methinic protons C*H* resonate at 4.97 ppm (two broad multiplets), methylenic protons CH_2 at 4.32 ppm (broad multiplet) and the methylic protons CH_3 at 1.35 ppm (broad multiplet).

The $^{31}P\{^1H\}$ NMR spectrum of complex **8** in $CDCl_3$, presents a broad doublet at 128.04 ppm with a constant $^1J_{RhP}$ = 260.4 Hz whose value proves the ligand chelation to the rhodium metal center.

The most important information is given by the ^1H NMR spectrum wherein the signals of the aromatic BINOL hydrogens appear to be split and separated in chemical shift with respect to the ligand because the steric hindrance between **L6** and cyclooctadiene ligands coordinated to the rhodium metal center. The hydrogen atoms of the N*H* group (broad singlet at 3.06 ppm) are shifted at lower fields than the free ligand and it was noted that the olefinic hydrogens of 1,5-cyclooctadiene give rise to two distinct signals at 5.84 and 4.45 ppm.

3.1 | Asymmetric hydrogenation of functionalized olefins

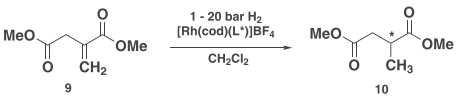
To evaluate the potential of the new chiral ligands **L4-L6** in the asymmetric hydrogenation of functionalized olefins, we initially used dimethyl itaconate **9** as model substrate (Scheme 4).

The pre-catalysts [Rh(cod)(P,P)]BF_4 **6–8** were first tested at 1 bar of H_2 pressure in CH_2Cl_2 and at 25 °C for 20 h, with a substrate:[Rh] ratio of 1000:1.

The results, reported in Table 1, show that only complex **6** quantitatively hydrogenated the dimethyl itaconate with low enantioselectivity (27% ee (*S*)) (Entry 1–3).

Interestingly, the complex [Rh(cod)(**L4**)]BF_4 **6** proved to be a very active catalyst. Indeed, complete reduction of substrate **9** was achieved in 6 h under the same catalytic conditions (Entry 4). Moreover, the rhodium catalyst derived from diphosphoramidite **L4** containing unsubstituted biphenol fragments turned out more active than that derived from diphosphoramidite **L3** containing bulky ortho *tert*-butyl groups.[14]

In view of significant catalytic activity displayed by the cationic complex **6** in the hydrogenation of dimethyl itaconate **9**, we decided studying the effect of H_2 pressure on stereoselectivity of the reaction.



SCHEME 4 Hydrogenation of dimethyl itaconate catalyzed by rhodium (I) complexes **6–8**

TABLE 1 Asymmetric hydrogenation of dimethyl itaconate **9** catalyzed by [Rh(cod)(**L4**)]BF_4 **6**, [Rh(cod)(**L5**)]BF_4 **7** and [Rh(cod)(**L6**)]BF_4 **8**[a]

Entry	Catalyst	P (bar)	t (h)	Conv. (%)	*ee.* (%)
1	**6**	1	20	100	27 (*S*)
2	**7**	1	20	0	-
3	**8**	1	20	60	45 (*R*)
4	**6**	1	6	100	27 (*S*)
5	**6**	20	6	100	87 (*S*)
6	**7**	10	20	100	37 (*R*)
7	**8**	5	20	100	27 (*R*)

[a]Substrate/Rh = 1000, 25 °C. Conversion was determined by ^1H NMR and GCMS-QP 5000 Shimadzu while ee values were measured by GC 8000 ThermoQuest and Shimadzu HPLC LC8A (for details see Experimental Section).

Previously,[14] we observed a significant positive effect of H_2 pressure on the enantioselectivity of the hydrogenation of dimethyl itaconate catalyzed by the cationic rhodium complex bearing diastereomeric diphosphoramidite ligand (R_c,R_c,S_a,S_a)–**L2**. In that case, an ee value of 88% (*S*) was reached at 60 bar.

With complex **6** a very good 87% ee (*S*) was obtained at 20 bar (Entry 5). Unfortunately, a further enhancement of the hydrogen pressure produced metallic rhodium in the autoclave.

In the complex **6**, the chelate diphosphoramidite **L4** contains a chiral diamine configurationally stable and two fluxional chiral biphenyl moieties.

Thus, a mixture of three rapidly interconverting (R_c,R_c,R_a,R_a), (R_c,R_c,S_a,S_a), (R_c,R_c,R_a,S_a) diastereomeric catalysts should be present in solution.[21]

It is likely that at 20 bar, one of three possible diastereomeric catalysts results most selective.

Rhodium complex **7** with diphosphoramidite **L5** which contains two (*S,S*) diethyltartrate groups completed the reduction of substrate **9** under 10 bar of H_2 with only 37% ee (*R*) (Entry 6).

Complex **8** bearing the BINOL-diphosphoramidite ligand **L6** with an achiral backbone, gave complete conversion at 5 bar with an ee value 27% (*R*) (Entry 7).

In both cases, no change in the enantioselectivity was observed when increasing the H_2 pressure to 30 atm.

The cationic complexes of rhodium(I) **6–8** were then assessed in the hydrogenation of (Z)-methyl-2-acetamido-3-phenylacrylate **11** and methyl 2-acetamido acrylate **12** (Scheme 5). The results summarized in Table 2 indicate that all pre-catalysts **6–8** are not very effective for hydrogenation of substrates **11** and **12**.

Complex **6** reduced quantitatively substrate **11** at 10 bar of H_2 (S/Rh = 500) giving very poor enantioselectivity (11% ee) (Entry 1). At higher hydrogen pressure, no effect was observed on the enantiomeric excess.

SCHEME 5 Hydrogenation of 2-methyl acetamidoacrylate derivatives catalyzed rhodium (I) complexes **6–8**

TABLE 2 Asymmetric hydrogenation of 2-methyl acetamidoacrylate derivatives **11–12** catalyzed by [Rh(cod)(**L4**)]BF_4 **6**, [Rh(cod)(**L5**)]BF_4 **7** and [Rh(cod)(**L6**)]BF_4 **8** [a]

Entry	Substr.	Catalyst	P (bar)	Conv. (%)	*ee.* (%)
1	**11**	**6**	10	100	11 (*R*)
2	**11**	**7**	10	75	68 (*S*)
3	**11**	**7**	20	100	65 (*S*)
4	**11**	**8**	10	0	-
5	**12**	**6**	10	0	-
6	**12**	**7**	10	0	-
7	**12**	**8**	10	0	-

[a]Substrate/Rh = 500, 25 °C, 20 h. Conversion was determined by ^{1}H NMR and GCMS-QP 5000 Shimadzu while ee values were measured by GC 8000 ThermoQuest and Shimadzu HPLC LC8A (for details see Experimental Section).

Using the diethyltartrate-derived complex **7**, a 20 bar pressure was necessary for obtaining complete reduction of substrate **11** with an ee value of 65% (*S*) (Entry 3).

Rhodium catalyst **8** derived from BINOL-diphosphoramidite **L6** proved to be inactive at 10 bar in the hydrogenation of (Z)-methyl-2-acetamido-3-phenylacrylate **11** (Entry 4).

No catalytic activity was observed using complexes **6–8** in the asymmetric hydrogenation of methyl 2-acetamido acrylate **12**.

A comparison of the results obtained in the asymmetric hydrogenation of dimethyl itaconate **9** and methyl 2-acetamidoacrylate derivatives **11** and **12** with new diphosphoramidite ligands **L4-L5** and the previously reported **L1-L3** shows that the axially chiral BINOL groups are crucial in determining the outcome of the reaction. Interestingly, substitution in the BINOL-derived diphosphoramidites **L1-L2** of the chiral (1*R*,2*R*)-diaminocyclohexane backbone with the achiral *o*-phenylenediamine has a detrimental effect on the catalyst performance.

4 | CONCLUSIONS

We have readily prepared three new C_2-symmetric chiral diphosphoramidite ligands using cheap and commercially available building blocks. They easily formed cationic rhodium(I) complexes useful as pre-catalysts for asymmetric hydrogenation of dimethyl itaconate.

In particular, a rhodium complex with a diphosphoramidite ligand which bears unsubstituted biphenol groups was more active than that with bulky ortho substituted *tert*-butyl biphenols.

Moreover, the same rhodium complex containing a chiral diamine configurationally stable and two fluxional chiral biphenyl units gives higher enantioselectivity with increasing hydrogen pressure (87% ee).

In contrast, these rhodium/diphosphoramidite catalysts showed poor performance in the hydrogenation of α-dehydroamino acid esters.

Comparing the results obtained with new ligands **L4-L5** and those previously reported **L1-L3** we noted that the BINOL group is determining for improving the catalytic outcome. Moreover, substitution of the chiral backbone in the BINOL-derived ligands **L1-L2** with achiral one produced a poorer catalyst.

We are currently studying the coordination chemistry of these new diphosphoramidites with other transition metals. Furthermore, other catalytic applications in asymmetric synthesis are currently in progress.

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