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Synthesis and characterization of new chiral Rh(I) complexes with N,N'-, and N,P-ligands. A study of anchoring on the modified zeolites and catalytic properties of heterogenized complexes

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Abstract

Novel chiral bidentate N,N'- and N,P- donors and their rhodium complexes were synthesised and characterized. The reactions of $[\{Rh(COD)Cl\}_2]$ and $[RhCl(PPh_3)_3]$ with different prepared chiral ligands: (*S*)-1-L-2-*t*-butylaminocarbonylpyrrolidine (**1a**, **1b**), (*S*)-1-L-2-diphenylphosphinomethylpyrrolidine (**2a**, **2b**), (*S*)-1-L-2-(1-naphthylaminocarbonyl)pyrrolidine (**5a**, **5b**), (*S*)-1-L-2-(1-naphthylaminomethyl)pyrrolidine (**7a**, **7b**) (**a**: L = *t*-butylaminocarbonyl, **b**: (3-trietoxysilylpropyl)aminocarbonyl) in the presence of a non-coordinating anion (PF_6^-) gave the cationic tetracoordinate $[Rh(L_2)(ligand)][PF_6]$ (L_2 = COD or PPh_3). The structures of these complexes were elucidated by elemental analysis, IR spectroscopy and ^1H, ^{13}C and ^{31}P NMR measurements. The metal complexes with **1b**, **2b**, **5b** and **7b**, were anchored to silica and modified USY-zeolite and Rh-heterogenized complexes were obtained. A comparative study (homogeneous vs. supported) was made for the catalytic activity and selectivity in several organic reactions.

Keywords: Rhodium; Supported catalysts; Zeolites; Asymmetric hydrogenation; Asymmetric hydroxylilation; Cyclopropanation

1. Introduction

Asymmetric syntheses with various transition metal complexes as catalysts have attracted much attention in the past two decades. Among them, rhodium(I) chiral diphosphine catalyst complexes have achieved very high stereoselection (up to 99% ee) in asymmetric hydrogenation of carbon–carbon double bonds [1]. In enantioselective catalysis with transition metal compounds, the optical activity in the organic products to be synthesized derives from the ligands. Although ligands that bind to the metal by P atoms, phosphines and mainly diphosphines, still dominate the field (P–P type ligands) [2], there are promising developments of ligands that bind to the metal atom by N atoms (N–N type) [3], and to a lesser extent, of ligands that bind to the metal atom by S or O atoms [4]. Aminoacids form the biggest group of compounds employed frequently as auxiliary agents in asymmetric synthesis. Aminoacids are of interest as ligands because of their biological importance, the variety of coordination modes they can display, and their easy availability [5].

Heterogenized homogeneous catalysts combine the properties of heterogeneous and homogeneous catalysts, although a heterogenized homogeneous catalyst may lose its activity owing to metal leaching [6]. Recently we reported the preparation of complexes $[Rh(L_2)(LL)]PF_6$, where LL represents a N,N'-bidentate ligand, that, when coordinated, forms a five-membered ring with the metal, through the reaction of chlorobridged rhodium dimers $[\{Rh(L_2)Cl\}_2]$ (L_2 = cycloocta-1,5-diene (COD), CO) with (*S*)-2-*t*-butylaminocarbonylpyrrolidine. These complexes have high reactivity and enantioselectivity in the hydrogenation of olefins [7].

In this paper we describe the synthesis, characterization and catalytic activity of a series of cationic

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rhodium complexes with *N,N'*- and *N,P*-bidentate ligands derived from l-proline (**1**, **2**, **5**, **7a** and **7b**). This type of ligand produces a seven-membered ring, as was confirmed by spectroscopic methods. We have studied the anchoring of this type of complex to silica and USY zeolite by forming a covalent bond, and we have studied their catalytic properties in several organic reactions.

2. Experimental details

All preparations of organometallic complexes were carried out under dinitrogen by standard Schlenk techniques. The starting complexes $[\{Rh(COD)Cl\}_2]$ and $[RhCl(PPh_3)_3]$ were prepared according to the literature method [8,9]. All solvents were carefully degassed before use. The silylating agent $OCN(CH_2)_3Si(OEt)_3$, obtained from Fluka 96% pure, was distilled before use. C, H and N analysis were carried out by the analytical department of the Institute of Organic Chemistry and Institute of Materials Science (C.S.I.C.) with an Heraeus and a Perkin-Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Unicam Philips SP9 apparatus. The conductivities were measured in DMF (ca. 10^{-3} M) and acetone (ca. 10^{-4} M) with a Philips Pw 5906 conductimeter. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr. ^1H, ^{13}C and ^{31}P NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; ^1H-NMR chemical shifts are given in parts per million with tetramethylsilane as an internal standard; ^{31}P-NMR chemical shifts are downfield from 85% H_3PO_4. Optical rotation values were measured with a Perkin-Elmer 241 MC polarimeter.

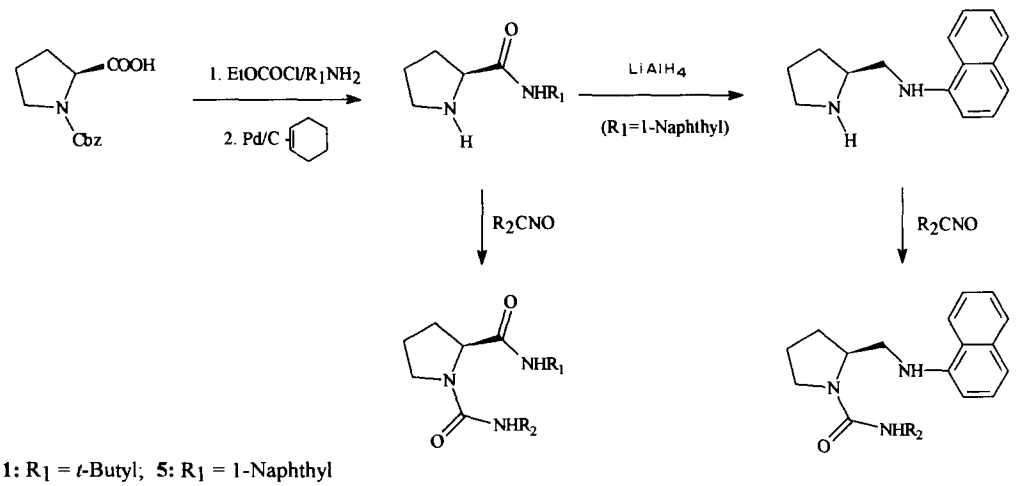
The inorganic supports taken as models were: SiO_2 Merck 60 (particle size 63–200 μm), and an ultrastable Y zeolite (USY) prepared by steam calcination at 1023 K of an 80% ammonium-exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min to remove extra-framework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite had a well-developed supermicroporemesopore system (pore diameter 12–30 Å besides the typical ca. 12 Å micropores). The controlled dealumination promotes destruction of some sodalite units, which allowed direct communication between α-cages generating cavities wider than 12 Å. The formation of supermicropores and large mesopores has been detected by N_2 adsorption–desorption. The main characteristics of the resultant zeolite are: unit cell size: 24.40 Å, bulk SiO_2/Al_2O_3: 4.2, crystallinity: greater than 95%. The inorganic supports were dried at 415 K under 0.01 torr before the anchoring process.

2.1. Synthesis of ligands

Scheme 1 shows a resumé of the synthesis of the ligands.

2.1.1. (S)-1-t-Butylaminocarbonyl-2-t-butylaminocarbonylpyrrolidine (1a)

Into a 15 ml CH_2Cl_2 solution containing 0.5 g of (*S*)-2-*t*-butylaminocarbonylpyrrolidine (2.94 mmol) was added 3.05 ml of 1 M *t*-butylisocyanate solution (3.09 mmol) with stirring. The mixture was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure and the resulting white solid was recrystallized (toluene/cyclohexane: 2/1). Yield greater than 85%; m.p. = 210°C. $[\alpha]_D^{25} = -62.2$ (EtOH, 1). Anal. Found: C, 63.0; H, 9.86; N, 15.45. $C_{14}H_{27}N_3O_2$ Calc.: C, 62.5; H, 10.04; N, 15.6%. IR (cm^{-1}); ν(NH)



1: R_1 = *t*-Butyl; **5**: R_1 = 1-Naphthyl

a: R_2 = *t*-Butyl; **b**: $R_2 = (CH_2)_3Si(OEt)_3$ **1,5a-b** **7a-b**

Scheme 1.

3340, 3275, ν(C=O) 1650, 1630. ^{1}H NMR ($CDCl_3$): δ = 7.0 (NH), 4.25 (t, 2H, C*H*-CONH,NH); 3.25 (m, 2H, -CH_2N-); 2.35 (m, 1H, -CH-CH_2-CH$_2$-); 1.9 (m, 3H, -CH-CH_2-CH_2-); 1.37, 1.33 (s, 9H, C-CH$_3$). ^{13}C NMR ($CDCl_3$) δ = 171.5 (*C*O); 157.0 (N-*C*O-NH); 60.7 (*C*H-CONH); 51.0 (*C*-CH$_3$); 50.8 (*C*-CH$_3$); 46.6 (*C*H$_2$-NCO-); 29.4, 28.8 (C-*C*H$_3$); 28.3 (-CH$_2$-*C*H$_2$-CH-); 24.9 (-*C*H$_2$-CH$_2$-CH).

*2.1.2. (S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-t-butylaminocarbonylpyrrolidine (**1b**)*

To a solution of 0.34 g (2 mmol) of (*S*)-2-*t*-butylaminocarbonylpyrrolidine in 10 ml of CH_2Cl_2 cooled at 0°C in argon, 4.94 ml of 1 M trietoxysilylpropylisocyanate solution was added. The mixture was stirred at room temperature over night. After solvent evaporation, a white solid was obtained. Yield 100%; m.p. = 207–209°C. $[\alpha]_D^{25} = -12.9$ (EtOH, 1). Anal. Found: C, 54.7; H, 9.2; N, 9.9. $C_{19}H_{39}N_3O_5Si$ Calc.: C, 54.6; H, 9.3; N, 10.0%. IR (cm^{-1}); ν(NH) 3280; ν(C=O) 1660, 1630. ^{1}H NMR ($CDCl_3$): δ = 4.33 (t, 1H, C*H*-CONH); 3.76 (q, 6H, CH_2-CH$_3$); 3.23 (m, 2H, CH_2-NCONH-); 2.56 (m, 2H, NH-CH_2-CH$_2$-); 1.7 (m, 4H, -CH-CH_2-CH_2-); 1.4 (m, 11H, CH$_2$-CH_2-CH$_2$-Si, C-CH_3); 1.16 (9H, -CH$_2$-CH_3); 0.65 (2H, CH_2Si).

*2.1.3. (S)-1-t-Butylaminocarbonyl-2-diphenylphosphinomethylpyrrolidine (**2a**)*

To a solution of (*S*)-2-diphenylphosphinomethylpyrrolidine [10] (0.36 g, 1.33 mmol) in dry CH_2Cl_2 (15 ml) was added a 1 M solution of *t*-butylisocyanate in CH_2Cl_2 (8.5 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated to dryness and the oily product was extracted with hexane to yield 0.33 g (100%) of a white solid. m.p. 142–143°C. $[\alpha]_D^{25} = -13.1$ (EtOH, 1). Anal. Found: C, 70.0; H, 7.3; N, 7.0. $C_{22}H_{29}N_2P$ Calc.: C, 71.7; H. 7.9; N. 7.6%. IR (cm^{-1}); ν(NH) 3460; ν(C=O) 1645. ^{1}H NMR ($CDCl_3$): δ = 7.9–7.3 (m, 10H, phenyl); 3.20 (m, 2H, CH$_2$-C*H*-CH$_2$P, -CH_2N-); 3.0 (m, 1H, -CH_2N-); 2.30 (m, 2H, -CH_2-PPh$_2$); 1.95 (m, 4H, -CH$_2$-CH_2-CH_2-CH-); 1.34 (s, 9H, CCH_3).

*2.1.4. (S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-diphenylphosphinomethylpyrrolidine (**2b**)*

This compound was prepared by a procedure similar to that described for **2a** except that trietoxysilylpropylisocyanate was used. The reaction is complete after 8 h. Yield 100%. d.p. = 225°C. $[\alpha]_D^{25} = -66.6$ (EtOH, 1). Anal. Found: C, 62.5; H, 7.9; N, 5.7. $C_{27}H_{41}N_2O_4PSi$ Calc.: C, 62.7; H, 7.9; N, 5.4%. IR (cm^{-1}); ν(NH) 3320, ν(C=O) 1645, 1635. ^{1}H NMR (C_6D_6): δ = 7.9–7.0 (m, 10H, phenyl); 4.1 (s, 1H, NH); 3.8 (m, 6H, OCH_2-CH$_3$); 3.4 (m, 2H, NH-CH_2-CH$_2$-CH$_2$-Si); 3.15 (m, 1H, CH$_2$-C*H*-CH$_2$-P); 2.85 (m, 2H, -CH_2N-); 1.85 (m, 5H, NH-CH$_2$-CH_2-CH$_2$-Si, -CH_2-PPh$_2$, CH$_2$-CH$_2$-CH_2-CH-); 1.65 (m, 2H, -CH$_2$-CH_2-CH_2-CH-); 1.35 (m, 1H, -CH$_2$-CH_2-CH$_2$-CH); 1.15 (t, 9H, CH$_2$-CH_3); 0.75 (m, 2H, -CH_2Si).

*2.1.5. (S)-1-Benzyloxycarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine (**3**) [11]*

A solution of (*S*)-1-benzyloxycarbonylproline (5 g, 0.02 mol) and triethylamine (2.05 g, 0.02 mol) in toluene/chloroform (1/1) was cooled in an ice-bath. Ethyl chloroformate (2.18 g, 0.02 mol) was added dropwise with vigorous stirring and the pasty reaction mixture stirred for an additional 30 min (temperature 5–10°C), obtained in situ the mixed anhydride. A solution of naphthyl amine (2.87 g, 0.02 mol) in $CHCl_3$ was added dropwise during 15 min. The mixture was stirred at 5°C for 17 h then, was washed successively with water. $NaHCO_3$ (10%), 1N HCl, and water. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give 6.22 g (83%) of **3**. M.p. = 138–140°C. $[\alpha]_D^{25} = -44$ ($CHCl_3$, 1). Anal. Found: C, 73.5; H, 5.7; N, 7.5. $C_{23}H_{22}N_2O_3$ Calc.: C, 73.8; H, 5.9; N, 7.5%. IR (cm^{-1}); ν(NH) 3275; ν(C=O)$_{cbz}$ 1714, ν(C=O)$_{amide}$ 1657. ^{1}H NMR ($CDCl_3$): δ = 8.14–7.26 (m, 12H, arom.); 5.26 (s, 2H, CH$_2$-O-); 4.69 (m, 1H, C*H*-CONH); 3–59–3.51 (m, 2H, CH$_2$N-); 2.67–2.63 (m, 1H, -CH$_2$-CH_2-CH$_2$-CH-); 2.17–1.92 (m, 3H, -CH$_2$-CH_2-CH_2-CH-).

*2.1.6. (S)-2-(1-naphthylaminocarbonyl)pyrrolidine (**4**)*

A mixture of **3** (5.5 g, 0.015 mol), cyclohexene (2.7 ml, 0.026 mol) and 0.24 g of commercial Pd/C (10%) in 55 ml of ethanol was heated under reflux for 6 h in argon, cooled and filtered over Celite. The catalyst was washed with ethanol, and filtrate and wash liquids were evaporated under reduced pressure to give 2.97 g of amide **4**. Yield: 70%. m.p. = 63–64°C. $[\alpha]_D^{25} = -7.2$ (EtOH, 1). Anal. Found: C, 74.3; H, 6.4; N, 11.4. $C_{15}H_{16}N_2O$ Calc.: C, 75.0; H, 6.7; N, 11.7%. IR (cm^{-1}); ν(NH) 3263, 3058, ν(C=O) 1688. ^{1}H NMR ($CDCl_3$): δ = 10.6 (s, br, 1H, NH$_{amide}$); 8.3–7.4 (m, 7H, arom); 4.0–3.9 (dd, 1H, C*H*-CONH); 3.2–3.0 (m, 2H, -CH$_2$N-); 2.3–2.1 (m, 3H, -CH$_2$-CH$_2$-CH_2-CH-, NH); 1.9–1.7 (m, 2H, -CH$_2$-CH_2-CH$_2$-CH-). ^{13}C NMR: δ = 173.3 (*C*O); 133.8, 132.4, 128.5, 125.9, 125.8, 125.7, 125.6, 124.3, 120.1, 117.7 (Carom., 10C); 61.3 (-*C*H-CH$_2$-); 47.2 (-*C*H$_2$-NH); 30.6 (-CH-*C*H$_2$-); 26.2 (-CH$_2$-*C*H$_2$-CH$_2$-).

*2.1.7. (S)-t-Butylaminocarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine (**5a**)*

To a dichloromethane solution of **4** (940 mg, 3.9 mmol) was added, under argon, 1 M *t*-butylisocyanate solution (3.9 mmol) with stirring. The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated and the product was extracted with hexane to yield a white solid (88%). M.p. = 160–161°C. $[\alpha]_D^{25} = -53.2$ (EtOH, 1). Anal. Found: C, 70.5; H, 7.4; N, 12.3. $C_{20}H_{25}N_2O_2$ Calc.: C, 70.8; H, 7.4; N, 12.4%.

IR (cm^{-1}); ν(NH) 3450; ν(C=O) 1705, 1620. ^1H NMR ($CDCl_3$): δ = 10.5 (s, br, 1H, NH); 8.2–7.4 (m, 7H, arom); 4.8 (d, 1H, C*H*–CONH); 4.4 (s, br, NH); 3.3–3.1 (m, 2H, $-CH_2N-$); 2.7–2.6 (m, 1H, $-CH_2-CH_2-CH_2-$ CH–); 2.2–1.8 (m, 3H, $-CH_2-CH_2-CH_2-CH-$); 1.3 (s, 9H, CCH_3).

2.1.8. (S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine (5b)

This product was prepared as **5a**. To a dichloromethane solution of **4** (509 mg, 2.12 mmol) was added triethoxysilylpropylisocyanate (523 mg, 2,12 mmol) under argon. Yield: 85%. m.p. = 95–96°C. $[\alpha]_D^{25} = -47.0$ (EtOH, 1). Anal. Found: C, 61.6; H, 7.7; N, 8.2. $C_{24}H_{37}N_2O_5Si$ Calc.: C, 61.0; H, 7.7; N, 8.6%. IR (cm^{-1}); ν(NH) 3330, 3210; ν(C=O) 1665, 1620. ^1H NMR ($CDCl_3$): δ = 10.5 (s, br, 1H, NH); 8.2–7.4 (m, 7H, arom.); 4.8 (m, 1H, C*H*–CONH); 4.2 (s, br, NH); 3.8–3.7 (q, 6H, $-OCH_2-CH_3$); 3.4–3.2 (m, 4H, $-CH_2N-$); 2.7 (m, 1H, $-CH_2-CH_2-CH_2-CH-$); 2.1–1.6 (m, 5H, $-CH_2-CH_2-CH_2-CH-$, $-CH_2-CH_2-CH_2Si$); 1.2 (s, 9H, $-CH_3$); 0.7–0.6 (t, 2H, $-CH_2Si$).

2.1.9. (S)-2-(1-naphthylaminomethyl)pyrrolidine (6)

To a solution of 2.5 g (0.010 mol) of **4** in tetrahydrofuran cooled in an ice-bath was slowly added 0.12 g (0.003 mol) of lithium aluminium hydride. The reaction mixture was stirred at room temperature for 36 h. The excess of $LiAlH_4$ was eliminated by adding a solution of sodium sulphate. The salts of lithium were filtered off and the filtrate was dried over anhydrous magnesium sulphate and evaporated under reduced pressure. The resulting oil product was purified by distillation. Yield: 81%. $[\alpha]_D^{25} = -27.2$ (EtOH, 1). Anal. Found: C, 79.5; H, 7.9; N, 12.1. $C_{13}H_{18}N_2$ Calc.: C, 79.6; H, 8.0; N, 12.4%. IR (cm^{-1}); ν(NH) 3360. ^1H NMR ($CDCl_3$): δ = 7.88–6.55 (m, 7H, arom.); 5.25 (broad, 1H, NH); 3.26 (m, 3H, C*H*–CONH, CH_2N-); 2.82 (m, 2H, CH_2NH); 1.88 (m, 4H, $-CH_2-CH_2-CH_2-CH-$). ^{13}C NMR: δ = 144.3, 134.3, 128.5, 126.7, 124.4, 123.6, 120.1, 116.6, 103.9 (arom.); 62.6 ($-CH-CH_2NH-$); 48.0 ($-CH_2-CH_2-NCO-$); 45.1 ($-CH_2NH$); 29.0, 23.0 ($-CH_2-CH_2-CH-$).

2.1.10. (S)-t-Butylaminocarbonyl-2-(1-naphthylaminomethyl)pyrrolidine (7a)

To a dichloromethane solution of (*S*)-2-(1-naphthylaminomethyl)pyrrolidine (0.42 g, 1.84 mmol) was added 1 M *t*-butylisocyanate solution (0.22 ml) with stirring. After 1 h the solution was evaporated to dryness and the resulting oil was extracted several times with hexane. Yield 83%. m.p. = 136–139°C. $[\alpha]_D^{25} = +6$ (EtOH, 1). Anal. Found: C, 72.9; H, 8.2; N, 12.5. $C_{20}H_{27}N_3O$ Calc.: C, 73.8; H, 8.4; N, 12.9%. IR (cm^{-1}); ν(NH) 3430, 3300; ν(C=O) 1635. ^1H NMR ($CDCl_3$): δ = 8.1–6.4 (m, 7H, arom.,); 6.7 (br, 1H, NH); 4.6 (m, 1H, $-CH-CH_2NH$); 4.29 (s, br, 1H, NH); 3.3–3.0 (m, 4H, $-CH_2-N-CO-$, $-CH-CH_2-NH$); 2.1–2.0 (m, 2H, $-CH_2-CH_2-CH-$); 1.8 (m, 1H, $-CH_2-CH_2-CH-$), 1.65 (m, 1H, $-CH_2-CH_2-CH-$); 1.5 (s, 9H, $-C(CH_3)$). ^{13}C NMR: δ = 158.1 (*C*O); 144.5, 134.3, 128.3, 126.5, 125.5, 124.2, 123.2, 121.4, 116.0, 102.0 (Carom., 10C); 60.3 ($C(CH_3)$); 52.9 ($-CH-CH_2-$); 50.9 ($-CH-CH_2-$); 46.3 (CH_2-NCO); 29.4 ($-C(CH_3)$; 29.3 ($-CH_2-CH_2-CH_2-$); 24.5 ($-CH_2-CH_2-CH_2-$).

2.1.11. (S)-1-(3-triethyloxysilylpropyl)aminocarbonyl-2-(1-naphthylaminomethyl)pyrrolidine (7b)

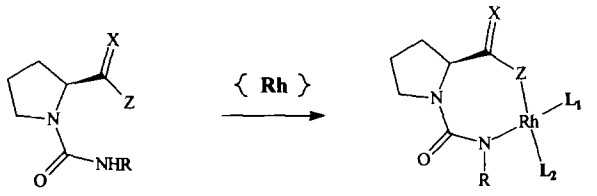
This compound was prepared by a procedure similar to that described for **7a**, except that triethoxysilylpropylisocyanate (0.37 ml of 1M solution) was used with (*S*)-2-(1-naphthylaminomethyl)pyrrolidine (0.7 g, 3.1 mmol). Yield 87%. m.p. = 68–70°C. $[\alpha]_D^{25} = +29.8$ (EtOH, 1). Anal. Found: C, 63.4; H, 8.3; N, 9.0. $C_{25}H_{39}N_3O_4Si$ Calc.: C, 63.4; H, 8.3; N, 8.9%. IR (cm^{-1}); ν(NH) 3450, 3300; ν(C=O) 1635. ^1H NMR ($CDCl_3$): δ = 8.1–6.4 (m, 7H, arom.); 6.6 (s, br, 1H, NH); 4.6 (NH, m, 2H, $-CH-CH_2NH-$); 3.8 (q, 6H, CH_2-CH_3); 3.4–3.2 (m, 6H; $-CH_2-N-CO-$, $-CH-CH_2NH-$, $-CH_2-NH-CO$); 2.2–2.0 (m, 3H, $-CH_2-CH_2-CH-$, $-CH_2-CH_2-CH_2Si-$); 1.85 (m, 1H, $-CH_2-CH_2-CH-$), 1.65 (m, 2H, $-CH_2-CH_2-CH-$); 1.2 (t, 9H, CH_3); 0.6 (t, 2H, CH_2Si). ^{13}C NMR: δ = 158.6 (CO); 144.3, 134.3, 128.1, 126.5, 125.5, 124.5, 123.3, 121.2, 116.0, 102.3 (Carom., 10C); 58.3 ($-CH_2-CH_3$); 56.4 ($-CH-CH_2-$); 50.8 ($-CH-CH_2-$); 46.1 (CH_2-NCO); 43.1 ($-CH_2-N-CO$); 24.5 ($-CH_2-CH_2-CH_2-$); 23.6 ($-CH_2-CH_2-CH_2Si$); 18.2 ($-CH_2-CH_3$); 7.6 (CH_2Si).

2.2. Preparation of complexes

The general synthesis of the complexes is presented in Scheme 2.

2.2.1. General synthesis of [Rh(COD)(LL)][PF_6]

To a solution of di-μ-chloro-bis(1,5-cyclooctadiene)dirhodium (0.4 mmol) in dry dichloromethane (20 ml) was added a solution of LL (0.8 mmol), then



8-15a,b

	8	9	10	11	12	13	14	15
X	O	H,H	O	H,H	O	H,H	O	H,H
Z	*t*-Bu	PPh_2	1-Naph	1-Naph	*t*-Bu	PPh_2	1-Naph	1-Naph
L_1,L_2	COD	COD	COD	COD	$2\cdot PPh_3$	$2\cdot PPh_3$	$2\cdot PPh_3$	$2\cdot PPh_3$

a: R = *t*-Bu; **b**: R = $(CH_2)_3Si(OEt)_3$

Scheme 2.

ammonium hexafluorophosphate (0.8 mmol) was added and the mixture stirred for 3 h at room temperature, and filtered. The filtrate was evaporated under reduced pressure to 5 ml. Careful addition of diethyl ether caused the precipitation of a yellow-orange solid which was collected by filtration, washed and dried in vacuo to give the desired complex.

*2.2.1.1. [Rh(COD){(S)-1-t-butylaminocarbonyl-2-t-butylaminocarbonylpyrrolidine}][PF_6] (**8a**).* Yield: 60%. Orange powder. $[\alpha]_D^{25} = -71.2$ ($CHCl_2$, 1). Anal. Found: C, 44.9; H, 7.1; N, 6.3; Rh, 17.1. $C_{22}H_{39}F_6N_3O_2PRh$ Calc.: C, 44.6; H, 7.0; N, 6.0; Rh, 16.5%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 158, Λ(acetone)(Ω^{-1} cm^{-1} mol^{-1}) = 134. IR (cm^{-1}); ν(NH) 3347, 3287; ν(C=O) 1662, 1635. ^{1}H NMR ($CDCl_3$): δ = 7.0 (1H, NH); 4.2 (6H, CH=, C*H*–CONH, NH); 3.3 (2H, CH_2N); 2.5 (4H, CH_2–CH=); 2.4 (1H, CH_2–CHCON); 1.9 (3H, CH_2–CHCON, CH_2–CH_2N); 1.8 (4H, CH_2–CH=); 1.4, 1.3 (18H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 171.4 (CH–*C*ONH); 157.0 (NCON); 78.6, 78.4 (*C*H=); 60.7 (*C*H–CONH); 51.0, 50.7 (NH*C*CH_3); 46.5 (*C*H_2N); 30.9 (*C*H_2–CH=); 29.4, 28.7 (CH_3); 28.8 (*C*H_2–CHCON); 24.8 (*C*H_2–CH_2N).

*2.2.1.2. [Rh(COD){(S)-1-(3-triethoxysilylpropyl)aminocarbonyl-2-t-butylaminocarbonylpyrrolidine}][PF_6] (**8b**).* Yield: 85%. Yellow-orange powder. $[\alpha]_D^{25} = -32.1$ ($CHCl_3$, 1). Anal. Found: C, 41.8; H, 6.3; N, 5.4; Rh, 13.8. $C_{27}H_{51}F_6N_3O_5PRhSi$ Calc.: C, 41.9; H, 6.6; N, 5.4; Rh, 13.3%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 56, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 89. IR (cm^{-1}); ν(NH) 3392, 3306; ν(C=O) 1668, 1652. ^{1}H NMR ($CDCl_3$): δ = 4.3–4.2 (5H, CH=, C*H*–CONH); 3.8 (6H, CH_2O); 3.3 (2H, CH_2N); 2.5 (6H, CH_2–CH=, CH_2–CH_2NHCO); 1.9 (4H, CH_2–CH=); 1.8 (4H, CH_2–CHCON, CH_2–CH_2N); 1.4 (11H, CH_2–CH_2Si, C–CH_3); 1.3 (9H, CH_2–CH_3); 0.7 (2H, CH_2–Si).

*2.2.1.3. [Rh(COD){(S)-1-t-butylaminocarbonyl-2-diphenylphosphinomethylpyrrolidine}][PF_6] (**9a**).* Yield: 85%. $[\alpha]_D^{25} = -12.5$ ($CHCl_3$, 1). Anal. (with 1 ethyl ether). Found: C, 51.8; H, 6.1; N, 3.6; Rh, 12.2. $C_{30}H_{41}F_6N_2P_2Rh$ Calc.: C, 51.8; H, 6.4; N, 3.5; Rh, 13.2%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 176, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 112. IR (cm^{-1}); ν(NH) 3430; ν(C=O) 1635. ^{1}H NMR ($CDCl_3$): δ = 8.3–7.2 (10H, ph); 4.1 (4H, CH=); 3.2 (2H, C*H*–CH_2P, CH_2N); 3.0 (1H, CH_2N); 2.5 (4H, CH_2–CH=); 2.3 (2H, CH_2–P); 2.0–1.8 (8H, CH_2–CH–CH_2P–, CH_2–CH_2N, CH_2–CH=); 1.3 (9H, CH_3). ^{13}C NMR ($CDCl_3$) δ = 156.3 (CO); 131.6, 130.7, 128.6(ph); 78.7, 78.4 (CH=); 53.8 (NH*C*$(CH_3)_3$); 52.7 (*C*H–CH_2P); 45.7 (CH_2N); 34.3 (CH_2–P); 32.0 (*C*H_2–CH–CH_2P); 30.9 (*C*H_2–CH=); 29.6 (*C*–CH_3); 23.6 (*C*H_2–CH_2N). ^{31}P NMR($CDCl_3$) = 26.8, 21.8 (PPh_2); –143.6 (PF_6).

*2.2.1.4. [Rh(COD){(S)-1-(3-triethoxysilylpropyl)aminocarbonyl-2-diphenylphosphinomethylpyrrolidine}][PF_6] (**9b**).* Yield: (83%). Yellow-orange powder $[\alpha]_D^{25} = -27.1$ ($CHCl_3$, 1). Anal. Found: C, 48.0; H, 5.9; N, 3.2; Rh, 11.0. $C_{35}H_{53}F_6N_2O_4P_2RhSi$ Calc.: C, 48.2; H, 6.1; N, 3.2; Rh, 11.8%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 186. Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 132. IR (cm^{-1}); ν(NH) 3430; ν(C=O) 1575, 1570. ^{1}H NMR ($CDCl_3$): δ = 7.8–7.1 (10H, ph); 5.3 (1H, NH); 3.9 (6H, CH_2O); 3.1 (2H, CH_2–CH_2NHCO); 3.0 (1H, C*H*–CH_2P); 2.9 (2H, CH_2N); 2.6 (4H, CH_2–CH=); 2.3 (2H, CH_2–P); 2.1 (4H, C*H*–CH=); 1.9 (6H, CH_2–CH–CH_2P, CH_2–CH_2N, CH_2–CH_2Si); 1.3 (9H, CH_2–CH_3); 0.9 (2H, CH_2–Si). ^{31}P NMR ($CDCl_3$): δ = 26.25; 21.6 (PPh_2); –143.6 (PF_6).

*2.2.1.5. [Rh(COD){(S)1-t-Butylaminocarbonyl-2-[(1-naphthylamino)carbonyl)pyrrolidine}]PF_6 (**10a**).* Yield: 81% Orange powder. $[\alpha]_D^{25} = +53.0$ ($CHCl_3$, 1). Anal. Found: C, 49.0; H, 5.8; N, 6.5; Rh, 14.8. $C_{28}H_{37}F_6N_2O_2Rh$ Calc.: C, 48.4; H, 5.4; N, 6.0; Rh, 14.1%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 173, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 112. IR (cm^{-1}); ν(NH) 3460; ν(C=O) 1690, 1610. ^{1}H NMR ($CDCl_3$): δ = 10.3 (s, br, 1H, NH); 8.1–7.1 (m, 7H, arom.); 4.7 (d, 1H, C*H*–CONH); 4.3 (s, br, NH); 4.1 (4H, CH=); 3.2 (m, 1H, –CH_2N–); 3.1 (m, 1H, –CH_2N); 2.6 (m, 1H, –CH_2–CH_2–CH_2–CH–); 2.4 (4H, CH_2–CH=); 2.2–1.9 (m, 2H, –CH_2–CH_2–CH_2–CH–); 1.8–1.6 (m, 6H, CH_2–CH=, –CH_2–CH_2–CH_2–CH–); 1.3 (s, 9H, CCH_3).

*2.2.1.6. [Rh(COD){(S)1-(3-trietoxysilylpropyl)aminocarbonyl-2-(1-naphthylaminocarbonylpyrrolidine}]PF_6 (**10b**).* Yield: 52%. Light-yellow powder. $[\alpha]_D^{25} = +57.0$ ($CHCl_3$, 1). Anal. Found: C, 47.8; H, 6.2; N, 5.4; Rh, 11.7. $C_{33}H_{45}F_6N_2O_5PRhSi$ Calc.: C, 47.0; H, 5.8; N, 5.0; Rh, 12.2%. Δ(DMF)(Ω^{-1} cm^{-2} mol^{-1}) = 69, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 91. IR (cm^{-1}); ν(NH) 3330, 3210; ν(C=O) 1665, 1620.

*2.2.1.7. [Rh(COD){(S)-1-t-butylaminocarbonyl-2-(1-naphthylamino)methylpyrroline}][PF_6] (**11a**).* The reaction time for the synthesis of this complex was 24 h. Yield: 63%. Light-yellow powder. D.p. = 134°C. $[\alpha]_D^{25} = +28.5$ ($CHCl_3$, 1). Anal. Found: C, 49.1; H, 5.7; N, 6.7; Rh, 14.6. $C_{28}H_{39}F_6N_3OPRh$ Calc.: C, 49.3; H, 5.8; N, 6.2; Rh, 15.1%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 170, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 105. IR (cm^{-1}): ν(NH) 3420, 3300; ν(C=O) 1635. ^{1}H NMR ($CDCl_3$): δ = 8.1–6.4 (m, 7H, arom.); 4.6 (m, 1H, –CH_2–CH_2NH–); 4.25–4.1 (4H, CH=); 3.3–3.1 (m, 4H, –CH_2–N–CO–, –CH–CH_2–NH); 2.4 (4H, CH_2–CH=); 2.1–2.0 (m, 3H, –CH_2–CH_2–CH–, CH_2–CH_2–CH–); 1.7–1.6 (m, 5H, –CH_2–CH_2–CH–, CH_2–CH=); 1.3 (s, 9H, –C(CH_3)). ^{13}C NMR: δ = 158.2 (*C*O); 144.1, 134.3, 128.1, 126.5, 125.6, 124.4, 123.2, 121.4, 116.2, 102.5 (Carom., 10C);

78.8, 78.5 (CH=); 55.9 (C(C(CH$_3$)$_3$); 51.2 (CH–CH$_2$–); 50.9 (CH–CH$_2$), 46.4 (CH$_2$–NCO); 30.8 (CH$_2$–CH=); 29.5 (–C(CH$_3$); 29.2 (–CH$_2$–CH$_2$–CH$_2$–); 24.5 (CH$_2$–CH$_2$–CH$_2$).

*2.2.1.8. [Rh(COD){(S)1-(3-trietoxysilylpropyl)aminocarbonyl-2-(1-naphthylamino)methylpyrrolidine}][PF$_6$] (**11b**).* The title compound was synthesized as follows: to a solution of [{RhCl(COD)}$_2$] in refluxing EtOH was added an equimolar amount of NH$_4$[PF$_6$] to give [Rh(COD)S][PF$_6$], then a solution of LL (in EtOH) was added at room temperature. The solvent was evaporated off and the resulting oil was extracted with hexane. Yield: 45%. Yellow-brown powder. d.p. = 163°C. $[\alpha]_D^{25}$ = +26.4(CHCl$_3$, 1). Anal. Found: C, 49.9; H, 6.8; N, 5.3; Rh, 12.3. $C_{33}H_{51}F_6N_3O_4RhSi$ Calc.: C, 49.4; H, 6.4; N, 5.2; Rh, 12.9%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 115, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 104. IR (cm^{-1}); ν(NH) 3400, 3300; ν(C=O) 1630. ^{1}H NMR (CDCl$_3$): δ = 7.7–6.5 (m, 7H, arom.); 6.6 (NH, s, 1H); 4.6 (m, 1H, –CH–CH$_2$NH–); 4.2 (4H, CH=); 3.8 (q, 6H, CH_2–CH$_3$); 3.4–3.2 (m, 6H, –CH_2–NCO–, –CH–CH_2–NH, –CH_2NHCO); 2.5–2.4 (m, 3H, CH_2–CH=, –CH$_2$–CH_2–CH–); 2.1 (m, 3H, CH_2–CH=, –CH$_2$–CH_2–CH–); 1.8–1.6 (m, 8H, CH_2–CH=, –CH$_2$–CH_2–CH–, CH$_2$–CH_2–CH$_2$Si–), 1.2 (t, 9H, CH$_2$–CH_3); 0.6 (CH$_2$Si).

2.2.2. General procedure for synthesis of Wilkinson-type derivatives [Rh(LL)(PPh$_3$)$_2$][PF$_6$]

To a solution of [RhCl(PPh$_3$)$_3$] (0.2 mmol) in dry CH$_2$Cl$_2$ (20 ml) the stoichiometric amount of the corresponding LL and NH$_4$[PF$_6$] were added. The mixture was heated under reflux for 3–5 h and the NH$_4$Cl filtered off. The filtrate was evaporated to dryness, diethyl ether was added and the yellow-orange powder thus formed collected, washed with ether and dried in vacuo.

*2.2.2.1. [Rh(PPh$_3$)$_2${(S)-1-t-butylaminocarbonyl-2-t-butylaminocarbonylpyrrolidine}][PF$_6$] (**12a**).* Yield: 88%. Orange powder. $[\alpha]_D^{25}$ = −7.7 (CH$_3$CN, 1). Anal. Found: C, 58.0; H, 5.2; N, 3.8; Rh, 11.0. $C_{50}H_{57}F_6N_3O_2P_3Rh$ Calc.: C, 57.6; H, 5.5; N, 4.0; Rh, 9.9%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 174, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 137. IR (cm^{-1}); ν(NH) 3350; ν(C=O) 1650, 1625. ^{1}H NMR (CDCl$_3$): δ = 7.8–7.4 (30H, ph); 4.3 (1H, NH); 4.2 (1H, CH–CONH); 3.3 (2H, CH$_2$N); 2.4 (1H, CH_2–CHCON); 1.9 (3H, CH_2–CHCON; CH_2–CH$_2$N); 1.3 (18H, CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 171.4 (CH–CONH); 157.0 (NCON); 60.7 (CH–CONH); 51.0, 50.7 (NHCCH$_3$); 46.5 (CH$_2$N); 29.4, 28.7 (CH$_3$); 28.8 (CH$_2$–CHCON); 24.8 (CH$_2$–CH$_2$N). ^{31}P NMR (CDCl$_3$): δ = 41.3 (PPh$_3$); −143.8 (PF$_6$).

*2.2.2.2. [Rh(PPh$_3$)$_2${(S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-t-butylaminocarbonylpyrrolidine}][PF$_6$] (**12b**).* Yield: 75%. $[\alpha]_D^{25}$ = +3.9 (CHCl$_3$, 1). Anal. Found: C, 56.0; H, 6.1; N, 3.1; Rh, 9.7. $C_{55}H_{69}F_6N_3O_5P_3RhSi$ Calc.: C, 55.5; H, 5.8; N, 3.5; Rh, 8.7%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 137, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 96. IR (cm^{-1}); ν(NH) 3340, 3390; ν(C=O) 1650, 1620. ^{1}H NMR (CDCl$_3$): δ = 7.8–7.2 (30H, ph); 4.3 (1H, CH-CONH); 3.5 (6H, CH$_2$O); 3.3 (4H, CH$_2$N, CH$_2$–CH$_2$–CH_2NHCO); 2.0 (4H, CH_2–CHCON, CH_2–CH$_2$N); 1.7 (2H, CH_2–CH$_2$Si); 1.3 (9H, C–CH$_3$); 1.2 (9H, CH$_2$–CH_3); 0.7 (2H, CH$_2$–Si). ^{31}P NMR (CDCl$_3$): δ = 41.0 (PPh$_3$); −143.7 (PF$_6$).

*2.2.2.3. [Rh(PPh$_3$)$_2${(S)-1-t-butylaminocarbonyl-2-diphenylphosphinomethylpyrrolidine}][PF$_6$] (**13a**).* Yield: 80%. $[\alpha]_D^{25}$ = +8.0 (CHCl$_3$, 1). Anal. Found: C, 59.4; H, 5.5; N, 2.1; Rh, 9.6. $C_{58}H_{59}F_6N_2OP_4Rh$ Calc.: C, 61.0; H, 5.2; N, 2.5; Rh, 9.0%. Λ(DMF) (Ω^{-1} cm^2 mol^{-1}) = 195, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 140. IR (cm^{-1}); ν(NH) 3450; ν(C=O) 1590. ^{1}H NMR (CDCl$_3$): δ = 8.3–7.2 (arom.); 3.2 (2H, CH–CH$_2$P, CH$_2$N); 3.0 (1H, CH$_2$N); 2.5 (4H, CH_2–CH=); 2.3 (2H, CH$_2$–P); 2.0–1.8 (8H, CH_2–CH–CH$_2$P, CH_2–CH$_2$N, CH_2–CH=); 1.3 (9H, CH$_3$). ^{13}C NMR δ = 156.3 (CO); 131.6, 130.7, 128.6 (arom.); 52.7 (CH–CH$_2$P); 45.7 (CH$_2$N); 34.3 (CH$_2$–P); 32.0 (CH$_2$–CH–CH$_2$P); 30.9 (CH$_2$–CH=); 29.6 (C–CH$_3$); 23.6 (CH$_2$–CH$_2$N). ^{31}P NMR (CDCl$_3$): δ = 46.6 (PPh$_3$); 26.3, 21.7 (PPh$_2$); −143.8 (PF$_6$).

*2.2.2.4. [Rh(PPh$_3$)$_2${(S)-1-(3-triethoxysilylpropyl)aminocarbonyl-2-diphenylphosphinomethylpyrrolidine}][PF$_6$] (**13b**).* Yield: 80%. Orange powder. $[\alpha]_D^{25}$ = −9.6 (CH$_3$CN, 1). Anal. Found: C, 58.0; H, 5.2; N, 2.5; Rh, 8.8. $C_{63}H_{71}F_6N_2O_4P_4RhSi$ calc.: C, 58.7; H, 5.5; N, 2.2; Rh, 8.0%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 105, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 93. IR (cm^{-1}); ν(NH) 3425; ν(C=O) 1590. ^{1}H NMR (CDCl$_3$): δ = 7.8–7.1 (arom.); 5.3 (1H, NH); 3.9 (6H, CH$_2$O); 3.1 (2H, CH$_2$–CH_2NHCO); 3.0 (1H, CH–CH$_2$P); 2.9 (2H, CH$_2$N); 2.3 (2H, CH$_2$–P); 1.9 (6H, CH_2–CH–CH$_2$P, CH_2–CH$_2$N, CH_2–CH$_2$Si); 1.3 (9H, CH$_2$–CH_3); 0.9 (2H, CH$_2$–Si). ^{31}P NMR (CDCl$_3$): δ = 46.7 (PPh$_3$); 26.4, 21.5 (PPh$_2$); −143.8 (PF$_6$).

*2.2.2.5. [Rh(PPh$_3$)$_2${(S)-1-t-butylaminocarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine}][PF$_6$] (**14a**).* Yield: 62%. Brown powder. $[\alpha]_D^{25}$ = +27.5 (EtOH, 1). Anal. Found: C, 59.9; H, 4.9; N, 3.4; Rh, 8.7. $C_{56}H_{55}F_6N_3O_2P_3Rh$ Calc.: C, 60.5; H, 5.0; N, 3.8; Rh, 9.3%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 194, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 139. IR (cm^{-1}); ν(NH) 3430, 3350; ν(C=O) 1680 (m), 1620. ^{1}H NMR (CDCl$_3$): δ = 10.3 (s, br, 1H NH); 8.1–7.1 (arom.); 4.7 (d, 1H, CH–CONH); 4.3 (s,

br, NH); 3.3 (m, 1H, $-CH_2N-$); 3.2–3.1 (m, 1H, $-CH_2N$); 2.6 (m, 1H, $-CH_2-CH_2-CH_2-CH-$); 2.1–1.9 (m, 2H, $-CH_2-CH_2-CH_2-CH-$); 1.9–1.6 (m, 3H, $-CH_2-CH_2-CH_2-CH-$); 1.4 (s, 9H, CH_3). ^{31}P NMR ($CDCl_3$): $\delta = 41.5$ (PPh_3); -143.7 (PF_6).

2.2.2.6. [Rh(PPh$_3$)$_2$\{(S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-(1-naphthylaminocarbonyl)pyrrolidine\}][PF$_6$] (14b). Yield: 68%. Orange powder. $[\alpha]_D^{25} = -37.8$ ($CHCl_3$, 1). Anal. Found: C, 57.7; H, 5.0; N, 3.2; Rh, 8.6. $C_{61}H_{67}F_6N_3O_5P_3Rh$ Calc.: C, 58.1; H, 5.4; N, 3.3; Rh, 8.2%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 162 Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 112. IR (cm^{-1}); ν(NH) 3400; ν(C=O) 1680 (m), 1620.

2.2.2.7. [Rh(PPh$_3$)$_2$\{(S)-1-t-Butylaminocarbonyl-2-(1-naphthylaminomethyl)pyrrolidine\}][PF$_6$] (15a). This product was obtained after 48 h under reflux. Yield: 67%. Yellow-green powder. $[\alpha]_D^{25} = +4.05$ (CH_3CN, 1). Anal. Found: C, 60.8; H, 4.8; N, 3.5; Rh, 8.9. $C_{56}H_{57}F_6N_3OP_3Rh$ Calc.: C, 61.3; H, 5.2; N, 3.8; Rh, 9.4%. Λ(DMF)(Ω^{-1} cm^2 mol^{-1}) = 120, Λ(acetone)-(Ω^{-1} cm^2 mol^{-1}) = 134. IR (cm^{-1}); ν(NH), 3430, 3380; ν(C=O), 1620. ^1H NMR ($CDCl_3$): δ = 8.0–6.8 (arom.); 4.5 (m, 1H, $-CH-CH_2NH-$); 3.4–3.2 (m, 4H, $-CH_2-N-CO-$, $-CH-CH_2-NH$); 3.0 (s, 1H, NH); 2.4–1.6 (m, 4H, $-CH_2-CH_2-CH-$); 1.4 (s, 9H, $-C(CH_3)$).

2.2.2.8. [Rh(PPh$_3$)$_2$\{(S)-1-(3-trietoxysilylpropyl)aminocarbonyl-2-(1-naphthylaminomethylpyrrolidine\}][PF$_6$] (15b). This complex was isolated after 24 h under reflux. Yield: 62%. Yellow-green powder. Anal. Found: C, 61.2; H, 5.7; N, 3.2; Rh, 8.0. $C_{61}H_{69}F_6N_3O_4P_3Rh$ Calc.: C, 58.8; H, 5.5; N, 3.4; Rh, 8.3%. Λ(DMF)-(Ω^{-1} cm^2 mol^{-1}) = 16, Λ(acetone)(Ω^{-1} cm^2 mol^{-1}) = 65. IR (cm^{-1}): ν(NH), 3420, 3380; ν(C=O), 1625. ^1H NMR ($CDCl_3$): δ = 7.8–7.0 (arom.); 4.4 (1H, NH); 3.8 (6H, CH_2O); 3.4–3.2 (6H, CH_2-CH_2NHCO, CH_2-CH_2NCO, $CH-CH_2NH$); 3.0 (1H, NH); 1.3 (9H; CH_2-CH_3); 0.7 (2H, CH_2-Si).

Table 1
Analytical data for the supported complexes

Complex	%C (found)	%H (found)	%N (found)	%Rh [a] (found)	%Anchoring
Sil-8b	4.3 (3.9)	1.3 (1.0)	0.6 (0.5)	0.9 (0.7)	78
Zeol-8b	3.4 (3.0)	0.8 (0.6)	0.5 (0.4)	0.6 (0.4)	54
Sil-8b	4.6 (4.3)	0.9 (0.8)	0.6 (0.4)	0.7 (0.6)	70
Zeol-9b	4.6 (4.4)	0.9 (0.6)	0.7 (0.5)	0.9 (0.8)	82
Sil-12b	4.6 (4.3)	0.7 (0.5)	0.4 (0.4)	0.6 (0.5)	63
Zeol-12b	4.4 (4.2)	0.8 (0.7)	0.6 (0.4)	0.6 (0.4)	60
Sil-13b	5.8 (5.6)	0.8 (0.7)	0.7 (0.6)	1.0 (1.0)	98
Zeol-13b	5.6 (5.5)	0.9 (0.7)	0.8 (0.6)	1.2 (1.0)	100

[a] Determined by atomic absorption.

2.3. Anchoring of complexes

A rhodium complex of **8–15b** bearing a triethoxysilyl group, (0.2 meq) in dry dichloromethane (2 ml) was added to a suspension of the inorganic support (silica or modified USY-zeolite dried at 140°C for 3–4 h in vacuo) (1 g) in dry toluene (40 ml) and the mixture was stirred under argon for 24 h at room temperature. The solid was then filtered and Soxhlet-extracted with CH_2Cl_2/ethyl ether (1:2) for 7 h to remove the remaining non-supported complex, and dried in vacuo. Analytical data for the supported catalysts are shown in Table 1.

2.4. Catalytic experiments

The catalytic properties of the rhodium complexes derived from l-proline were examined under usual conditions for test reactions. The reactions were carried out as follows.

2.4.1. Hydrogenation of olefins

2.4.1.1. Hydrogenation of simple olefins. Hex-1-ene, cyclohexene and 1-methylcyclohexene (high purity Merck) were hydrogenated in a batch reactor (Autoclave Engineers) of 100 ml capacity, at 323 K and 6 atm of dihydrogen pressure, the Rh/substrate molar ratio being 1/50000 for hex-1-ene and cyclohexene, and 1/20000 for methylcyclohexene. The olefins were added to a solution or suspension of the catalyst in methyl isobutyl ketone (50 ml). After hydrogenation, the catalyst, if supported, was separated by filtration and used again. The reaction products were analysed in a Siemens glc apparatus using a 0.5 inch/4 m column, packed with β,β'-oxydipropionitrile at 317 K (Table 2).

2.4.1.2. Hydrogenation of prochiral olefins. Ethyl (Z)-α-acetylaminocinnamate, selected as a model compound, was hydrogenated in a batch reactor at 338 K and 5 atm of dihydrogen pressure. The molar ratio of catalyst/substrate was 1/100. The olefin was added to a solution or suspension of the catalyst in ethanol (45 ml). After hydrogenation, the catalyst, if supported, was separated by filtration and used again. The reaction products were analysed by HPLC (Table 3).

2.4.2. Hydroboration

A typical procedure is given for styrene. A mixture of styrene (2 mmol), catalyst (0.02 mmol) and 1 mmol

Table 2
Turnover numbers (mmol substrate mmol cat.$^{-1}$ min^{-1}) in the maximum rate for the hydrogenation of hex-1-ene, cyclohexene and methyl cyclohexene [a]

Catalyst	Hex-1-ene	Cyclohexene	Methylcyclohexene [b]
8a	1512	1333	33(10)
Sil-8b	2750	1150	29(75)
Zeol-8b	4400	3650	35
9a	2460	1917	59(10)
Sil-9b	2625	1100	90(100)
Zeol-9b	4642	3650	68
12a	4374	900	22(30)
Sil-12b	3350/750	825	45(50)
Zeol-12b	6875/750	1000	40
13a	4142	900	7
Sil-13b	1400/933	750	26(50)
Zeol-13b	8000/820	928	23

[a] Cat./sus. = 1/50000 (hex-1-ene, cyclohexene), 1/20000 (methylcyclohexene); T = 323 K, P_{H_2} = 6 atm.
[b] Induction time (min.) in parenthesis.

of decane (used as reference standard) in 4 ml of dry THF was stirred under argon. Catechol-borane (4 mmol of a 1 M THF solution) was added at room temperature and the mixture was stirred at the same temperature until the starting product disappeared (analysed by glc) and then quenched with 4 ml of THF/EtOH: 1/1. To the mixture was added 4 ml of 2 M NaOH and 4 ml of 30% H_2O_2, and it was stirred at room temperature for 1 h. Extraction with ether followed by flash chromatography on silica gel (AcOEt/Hexane: 1/10) gave 100% yield of 1-phenylethanol.

2.4.3. Hydrosilylation

To a solution of styrene (2 mmol) in dry benzene (1 ml) were added under argon the catalyst (0.002 mmol), decane (1 mmol as reference standard) and the silane (2.5 mmol). The mixture was stirred at 38°C and 50°C. The products were evaluated by glc. The final product was obtained by distillation (Table 4).

2.4.4. Cyclopropanation

To styrene (3 mmol) and the catalyst (0.02 mmol), ethyl diazoacetate (4.12 mmol) was added dropwise with a syringe over 2 h under N_2. The reaction was carried out at 50°C with magnetic stirring. After evolution of N_2 ceased, the product ethyl *cis/trans*-2-phenylcyclopropanecarboxylate was obtained by distillation (94°C, 0.3 torr). Chemical yield was determined by glc. The enantiomeric excess was measured by gas chromatography with a chiral glass capillary cyclodextrin column [12] (Table 5).

Table 3
Asymmetric hydrogenation of *Z*-(α)-ethyl acetamidocinnamate. (cat./subs = 1/100, T = 60°C; PH_2 = 6 atm.)

Catalyst	t (h) [a]	Induction time	TOR	Optical yield [b] (% ee)	Leaching (% Rh)
9b	24	3	0.11	34.4	
Sil-9b	30	3	0.12	84.5	19
Zeol-9b	20	0	0.12	53.3	13

[a] Total conversion.
[b] Optical yields were determined on the basis of the reported maximum rotation $[\alpha]_D^{25} = +85.9$ ($CHCl_3$, l).

Table 4
Asymmetric hydrosilylation of styrene (cat./subs. = 1/1000, benzene, T = 38°C)

Catalyst	t(h) [a]	Silane	% Hydrosilylation
8a	5	$PhMe_2SiH$	83
Zeol-8b	7	$PhMe_2SiH$	88
9a	8	$PhMe_2SiH$	80
Zeol-9b	9	$PhMe_2SiH$	80
8a	8	Ph_2SiH_2	81
Zeol-8b	28	Ph_2SiH_2	67
9a	24	Ph_2SiH_2	88
Zeol-9b	71	Ph_2SiH_2	45

[a] Total conversion was achieved for all substrates if more silane was added.

3. Results and discussion

3.1. Donor synthesis

Optically pure compounds (*S*)-1-l-2-*t*-butylaminocarbonylpyrrolidines (**1a**, **1b**), (*S*)-1-l-2-diphenylphosphinomethylpyrrolidines (**2a**, **2b**), (*S*)-1-l-2-(1-naphthylaminocarbonyl)pyrrolidines (**5a**, **5b**), (*S*)-1-l-2-(1-naphthylaminomethyl)pyrrolidines (**7a**, **7b**), (**a**: l = *t*-butylaminocarbonyl, **b**: l = (3-trietoxysilylpropyl)aminocarbonyl) were prepared by previously described methods [7] in several steps starting from L-proline. The procedures are outlines in Scheme 1.

3.2. Preparation of the complexes

Reactions of *N,N'*- and *N,P*-donors prepared above, with $[\{RhCl(COD)\}_2]$ or $[RhCl(PPh_3)_3]$ yields different complexes, which were characterized by analytical and spectroscopic data. All ligands form seven-membered chelate rings with rhodium (Scheme 2).

3.2.1. [Rh(COD)(ligand)][PF_6]

Addition of a stoichiometric amount of donor to a dichloromethane solution of $[\{RhCl(COD)\}_2]$ in the presence of a non-coordinating anion leads to the formation of [Rh(COD(ligand)][PF_6] by cleavage of the

Table 5
Enantioselective cyclopropanation of styrene (3 mmol) with ethyldiazoacetate (4.2 mmol) using catalysts **8a** and **Zeol-8b** (0.02 mmol) at 50°C

Catalyst	Yield % [a]	*cis / trans* ratio	% ee *cis / trans*
8a	90	1/1.4	< 1 %
Zeol-8b	75	1/1.8	2.4/3.7

[a] Total conversion is achieved if more ethyldiazoacetate is added.

chloride bridge. The complexes were isolated as yellow, relatively air-stable solids. Microanalytical, conductivity and IR spectroscopic data are given in the experimental section.

The IR spectra show the presence of the coordinated diene and bands for the coordinated l–l donors. The spectra show ν(N–H) at 3480–3200 cm^{-1} at higher frequencies than the free donors which suggests Rh–N coordination; ν(C=O) at 1660–1640 cm^{-1}, which is close to the values of the free bases, excludes linkage through the C=O groups (Rh–O bond). No bands owing to the Rh–Cl stretching vibrations were observed in the far IR. The spectra also show the ν(P–F) at 830–840 cm^{-1}.

The ^{1}H and ^{13}C NMR spectra show signals corresponding to ring protons and carbons atoms slightly shifted with respect to the free bases. The ^{1}H and ^{13}C NMR signals of the atoms close to the metal are remarkably broadened because of the metal and the conformational non-rigidity on the NMR time scale. For compounds with triethoxysilyl groups, the signals of the atoms close to the coordinated atoms have even higher coordination chemical shifts $\Delta\delta = -0.06$ for $-NH-CH_2-$, -0.12 for $-CH-CONH-$ in compound **8b**; -0.1 for $-CH_2P$ in compound **9a**; -0.3 for $-NH-CH_2-$, $+0.45$ for $-CH_2P$ in compound **9b**. In compounds **10a**, **10b**, **11a** and **11b** the naphthyl protons resonances are shifted -0.4–0.1 ppm upfield. The $-NH-CH_2-$ signal for compound **11b** is shifted 0.4 ppm upfield on coordination, but the cyclooctadiene shows resonances in the expected positions. The COD vinylic hydrogen atoms give rise to a broad signal ($\delta = 4.24$, 4.21 for the complexes **8a**, **8b**, 4.2, 4.1 for **9a**, **9b**, 4.1 for **10a** and 4.25, 4.1 for **11a**, **11b**), shifted upfield with respect to the original dimer ($\delta = 4.3$ ppm). The two signals for the methylene protons, at 2.5–2.4 ppm and 1.9–1.8 ppm are also shifted with respect to the starting dimer (2.6–1.7), which suggests the presence of only one COD molecule. Heteronuclear COSY experiments of the compounds are consistent with the proposed structures, and they confirm the assignments. We have not observed any correlation through the metal. An example is shown in Fig. 1.

The ^{13}C NMR spectra of the carbon atoms close to the metal show a higher coordination chemical shifts, $\Delta\delta = -0.05$, -0.07 for *C*-*t*-Bu and -0.06, -0.12 for CH_3 groups in compound **8a**, the ring carbons are shifted $+0.47$, -0.12. Compound **9a** has a high shift for the aromatic carbons (-6.15, -1.85, $+0.12$ ppm), the *C*-*t*-Bu shifts $+2.8$ downfield and $-CH_2P$ shifts -6.04 on coordination. The ring carbons also show coordination shifts (-0.86, -1.01, -1.36). Compound **11a** has a shift for *C*-*t*-Bu of -4.4 ppm and -1.7 ppm for $-NH-CH_2-$. These spectra show no displacement of the CO resonances with respect to the free donors which indicates no coordinates by the CO groups. The

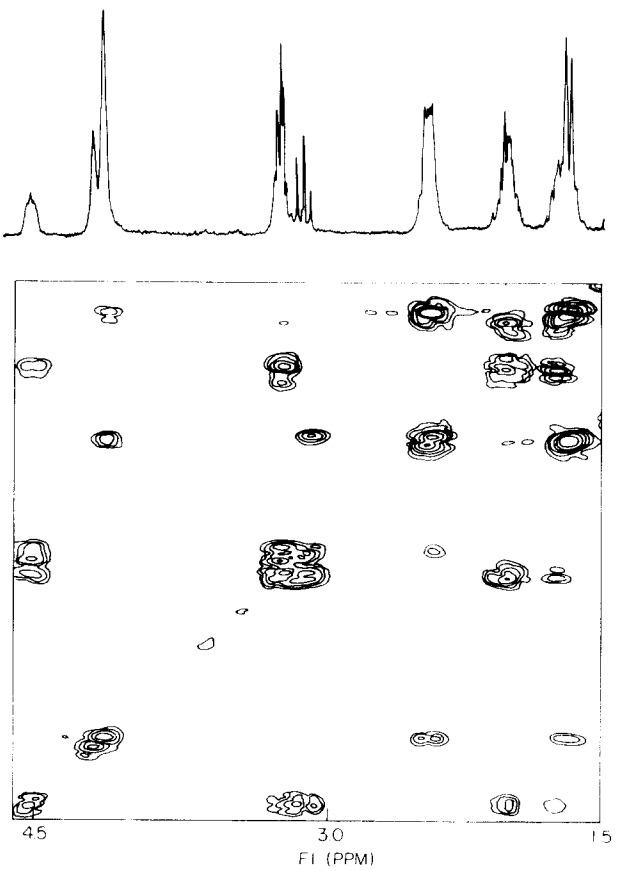


Fig. 1. COSY experiment of compound [Rh(COD)((S)1-t-Butylaminocarbonyl-2-(1-naphthylaminomethyl)pyrrolidine)][PF_6] (**11a**).

coordination chemical shifts of the COD are $\Delta\delta^{13}C(C=C)$ of -50 and $\Delta\delta^{13}C(CC)$ at 2.5. With resonances for uncoordinated cyclooctadiene at $\delta = 128.8$ ppm and $\delta = 28.5$ ppm. These values are consistent with either a boat [13] or twist-boat conformation of the COD [14].

The ^{31}P NMR spectrum of **9a** shows a doublet at 26.8 and 21.8 ppm, and **9b** shows a doublet at 26.25 and 21.60 ppm, corresponding to phosphorus bonded to pyrrolidine coupled with the rhodium atom (J(P–Rh) = 151 Hz). The signal of [PF_6]$^-$ appears consistently at -143.6 ppm (J(P–F) = 714 Hz).

The conductivity data suggest 1 : 1 electrolytes [15].

Attempts to grow crystals of the cationic complexes for X-ray diffraction studies have so far been unsuccessful.

3.2.2. *[Rh(PPh$_3$)$_2$(ligand)][PF$_6$]*

The IR spectra of the various derivatives show phosphine free CO (1660–1650 cm^{-1}) bands and coordinated NH (ν(NH) = 3400–3200 cm^{-1}). We also observed the ν(PF) bands, but no Rh–Cl stretching vibrations. Elemental analysis and ^{1}H NMR data clearly indicate the presence of two phosphine groups and one chiral ligand per Rh atom.

The NMR spectra of complexes are simple and

informative. These compounds have NMR coordination chemical shifts similar to those of the analogous COD-derivatives.

The ^{31}P NMR spectra of these complexes show a triphenylphosphine signal (double, $J(P-Rh) = 115$ Hz), and a $[PF_6]^-$ resonance at -143.8 ppm ($J(P-F) = 714$ Hz). The signal for the phosphorus bonded to pyrrolidine appears at 26.3 ppm and 21.7 ppm (doublet, $J(P-Rh) = 151$ Hz). These results are consistent with previous data.

3.2.3. Complexes supported on inorganic matrices

The supported complexes were obtained by the controlled hydrolysis of Si–OEt bonds of complexes **8–15b** and reaction of free silanols (Si–OH) on the surface of an inorganic matrix (silica and USY-zeolite). The resulting products are very stable.

The sequence of reactions we have followed for preparing the catalysts is: ligand → organometallic compound → anchored complex. The ligand- to -metal ratio may be rigorously controlled, the structure of the organometallic compound can be determined by conventional methods, and, once the complex is formed, it can easily be immobilized on the support. The structure of the metal species is maintained when it is attached to the surface, as confirmed by analytical and spectroscopic data. It is unlikely that the complex is substantially altered under the relatively mild conditions of the anchoring reaction. The supported complexes were characterized by elemental analysis (Table 1). The loading of the metal is always ca. 1%. IR spectroscopy confirms that the soluble complex has not been altered by anchoring.

The supported complexes can be used as catalysts, combining the advantages of the homogeneous catalysts with the easy handling of the heterogeneous catalysts. Much work has been done with organic polymers as macromolecular supports, whereas inorganic matrices, such as silica and zeolites, have been utilized less although they have physical properties that offer considerable advantages as supports for large-scale applications [16]. The inorganic matrices are mechanically rigid and remain unaffected by the most severe solvent and temperature conditions.

Metal-containing zeolite materials have long been used as catalyst systems. A zeolite catalyst species can exhibit properties different from those of simple oxide-bound ones. This may derive from "the molecular sieve" property of the zeolite microcrystals, concentration effects, and from the possibility that the three-dimensional nature of the supercage can influence substrate-catalyst interactions. For example, silica-supported rhodium hydride complexes catalyse hydrogenation of substituted olefins with relative rates depending solely on local steric congestion about the double bond. Whereas *Z*-complexes exhibit high catalytic activity for olefin hydrogenation, size and shape selectivity for the substrate (attributed to the "molecular sieve" nature of the zeolite support) was also noted [17]. Of particular interest to us is the possibility that the cage environment has an effect on the reactivity of substrate molecules through specific substrate and environment interactions.

4. Reactivity

The experimental conditions for the catalytic study are detailed in the experimental section.

4.1. Catalytic hydrogenation of simple olefins

Hex-1-ene, cyclohexene, and 1-methylcyclohexene were hydrogenated in the presence of catalysts **8**, **9**, **12**, **13a** and the corresponding silica and zeolite heterogenized complexes. In all experiments with *soluble* catalysts we observed an induction period, depending on the catalyst, from 5 to 10 min for hex-1-ene and cyclohexene, and higher for methyl cyclohexene. The maximum rates of hydrogenation were in the order: hex-1-ene > cyclohexene ≫ 1-methylcyclohexene.

Amongst the *soluble* catalysts, the phosphine derivatives were found to have the highest activity, but their composition changes with the reaction time, and the maximum rates correspond to the initial rates. By anchoring complexes to a silica and zeolite supports, the activities in a single run increased.

Soluble complexes could be used only once, because they deteriorate completely by the end of the first catalytic run, but silica- or zeolite-complexes could be recovered for recycling, and used in further runs without loss of activity.

Complete absence of induction periods was also characteristic of those processes in which zeolite-supported catalysts were used. This implies that once the active species is formed it does not regenerate the starting catalyst even if the hydrogen source is removed.

In the homogeneous reactions, the colour gradually darkened, and sometimes brown or black particles of Rh(O) separated towards the end. If more olefin was added in this stage no hydrogenation occured. All the complexes were highly active hydrogenation catalysts. New bands in the IR spectra at 2040–2100 cm^{-1} suggest the formation of Rh^{III} hydrides.

Isomerization products (until 20% conversion) of hex-1-ene were detected at the initial stages of the reaction, during the induction period.

4.2. Hydrogenation of dehydroaminoacid derivatives

Z(α)-ethylacetamidocinnamate is the substrate of choice to test the efficiency of new optically active

ligands or catalysts. We carried out asymmetric hydrogenation by using complexes **9a**, **Sil-9b**, **Zeol-9b**. The results are summarized in Table 3. Homogeneous hydrogenation in EtOH with **9a** as catalyst proceded with 34.4% ee. The use of heterogenized silica and zeolite compounds gave values higher than the homogeneous systems. These catalysts are less stereoselective than previously described Rh complexes [7].

4.3. Hydroboration of styrene

The reaction of styrene with catechol borane in THF at various temperatures in the presence of 1 mol% of rhodium catalyst followed by oxidation gave 1-phenylethanol. The hydroboration of styrene was complete in less than 24 h. The regioselectivity forming 1-phenylethanol was greater than 99/1. Surprisingly under these reaction conditions, no enantioselectivity was found.

4.4. Hydrosilylation

The new rhodium complexes are also catalytically active in the hydrosilylation of styrene, and we have selectively obtained the β-addition products $PhCH_2CH_2Si(CH_3)_2Ph$ and $PhCH_2CH_2SiHPh_2$ (Table 4).

4.5. Cyclopropanation

The complexes isolated were also used as catalyst for cyclopropanation reactions by reported methods [18].

As shown in Table 5, the product of the cyclopropanation is a mixture of *cis/trans* isomers, the *trans* isomer being the main component. Diethyl fumarate and diethyl maleate were also formed in yields lower than 3%. The chemical yield is in the range 75–90% (100% if more ethyl diazoacetate was added). The enantiomeric excess if 0.1–2.4 for the *cis* isomer and 0–3.7 for the *trans* isomer.

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