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Journal of Organometallic Chemistry 601 (2000) 284–292

Journal of Organometallic Chemistry

Rh and Ir complexes containing multidentate, C_2-symmetry ligands. Structural and catalytic properties in asymmetric hydrogenation

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Received 9 December 1999; received in revised form 23 January 2000

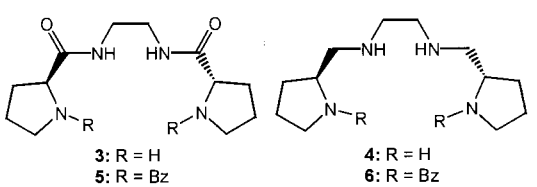
Abstract

A comparative investigation of the interaction of Rh(I) and Ir(I) with a series of mixed-donor multidentate, C_2-symmetry ligands has been carried out. The complexes have been prepared by the reaction of $[MCl(cod)]_2$ (cod = 1,5-cyclooctadiene) with $AgPF_6$ and further treatment with the ligand. All ligands form 1:1 (metal:ligand) species with the above metal ions although, in a few instances, species of type $[M_2L_2]^{2+}$ were also detected. The structures of these complexes were elucidated by analytical and spectroscopic data (elemental analysis, mass spectroscopy, IR, ^{1}H- and ^{13}C-NMR). Complexes were tested in the asymmetric hydrogenation of prochiral olefins, providing enantioselectivities up to 36%.

Keywords: Rhodium; Iridium; Asymmetric hydrogenation; Multidentate ligands

1. Introduction

Nitrogen-containing ligands are being used more and more in asymmetric catalysis [1]. They turn out to be suitable for any type of catalysis and especially for heterogeneous catalysis, which is one of their main advantages over phosphines. If we consider the latest new methodologies developed to obtain easy separation of the catalyst from the reaction products (i.e. heterogeneous catalysts with modifiers, homogeneous supported catalysts, liquid polyphasic catalysts, molecular imprinting…), nitrogen-containing ligands appear to offer many more possibilities than phosphorus compounds. Serious attempts are now being made to evaluate the possibilities of these ligands in both catalytic systems where the efficiency of phosphines has already been demonstrated and for new specific catalytic reactions. This last point, especially when non-precious transition metals are used, offers a great potential interest.



3: R = H
5: R = Bz

4: R = H
6: R = Bz

Fig. 1. C_2-symmetry ligands.

C_2-symmetric diamines could be used in carbonyl reduction by hydride transfer with more than 99% ee [2]. It is noticeable that even groups known for their work on the use of chiral phosphines have turned their attention to nitrogen-containing ligands. Thus, in 1995, Noyori and his group used a synergetic effect of diamines and phosphines in carbonyl reduction by hydrogenation with molecular H_2 [3]. Chiral diureas with the C_2-diamine basic structure gave also promising results [4]. Nitrogen-containing ligands may be used in asymmetric catalysis with transition metals less expensive than noble metals. Thus, semicorrins were used in cobalt complexes by Pfaltz and co-workers [5] for the reduction of α,β-unsaturated molecules with $NaBH_4$.

With these facts in mind (nitrogen ligands as efficient alternatives to phosphorus ligands and the importance of the C_2-symmetry of the ligands), we decided to

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0022-328X/00/$ - see front matter
PII: S0022-328X(00)00083-8

investigate the preparation and use, as catalytic precursors in some enantioselective reactions, of rhodium(I) and iridium(I) cationic complexes containing C_2-symmetry ligands. In previous papers we have conducted an extensive study of the synthesis of new chiral ligands in order to apply them in asymmetric synthesis. For that purpose, special efforts have been devoted toward the synthesis of easily accessible ligands based on natural aminoacids [6]. These ligands have been applied with success in asymmetric catalysis like addition of diethylzinc to enones [7], hydrogenation [8], cyclopropanation [9] and oxidation of olefins [10]. Here, we report on the preparation of some chiral multidentate, C_2-symmetry ligands (Fig. 1) and their Rh(I) and Ir(I) complexes, structural data for the ligands and complexes, and catalytic properties of the new metal complexes. The complexes have proven to be active in the asymmetric hydrogenation of prochiral olefins at 4 bar and 313 K. A motivation for the present study was to investigate the effect on complex formation of the structural variation that occurs along this series of ligands.

2. Experimental

All preparations of organometallic complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. The starting complexes $[Rh(cod)Cl]_2$ and $[Ir(cod)Cl]_2$ were prepared according to the literature methods [11,12]. All solvents were carefully degassed before use. C, H and N analysis was carried out by the analytical department of the Institute of Materials Science (CSIC) with a Perkin–Elmer 240 apparatus. Metal contents were analysed by atomic absorption using a Unicam Philips SP9 apparatus and a plasma ICP Perkin–Elmer 40. Mass spectra were performed on a Hewlett–Packard 1100 MSD mass spectrometer (ESI-MS, APCI-MS) with positive mode and VG-Autospec (FAB^+). IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^1H and ^{13}C spectra were taken on Varian XR300 and Bruker 200 spectrometers, repectively. ^1H-NMR chemical shifts are given in ppm using tetramethylsilane as an internal standard. High-resolution ^{13}C-MAS or CP/MAS-NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and 5–10 ms recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 KHz. Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin–Elmer 241 MC polarimeter. Gas chromatography analysis was performed using a Hewlett–Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column [13].

2.1. Synthesis of ligands

2.1.1. *N,N′-Bis[(S)-N-benzyloxycarbonyl-prolyl]ethylenediamine (2)*

To a solution of (*S*)-*N*-benzyloxycarbonylproline (**1a**) (3.7 g, 14.8 mmol) and triethylamine (1.5 g, 14.8 mmol) in THF (80 ml), ice-cooled ethyl chloroformate (1.6 g, 14.8 mmol) was added dropwise with vigorous stirring. When the addition was finished the pasty reaction mixture was stirred for 30 min (temperature 5–10°C), and a very reactive mixed anhydride was obtained. To the anhydride solution, ethylenediamine (0.5 ml, 7.4 mmol) in THF (5 ml) was added dropwise for 15 min and the mixture was stirred at 0°C for 1 h, and filtered. The solvent was evaporated and the residue extracted with ethyl acetate and washed successively with water, aqueous $NaHCO_3$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give 3.6 g (94%) of **2**. M.p. 163–164°C. $[\alpha]_D^{20}$ −42.4° (*c* 1, CH_2Cl_2). $C_{28}H_{34}N_4O_6$ (522): calc. C, 64.4; H, 6.6; N, 10.7. Found: C, 64.6; H, 6.8; N, 11.0%. IR (cm^{-1}): $\nu = 3380$, 3340 (NH); 1710 ($C{=}O_{Cbz}$); 1670 (amide I); 1530 (amide II). ^1H-NMR ($CDCl_3$, 50°C): δ 7.35–7.26 (m, 10H, Ph); 7.26–6.53 (s, br, 2H, N–H); 5.18 (d, 2H, 12.5 Hz, OCH_2Ph); 5.10 (d, 2H, 12.5 Hz, OCH_2Ph); 4.24–4.21 (m, 2H, H_2); 3.57–3.34 (m, 4H, H_5); 3.20–3.19 (m, 4H, CH_2–NH); 2.17–2.15 (m, 2H, H_3); 2.07–1.96 (m, 4H, $H_{3'}$, H_4); 1.89–1.83 (m, 2H, $H_{4'}$). ^{13}C-NMR ($CDCl_3$, 50°C): δ 172.90 ($C{=}O_{amide}$); 155.37 ($C{=}O_{ester}$); 136.49 (C_{Ph}–R); 128.38–127.68 (C_{Ph}–H); 67.06 (OCH_2Ph); 60.79 (C_2); 47.07 (C_5); 39.22 (CH_2–NH); 29.22 (C_3); 24.43 (C_4). MS (*m*/*z*, %): 522 [M^+, 0.5]; 306 (43); 204 (3); 108 (77); 79 (100); 77 (63); 70 (37).

2.1.2. *N,N′-Bis[(S)-prolyl]ethylenediamine (3)*

A mixture of *N,N′*-bis[(*S*)-*N*-benzyloxycarbonylprolyl]ethylenediamine (**2**) (1 g, 1.9 mmol), cyclohexene (0.31 g, 3.8 mmol) and 180 mg of commercial Pd–C (10%) in 20 ml of ethanol was heated under reflux for 1 h in argon, cooled and filtered over Celite. The catalyst was washed with ethanol, and the filtrate and wash liquids were evaporated under reduced pressure to give 405 mg of **3**. Yield: 0.46 g (94%). M.p. 92–93°C. $[\alpha]_D^{20}$ −76.8° (*c* 1, CH_2Cl_2). $C_{12}H_{22}N_4O_2$ (254): calc. C, 56.7; H, 8.7; N, 22.0. Found: C, 56.30; H, 8.6; N, 22.3%. IR (KBr, cm^{-1}): $\nu = 3278$ (NH); 1646 (amide I); 1552 (amide II). ^1H-NMR ($CDCl_3$, 50°C): δ 7.81–7.63 (s, br, 2H, N–H); 3.67 (dd, 2H, 5.1, 8.9 Hz, H_2); 3.36–3.34 (m, 4H, CH_2–NH); 2.97 (ddd, 2H, 10.2, 6.6, 7.0 Hz, H_5); 2.88 (ddd, 2H, 10.2, 5.4, 7.3 Hz, $H_{5'}$); 2.6–2.3 (s, br, 2H, N–H); 2.16–2.02 (m, 2H, H_3); 1.94–1.82 (m, 2H, $H_{3'}$); 1.72–1.63 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50°C): δ 175.81 (C=O); 60.61 (C_2); 47.05 (C_5); 39.05 (CH_2–NH); 30.56 (C_3); 25.96 (C_4). MS (*m*/*z*, %): 255 ([$M^+ + 1$], 5.62); 185 (15); 157 (6); 142 (5); 115 (2); 98 (5); 70 (100).

2.1.3. *N,N′-Bis{[(S)-pyrrolidin-2-yl]methyl}-ethylenediamine (4)*

To a solution of *N,N′*-bis[(*S*)-prolyl]ethylenediamine (**3**) (1 g, 4 mmol) in THF (25 ml) ice-cooled Li[AlH_4] (1.4 g, 36 mmol) was added dropwise. When the addition was finished the reaction mixture was stirred for 24 h under reflux. The reaction products were analysed by GC–MS. The product was isolated as an air-sensitive yellow oil. Yield: 0.62 g (70%). $[\alpha]_D^{20}$ +19.3° (*c* 5.5, CH_2Cl_2). $C_{12}H_{26}N_4$ (226): calc. C, 63.7; H, 11.5; N, 24.8. Found: C, 63.8; H, 11.2; N, 24.4%. IR (film, cm^{-1}): $\nu = 3288$ (N–H). ^{1}H-NMR ($CDCl_3$, 50°C, D_2O): δ 3.18–3.11 (m, 2H, H_2); 2.93–2.71 (m, 4H, H_5); 2.70–2.65 (m, 4H, CH_2–NH); 2.57 (dd, 2H, 4.9 Hz, 11.6 Hz, H_6); 2.48 (dd, 2H, 7.9 Hz, 11.6 Hz, $H_{6'}$); 1.87–1.73 (m, 4H, H_3); 1.73–1.59 (m, 4H, $H_{4'}$). ^{13}C-NMR ($CDCl_3$, 50°C): δ 58.17 (C_2); 54.72 (C_6); 49.36 (NH–*C*H_2–*C*H_2–NH); 46.11 (C_5); 29.43 (C_3); 25.35 (C_4). MS (*m*/*z*): 227 [$M^+ + 1$], 156, 113, 84, 70.

2.1.4. *N,N′-Bis[(S)-N-benzylprolyl]ethylenediamine (5)*

To a solution of *N,N′*-bis[(*S*)-prolyl]ethylenediamine (**3**) (1 g, 4 mmol) and triethylamine (0.8 g, 1.12 ml, 8 mmol) in ice-cooled THF (25 ml), benzyl bromide (1.37 g, 0.95 ml, 8 mmol) was added dropwise with vigorous stirring. When the addition was finished the reaction mixture was stirred for 2 h at 0°C. The solvent was evaporated and the residue extracted with ethyl acetate and washed successively with water, aqueous $NaHCO_3$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give **5** as a white solid. The product was purified by flash chromatography with 1:1 THF–hexane. Yield: 1.63 g (97%); m.p. 103–104°C. $[\alpha]_D^{20}$ −67.2° (*c* 1, CH_2Cl_2). $C_{26}H_{34}N_4O_2$ (434): calc. C, 71.9; H, 7.9; N, 12.9. Found: C, 72.1; H, 7.7; N, 12.7%. IR (KBr, cm^{-1}): $\nu = 3312$ (NH); 1656 (amide I); 1524 (amide II). ^{1}H-NMR ($CDCl_3$, 50°C): δ 7.62–7.49 (s, br, 2H, N–H); 7.38–7.15 (m, 10H, Ph); 3.79 (d, 12.9 Hz, 2H, CH_2Ph); 3.51 (d, 12.9 Hz, 2H, CH_2Ph); 3.37–3.28 (m, 4H, HN–CH_2–CH_2–NH); 3.22–3.13 (m, 2H, H_2); 3.08–2.99 (m, 2H, H_5); 2.42–2.32 (m, 2H, $H_{5'}$); 2.26–2.11 (m, 2H, H_3); 1.91–1.78 (m, 2H, $H_{3'}$); 1.78–1.61 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50°C): δ 175.18 (C=O); 138.42 (C_{Ph}–R); 128.70–127.21 (C_{Ph}–H); 67.15 (C_2); 59.88 (CH_2Ph); 54.01 (C_5); 38.81 (HN–*C*H_2–*C*H_2–NH); 30.75 (C_3); 24.05 (C_4). MS (*m*/*z*): 435 [$M^+ + 1$]; 252, 91.

2.1.5. *N,N′-Bis{[(S)-N-benzyl-pyrrolidin-2-yl]methyl}ethylenediamine (6)*

The diamine **6** was prepared by a procedure similar to that given for **4** starting from *N,N′*-bis[(*S*)-*N*-benzylprolyl]ethylenediamine (**5**) (1.74 g, 4 mmol). The product was isolated as an air-sensitive yellow oil. Yield: 1.42 g (87%). $[\alpha]_D^{20}$ +23.6° (*c* 1, CH_2Cl_2). $C_{26}H_{38}N_4$ (406): calc. C, 76.8; H, 9.4; N, 13.8. Found: C, 76.2; H, 9.4; N, 13.6%. IR (film, cm^{-1}): $\nu = 3360$ (N–H). ^{1}H-NMR ($CDCl_3$, 50°C): δ 7.58–7.12 (m, 10H, Ph); 3.93 (d, 12.9 Hz, 2H, CH_2Ph); 3.23 (d, 12.9 Hz, 2H, CH_2Ph); 2.93–2.78 (m, 2H, H_5); 2.20–2.02 (m, 2H, $H_{5'}$); 2.73–2.42 (m, 10H, HN–CH_2–CH_2–NH, H_6, H_2); 2.20–2.02 (m, 2H, $H_{5'}$); 2.02–1.75 (m, 4H, H_3); 1.75–1.56 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50°C): δ 139.9 (C_{Ph}–R); 128.9–126.7 (C_{Ph}–H); 63.8 (C_2); 59.4 (*C*H_2-Ph); 54.5 (C_5); 53.1 (C_6); 49.7 (HN–*C*H_2–*C*H_2–NH); 29.2 (C_3); 22.8 (C_4). MS (*m*/*z*): 407 [$M^+ + 1$], 316, 225, 91.

2.2. Preparation of *{[M(C$_2$-ligand)(THF)]PF$_6$}$_n$ complexes (M = Rh, Ir; n = 1, 2) (I–VIII)*

Only the preparation of {[Rh(**3**)$(THF)_2$]PF_6}$_2$·THF (**I**) is described in detail, the experimental procedure being the same for all the other complexes. Silver hexafluorophosphate (0.4 mmol) in THF (40 ml) was added to $[Rh(cod)Cl]_2$ (0.2 mmol) in THF (10 ml) and the mixture was stirred vigorously at room temperature for 30 min. Precipitated silver chloride was filtered off and the yellow solution was treated with the ligand (0.4 mmol) in THF. The mixture was stirred for 24 h under reflux. The solvent was evaporated under reduced pressure to 2 ml. Careful addition of diethyl ether caused the precipitation of a yellow–orange solid which was collected by filtration, washed with diethyl ether and dried under vacuum (10^{-3} mmHg) to give the yellow cationic complex. Yield: 68%; m.p. > 230°C. $C_{24}H_{44}F_{12}N_8O_4P_2Rh_2$·5THF (1365): calc. C, 38.7; H, 6.2; N, 8.2; Rh, 15.1. Found: C, 38.5; H, 6.3; N, 8.6; Rh, 14.6%. IR (KBr, cm^{-1}): $\nu = 3400$, 3200 (N–H); 1670, 1600 (amide I); 1550 (amide II); 840 (P–F). ^{13}C-NMR (solid): δ 183.95, 168.66 (C=O); 76.33 (C_2); 65.29 (C_5); 30.47 (*C*H_2–NH, C_3, C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 378 nm (3.37), 292 (3.93). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 142–158. MS^+ (*m*/*z*): 821 ({[Rh(**3**)]PF_6}$_2$ − PF_8); 675 ({[Rh(**3**)]PF_6}$_2$ − **3** − 4F); 465 ({[Rh(**3**)]PF_6}$_2$ − **3** − 2PF_6); 255 (**3** + 1).

Complexes **II–VIII** were prepared through a procedure similar to that given for (**I**) using 0.2 equivalents of $[Rh(cod)Cl]_2$ or $[Ir(cod)Cl)]_2$ and 0.4 equivalents of the appropriate ligand.

2.2.1. *[Rh(4)(THF)$_2$]PF$_6$ (II)*

Yellow. Yield: 61%; m.p. > 230°C. $C_{12}H_{26}F_6N_4$-PRh·2THF (618): calc. C, 38.8; H, 6.9; N, 9.1; Rh, 16.6. Found: C, 38.7; H, 6.3; N, 8.7; Rh, 16.3%. IR (KBr, cm^{-1}): $\nu = 3400$, 3260 (N–H); 840 (P–F). ^{13}C-NMR (solid): δ 59.33 (C_2); 50.12 (br, NH–*C*H_2–*C*H_2–NH, C_6, C_5); 27.34 (br, C_3, C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 377.5 (2.36); 288.5 nm (3.39), 292 (3.93). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 132–143. MS^+ (*m*/*z*): 455 ([Rh(**4**)]PF_6 − F); 329 ([Rh(**4**)]$^+$).

*2.2.2. {[Rh(**5**)(THF)]PF_6}$_2$ (**III**)*

Yellow. Yield: 68%; m.p. 123–126°C. $[\alpha]_D^{20}$ −60° (*c* 0.5, EtOH); $C_{52}H_{68}F_{12}N_8O_4P_2Rh_2{\cdot}2THF$ (1504): calc. C, 47.9; H, 5.6; N, 7.4; Rh, 13.7. Found: C, 48.4; H, 5.3; N, 7.2; Rh, 13.3%. IR (KBr, cm^{-1}): $\nu = 3376$, 3260 (N–H); 1660, 1612 (amide I); 1526 (amide II); 834 (P–F). ^{13}C-NMR (solid): δ 183.7, 177.04 (C=O); 129.47 (Ph); 66.62 (C_2, CH_2Ph, C_5); 28.28 (CH_2–NH, C_3, C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 348.0 nm (3.27), 289.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 144–157. MS^+ (*m*/*z*): 855 ({[Rh(**5**)]PF_6}$_2$} − PF_6 − 4Bz); 663 ([Rh(**5**)]PF_6 − F); 435 ((**5**) + 1).

*2.2.3. [Rh(**6**)]PF_6 (**IV**)*

Yellow. Yield: 67%; m.p. 165–170°C (dec.). $C_{26}H_{38}F_6N_4PRh$ (654.5): calc. C, 47.7; H, 5.9; N, 8.6; Rh, 15.7. Found: C, 47.3; H, 5.6; N, 8.1; Rh, 15.2%. IR (KBr, cm^{-1}): $\nu = 3420$ (N–H); 850 (P–F). ^{13}C-NMR (solid): δ 140–125 (C_{Ph}–R, C_{Ph}–H); 65.1 (C_2); 60–45 (CH_2Ph, C_5, C_6, HN–CH_2–CH_2–NH); 29.0 (C_3); 22.0 (C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 375.9 nm (2.64); 288.0 (3.32). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 146–159. MS^+ (*m*/*z*): 635 ([Rh(**6**)]PF_6–F); 404 ((**6**) − 2).

*2.2.4. [Ir(**3**)(THF)]PF_6 (**V**)*

Brick-red. Yield: 61%; m.p. > 230°C. $C_{12}H_{22}F_6IrN_4O_2P{\cdot}THF$ (664): calc.: C, 29.0; H, 4.6; N, 8.4; Ir, 29.0. Found: C, 28.9; H, 4.6; N, 8.9; Ir, 28.6%. IR (KBr, cm^{-1}): $\nu = 3360$ (N–H); 1670 (amide I); 1560 (amide I, II); 850 (P–F). ^{13}C-NMR (solid): δ 168.7 (C=O); 60.7 (C_2); 46.3 (C_5); 39.4 (CH_2–NH); 30.1 (C_3); 25.2 (C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 410.5 nm (3.13), 287.5 (3.46). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, DMF) 145. MS^+ (*m*/*z*): 664 ([Ir(**3**)(THF)]PF_6); 591 ([Ir(**3**)]PF_6); 572 ([Ir(**3**)]PF_6–F); 553 ([Ir(**3**)]PF_6–2F); 255 (**3** + 1).

*2.2.5. [Ir(**4**)(THF)]PF_6 (**VI**)*

Brick-red. Yield: 65%; m.p. > 230°C. $C_{12}H_{26}F_6IrN_4P{\cdot}THF$ (636): calc. C, 30.2; H, 5.4; N, 8.8; Ir, 30.2. Found: C, 30.3; H, 5.0; N, 8.9; Ir, 29.5%. IR (KBr, cm^{-1}): $\nu = 3440$ (N–H); 850 (P–F). ^{13}C-NMR (solid): δ 60.0–40.0 (C_2, NH–CH_2–CH_2–NH, C_6, C_5); 27.7 (C_3, C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 356 nm (2.97), 289 (3.21). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, DMF) 170. MS^+ (*m*/*z*): 655 ([Ir(**4**)(THF)]PF_6 + H_2O); 583 ([Ir(**4**)(H_2O)]PF_6); 543 ([Ir(**4**)]PF_6–F); 418 ([Ir(**4**)]$^+$).

*2.2.6. [Ir(**5**)(THF)]PF_6 (**VII**)*

Light brown. Yield: 60%; m.p. 138–140°C. $C_{26}H_{34}F_6IrN_4O_2P{\cdot}THF$ (844): calc.: C, 42.7; H, 5.0; N, 6.6; Ir, 22.8. Found: C, 42.7; H, 4.6; N, 6.3; Ir, 22.4%. IR (KBr, cm^{-1}): $\nu = 3372$ (N–H); 1670 (amide I); 1560 (amide I, II); 850 (P–F). ^{13}C-NMR (solid): δ 167.0 (C=O); 142.2 (C_{Ph}–R); 130.0–120.0 (Ph); 64.0 (C_2); 57.5 (CH_2Ph), 49.4 (C_5); 44.1 (CH_2–NH); 34.7 (C_3); 25.0 (C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ε) 399.5 nm (2.17); 289.0 (3.44). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 110. MS^+ (*m*/*z*): 627 ([Ir(**5**)]$^+$), 435 (**5**).

*2.2.7. [Ir(**6**)(THF)]PF_6 (**VIII**)*

Light brown. Yield: 61%; m.p. 135–140°C. $C_{26}H_{38}F_6IrN_4P{\cdot}THF$ (816): calc.: C, 44.2; H, 5.8; N, 6.9; Ir, 23.6. Found: C, 44.0; H, 5.7; N, 7.0; Ir, 23.1%. IR (KBr, cm^{-1}): $\nu = 3450$ (N–H); 845 (P–F). ^{13}C-NMR (solid): δ 138.7 (C_{Ph}–R); 130–125 (C_{Ph}–H); 65–45 (C_2, CH_2Ph, C_5, C_6, HN–CH_2–CH_2–NH); 30.0–20.0 (C_3, C_4). UV–vis (DMF, 10^{-3} M): λ_{max} (log ϵ) 352.3 nm (2.47); 288.0 (3.32). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN) 115. MS^+ (*m*/*z*): 725 ([Ir(**6**)]PF_6 − F); 706 ([Ir(**6**)]PF_6 − 2F); 407 (**6**).

*2.3. Preparation of {[Rh(CO)$_2$(**ligand**)]PF_6}$_n$ (n = 1, 2)*

Carbon monoxide (3 ml min^{-1}) was bubbled through a thoroughly stirred dichloromethane solution of the corresponding Rh complex for 3 h, during which period colour intensification occurred. The precipitated complexes were filtered off, washed with diethyl ether and vacuum dried (10^{-3} mmHg). Yield: > 95%.

2.4. Catalytic experiments

The catalytic properties, in hydrogenation reactions, of the above Rh and Ir complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 ml capacity at 313 K temperature, 4 atm dihydrogen pressure and a metal:substrate molar ratio of 1:500. The results were monitored by GLC. The kinetics results are shown in Table 1.

3. Results and discussion

3.1. Synthesis and characterisation of ligands

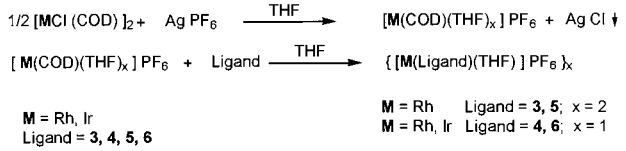
The ligands were prepared and well characterised by modifying the synthesis described previously [14]. All reaction steps were fine tuned for high yield and selectivity. The preparation of the diamides *N*,*N*′-bis[(*S*)-prolyl]ethylenediamine (**3**) and *N*,*N*′-bis[(*S*)-*N*-benzylprolyl]ethylenediamine (**5**) was achieved starting from the easily available L-proline, protected as the *N*-carbobenzyloxy (**1a**) or *N*-benzyl (**1b**) derivative, according to Scheme 1. The corresponding amines *N*,*N*′-bis{[(*S*)-pyrrolidin-2-yl]methyl}ethylenediamine (**4**) and *N*,*N*′-bis{[(*S*)-*N*-benzyl-pyrrolidin-2-yl]methyl}ethylenediamine (**6**) were obtained by reduction of the respective amide with lithium aluminium hydride. The ligands have two optically active centres; both have the *S*

Table 1
Asymmetric hydrogenation of diethyl 2-methylbut-2-enedioate (cat./subs. = 1/500, $T = 313$ K; $pH_2 = 4$ atm)

Catalyst	Induction time (min)	Conversion (%)	TOR [a]	Optical yield [b] (% ee)
I	30	78	304	5.5
II	15	80	405	20.0
III	30	82	800	4.2
IV	5	94	1467	21.5
V	3	100	6800	36.0
VI	0	85	5000	35.4
VII	0	78	5000	9.0
VIII	0	95	6333	19.5

[a] mmol substrate mmol cat.$^{-1}$ min^{-1}.
[b] Optical yield was determined by GLC using capillary a chiral column based on alkylated cyclodextrins [13].

absolute configuration. All intermediates and final products has been obtained with a total yield of >80%. Diamides **3** and **5** were isolated as white solids and amines **4** and **6** were isolated as colourless oils that are stable at low temperature in an inert atmosphere. The ligands were characterised unequivocally by mass spectrometry, IR, and ^{1}H- and ^{13}C-NMR spectroscopy and gave satisfactory elemental analyses. Mass spectrometry shows the highest ions at m/z 254, 226, 434 and 406, which corresponds to the molecular weights of compounds **3–6**, respectively. The ^{1}H- and ^{13}C-NMR spectra obtained are in agreement with those expected for these C_2-symmetrical ligands.



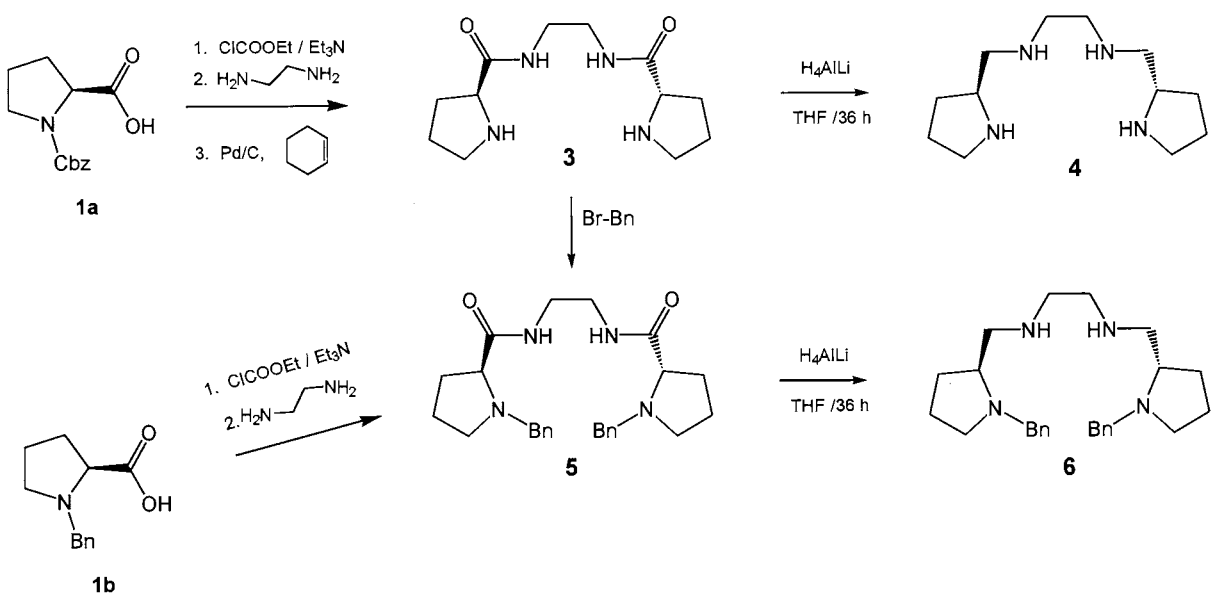
Scheme 2.

3.2. Synthesis of metal complexes

The complexes $\{[M(ligand)(solvent)]PF_6\}_n$ (M = Rh, Ir; $n = 1$, 2) **I–VIII**, have been prepared as shown in Scheme 2 following a general procedure.

The dimeric $[M(cod)Cl]_2$ and two equivalents of $AgPF_6$ were reacted in THF for 2 h and the precipitated AgCl was filtered off. The ligand was added to the filtrate containing the cationic mononuclear $[M(cod)(THF)_x]PF_6$ complex. The isolated complexes, **I–VIII**, were characterised by elemental analysis, mass spectrometry (FAB^+, ESI-MS and APCI-MS with positive mode), IR and ^{13}C-NMR spectroscopy, which present values in accordance with the proposed structures depicted in Fig. 2.

Thus, the mononuclear complexes $[M(\mathbf{L})(THF)]PF_6$ (M = Rh, Ir) (**II**, **IV–VIII**) were prepared in good yield (>60%) by ligand exchange of **L** with $[M(cod)(THF)_2]PF_6$ in THF. The complexes were isolated as yellow, microcrystaline, and air-stable solids. On the other hand, the dinuclear yellow complexes $\{[Rh(\mathbf{L})(THF)]PF_6\}_2$, (**I**, **III**), were obtained in 68% yield by reaction of $[Rh(cod)(THF)_2]PF_6$ and one equivalent of ligand (**3**, **5**) in THF. Mass spectrometry and elemental analysis of these products indicated a dimeric formula



Scheme 1.

($C_{24}H_{44}F_{12}N_8O_4P_2Rh_2$ (**I**), $C_{52}H_{68}F_{12}N_8O_4P_2Rh_2$ (**III**)), suggesting that two rhodium atoms were bound to two ligands in accordance with the results of the IR and NMR studies. These microcrystaline products are very stable but crystals suitable for X-ray analysis could not be obtained.

The IR spectra of the free ligands exhibit the characteristic bands of amides and amines. The amide I band appears at about 1650–1670 cm^{-1} and amide II at 1530–1550 cm^{-1}. The IR spectrum of dinuclear complex **I** show a ν(N–H) band at 3400 cm^{-1}, shifted to higher frequencies, due to Rh-coordinated NH of pyrrolidine ring and a broad band at 3200 cm^{-1} shifted to lower frequencies that corresponds to the ν(N–H) amide band. The amide I band was split at 1664 and 1600 cm^{-1}; the band at 1664 cm^{-1} was attributed to the uncoordinated keto function and the band at 1600 cm^{-1} shifted to lower frequencies and is due to the C=O group coordinated to the Rh atom. The amide II band appears in the same position as the free ligand. The ν(P–F) frequency appears at 840 cm^{-1}.

The IR spectrum of complex **III** shows ν(N–H) bands at 3376–3260 cm^{-1}. The amide I band splits in two, the band at higher frequencies (1660 cm^{-1}) corresponds to uncoordinated C=O group and the band shifted to lower frequencies (1612 cm^{-1}) indicates that exits Rh←O bond. The band at 1526 is attributed to amide–N coordination.

These complexes are almost insoluble in organic solvents and we have obtained the ^{13}C-MAS and CP/MAS-NMR spectra of powdered samples. The ^{13}C-NMR spectra of free ligands exhibits a single signal for the C=O at about 174–175 and in the spectra of Rh–amide complexes (**I**, **III**) two peaks are found for the amide carbons. The spectrum of dinuclear complex **I** displays two separate resonances at 184.0 and 168.7 ppm indicating the presence of two inequivalent C=O moieties which is in agreement with the structural proposal show in Fig. 2. The signal at 184.0 ppm is downfield shifted as corresponds to C=O coordination and the signal at 168.7 shifted at high field due to *N*-amide coordination and the existence of intermolecular –C=O···HN– interaction (as we have determined by X-ray analysis in the analogous Cu complex [15]). This shift to high field indicates a higher electron density in this complex. The ^{13}C-NMR spectrum of complex **III** also shows two carbonyl signals at 183.7 and 177.0 ppm. The signal downfield shifted (+8.5 ppm) corresponds to the Rh←O=C– bond and the resonance at 177.0 ppm with a low high field shift (−1.9) corresponds to amide–N coordination.

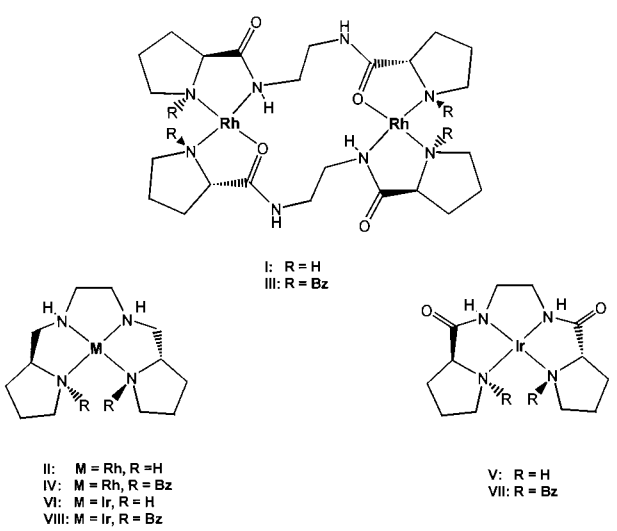


Fig. 2. Proposed structures for the rhodium and iridium complexes **I**–**VIII**.

The IR spectra of Rh–amine complexes (**II**, **IV**) show ν(N–H) bands shifted at higher frequencies (3400 cm^{-1}) and medium bands at 840 cm^{-1} characteristic of the non-coordinated PF_6^- anion. The ^{13}C-NMR spectra of these complexes show only small chemical shift differences compared with the free ligands.

The IR spectra of the mononuclear Ir complexes show the expected ν(N–H) bands shifted to higher frequencies. There is also no doubt that in the Ir–amide complexes (**V**, **VII**) the C=O unit of the amide groups is not involved in the coordination to the metal, since in the IR spectra only one C=O stretching frequency at 1670 cm^{-1} appears. The band at 1570 cm^{-1} is due to amide–N coordination. The ^{13}C-NMR spectra of **V**, **VII** exhibit only one signal for the amide carbons at δ 168.7, 167.0 ppm shifted at higher field (−7.1, −8.8 ppm) that indicates a high electron density in these complexes. In the Ir–amine complexes (**VI**, **VIII**) the ^{13}C-NMR signals show only small chemical shift differences compared with the free ligands.

Electronic absorption spectra of the rhodium and iridium complexes, measured between 800 and 200 nm, show a clear maximum at ca. 300 nm (ϵ 6000–8000) and one shoulder at ca. 400 nm (ϵ 1500–2000). Taking into account their energy position and intensity the bands at 400 nm could be assigned [16] to d–d transitions localised on the metal ion. At shorter wavelengths, the bands at 300 nm may be assigned to the Rh→ligand charge-transfer transition and intra-ligand transitions. The conductivity data suggest 1:1 electrolytes for all cationic complexes.

In order to confirm the nuclearity, the mass spectra of new complexes were examined. In the case of complex $\{[Rh(\mathbf{3})(THF)_2]PF_6\}_2 \cdot THF$ (**I**) the spectrum shows a peak at $m/z = 821$ (2) corresponding to a dinuclear cationic species; two peaks at $m/z = 675$ (98), 465 (100) correspond to the loss of a ligand and the PF_6 anion in the dinuclear complex. For complex $[Rh(\mathbf{4})(THF)_2]PF_6$ (**II**) the spectrum shows a peak at $m/z = 453$ (37) that corresponds with the molecular formula ($[Rh(\mathbf{4})]PF_6$); a

peak at 329 (41) corresponds to the mononuclear cationic species $[Rh(\mathbf{4})]^+$. In the case of complex $\{[Rh(\mathbf{5})(THF)]PF_6\}_2$ (**III**) the mass spectrum shows peaks at $m/z = 855$ and 661 that correspond, respectively, to the dinuclear species with loss of the PF_6 anion and the benzyl groups and the mononuclear complex. The spectrum of $[Rh(\mathbf{6})]PF_6$ (**IV**) shows a peak at $m/z = 635$, corresponding to the mononuclear cationic species; for all complexes solvent molecules are also lost. The iridium complexes are mononuclear species. Their mass spectra show peaks at m/z 664 for $[Ir(\mathbf{3})(THF)]PF_6$, 655 for $[Ir(\mathbf{4})(THF)]PF_6 \cdot H_2O$, 627 for $[Ir(\mathbf{5})]^+$ and 725 for $[Ir(\mathbf{6})]PF_6 - F$.

3.3. Reactivity towards H_2 and CO

Transition-metal hydride complexes have been the focus of considerable research because of their prominent role in many catalytic hydrogenation processes. The oxidative addition of hydrogen is, usually, the rate-determining step for the asymmetric hydrogenation of olefins using rhodium complexes, which contain chiral diphosphines and diphosphites. For this reason we believe that is interesting to study the reactivity of the diamide, amine complexes synthesised with the H_2. The corresponding *cis*-dihydrido complexes were formed at lower temperature, but they are only stable in solution under a H_2 atmosphere, to the effect that attempts at their isolation in crystalline form rapidly restored the starting product as the H_2-loss product. This behaviour has also been observed for related complexes; *cis*-$[IrH_2(cod)L_2]PF_6$ ($L = PMePh_2$, PPh_3, 0.5-dppe, PBu^n_3 or 0.5DIOP) also behave similarly [17].

On the other hand, we have also studied the reactivity of above described complexes towards CO. Thus, bubbling carbon monoxide through dichloromethane solutions of Rh–amide complexes leads to the displacement of the THF molecules and to the formation of the carbonyl derivatives. The $\{[Rh(\mathbf{3})(THF)_2]PF_6\}_2$ complex maintains its dimer structure in the carbonyl derivative; in effect, the mass spectra of this compound shows a peak at $m/z = 1116$ that corresponds to $\{[Rh(\mathbf{3})(CO)_2]PF_6\}_2$, and peaks at 767, 639 corresponds to the loss of fluorine and anion PF_6, also, a peak at 413 is due to the mononuclear cationic species ($[Rh(\mathbf{3})(CO)_2]^+$). Also, the dimer $\{[Rh(\mathbf{5})(THF)]PF_6\}_2$ complex yields the carbonyl complex $[Rh(\mathbf{5})(CO)_2]PF_6$, which shows in their mass spectra peaks at m/z 891, that (corresponding to the loss of benzyl groups, anion PF_6 and four fluorine atoms) 662 that corresponds to the loss of four fluorine anions. Also, a peak at 593 is due to the mononuclear cationic species.

These carbonyl complexes exhibit in their IR spectra two symmetrical bands at 2070, 2000 cm^{-1} that correspond to two *cis*-carbonyls in the molecule and bands for uncoordinated keto group at 1674 cm^{-1}; these complexes do not present chelating keto groups in the IR spectra. The carbonyl stretching frequency is independent of the nature of the ligand. The value for the carbonyl stretch (2070, 2000 cm^{-1}) indicates a low electron density on the rhodium centre. The ^1H- and ^{13}C-NMR spectra show the signals corresponding to pyrrolidine protons and carbons slightly downfield shifted as well as broadened signals for the atoms spatially close to the metal. The two carbonyl ligands appear as a sharp single resonance at δ 190.6 ppm.

Rh–amine complexes and all Ir complexes do not react with CO, probably due to the stability of the tetracoordinated mononuclear structure of these compounds, which present ligands coordinated through the N–H–Rh bonds.

3.4. Catalytic activity

In the first stage, metal complexes were evaluated as catalysts in the hydrogenation of cyclohexene. In the presence of 1 mol% of catalysts in ethanol at 313 K under a pressure of 4 bar H_2, the substrate was fully converted to the alkane in 1 h. All complexes gave similar results.

Multidentate ligands **3–6** have been used in the rhodium, iridium asymmetric hydrogenation of diethyl 2-methylbut-2-enedioate at 313 K under 4 bar of H_2. Conversion and enantioselectivity results are shown in Table 1.

Investigation of enantioselective hydrogenation of diethyl 2-methylbut-2-enedioate was carried out to optimise parameters. The precision of gas chromatographic estimation of enantiomers allowed us to observe the influence of the temperature on the ee with high accuracy. We observed an increase in ee with decreasing temperature (8–9% ee at 293 K and 5–6% ee at 313–323 K). A second effect is seen in the influence of H_2 pressure. While several authors reported a pronounced decrease or even a reversal [18] of the enantioselectivity with increasing pressure, we found almost no dependence of ee on pH_2 between 1 and 10 atm.

In all experiments with these homogeneous catalysts we observed an induction period, depending on the catalyst, from 5 min for amine derivatives to 30 min for Rh–amide complexes **I**, **III** (Fig. 3). The reactivity and enantioselectivity of the hydrogenation of diethyl mesaconate turned out to be dependent on the type of chelate ring formed by the ligand with the rhodium metal. Chelating ligands forming a five-membered ring with *N*,*O*-coordination such as **3** and **5** gave only poor enantioselectivities of 5 and 4% ee, and low chemical yields (78 and 82%). With the ligands **4** and **6**, constituting a five-membered ring with *N*,*N*-coordination, an enantioselectivity of 20 and 21.5% ee and chemical yields of $> 80\%$ were obtained.

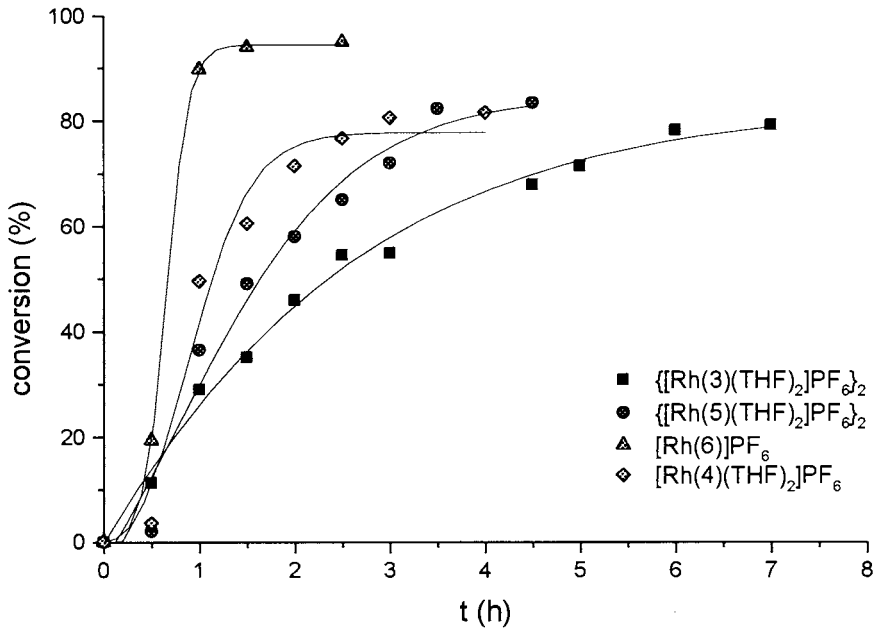


Fig. 3. Catalytic activity of the complexes **I–VIII** in the asymmetric hydrogenation of diethyl 2-methylbut-2-enedioate (cat./subs. = 1/500, $T = 313$ K; $pH_2 = 4$ atm).

Iridium complexes are more efficient than rhodium complexes. The hydrogenation with the iridium complexes is completed in 30 min with higher ee (36%). The higher ee obtained with iridium complexes could be due to the Ir-*N*,*N*-coordination (absence of the Ir–O bond for amide complexes).

On the other hand, some complexes of ruthenium with chiral nitrogen ligands were shown to be excellent catalysts for enantioselective transfer hydrogenation and the synthesis of Ru complexes with the multidentate ligands described here would be interesting.

4. Conclusions

A series of new microcrystalline air-stable rhodium and iridium complexes with multidentate C_2-symmetry ligands has been synthesised and characterised by spectroscopic methods. We have shown that these cationic Rh(I) and Ir(I) complexes are efficient catalysts for the hydrogenation of olefins. The complexes are easily handled and approaching up to 7000 turnover numbers could be achieved with the diethyl 2-methylbut-2-enedioate. Although the enantioselectivities are lower, our results indicate a considerable potential for this class of catalysts, which merits further investigation. We have heterogenised these compounds on inorganic supports and found that the corresponding zeolite-supported complexes are also promising catalysts for the enantioselective hydrogenation of C=C double bonds. The results of these studies will be reported in due course.

Acknowledgements

The authors are grateful for the financial support from Dirección General de Investigación Científica y Técnica of Spain (Project MAT97-1016-C02-02).

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