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Synthesis of Rh(I) and Ir(I) complexes with chiral C_2-multitopic ligands
Structural and catalytic properties

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Abstract

Four multitopic ligands, *N*,*N*′-bis[(*S*)-prolyl)phenylenediamine, *N*,*N*′-bis{[(*S*)-pyrrolidin-2-yl]methyl}phenylenediamine, *N*,*N*′-bis[(*S*)-*N*-benzylprolyl]phenylenediamine, *N*,*N*′-bis{[(*S*)-*N*-benzyl-pyrrolidin-2-yl]methyl}phenylenediamine, were synthesised and their co-ordination properties with Rh(I) and Ir(I) studied. The complexes were prepared by the reaction of $[MCl(cod)]_2$ with $AgPF_6$ and further treatment with the ligand. All ligands form one to one [ML] species with the above metal ions. The structures of these complexes were elucidated by analytical and spectroscopic data (elemental analysis, mass spectroscopy, IR, ^{1}H- and ^{13}C-NMR). Complexes show excellent activities and enantioselectivities up to 30% for the hydrogenation of prochiral olefins under mild reaction conditions.

Keywords: Rhodium; Iridium; Asymmetric hydrogenation; Multitopic ligands

1. Introduction

Catalytic asymmetric synthesis using organometallic complexes has become one of the most active areas of research in modern organic synthesis [1]. In this area the search for and development of new chiral complexes and a better understanding of their properties, play a fundamental role in revealing the mechanisms of catalytic processes [2].

The most commonly studied and employed organometallic complexes contain phosphorus ligands. This is mainly due to the excellent results obtained with phosphines in different catalytic reactions [1]. However, interest in nitrogen ligands has increased over the recent years because of their higher stability, easier preparation and promising results [3]. Nitrogen-containing ligands present several distinct advantages. First, they are largely available in enantiomerically pure form, both in the chiral pool and as cheap industrial chemical intermediates. The second advantage lies in the chemistry of the nitrogen functional group itself. The chemistry of nitrogen is not always easy but has received abundant attention such that there exist, in most cases, numerous synthetic solutions to each possible transformation of these compounds. As a result, these synthetic facilities allow tailor-made modifications toward the preparation of ligands with specific physicochemical properties.

C_2-symmetric diamines could be used in carbonyl reduction by hydride transfer with more than 99% ee [4]. 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 co-workers used a synergetic effect of diamines and phosphines in carbonyl reduction by hydrogenation with molecular H_2 [5]. Chiral diureas with the C_2-diamine basic structure also gave promising results [6]. Nitrogen-containing ligands may be used in asymmetric catalysis with transition metals less expensive than the noble metals. Thus, semicorrins were used in cobalt complexes by Pfaltz and co-workers [7] for the reduction of α,β-unsaturated molecules with $NaBH_4$.

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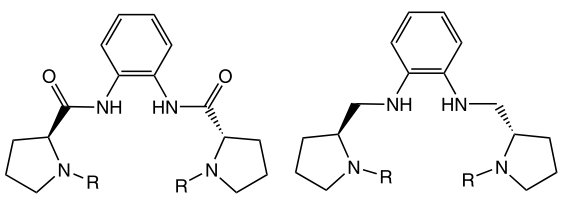
An extensive study of the synthesis of new chiral ligands to be applied in asymmetric synthesis has been carried out in our earlier papers. For that purpose, special efforts have been taken toward the synthesis of easily accessible ligands based on natural aminoacids [8]. These ligands have been applied with success in asymmetric catalysis like the addition of diethylzinc to enones [9], hydrogenation [10], cyclopropanation [11] and oxidation of olefins [12]. In this context we have developed the synthesis of a family of chiral C_2-multitopic ligands (Fig. 1) with rigidity in the backbone as an alternative to the more flexible family of C_2-nitrogen ligands that we have described recently [13]. To direct our research toward obtaining further information on the stability and structure of catalyst precursors, we report the preparation of new C_2-chiral ligands and their Rh(I) and Ir(I) complexes and investigate their co-ordination chemistry and catalytic properties in detail.

2. Results and discussion

2.1. Synthesis of ligands

The ligands were prepared and well characterised following a modified procedure described in Ref. [13]. All reaction steps were fine-tuned for high yield and selectivity. The preparation of diamides *N*,*N*′-bis[(*S*)-prolyl]phenylenediamine (**3**), and *N*,*N*′-bis[(*S*)-*N*-benzylprolyl]phenylenediamine (**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}phenylenediamine (**4**), *N*,*N*′-bis{[(*S*)-*N*-benzyl-pyrrolidin-2-yl]methyl}-phenylenediamine (**6**) were obtained by the reduction of the respective amide with lithium aluminium hydride or alternatively with sodium borohydride/trifluoroacetic acid in dioxane at reflux. All intermediates and final products have been obtained with a total yield of 70–80%. Diamides **3** and **5** are white solids while 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-, ^{13}C-NMR spectroscopy and gave satisfactory elemental analyses. Mass spectrometry shows the highest ions at m/z 302, 275, 484 and 455, 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. The ligands have two optically active centres; both have the *S* absolute configuration.



3: R = H **4:** R = H
5: R = Bn **6:** R = Bn

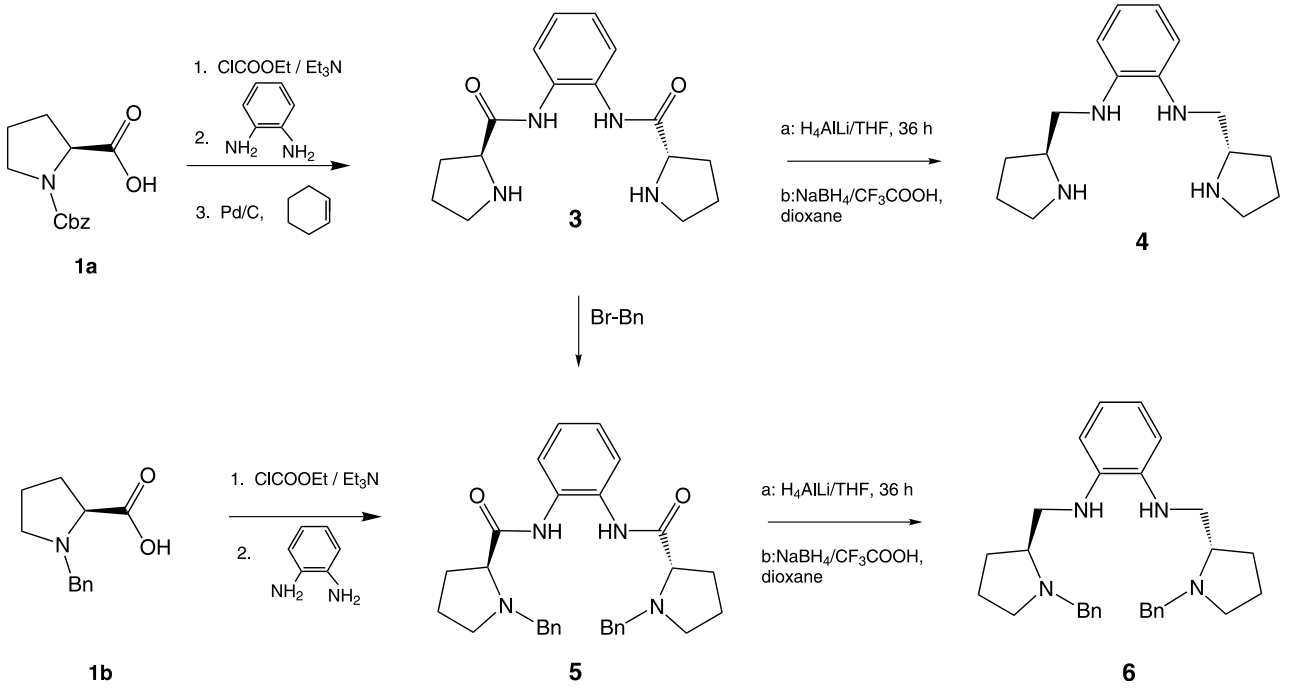
Fig. 1. C_2-multitopic ligands.

2.2. Preparation of complexes

The rhodium and iridium complexes [M(ligand)(L′)]PF_6 (L′ = cod, THF) (**7**–**14**), were obtained by treating the dimeric $[M(cod)Cl]_2$ with two equivalents of $AgPF_6$ in tetrahydrofurane. An equimolar amount of the corresponding multitopic ligands was added to the solution containing the cationic mononuclear $[M(cod)(THF)_x]PF_6$ species (Scheme 2). The mononuclear complexes [M(**L**)(L′)]PF_6 (M = Rh, Ir) were prepared in good yield (> 60%) by the ligand exchange of **L** with $[M(cod)(THF)_2]PF_6$ in THF. The complexes were isolated by precipitation from diethyl ether as microcrystaline air stable solids. Rhodium and iridium complexes were moderately unstable in solution and ^{13}C-NMR could be obtained only in the solid state. Elemental analysis of C, H, N and metal is consistent with the proposed stoichiometry (Fig. 2). Mass spectrometry (ESI-MS and APCI-MS with positive mode) indicated a monomeric formula in accordance with the results of IR and NMR studies. The complexes have their highest ions at m/z values corresponding to the loss of F^-, and PF_6^- in the molecular species.

The IR spectra of the free ligands exhibit the characteristic bands of amides and amines. The amide I band appears at about 1660–1680 cm^{-1} and amide II at 1520 cm^{-1}. The IR spectra of amide complexes (**7**, **9**) show ν(N–H) bands in the range of 3260–3376 cm^{-1}, shifted with respect to the free ligands, due to Rh–NH coordination. The amide I band at 1682 cm^{-1} is attributed to the uncoordinated keto function and the band at 1600 cm^{-1} is due to the C=C frequency. The amide II band appears in the same position as the free ligand. Also, the IR spectra of Rh–amine complexes **8** and **10** show ν(N–H) bands shifted at higher frequencies (3400 cm^{-1}). The ν(P–F) frequency appears at 835 cm^{-1} as medium bands characteristic of the non-coordinated PF_6^- anion.

These complexes are moderately unstable 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 173–174 ppm and in the spectra of Rh–amide complexes **7** and **9** two peaks are found for the amide carbons. The spectrum of complex **7** displays



Scheme 1.

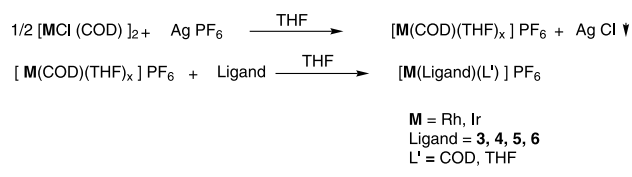
two separate resonances at 183.6 and 166.1 ppm. The downfield shift is due to the Rh←NH–CO coordination and the signal high field shifted indicating that a higher electron density in this complex may be due to the hydrogen bond between the NH and the uncoordinated C=O group. The ^{13}C-NMR spectrum of **9** also shows two carbonyl signals at 180.9 (+7.2) and 166.4 (−7.3) ppm. The ^{13}C-NMR spectra of amine complexes show only small chemical shift differences compared with the free ligands.

The IR spectra of the mononuclear Ir complexes show that the expected ν(N–H) bands shift to higher frequencies. There is also no doubt that in the Ir–amide complexes **11** and **13** the C=O unit of the amide groups is not involved in the coordination to the metal, as in the IR spectra only one C=O stretching frequency at 1690, 1683 cm^{-1} appears. The band at 1540–1520 cm^{-1} is due to the amide–N coordination. The ^{13}C-NMR spectra of **11** and **13** exhibit only one signal for the amide carbons at δ 167.0, 172.0, 167.0 ppm shifted at higher field (−7.1 ppm) which also indicates a high electron density in these complexes. In the Ir–amine complexes **12** and **14** the ^{13}C-NMR signals show only small chemical shift differences compared with the free ligands.

Electronic absorption spectra of 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 [14] 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.

2.3. Catalytic activity

The use of cationic complexes with chiral nitrogen-containing ligands is an attractive approach for the catalytic hydrogenation of prochiral olefins. In the first stage, metal complexes were evaluated as catalysts in the hydrogenation of diethyl citraconate to investigate the potential of ligands **3**–**6** for asymmetric catalysis (Table 1, Fig. 3). In the presence of 0.2 mol% of catalysts in ethanol at 313 K under a pressure of 4 bar H_2, the substrate was fully converted to alkane in 30 min. The results of these studies reveal that cationic catalysts are very effective for this transformation forming a product with higher rate and comparable enantioselectivity to that achieved with the analogous ethylenediamine derivative [13]. The results show that iridium complexes are more efficient than rhodium complexes. The hydrogenation is completed in less than



Scheme 2.

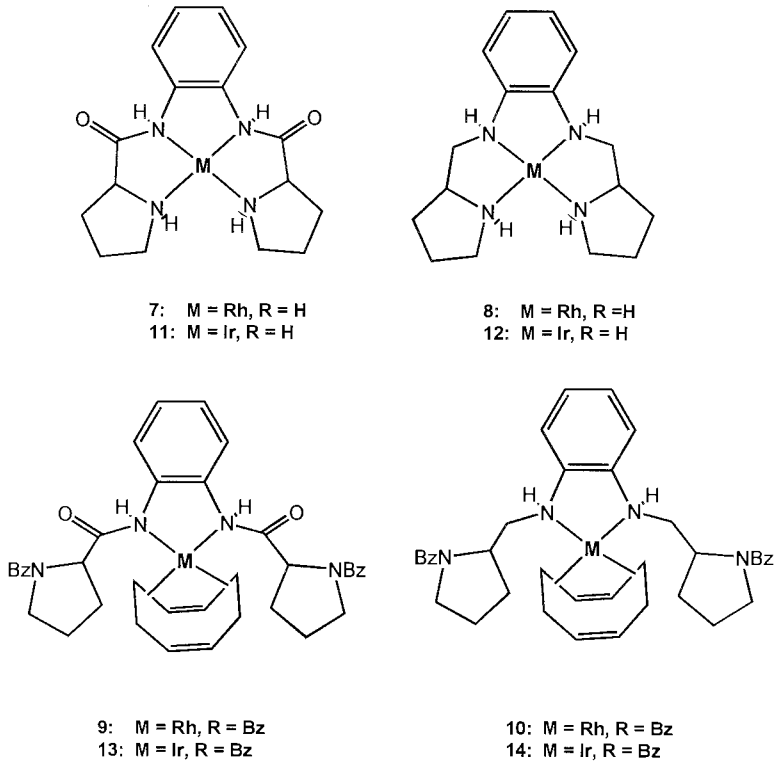


Fig. 2. Proposed structures for the rhodium and iridium complexes **7**–**14**.

30 min with higher ee (30%). Changing the substituents in the ligands produces an important effect on the optical induction. Thus, the optical induction is higher for the catalysts containing the benzyl groups as pyrrolidine substituents. The results of these studies reveal that cationic catalysts are very effective for this transformation forming a product with higher rate and moderate enantioselectivity.

The effect of the characteristics of substrate (Fig. 4) on reactivity and enantioselectivity was tested using **7** as a model catalyst and the results summarised in Fig. 5. The hydrogenation of diethyl mesaconate, diethyl citraconate and citraconic anhydride was quantitative in less than 20 min with modest enantioselectivity (ee = 13.4, 9.0, 26%), while the hydrogenation of more steric demanding diethyl 2-benzylidene succinate proceeds more slowly (ee = 22%).

The iridium complexes have shown higher rates (TOF) and enantioselectivity (ee 30%) than the Rh complexes. The change of substituents on the pyrrolidine nitrogen plays a significant role on optical induction that increases when moving from hydrogen to benzyl group, indicating that an enhanced steric volume around the metallic centre is a decisive effect for high enantioselectivity.

A study about the influence of structural characteristics of ligand and substrates with these promising catalysts in homogeneous media or supported on zeolites are in progress and will be presented extensively in future.

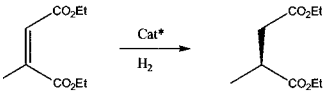
3. Conclusions

A series of new microcrystalline air-stable rhodium and iridium complexes with multitopic C_2-symmetry nitrogen ligands has been synthesised and characterised fully even in an optically pure form. The complexes are mononuclear species with the ligand coordinated in a tetradentate manner through the amine–amide groups. The metal–nitrogen bond is sufficiently stable for a transfer of chirality from the optically active catalyst to the product. We have shown that these cationic Rh(I) and Ir(I) complexes are efficient catalysts for the hydrogenation of olefins. The complexes are handled easily and the turnover numbers approaching up to 11 000 could be achieved with the diethyl 2-citraconate. These results constitute a firm ground for the design of more efficient enantioselective systems, based on C_2-symmetry nitrogen ligands.

4. Experimental

The preparation of organometallic complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. The starting complexes $[Rh(cod)Cl]_2$

Table 1
Asymmetric hydrogenation of diethyl citraconate



Catalyst	TOF (mmol substrate mmol catalyst^{-1} min^{-1})	ee (%) [a]
7	4062	9.1
8	8000	13.4
9	4070	13.6
10	10 000	19.4
11	3625	13.4
12	9600	16.5
13	9700	25.8
14	11 000	29.3

All reactions were performed in EtOH at 40 °C, S/C = 500 and 4 atm H_2. All reactions were complete after 30 min reaction time.

[a] Enantiomeric excess (ee) was determined by chiral GC using a chiral column based on alkylated cyclodextrin [17].

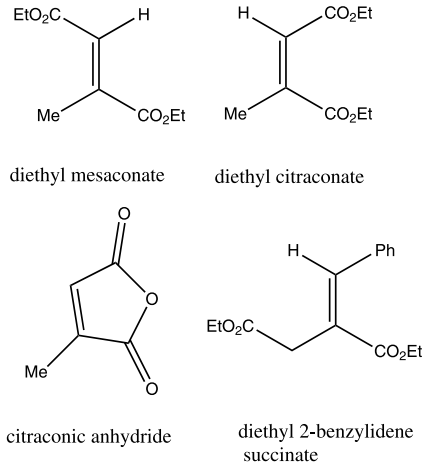


Fig. 4. Prochiral olefins for the catalytic hydrogenation.

[15] and $[Ir(cod)Cl]_2$ [16] were prepared using the methods reported earlier. 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). Metal contents were analysed by atomic absorption using a Perkin–Elmer 1100 B 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. IR spectra were recorded on a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^{1}H-, ^{13}C-NMR spectra were taken on a Varian XR300 and a Bruker 200 spectrometers. ^{1}H-NMR chemical shifts are given in parts per million (ppm) using Me_4Si 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 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 chromatographic analysis was performed using a Hewlett–Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column [17].

4.1. Synthesis of ligands

The amides **3** and **5** were prepared by modifying the procedure given for 1,6-bis[2(*S*)-2-pyrrolidinyl-

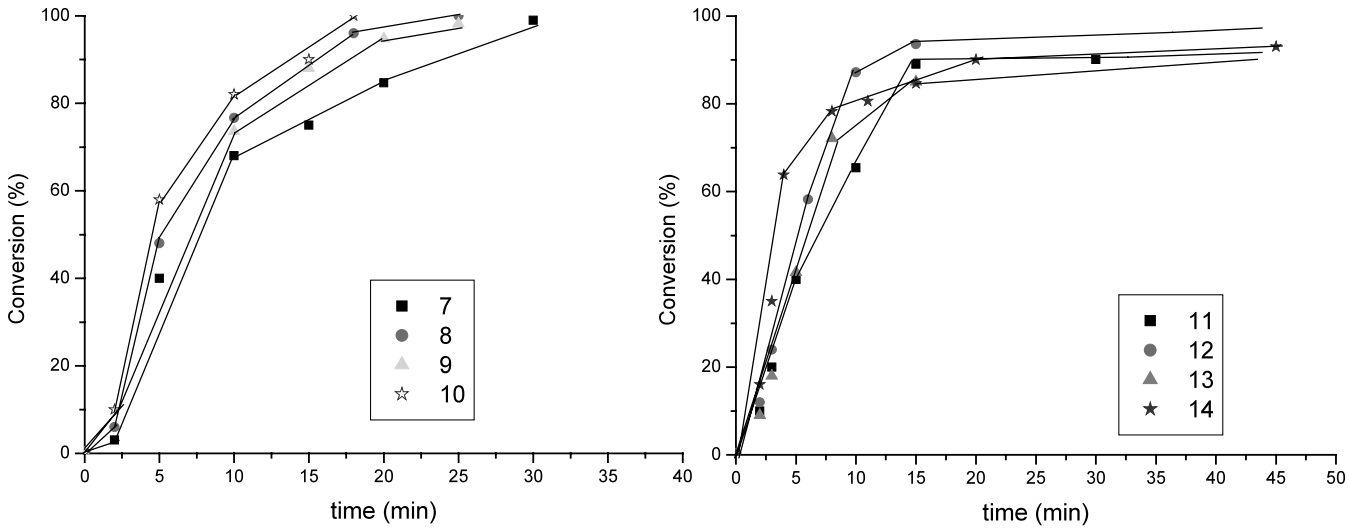


Fig. 3. Catalytic activity of the complexes **7**–**14** in the asymmetric hydrogenation of ethyl citraconate (catalyst–substrate = 1:500; $T = 313$ K, $pH_2 = 4$ atm).

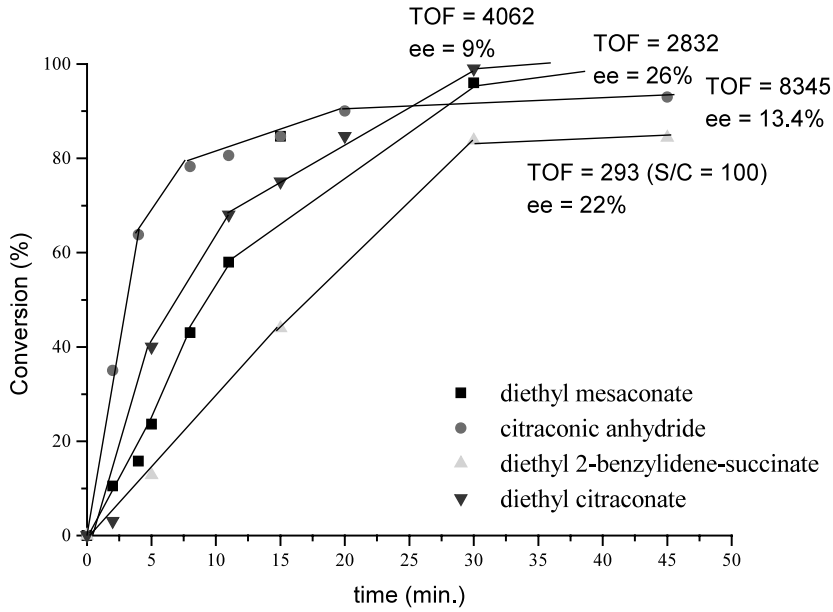


Fig. 5. Kinetic profile of catalytic hydrogenation of prochiral olefins with **7**. All reactions were performed in EtOH at 40 °C, S–C = 500 and $pH_2 = 4$ atm.

methyl]ethylenediamine starting from phenylenediamine [13].

*4.1.1. N,N′-Bis[(S)-N-benzyloxycarbonyprolyl]-phenylenediamine (**2**)*

Ethyl chloroformate (1.41 ml, 14.8 mmol) was added dropwise with vigorous stirring to an ice-cold solution of (*S*)-*N*-benzyloxycarbonylproline (**1a**) (3.7 g, 14.9 mmol) and triethylamine (2.07 ml, 14.9 mmol) in THF (80 ml). When the addition was complete 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, recrystallised *o*-phenylenediamine (0.8 g, 7.4 mmol) in cold THF (3 ml) was added dropwise for 15 min and the mixture was stirred for 2 h at 0 °C, and then filtered. The solvent was evaporated and the residue extracted with EtOAc and washed successively with water, aq. $NaHCO_3$ and brine. The organic layer was dried over magnesium sulphate and evaporated in vacuo to give 3.39 g (80%) of a white solid. The product was purified by flash-chromatography with hexane–EtOAc (1:2). M.p. (dec.): 66–67 °C. $[\alpha]_D^{20} - 93.3$ (CH_2Cl_2, 1). Anal. Found: C, 66.8; H, 6.8; N, 10.4. Calc. for $C_{32}H_{34}N_4O_6$ (MW 570): C, 67.3; H, 6.8; N, 10.4%. IR (cm^{-1}): ν(NH) 3272, ν(C=O_{Cbz}) 1696, ν(amide I) 1677; ν(C=C) 1590; ν(amide II) 1518. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 8.48–8.52 (m, 2H, N–H), 7.38–7.10 (m, 10H, Ph Cbz), 7.10–6.96 (m, 4H, Ph *o*-phenylenediamine), 5.18–5.07 (m, 4H, OCH_2), 4.41–4.20 (m, 2H, H_2), 3.68–3.35 (m, 4H, H_5), 2.46–2.04 (m, 2H, H_3), 2.04–1.86 (m, 2H, $H_{3'}$), 1.86–1.74 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50 °C): δ 170.97 (C=O amide), 156.29 (C=O ester), 140.22 (C_{Ph}–R Cbz), 136.39 (C_{Ph}–R *o*-phenylenediamine), 128.58–127.88 (C_{Ph}–H Cbz), 125.01–124.63 (C_{Ph}–H *o*-phenylenediamine), 67.36 (O*C*H_2Ph), 61.13 (C_2), 47.22 (C_5), 28.41 (C_3), 24.59 (C_4). MS; *m*/z: 324, 250, 220, 205, 154, 57.

*4.1.2. N,N′-Bis[(S)-prolyl]phenylenediamine (**3**)*

A mixture of *N*,*N*′-bis[(*S*)-*N*-benzyloxycarbonyl prolyl]phenylenediamine (**2**) (7.3 g, 12.8 mmol), cyclohexene (6 ml, 76 mmol) and 2 g of commercial Pd/C (10%) in 160 ml of EtOH was heated under reflux for 1 h in argon, cooled and filtered over celite. the catalyst was washed with EtOH, and the filtrate and wash liquids were evaporated under reduced pressure to give 3.64 g of **3**. Yield: 84%; m.p. (dec.): 123–125 °C. $[\alpha]_D^{20} - 27.7$ (CH_2Cl_2, 1). Anal. Found: C, 62.5; H, 6.8; N, 17.9. Calc. for $C_{16}H_{22}N_4O_2$ (MW 302): C, 63.6; H, 7.3; N, 18.5%. IR (KBr, cm^{-1}): ν(NH) 3304, 3238, ν(amide I) 1662, ν(C=C) 1590, ν(amide II) 1522. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 9.68–9.59 (s, br, 2H, N–H), 7.68–7.63 (m, 2H, *p*-Ph), 7.21–7.11 (m, 2H, *o*-Ph), 3.86 (dd, 2H, H_2, $J = 5.28$ Hz, $J = 9.22$ Hz), 3.07–2.99 (m, 2H, H_5), 2.97–2.93 (m, 2H, $H_{5'}$), 2.37–2.13 (m, 4H, H_3, N–H), 2.06–1.97 (m, 2H, $H_{3'}$), 1.82–1.69 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50 °C): δ 174.09 (C=O), 129.72 (C_{Ph}–R), 125.59 ($C_{o\text{-}Ph}$), 123.98 ($C_{p\text{-}Ph}$), 61.03 (C_2), 47.35 (C_5), 30.82 (C_3), 26.23 (C_4). MD; *m*/z: 302 ([M^+]), 220, 205, 145, 57.

*4.1.3. N-N′-Bis{[(S)-pyrrolidin-2-yl]methyl}-phenylenediamine (**4**)*

Procedure a: to a solution of *N*,*N*′-bis[(*S*)-prolyl]phenylenediamine (**3**) (1 g, 3.3 mmol) in ice-cold

THF (25 ml), $LiAlH_4$ (1.3 g, 34 mmol) was added dropwise. When the addition was complete 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 oil. Yield: 0.62 g (70%). Anal. Found: C, 69.8; H, 9.9; N, 20.7. Calc. for $C_{16}H_{26}N_4$ (MW 274): C, 70.1; H, 9.5; N, 20.4%. IR (film, cm^{-1}): ν(N–H) 3288. ^{1}H-NMR ($CDCl_3$, D_2O, 50 °C): δ 7.03–6.58 (4H, C*H*Ph.), 3.68–3.46 (m, 4H, CH_2–NH_{Ph}), 3.26–3.17 (m, 2H, H_2), 3.14–3.09 (m, 4H, H_5), 1.97–1.88 (m, 4H, H_3), 1.86–1.72 (m, 4H, H_4). MS; m/z: 275 ($[M^+ + 1]$).

Procedure b: to an ice-cold suspension of 2.19 g (0.0579 mol) of $NaBH_4$ in dry dioxane (30 ml), trifluoroacetic acid was added dropwise (0.0579 mol or 28.95 ml of a 2 M dioxane solution) and the mixture was stirred for 10 min at room temperature (r.t.). The amide (3.86 mmol) was added to the solution and the mixture was stirred for 48 h under reflux. The solvent was evaporated under reduced pressure. Water was carefully added to the residue, which was extracted with $CHCl_3$ and dried over $MgSO_4$. The solvent was eliminated and the final product was purified by flash chromatography. Yield: 79%.

4.1.4. *N,N′-Bis[(S)-N-benzylprolyl]phenylenediamine* (**5**)

Procedure a: to a solution of *N,N′*-bis[(*S*)-prolyl]phenylenediamine (**3**) (2.16 g, 4 mmol) and triethylamine (2.37 ml, 2 mmol) in ice-cold THF (25 ml), benzyl bromide (2 ml, 2 mmol), was added dropwise with vigorous stirring. When the addition was complete the reaction mixture was stirred for 6 h at 0 °C. The solvent was evaporated and the residue extracted with $CHCl_3$ and washed successively with water, aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give **5** as a white solid. The product was purified by flash chromatography with 1:1 hexane–EtOAc. Yield: 3.4 g (93%); m.p. (dec.): 101–102 °C; $[\alpha]_D^{20} - 58.1$ ($CHCl_3$, $c = 1$); Anal. Found: C, 74.5; H, 7.1; N, 11.8. Calc. for $C_{30}H_{34}N_4O_2$ (MW 483): C, 74.7; H, 7.1; N, 11.6%. IR (KBr, cm^{-1}): ν(NH) 3328, 3214, ν(amide I) 1680, 1660, ν(C=C) 1594, ν(amide II) 1520, 1510. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 9.32 (s, br, 2H, N–H), 7.34–7.05 (m, 14H, Ph), 3.80 (d, 2H, CH_2Ph, $J = 15.16$ Hz), 3.54 (d, 2H, CH_2Ph, $J = 14.99$ Hz), 3.30–3.25 (m, 2H, H_2), 3.03–2.97 (m, 2H, H_5), 2.41–2.32 (m, 2H, $H_{5'}$), 2.21–2.11 (m, 2H, H_3), 1.92–1.83 (m, 2H, $H_{3'}$), 1.70–1.60 (m, 4H, H_4). ^{13}C-NMR ($CDCl_3$, 50 °C): δ 173.70 (C=O), 137.87 (C_{Ph}–NH), 129.97 (C_{Ph}–C), 129.04–124.64 (C_{Ph}–H), 67.52 (C_2), 59.92 (CH_2Ph), 53.99 (C_5), 30.89 (C_3), 24.03 (C_4). MS; m/z: 484 ($[M^+ + 1]$), 160, 91.

Procedure b. a solution of (*S*)-*N*-benzylproline (**1b**) (1 g, 4.88 mmol) and Et_3N (685 μl, 4.88 mmol) in $CHCl_3$ (50 ml), was stirred at r.t. for 15 min and cooled. Ethyl chloroformate (466 μl, 4.88 mmol) was added dropwise to the mixture with vigorous stirring. When the addition was complete the pasty reaction mixture was stirred for 1 h (temperature 5–10 °C), and a very reactive mixed anhydride was obtained. To the anhydride filtered solution, recrystallised *o*-phenylenediamine (2.44 mmol) in cold THF (1 ml) was added for 15 min and the mixture was stirred at 0 °C for 10 h, and washed successively with water, aq. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and evaporated in vacuo to give a white solid. The product was purified by flash-chromatography with hexane–EtOAc (1/2). Yield:75%

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

The diamine **6** was prepared through procedures (a and b) similar to those given for **4** starting from *N,N′*-bis[(*S*)-*N*-benzylprolyl]phenylenediamine (**5**) (1.20 g, 2.49 mmol). The product was purified by flash chromatography with EtOAc–NEt_3 (95/5) and isolated as an air sensitive colourless oil. Yield: procedure a: 1.02 g (87%), procedure b: 80%. Anal. Found: C, 79.2; H, 8.7; N, 12.6. Calc. for $C_{30}H_{38}N_4$ (MW 454): C, 79.3; H, 8.4; N, 12.3%. IR (film, cm^{-1}): ν(N–H) 3307, ν(C=C) 1594. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 7.29–7.07 (m, 10H, Ph), 6.70–6.67 (m, 2H, C_{Ph}), 6.56–6.53 (m, 2H, C_{Ph}), 4.30 (s, br, NH), 3.92–3.89 (d, 2H, CH_2Ph), 3.18–3.06 (m, 8H, CH_2Ph, H_2, H_5, H_8), 2.87–2.77 (m, 4H, H_5, H_8), 2.20–1.86 (m, 4H, $H_{3,3'}$), 1.62–1.44 (m, 4H, $H_{4,4'}$). ^{13}C-NMR ($CDCl_3$, 50 °C): δ 139.56, 137.88 (C_{Ph}–NH), 128.62, 128.02, 126.74, 118.04, 109.62 ($C_{Ph.}$), 62.08 (C_2), 58.00 (C_5), 54.42 (CH_2Ph), 44.08 (C_8), 28.64 (C_3), 23.46 (C_4). MS; m/z: 455($[M^+ + 1]$), 91.

4.2. *Preparation of [M(C$_2$-ligand)(THF)]PF$_6$ complexes (M = Rh, Ir)* (**7**–**14**)

4.2.1. *General procedure*

The preparation of [Rh(**3**)]PF_6·(THF) (**7**) is described in detail, and the experimental procedure is a model 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 r.t. for 30 min. Precipitated silver chloride was filtered 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 Et_2O caused the precipitation of a solid which was collected by filtration, washed with Et_2O and dried under vacuum (10^{-3} mmHg) to give the wine cationic complex. Yield: 85%; m.p. (dec.): > 230 °C. Anal. Found: C, 41.3; H, 5.2; N, 8.0; Rh, 14.5. Calc. for $C_{24}H_{38}F_6N_4O_4PRh$ (MW 694): C, 41.5; H, 5.5; N, 8.1; Rh, 14.8%. IR (KBr, cm^{-1}): ν(N–H) 3362, 3303, ν(amide I) 1682, ν(C=C) 1594, ν(amide II) 1549,

ν(amide II) 1520, ν(P–F) 834. ^{13}C-NMR (solid): δ 183.6, 166.1 (C=O), 144.1 ($C–O_{THF}$), 142.1 (C_{Ph}–R), 129.2 ($C_{Ph}o$), 126.0 ($C_{Ph}p$), 110.1 ($C–C_{THF}$), 78.7 (C_2), 64.9, 60.3 (C_5), 30.5 (C_3, C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 381.5 (3.06), 294.5 (3.77). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 154–167. MS; m/z: 405 ([Rh(**3**)]$^+$), 303 ([(**3**) + 1]).

Complexes **8**–**14** were prepared by a procedure similar to that given for **1** using 0.2 equivalents of the appropriate ligand.

4.2.2. [Rh(**4**)(THF)]PF_6 (**8**)

Yellow. Yield: 75%; m.p. (dec.) > 200 °C. Anal. Found: C, 40.0; H, 6.3; N, 8.7; Rh, 16.9. Calc. for $C_{20}H_{34}F_6N_4PRh$ (MW 594): C, 40.4; H, 6.0; N, 8.9; Rh, 17.3%. IR (KBr, cm^{-1}): ν(N–H) 3400, 3296, ν(P–F) 836. ^{13}C-NMR (solid): δ 144.1 (C_{Ph}–R), 142.7 ($C–O_{THF}$), 129.0 ($C_{Ph}o$), 127.0 ($C_{Ph}p$), 109.3 ($C–C_{THF}$), 68.7 (C_2), 64.9, 60.3 (C_5), 28.5 (C_3, C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 377.5 (2.36), 288.5 (3.39), 292 (3.93). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 122. MS; m/z: 503 ([Rh(**4**)]PF_6 − F), 377 ([Rh(**4**)]$^+$).

4.2.3. [Rh(**5**)(cod)]PF_6 (**9**)

Yellow. Yield: 68%; m.p. (dec.): 120–122 °C. Anal. Found: C, 54.4; H, 5.3; N, 6.4; Rh, 12.8. Calc. for $C_{38}H_{46}F_6N_4O_2PRh$ (MW 839): C, 54.3; H, 5.5; N, 6.7; Rh, 12.3%. IR (KBr, cm^{-1}): ν(N–H) 3376, 3260, 1686, ν(amide I) 1612, ν(C=C) 1570, ν(amide II) 1526, ν(P–F) 840. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 7.8–6.6 (m, 14H, Ph.), 4.3–4.0 (m, 6H, C*H*=, CH_2Ph), 3.50–3.48 (m, 2H, CH_2Ph), 2.95–1.50 (m, H_5, H_3, H_4, CH_{cod}).^{13}C-NMR (solid): δ 180.9, 166.4 (C=O), 129.35 (C_{Ph}), 76.7 (C_2), 68.82 (C=C_{cod}), 66.62 (CH_2Ph), 55.82 (C_5), 31.68 (C_3), 29.81 ($C–C_{cod}$), 29.03 (C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 348.0 (3.27), 289.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 124–127. MS; m/z: 693 ([Rh(**5**)(cod)]$^+$), 483 ([(**5**) + 1]).

4.2.4. [Rh(**6**)(cod)]PF_6 (**10**)

Yellow. Yield: 75%; m.p. (dec.): > 210 °C. Anal. Found: C, 56.0; H, 5.8; N, 7.2; Rh, 12.9. Calc. for $C_{38}H_{50}F_6N_4O_2PRh$ (MW 810): C, 56.3; H, 6.2; N, 6.9; Rh, 12.7%. IR (KBr, cm^{-1}): ν(N–H) 3350, 3260, ν(C=C) 1600, ν(P–F) 836. ^{13}C-NMR (solid): δ 135.6 (C_{Ph}–NH), 128.99 ($C_{Ph.}$), 64.68 (C_5), 59.10 (C_2), 50.37 (*C*H_2Ph), 41.51 (C_8), 28.89 (C_3, C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 345.0 (3.27), 288.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 114–117. MS; m/z (MeOH–CH_3CN): 714 ([Rh(**6**)(MeOH)]PF_6] − F), 558 ([Rh(**6**)]$^+$ + 1), 455 ([(**6**)] + 1).

The iridium complexes were prepared following the general procedure starting from [IrCl(cod)]$_2$ and the corresponding ligand.

4.2.5. [Ir(**3**)(THF)]PF_6 (**11**)

Beige. Yield: 85%; m.p. (dec.): > 200 °C. Anal. Found: C, 33.1; H, 4.0; N, 7.6; Ir, 27.1. Calc. for $C_{20}H_{30}F_6IrN_4O_3P$ (MW 711): C, 33.7; H, 4.2; N, 7.9; Ir, 27.0%. IR (KBr, cm^{-1}): ν(N–H) 3402, 3184, ν(amide I) 1690, ν(C=C) 1604, ν(amide II) 1540, ν(P–F) 842. ^{13}C-NMR (solid): δ 167.0 (C=O), 143.9 ($C–O_{THF}$), 142.4 (C_{Ph}–R), 128.2 ($C_{Ph}o$), 126.9 ($C_{Ph}p$), 110.6 ($C–C_{THF}$), 76.7 (C_2), 63.6, 59.9 (C_5), 27.8, 25.7 (C_3, C_4). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 110. MS; m/z (^{191}Ir): 562 ([Ir(**3**)]PF_6 − 4F), 303 ([(**3**)] + 1).

4.2.6. [Ir(**4**)]PF_6 (**12**)

Light yellow. Yield: 75%; m.p. (dec.): > 200 °C. Anal. Found: C, 36.8; H, 4.8; Ir, 36.1; N, 10.4. Calc. for $C_{16}H_{26}F_6IrN_4P$ (MW 522): C, 36.8; H, 5.0; Ir, 36.8; N, 10.7%. IR (KBr, cm^{-1}): ν(N–H) 3394, ν(P–F) 836. ^{13}C-NMR (solid): δ 140.1 (C_{Ph}–R), 129.39 (C_{Ph}), 66.7 (C_2), 60.3 (C_5), 28.5 (C_3, C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 378.5 (2.36), 289.5 (3.39), 290 (3.93). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 103. MS; m/z (^{191}Ir): 591 ([Ir(**4**)]PF_6 − F), 465 ([Ir(**4**)]$^+$), 275 ([(**4**)] + 1).

4.2.7. [Ir(5)(cod)]PF_6 (**13**)

Light brown. Yield: 80%; m.p. (dec.): 130–132 °C. Anal. found: C, 49.4; H, 5.0; Ir, 20.1; N, 6.2. Calc. for $C_{38}H_{46}F_6IrN_4O_2P$ (MW 927): C, 49.2; H, 5.0; Ir 20.7; N, 6.0%. IR (KBr, cm^{-1}): ν(N–H) 3376, 3260, ν(amide I) 1683, 1679, ν(C=C) 1600, ν(amide II) 1548, ν(P–F) 840. ^{1}H-NMR ($CDCl_3$, 50 °C): δ 7.84–6.65 (m, 14H, Ph), 4.25–4.05 (m, 6H, C*H*=, CH_2Ph), 3.50 (m, 2H, CH_2Ph), 2.90–1.60 (m, H_5, H_3, H_4, CH_{cod}). ^{13}C-NMR (solid): δ 172.0, 167.0 (C=O), 129.60 (C_{Ph}), 78.7 (C_2), 68.42 (C=C_{cod}), 62.86 (CH_2Ph), 56.82 (C_5), 29.61(C_3, $C–C_{cod}$), 26.33 (C_4). UV–vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 346.0 (3.27), 292.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 114–117. MS; m/z (^{191}Ir): 781 ([Ir(**5**)(cod)]$^+$), 484 ([(**5**)] + 1).

4.2.8. [Ir(**6**)(cod)]PF_6 (**14**)

Yellow. Yield: 75%; m.p. (dec.): 133–136 °C. Anal. Found: C, 50.7; H, 5.3; Ir, 20.9; N, 6.4. Calc. for $C_{38}H_{50}F_6IrN_4O_2P$ (MW 899): C, 50.7; H, 5.6; Ir, 21.4; N, 6.2%. IR (KBr, cm^{-1}): ν(N–H) 3378, ν(C=C) 1600, ν(P–F) 822. ^{13}C-NMR (solid): δ 135.6 (C_{Ph}–NH), 129.84 ($C_{Ph.}$), 67.52 (C=C_{cod}), 60.68 (C_5), 58.25 (C_2), 50.07 (*C*H_2Ph), 43.51 (C_8), 29.37, 28.56, 26.45 (C_3, C_4, *C*H_{2cod}). UV–Vis: λ_{max} (nm) (log ε, 10^{-3} M) (DMF): 345.0 (3.27), 288.0 (3.70). Λ_M (Ω^{-1} cm^2 mol^{-1}, 10^{-3} M, CH_3CN): 124–127. MS; m/z (^{191}Ir) (MeOH–CH_3CN): 772 ([Ir(**6**)]PF_6 − F), 677 ([Ir(**6**)(MeOH)]$^+$), 645 ([Ir(**6**)]$^+$), 455 ([(**6**)] + 1).

4.3. Catalytic experiments

The catalytic properties, in hydrogenation reactions,

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

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