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Synthesis, chirooptical properties and catalytic activity of diene–rhodium(I) and –iridium(I) cationic complexes containing binaphthyl, C_2-symmetric diamine ligands

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Abstract

New cationic rhodium(I) and iridium(I) complexes [M(diene)(diamine)]BF_4 containing chiral C_2-symmetric diamines [M = rhodium; diamine = 2,2′-diamino-1,1′-binaphthyl (BNDA), diene = cycloocta-1,5-diene (COD), **1a**, bicyclo[2,2,1]hepta-2,5-diene (NBD), **1b**, hexa-1,5-diene (HEX), **1c**; diamine = N,N′-dimethyl-2,2′-diamino-1,1′-binaphthyl (DMBNDA), diene = COD, **1d**. M = iridium; diamine = BNDA, diene = COD, **2a**; diamine = DMBNDA, diene = COD, **2b**] have been prepared by the reaction of $[MCl(diene)]_2$ with $AgBF_4$ and further treatment with the diamine. Using *N,N,N′,N′*-tetramethyl-2,2′-diamino-1,1′-binaphtyl (TMBNDA), no cationic complex was obtained. With the exception of the complex **1c**, complexes **1** and **2** are stable in solution under inert atmosphere. Acetonitrile removes bonded DMBNDA but not BNDA from the metal; KOH removes both the diamines but not the diene. Complexes **1a**, **1b**, and **2a**, containing (+)(*R*)-BNDA, catalyze the enantioselective hydrogenation of (*Z*)-α-acetamidocinnamic acid to acetamidodihydrocinnamic acid (o.p. = 9%; room temperature; hydrogen pressure, 35 atm).

Keywords: Rh; Ir; Catalytic activity; Circular dichroism; Hydrogenation

1. Introduction

Since the pioneering work of Knowles and co-workers [1] who developed the first efficient asymmetric catalytic hydrogenation of functionalized olefin substrates, the methods of asymmetric catalysis have developed very rapidly leading to impressive achievements in important organic reactions such as the reduction of olefin and carbonyl double bonds [2] and the oxidation [3], hydroformylation [4] and cyclopropanation [5] of olefins. Generally, the catalytic precursors are organometallic complexes of Rh, Ir, Ru with chiral bidentate phosphine, C_2-symmetric ligands (Chiraphos, Binap) providing the highest level of enantioselection.

Only very recently, however, has the importance of nitrogen donors in organometallic chemistry and, most importantly, in homogeneous catalysis been fully recognized: Togni and Venanzi have reviewed the role played by nitrogen ligands in asymmetric catalysis [6].

With these facts in mind (nitrogen ligands as efficient alternative to phosphorus ligands and the importance of the C_2-symmetry of the ligands) we decided to investigate the preparation and use, as catalytic precursors in some enantioselective reactions, of diene-rhodium(I) and -iridium(I) cationic complexes containing the C_2-symmetric ligands 2,2′-diamino-1,1′-binaphthyl (BNDA), *N,N′*-dimethyl-2,2′-diamino-1,1′-binaphthyl (DMBNDA), and *N,N,N′,N′*-tetramethyl-2,2′-diamino-1,1′-binaphthyl (TMBDNA) (Scheme 1). We noted that ligands based on the 1,1′-binaphthalene skeleton have provided a list of successes in asymmetric synthesis and catalysis [7].

In this paper we report the results obtained in our attempts to prepare the complexes [M(diene)(diamine)]-BF_4 by reaction between the dimeric diolefin compounds $[MCl(diene)]_2$ (M = Rh, diene = cycloocta-1,5-diene (COD), bicyclo-2,2,1-hepta-2,5-diene (NBD),

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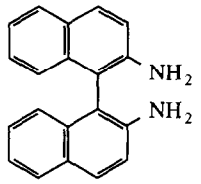
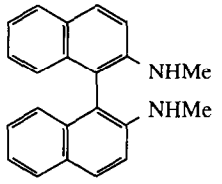
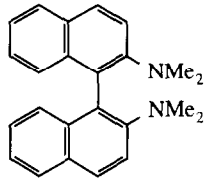


2,2′-Diamino-1,1′-binaphthyl
BNDA



N,N′-Dimethyl-2,2′-Diamino-1,1′-binaphthyl
DMBNDA



N,N,N′,N′-tetramethyl-2,2′-diamino-1,1′-binaphthyl
(TMBNDA)

Scheme 1.

hexa-1,5-diene (HEX); M = Ir, diene = COD) and the diamine ligands BNDA, DMBNDA and TMBNDA. Their complete characterization, including a study of their behaviour in the presence of strong bases, is also described. Finally, the catalytic activity of some optically active complexes of this kind in the asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid (AAZ) and in the reduction of acetophenone by hydrogen transfer from 2-propanol is reported.

2. Results and discussion

*2.1. Synthesis of complexes [M(diene)(diamine)]BF_4 (M = Rh; diamine = BNDA; diene = COD, **1a**, NBD, **1b**, HEX, **1c**; diamine = DMBNDA, diene = COD, **1d**. M = Ir; diamine = BNDA, diene = COD, **2a**; diamine = DMBNDA, diene = COD, **2b**)*

The complexes [M(diene)(diamine)]BF_4 **1a–d**, **2a** and **2b** have been prepared as shown in Scheme 2 following a general procedure [8].

The appropriate diene-metal chloride dimer was dissolved in the solvent (THF or acetone) and treated with $AgBF_4$. The precipitated AgCl was filtered off and the diamine was added to the filtrate containing the species [M(diene)(solvent)$_x$]BF_4 to give the [M(diene)(diamine)]BF_4 complex. Complexes **1a–d**, **2a** and **2b** were characterized by elemental analysis, ^{1}H-NMR spectroscopy and MS-FAB spectrometry (Table 1).

With rhodium, very good results have been obtained in THF at room temperature. Only the complex **1c**, containing 1,5-hexadiene, is more conveniently prepared at −10°C, because, like its dimeric precursor $[RhCl(HEX)]_2$, it is unstable in solution [9,10]. With iridium, high yields of **2a** and **2b** have been obtained using acetone as solvent and preparing the intermediate species [Ir(COD)(acetone)$_x$]BF_4 under reflux [11].

2.2. Reaction between [MCl(diene)]$_2$ (M = Rh, Ir) and TMBNDA: attempts to prepare [M(diene)(TMBNDA)]-BF_4 complexes

The reaction between $[MCl(diene)]_2$ compounds (M = Rh; diene = COD, NBD, HEX, M = Ir; diene = COD) and TMBNDA was carried out following the procedure of Scheme 2 using different temperatures and solvents (THF, acetone, CH_2Cl_2): no cationic complex was obtained in this case and the free ligand was recovered from the reaction mixture. Alternative synthetic pathways were tested, such as the reaction between TMBNDA and $[MCl(diene)]_2$ in methanol followed by addition of $NaBF_4$ [12,13] or the replacement of 1 mol of diolefin in the performed [14,15] complex $[M(diene)_2]BF_4$ by TMBNDA; however, in no case was the diamine–metal complex isolated.

The poor complexing ability of TMBNDA with respect to BNDA and DMBNDA can be attributed to an important structural difference between BNDA and DMBNDA on the one hand and TMBNDA on the other. It has been shown recently that in the conformation of BNDA and DMBNDA the naphthalene planes form a dihedral angle of about 90° [16]. At the same time the fragments NH_2 and NHMe are perfectly coplanar with the aromatic rings, so that there is complete conjugation between the nitrogen lone pair and the aromatic electrons. The conformation of TMBNDA is very different [16]: the dihedral angle is now 75° and the fragments of NMe_2 are not coplanar with the naphthalene planes but twisted by about 30°, i.e. the conjugation between the nitrogen lone pairs and the aromatic electrons is only partial. This structural difference is a consequence of the different steric hindrance due to a NH_2 or NHMe group vs a NMe_2 group. In the case of BNDA and DMBNDA a small substituent (hydrogen) can be placed in a crowded region (near to the naphthyl group which acts as an ortho substituent) and the conju-

$$1/2[MCl(diene)]_2 + AgBF_4 \xrightarrow{\text{solvent}} [M(diene)(solvent)_x]BF_4 + AgCl\downarrow$$

$$[M(diene)(solvent)_x]BF_4 + \text{diamine} \longrightarrow [M(diene)(diamine)]BF_4$$

Scheme 2. M = Rh; diamine = BNDA, diene = COD, **1a**, NBD, **1b** and HEX, **1c**; diamine = DMBNDA, diene = COD, **1d**; solvent, THF; room temperature. M = Ir; diene = COD, diamine = BNDA, **2a**, and DMBNDA, **2b**; solvent, acetone; 65°C.

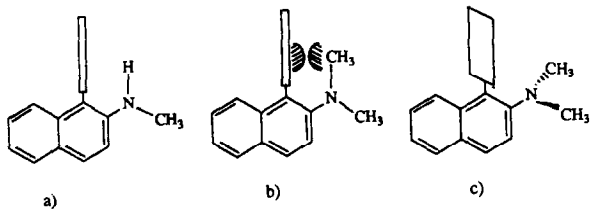


Fig. 1. (a) Stable conformation of DMBNDA. The smallest group, H, can be placed in the hindered region (i.e. near to second naphthyl fragment linked to the α position). The 'small rectangle' represent the second half of the molecule which is orthogonal to the first. (b) In the case of TMBNDA such conformation causes several steric hindrances between the above described counterparts. (c) To relieve such steric repulsive interaction the NMe_2 fragment of each half is twisted (ca. 75°) with respect to its own naphthyl group. In this case the 'large rectangle' represents the second half of the molecule which is not orthogonal to the first.

gation between the nitrogen atom and the naphthalene can be maintained (see Fig. 1(a)). In the case of the more sterically demanding NMe_2 group, this cannot occur (see Fig. 1(b)) owing to the steric repulsion between a methyl group and the naphthyl group which is the ortho substituent. To reduce such steric repulsion, a significant twist (ca. 30°) between the plane of the NMe_2 group and the naphthalene ring is introduced (Fig. 1(c)). The minimum-energy conformation of TMBNDA is thus the result of a subtle compromise between electronic and steric factors, giving rise to a stable situation; as a consequence, TMBNDA behaves as a rigid molecule. In contrast, coordination to a metallic centre can require significant changes in the conformation of the organic ligand (for instance, 6,6′-di-

Table 1
Analytical and spectroscopic data for [M(diene)(diamine)]BF_4 complexes **1a–d**, **2a**, **2b** and **3**

Compound	Yield (%)	Analysis (%) [a]			^{1}H-NMR data [b]			FAB-MS m/z (% rel. int.)
		C	H	N	Diamine	Diene		
						Olefinic	Other	
[Rh(COD)(BNDA)]BF_4	85	57.12	4.78	4.35	8.09 (d, 2H)	4.40 (m, 2H)	2.40 (br m, 4H)	495, M^+ (80)
1a		(57.75)	(4.85)	(4.81)	7.97 (d, 2H)	4.05 (m, 4H)	1.82 (br m, 4H)	387, M^+-COD (100)
					7.53 (d, 2H)			
					7.42 (t, 2H)			
					7.24 (t, 2H)			
					6.95 (d, 2H)			
[Rh(NBD)(BNDA)]BF_4	85	56.88	4.15	4.53	8.09 (d, 2H)	4.30 (m, 2H)	3.86 (m, 2H, CH)	479, M^+ (100)
1b		(57.27)	(4.27)	(4.95)	7.98 (d, 2H)	4.03 (m, 2H)	1.26 (m, 2H, CH_2)	387, M^+-NBD (85)
					7.58 (d, 2H)			
					7.42 (t, 2H)			
					7.24 (t, 2H)			
					6.9 (d, 2H)			
[Rh(HEX)(BNDA)]BF_4 [c]	70	55.88	4.45	5.41	8.09 (d, 2H)	3.43 (m, 2H, =C*H*=)	2.26 (m, 2H, C*H*H)	469, M^+ (30)
1c		(56.14)	(4.71)	(5.03)	8.01 (d, 2H)	2.50 (d, 2H, =CH*H*)	1.63 (m, 2H, CH*H*)	387, M^+-HEX (100)
					7.54 (d, 2H)	2.26 (m, 2H, =CH*H*) [d]		
					7.46 (t, 2H)			
					7.27 (t, 2H)			
					6.96 (d, 2H)			
[Rh(COD)(DMBNDA)]BF_4	85	58.90	5.19	4.22	8.05 (d, 2H)	4.15 (m, 2H)	2.50 (br m, 4H)	523, M^+ (100)
1d		(59.04)	(5.28)	(4.59)	7.90 (d, 2H)	3.98 (m, 2H)	1.81 (br m, 4H)	415, M^+-COD (70)
					7.44 (d, 2H)			
					7.26 (t, 2H)			
					7.15 (t, 2H)			
					6.90 (d, 2H)			
[Ir(COD)(BNDA)]BF_4	85	49.88	4.03	4.56	8.10 (d, 2H)	4.16 (m, 2H)	2.20 (br m, 4H)	583, M^+ (85) [e]
2a		(50.07)	(4.20)	(4.17)	8.01 (d, 2H)	3.82 (m, 2H)	1.71 (br m, 4H)	476, M^+-COD (100)
					7.56 (d, 2H)			
					7.47 (t, 2H)			
					7.28 (t, 2H)			
					6.99 (d, 2H)			
[Ir(COD)(DMBNDA]BF_4 [f]	80	51.00	4.52	3.68	8.25 (d, 2H)	4.51 (m, 2H)	2.23 (br m, 4H)	611, M^+ (85) [e]
2b		(51.50)	(4.61)	(4.00)	8.12 (d, 2H)	3.95 (m, 2H)	1.50 (br m, 4H)	503, M^+-COD (100)
					7.73 (d, 2H)			
					7.60 (t, 2H)			
					7.44 (t, 2H)			
					7.18 (d, 2H)			
[Rh(COD)(TMEDA)]BF_4	90	39.87	6.70	6.52	2.62 (s, 4H)	4.05 (m, 4H)	2.48 (br m, 4H)	327, M^+ (100)
3		(40.55)	(6.80)	(6.75)	2.57 (s, 12H)		1.86 (br m, 4H)	219, M^+-COD (10)

[a] Calculated values are given in parentheses. [b] Spectra were measured at 200 MHz using Me_4Si as internal standard in methanol-d_6; δ scale; s = singlet, d = doublet, t = triplet, br = broad. [c] The ^{1}H-NMR spectrum was recorded at −10°C. [d] Observed by double resonance. [e] Based on ^{191}Ir. [f] The ^{1}H-NMR spectrum was recorded in acetone-d_6.

methyl-2,2'-diaminobiphenyl shows a dihedral angle between the two phenyl rings of about 90° when free, but when coordinated to rhodium this angle is reduced to 65° [17]). Thus, the rigidity of TMBNDA prevents conformational variations of this kind and hinders the coordination.

2.3. Physico-chemical properties of complexes 1a–d, 2a and 2b

The complexes **1a–d**, **2a** and **2b** are yellow-orange solids with decomposition temperatures between 150 and 200°C. They are air-stable in the solid state but not in solution. They are very soluble in alcoholic solvents (methanol and ethanol) and dichloromethane, soluble in acetone, acetonitrile and THF, slightly soluble in chloroform, and insoluble in diethyl ether, aromatic and aliphatic solvents. With the sole exception of $[Rh(HEX)(BNDA)]BF_4$, **1c**, whose instability in solution has been pointed out previously, the other complexes are stable in alcoholic solvents and dichloromethane at room temperature and under reflux under inert atmosphere.

Of particular interest is their behaviour in acetonitrile, a strongly coordinating solvent that is able to displace amines from a transition metal [18]. Complexes **1a**, **1b** and **2a**, containing BNDA, dissolve in acetonitrile at room temperature and are stable in this solvent both at room temperature and under reflux; they are recovered unchanged as shown by MS-FAB and ^{1}H-NMR analysis of the residue obtained after removal of solvent. In contrast, acetonitrile displaces DMBNDA at room temperature from the complexes **1d** and **2b**; the signals due to the free amine appear after some hours in the ^{1}H-NMR spectrum of these complexes recorded in CD_3CN. These data indicate the stability of the metal–primary amine bond and suggest that the complexes **1a**, **1b** and **2a**, in the optically active form, could be employed as catalytic precursors in asymmetric synthesis.

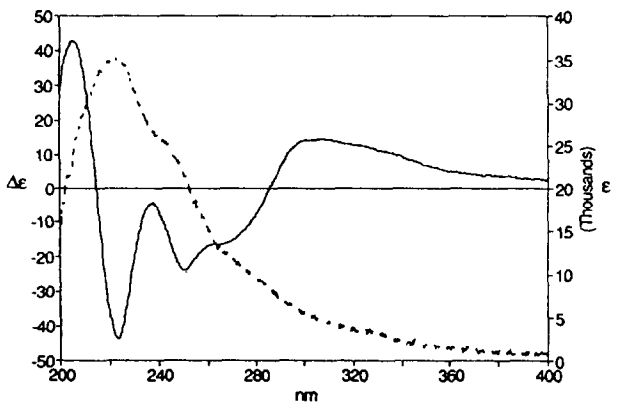


Fig. 2. Absorption (-----) and CD (———) spectrum of [Rh(COD){(*R*)-BNDA}]BF_4 in methanol.

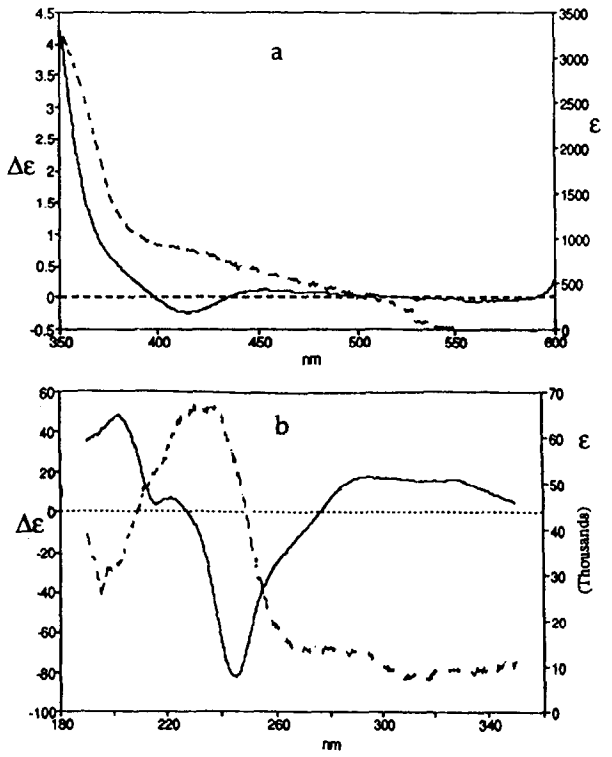


Fig. 3. Absorption (-----) and CD (———) spectrum of [Ir(COD){(*R*)-BNDA}]BF_4 in methanol: (a) between 600 and 350 nm; (b) between 360 and 190 nm.

2.4. Synthesis and chirooptical properties of the optically active complexes [Rh(COD){(R)-BNDA}]BF_4, (R)-1a, [Rh(NBD){(R)-BNDA}]BF_4, (R)-1b, and [Ir(COD){(R)-BNDA}]BF_4, (R)-2a

The optically active complexes (*R*)-**1a**, (*R*)-**1b** and (*R*)-**2a** have been prepared by reaction of the corresponding rhodium- or iridium- dimer with (+)(*R*)-BNDA following the procedure previously reported for the synthesis of the racemic complexes. Figs. 2 and 3 show the absorption and circular dichroism (CD) spectra recorded in methanol, of the complexes (*R*)-**1a** and (*R*)-**2a** respectively.

The UV–VIS spectrum of (*R*)-**1a**, measured between 400 and 200 nm, shows (Fig. 2) a clear maximum at 225 nm ($\varepsilon = 35\,000$) and two shoulders at 250 and 280 nm. This spectrum differs from that of (*R*)-BNDA, where four main absorptions are recognizable [16] at 370, 270, 240 and 215 nm. The difference is particularly evident in the high-energy region. The most intense absorption is clearly blue-shifted in the complex with respect to the free ligand. This observation can be interpreted as follows: the lone pair, which in BNDA is fully conjugated with the aromatic electrons giving rise to a 'strongly perturbed' naphthalene chromophore, characterized by a strong absorption at 245 nm, in the complex (*R*)-**1a** is engaged in the formation of the N–metal bond. Then the perturbation of the naphthalene

cromophore is strongly reduced leading to a 'weakly perturbed' chromophore, whose absorption will resemble the 220 nm band of the naphthalene; this accounts for the blue shift. The CD spectrum shows, in the same range, Cotton effects at 310 nm ($\Delta\varepsilon = +15$), 270 nm ($\Delta\varepsilon = -15$), 250 nm ($\Delta\varepsilon = -25$), 225 nm ($\Delta\varepsilon = -45$), 210 nm ($\Delta\varepsilon = +45$). The first two absorptions are also present in the spectrum of (*R*)-BNDA and are assignable to $\pi-\pi^*$ transitions of the free ligand. The intense negative couplet at 210 nm can be related to the coupling of the long-axis polarized ^{1}B transition of the naphthalene chromophore: the negative sign is an indication of a cisoid conformation [16] of the binaphthyl ligand, which is required for complexing to the metal.

The Ir(I) complex (*R*)-**2a** shows (Fig. 3(a)) between 500 and 400 nm an absorption tail with $\varepsilon = 500-1000$; correspondingly, in the CD spectrum, two weak Cotton effects can be observed. Taking into account their energy position and intensity these bands could be assigned [19] to d–d transitions localized on the metal ion. At shorter wavelengths (Fig. 3(b)) the absorption spectrum shows bands at 330 nm ($\varepsilon = 10000$), 290 nm ($\varepsilon = 12000$) and 240 nm ($\varepsilon = 65000$). In the CD spectrum, Cotton effects can be observed at 330 nm ($\Delta\varepsilon = +20$), 290 nm ($\Delta\varepsilon = +20$), 245 nm ($\Delta\varepsilon = -80$), 230 nm ($\Delta\varepsilon = +10$), and 210 nm ($\Delta\varepsilon = +45$). The clear couplet effect present in the CD spectrum of the Rh(I) complex **1a** is not observable in the case of the Ir(I) counterpart. It is not easy to provide a satisfactory explanation of this observation, although there are two possibilities. First, the different nature of the metal ion (i.e. Ir vs. Rh) can cause the presence of additional transitions (e.g. charge transfer excitations) which can mask or even cancel the couplet. The difference could also arise form dissimilar structures for the two complexes, which could cause different perturbations of the naphthalene chromophores, and hence different absorption features and different Cotton effects.

2.5. Catalytic activity

The enantioselective reduction of double bonds by molecular hydrogen, or of carbonyl groups by hydrogen transfer from 2-propanol, are widely investigated reactions which are catalyzed by rhodium and iridium complexes containing optically active phosphine or nitrogen donors [20]. In this context we studied the catalytic activity of the optically active complexes (*R*)-**1a**, (*R*)-**1b** and (*R*)-**2a** in the reduction of acetophenone by hydrogen transfer from 2-propanol and in the hydrogenation of AAZ.

Table 2
Reduction of acetophenone to 1-phenylethanol by hydrogen transfer from 2-propanol in the presence of [M(diene)(BNDA)]BF_4 complexes **1a**, **1b** and **2a** [a,b]

Run	Catalyst	KOH/catalyst (mol/mol)	*T* (°C)	Conv. (%)	e.e (%)
1	(*R*)(*S*)-**1a**	—	65	0	
2	(*R*)(*S*)-**1b**	—	65	0	
3	(*R*)(*S*)-**2a**	—	65	0	
4	(*R*)(*S*)-**1a**	5	20	< 5	
5	(*R*)(*S*)-**1b**	5	20	< 5	
6	(*R*)(*S*)-**2a**	5	20	< 5	
7	(*R*)(*S*)-**1a**	5	65	100	
8	(*R*)(*S*)-**1b**	5	65	100	
9	(*R*)(*S*)-**2a**	5	65	100	
10	(*R*)-**1a**	5	65	100	0.0
11	(*R*)-**1b**	5	65	100	0.0
12	(*R*)-**2a**	5	65	100	0.0

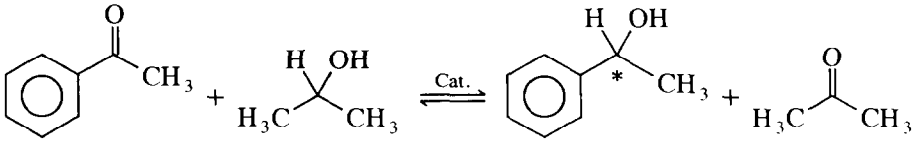
[a] **1a**, [Rh(COD)(BNDA)]BF_4; **1b**, [Rh(NBD)(BNDA)]BF_4; **2a**, [Ir(COD)(BNDA)]BF_4.
[b] Catalyst, 0.034 mmol; acetophenone, 0.8 ml (6.8 mmol); 2-propanol, 40 ml; reaction time, 24 h.

2.5.1. Reduction of acetophenone by hydrogen transfer from 2-propanol

The results obtained in the catalytic reduction of acetophenone to 1-phenylethanol by hydrogen transfer from 2-propanol with racemic (*R*)(*S*)-**1a**, (*R*)(*S*)-**1b** and (*R*)(*S*)-**2a** (Scheme 3) are reported in Table 2.

No reaction is observed under reflux for 24 h (runs 1–3). In the presence of KOH, often used as promoter for this reaction [21], the conversion to 1-phenylethanol is low at room temperature (runs 4–6) but becomes complete under reflux (runs 7–9). Using (*R*)-**1a**, (*R*)-**1b** and (*R*)-**2a** as optically active catalytic precursors, racemic 1-phenylethanol was obtained (runs 10–12).

The necessity to operate in the presence of a base, which could displace the amine from the metal, prompted us to investigate the behaviour of the complexes with KOH in alcoholic solution. As a representative example, we report the NMR spectra of the complex [Rh(COD)(BNDA)]BF_4, **1a**, before and after treatment with KOD. Complex **1a** (Fig. 4(a)) exhibits, between 8.2 and 6.9 ppm, a group of signals due to pairs of equivalent aromatic protons of the amine, at 4.4 and 4.05 ppm, two multiplets assigned to the olefinic protons of COD and, at 2.4 and 1.82 ppm, two multiplets due to the methylenic protons of COD. After KOD is



Scheme 3.

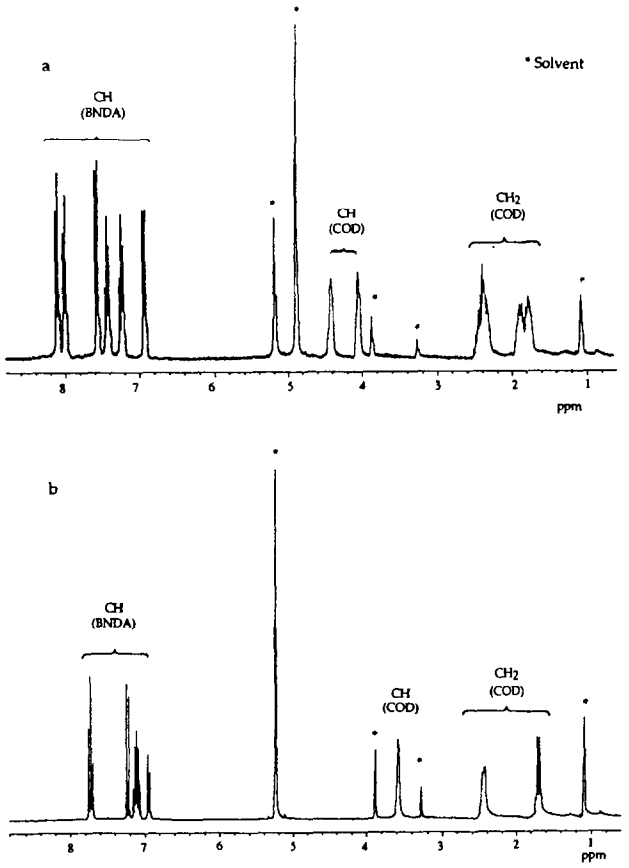


Fig. 4. ^{1}H-NMR spectra (300 MHz; solvent: 1:1 mixture of 2-propanol-d_8 and methanol-d_4) of: (a) [Rh(COD)(BNDA)]BF_4; (b) [Rh(COD)(BNDA)]BF_4 + KOD.

added, the NMR spectrum shows significant changes (Fig. 4(b)). The signals of the aromatic protons of the amine are considerably different from those observed in the complex and are similar to those of the free ligand. The two multiplets of the olefinic protons of COD collapse to a single signal at 3.58 ppm and the resonances of the methylenic protons are shifted at 2.46 and 1.69 ppm (relative intensity 1 : 1), showing also a different multiplicity. It is important to note that the COD resonances are similar to those of the dimeric complex [Rh(OMe)(COD)]$_2$, formed by reaction of [RhCl(COD)]$_2$ and KOH in methanol [22]. These results indicate that KOD causes the removal of the amine from rhodium, whereas the diolefin remains still bonded to it. Analogous behaviour has also been found for the other rhodium and iridium complexes containing BNDA and DMBNDA.

In order to obtained more insight into this phenomenon, we have studied the behavior of the complex [Rh(COD)(TMEDA)]BF_4, **3**, containing the tertiary amine *N,N,N′,N′*-tetramethylethylenediamine TMEDA [15], with KOD. Complex **3** exhibits (Table 1) a multiplet at 4.05 ppm, assigned to the olefinic protons of COD, two singlets at 2.62 and 2.57 ppm due respectively, to the methylene and methyl protons of TMEDA and two multiplets at 2.48 and 1.86 ppm assigned to the methylene protons of COD. On adding KOD the signals of TMEDA are shifted to 2.42 and 2.22 ppm characteristic of the free ligand; the signals of COD are present at 3.58 ppm (olefinic protons) and at 2.46 and 1.70 ppm (methylene protons), as observed in the previous experiment (see Fig. 4(b)). In conclusion these results indicate that the base removes the amine with formation of a diene–metal compound that can reasonably act as the catalytic precursor in the hydrogen transfer reaction.

It is interesting to note that similar ionic diene–rhodium complexes [Rh(NBD)L_n]ClO_4, in which **L** is a mono- ($n = 2$) or a diamine ($n = 1$), have been used as catalysts in the hydrogen transfer reaction of ketones from 2-propanol in the presence of KOH by Uson et al. [23]; they found that the activity depends on the amine, indicating that it remains bonded to the metal. In addition, while this work was in progress, Gamez and co-workers [24] reported the enantioselective reduction of ketones from 2-propanol, in the presence of KOH, using [RhCl(HEX)]$_2$ with C_2-symmetric 1,2-diamines as a chiral catalytic precursor. In particular, with acetophenone and (*S,S*)-1,2-diphenylethylendiamine, they obtained (*R*)-1-phenylethanol with 67% e.e. On the contrary, working in presence of optically active BNDA also these authors obtained only the racemic product.

Comparison of our results with those reported in the literature indicates that the nature of the amine and of the diolefin plays an important role in determining the stability of the catalyst in the presence of a strong base and, consequently, its enantioselective ability.

2.5.2. *Hydrogenation of AAZ*

The results obtained in the hydrogenation of AAZ to acetamidodihydrocinnamic acid are reported in Table 3. The runs 13–18 have been carried out with racemic **1a**, **1b** and **2a** to find the best reaction conditions to be employed with the optically active catalysts. The results show that it is necessary to work under hydrogen pressure (35 atm) to have complete reduction of the substrate (compare runs 13–15 and 16–18). They indicate also that rhodium complexes **1a** and **1b**, containing different dienes bonded to the metal, have the same catalytic activity and they are more active than iridium complex **2a** (runs 16–18). Using (*R*)-**1a**, (*R*)-**1b** and (*R*)-**2a** as optically active catalytic precursors, the optical purity of the acetamidodihydrocinnamic acid is very low (2%) (runs 19–21). Slightly better results (o.p = 9%) are obtained working in the presence of free (+)(*R*)-BNDA ((+)(*R*)-BNDA–complex, molar ratio = 1) (runs 22–24). However, by increasing the molar ratio between free amine and complex a reduction of both the optical purity of the product and the reaction rate are observed (runs 25–27); probably, the amine in

Table 3
Catalytic hydrogenation of AAZ in the presence of [M(diene)(BNDA)]BF_4 complexes **1a**, **1b** and **2a** [a,b]

Run	Catalyst	(*R*)-BNDA/ catalyst (mol/mol)	*P* (atm)	*t* (h)	Conv. (%)	o.p. (%)
13	(*R*)(*S*)-**1a**	—	1	24	—	—
14	(*R*)(*S*)-**1b**	—	1	24	—	—
15	(*R*)(*S*)-**2a**	—	1	24	—	—
16	(*R*)(*S*)-**1a**	—	35	24	100	—
17	(*R*)(*S*)-**1b**	—	35	24	100	—
18	(*R*)(*S*)-**2a**	—	35	30	100	—
19	(*R*)-**1a**	—	35	24	100	2
20	(*R*)-**1b**	—	35	24	100	2
21	(*R*)-**2a**	—	35	30	100	2
22	(*R*)-**1a**	1	35	24	100	9
23	(*R*)-**1b**	1	35	24	100	9
24	(*R*)-**2a**	1	35	30	100	8
25	(*R*)-**1a**	4	35	24	100	4
26	(*R*)-**1a**	20	50	24	100	2
27	(*R*)-**2a**	20	35	30	100	2

[a] **1a**, [Rh(COD)(BNDA)]BF_4; **1b**, [Rh(NBD)(BNDA)]BF_4; **2a**, [Ir(COD)(BNDA)]BF_4.
[b] Catalyst, 0.01 mmol; AAZ, 0.41 g (2 mmol); ethanol, 20 ml; temperature, 20°C.

excess binds to the metal, reducing the free cordination sites and slowing down the reaction.

3. Conclusion

The 2,2′-diamino-1,1′-binaphthyl ligands give rise, when reacted with suitable diene–rhodium(I) and –iridium(I) compounds, to new organometallic complexes which are quite stable and have been fully characterized even in optically active form. However, the metal–nitrogen bond is not sufficiently stable in the presence of strong nucleophiles, such as OH^-, for these complexes to act as catalytic precursors in hydrogen transfer reactions where these nucleophiles are present. However, in a reaction (hydrogenation) where such bond is stable, a transfer of chirality from the optically active catalytic precursor to the product has been observed. This result constitutes a firm ground for the design of more efficient enantioselective catalytic precursors, based on binaphthyl, C_2-symmetric nitrogen ligands.

4. Experimental details

All reactions were carried out under dry oxygen-free atmosphere, using conventional Schlenk-tube techniques. Solvents were purified by conventional methods, distilled and stored under nitrogen. 2,2′-Diamino-1,1′-binaphthyl, (+)(*R*)-2,2′-diamino-1,1′-binaphthyl (e.e. = 99%) and *N*,*N*′-dimethyl-2,2′diamino-1,1′-binaphthyl were prepared following the procedure of Miyano et al. [25]. *N*,*N*,*N*′,*N*′-Tetramethyl-2,2′-diamino-1,1′-binaphthyl was obtained as reported by Benson et al. [26]. AAZ and silver tetrafluoroborate were used as-received from commercial suppliers. [MCl(diene)]$_2$ complexes were prepared as reported in the literature (M = Rh; diene = COD [10], NBD [27], HEX [10]. M = Ir; diene = COD [28]). [Rh(COD)(TMEDA)]-BF_4, **3**, was prepared by reaction of [Rh(COD)$_2$]BF_4 and TMEDA as describe by Uson et al. [15]; the ^{1}H-NMR and FAB-MS parameters of **3**, not previously reported, are presented in Table 1.

The ^{1}H-NMR spectra were recorded on a Gemini 200 instrument at 200 MHz and on a Varian VXR-300 at 300 MHz; proton chemical shifts were determined relative to internal TMS (δ 0 ppm). CD spectra were recorded for CH_3OH solutions on a Jasco J-600 C dichrograph. UV–VIS spectra, in the same solvent, were recorded on a Jasco uvidec 710 spectrometer. Mass spectra (FAB) were measured on a VG 7070 E spectrometer. The GLC analyses of the hydrogen transfer experiments (Table 2) were carried out with a Perkin–Elmer 8600 gas chromatograph equipped with a 30 m × 0.52 mm DB-1 capillary column, using helium as carrier gas. Optical rotations were determined with a JASCO DIP-360 polarimeter. Decomposition points were measured on a Kofler hot-stage apparatus. Microanalyses were performed by the Laboratorio di Microanalisi, Facoltá di Farmacia, Universitá di Pisa, Italy.

Proton NMR spectroscopic studies of the reaction between the [M(diene)(diamine)]BF_4 complexes and KOD were carried out by dissolving the complex in a 1 : 1 mixture of 2-propanol-d_8 and methanol-d_4 in a 5 mm o.d. NMR tube to which KOD was added. The course of the reaction was monitored on a Varian VXR-300 NMR spectrometer.

Yields, elemental analyses, ^{1}H-NMR and mass data for the complexes [M(diene)(diamine)]BF_4, **1a–d**, **2a**, **2b** and **3** are reported in Table 1.

*4.1. Preparation of complexes [Rh(diene)(diamine)]BF_4 (diamine = BNDA, diene = COD, **1a**, NBD, **1b**, HEX, **1c**; diamine = DMBNDA, diene = COD, **1d**)*

Only the preparation of [Rh(COD)(BNDA)]BF_4, **1a**, is described in detail, the experimental procedure being the same for all the other complexes. Silver tetrafluoroborate (0.21 g, 1.07 mmol) in THF (40 ml) was added to [RhCl(COD)]$_2$ (0.26 g, 0.53 mmol) in THF (30 ml) and the mixture was stirred vigorously at room temperature for 1 h. Precipitated silver chloride was filtered off and the yellow solution was treated with BNDA (0.3 g, 1.06 mmol) in THF. The mixture was stirred for 1 h. Addition of pentane caused the precipitation of **1a** as a yellow solid that was filtered, washed with diethyl ether

and recrystallized from dichloromethane–pentane (0.524 g, 0.9 mmol).

4.2. Preparation of complexes [Ir(COD)(BNDA)]BF_4, 2a, and [Ir(COD)(DMBNDA)]BF_4, 2b

The complexes **2a** and **2b** were synthesized following the same experimental procedure; only the preparation of **2b** is describe in detail. Silver tetrafluoroborate (0.174 g, 0.89 mmol) in acetone (20 ml) was added to $[IrCl(COD)]_2$ (0.295 g, 0.44 mmol) in acetone (25 ml) and the mixture was heated under reflux for 1 h. After cooling to room temperature, the precipitated silver chloride was filtered off and the red solution was treated with DMBNDA (0.275 g, 0.88 mmol) in acetone (15 ml). The mixture was stirred for 1 h at room temperature and pentane was added to the resulting orange solution. Complex **2b** precipitated as a red-orange solid that was filtered, washed with diethyl ether and recrystallized from dichloromethane–pentane (0.493 g, 0.7 mmol).

4.3. Catalytic reduction of acetophenone by hydrogen transfer from 2-propanol in the presence of complexes 1a, 1b, and 2a

All experiments were carried out under argon in a 100 ml three-necked round bottom flask, fitted with a reflux condenser and provided with a serum cap and magnetic stirrer. In a typical experiment (run 12, Table 2) [Ir(COD){(*R*)-BNDA}]BF_4, *R*-**2a** (0.023 g, 0.034 mmol), 2-propanol (40 ml) and acetophenone (0.8 ml, 6.8 mmol) were introduced into the flask. Then, 1 ml of a 2-propanol solution of 0.17 M KOH was added. The resulting orange solution was heated under reflux. The progress of reaction was checked by withdrawing samples of the reaction mixture and analysing them by GLC. At the end of the reaction the solution was neutralized with acetic acid and the solvent was evaporated. 1-Phenylethanol was quantitatively recovered by distillation under reduced pressure, $[\alpha]_D^{25} = 0$ (neat).

4.4. Catalytic hydrogenation of AAZ in the presence of complexes 1a, 1b and 2a

All experiments were performed in a 125 ml stainless steel rocking autoclave. In a typical experiment (run 22, Table 3) a glass vial, containing [Rh(COD){(*R*)-BNDA}]BF_4, *R*-**1a** (0.006 g, 0.01 mmol), ethanol (20 ml), (+)(*R*)-BNDA (0.003 g, 0.01 mmol), AAZ (0.41 g, 2 mmol), was introduced into the autoclave under nitrogen. The gas was removed in a vacuum and the autoclave was charged with hydrogen (35 atm). The autoclave was stirred at room temperature for 24 h. It was discharge and the solid material present in the reaction mixture was filtered off. The filtrate was treated successively with NaOH (10%) and with diethyl ether. The alkaline washings were separate from the organic phase and acidified with HCl (10%). Then the aqueous solution was extracted with diethyl ether and the organic phase was dried over magnesium sulphate. The solvent was removed in a vacuum giving white crystals of acetamidodihydrocinnamic acid (0.41 g) $[\alpha]_D^{25} = -4.7$ ($c = 1$, C_2H_5OH), o.p. = 9% [29].

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