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Optically Active Phenanthrolines in Asymmetric Catalysis. III. Highly Efficient Enantioselective Transfer Hydrogenation of Acetophenone by Chiral Rhodium/3-Alkyl Phenanthroline Catalysts.

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Abstract: The *in situ* catalysts prepared from [Rh(Diol)Cl]$_2$ (Diol = 1,5-Hexadiene or 1,5-Cyclooctadiene) and 3-alkylphenanthrolines display an extremely high catalytic activity in the transfer hydrogenation of acetophenone. Turn over rates up to 10,000 cycles-per-hour (c/h) have been recorded in 2-propanol solution at 83°C in the presence of KOH as a promoter. Asymmetric inductions up to 65% e.e. are obtained with the ligand **3c** bearing a chiral trimethylpropyl substituent. This is an extraordinarily high value in view of the long distance existing between the chiral carbon atom and the reactive site of the catalyst. Experimental evidences suggest that in the asymmetric process the most active and stereoselective catalytic species might be a rhodium hydride complex containing two phenanthroline ligands in a chiral C_2 array.

In recent years optically active nitrogen compounds have attracted increased interest as ligands for transition metal ions in asymmetric catalysis[1]. This attention stems from the consideration that nitrogen derivatives can be chiral modifiers as efficient as chiral phosphines in several asymmetric reactions and that, additionally, they can be profitably employed even in few catalytic processes where the use of phosphines is incompatible with the operative conditions[2].

Optically active alkylphenanthrolines have been recently shown to be efficient chiral ligands in promoting the asymmetric transfer hydrogenation of acetophenone in the presence of rhodium catalysts[3].

The prominent features of the catalytic system originated by these new ligands are the high catalytic activity, up to 500 cycles per hour (c/h), and the complete selectivity displayed in the reduction.

The stereoselectivity is apparently less satisfactory since the highest optical yield so far recorded does not exceed 31% e.e., to be compared with 75% e.e and 84% e.e. that are the highest values obtained in the asymmetric transfer hydrogenation of alkyl aryl ketones with rhodium[4] and iridium[5] catalysts, respectively.

A more careful examination, however, shows that the significance of this stereochemical result lies well beyond its extent for three reasons. First, because the best value has been obtained with a phenanthroline with a 3-*sec.*butyl substituent and this group is usually poorly efficient in transferring the chiral information because of the small structural differentiation responsible for its chirality (a methyl *vs.* an ethyl group). Second, the asymmetric carbon atom of the *sec.*butyl group is not less than four bonds far away from the reactive site where enantioselection takes place. Last but not least, this seems one of the rare case in asymmetric catalysis where the proximity effect does not hold, since 3-substituted phenanthrolines are more efficient than the corresponding 2-substituted[3].

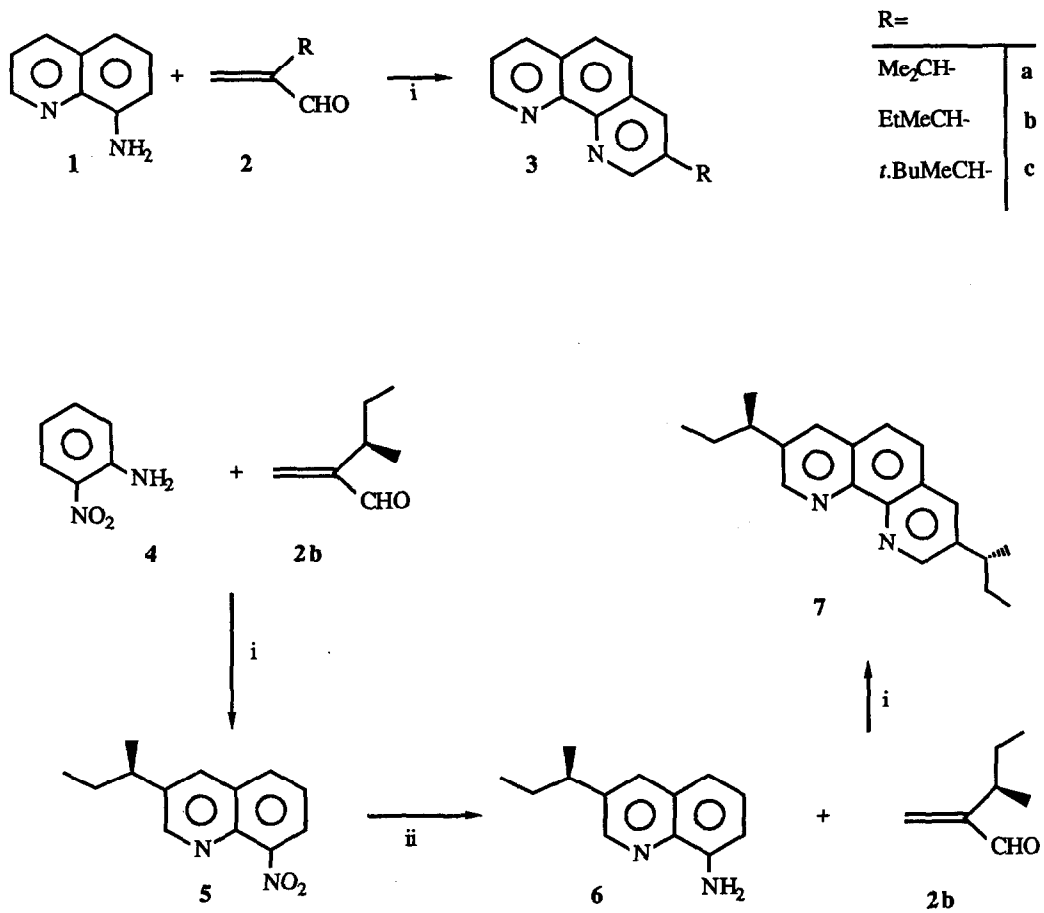
We reasoned that a deeper understanding of this intriguing behavior and, hopely, an improved efficiency in the enantioselectivity of this catalytic system could be attained either by introducing a more demanding chiral substituent on the phenanthroline backbone or by providing a C_2 symmetry to the ligand. Thus, we have undertaken the synthesis of (-)-(S)-3-(1,2,2-trimethylpropyl)-1,10-phenanthroline **3c** and (+)-(S,S)-3,8-di-*sec.*butyl-1,10-phenanthroline **7** (Scheme).

Compound **3c** was synthesized from 8-aminoquinoline **1** and (+)-(R)-2-(1,2,2-trimethylpropyl)acrolein **2c** according to the procedure previously employed for the preparation of the 3-*sec.*butyl analogue **3b**. The necessary intermediate **2c** is easily accessible in three steps from (+)-(R)-3,4,4-trimethylpentanoic acid, obtained in 92% e.e. by optical resolution of the racemic product with dehydroabiethylamine[6].

The preparation of the disubstituted phenanthroline **7** was readily accomplished in three steps. Condensation of 2-nitro aniline **4** with 96% optically pure (+)-(S)-2-*sec.*butylacrolein **2b** gave (+)-(S)-3-*sec.*butyl-8-nitroquinoline **5** which was then hydrogenated to the corresponding amino derivative **6**. A further Doebner-Miller reaction of this compound with one more equivalent of the optically active acrolein **2b** gave the expected derivative. Despite the overall yield of this reactions sequence was lower than 10%, this procedure was by far more expedient than the direct condensation of *o.*phenylendiamine with **2b** which produced almost intractable tars containing only traces of the desired product.

Several attempts have been carried out to get a direct measure of the enantiomeric excesses of the new ligands by chromatographic as well as by spectroscopic methods. No apparent peak separation could be obtained for both the ligands by HPLC and GLC on chiral stationary phases and chiral shift reagents also did not succeed in separating any of the proton resonances of the alkylphenanthrolines **3b**, **3c** and **7**. Compound **3b**, however, was able to induce a partial separation in one of the peaks of the chiral ligand of the shift reagent $Eu(hfc)_3$, as confirmed by using a racemic sample. Unfortunately, this effect was not so pronounced as to allow an evaluation of the integrals of the separate peaks more accurate than 90 ±10%. This value substantially corresponds to the optical purity of the starting material (96% e.e.) and, within the boundaries of the reliability of the N.M.R. determination, this fact confirms that the synthetic process employed for the preparation of 3-alkyl-1,10-phenanthrolines is racemization free[3].

SCHEME

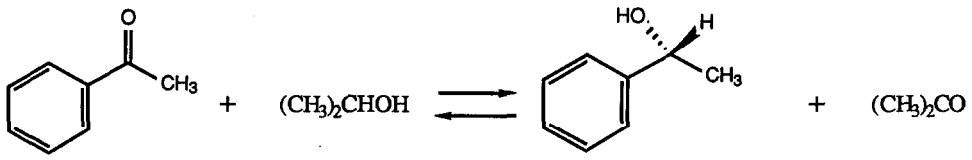


i) H_3PO_4 85%, As_2O_5

ii) H_2, Pd/C

The Rhodium catalyzed asymmetric hydrogen transfer from 2-propanol (DH_2) to acetophenone (S) (Scheme 2) is the reaction of choice for testing the efficiency of the new ligands. The reaction is carried out under inert atmosphere at reflux temperature (83°C) using a high excess of 2-propanol (DH_2/S = 81.5) in order to obtain high conversions of the substrate despite of the unfavorable equilibrium constant. A basic cocatalyst, KOH in our case, is essential otherwise no reaction takes place. The rate and the enantioselectivity of this process are markedly dependent on several parameters and most of them have been investigated in this work.

SCHEME 2



Catalytic precursor.

Two Rhodium complexes of the same general structure [Rh(Diol)Cl]2, **8**, Diol = 1,5-Cyclooctadiene (Cod) or 1,5-Hexadiene (Hex), were employed as catalytic precursors. Selected results obtained in the presence of (+)-(S)-3-*sec*.butyl-, (-)-(S) 3-(1,2,2-trimethylpropyl)- and (+)-(S,S)-3,8-di-*sec*.butyl-1,10-phenanthrolines, **3b** , **3c** and **7** respectively, are summarized in Table 1. With all the ligands the Cod precursor is much less active, but more stereoselective than the Hex. The difference in the catalytic activity is quite high, covering almost two orders of magnitude and can be attributed to the different stability of the coordinated olefin. The difference in stereoselectivity is less pronounced and may ultimately rest on the same reason (vide infra).

TABLE 1

REDUCTION OF ACETOPHENONE CATALYZED BY [Rh(Diol)Cl]2 AND 3-ALKYLSUBSTITUTED-1,10-PHENANTHROLINES ([Rh] = 3.2×10^{-4} M; [S]/[Rh] = 500; [KOH]/[Rh] = 6; [Phen]/[Rh] = 2)

Run	Diol	Phen	Conv.(%)	Time (m)	r (c/h)[a]	e.e (%)[b]
1	Hex	**3 b**	95	10	2850	18.5
2	Cod	**3 b**	66	420	47[c]	31.5
3	Hex	**3 c**	97	10	2900	57.5
4	Cod	**3 c**	89	240	60[c]	63.0
5	Hex	**7**	16	360	n. d.	0

a) Specific rate (turnover number) in cycles (or moles of substrate consumed) x $hour^{-1}$ x g atom of Rh^{-1}. Average value between 0 and 10 min b) Prevailing configuration is always (-)-(S). c) Calculated on the total reaction time.

Structure of the ligand.

The introduction of one bulky chiral group in position 3 onto the phenanthroline framework as in **3c** results in a sharp improvement of the enantioselectivity of the reaction without any unfavorable effect on the reaction rate. On the contrary, the C_2 symmetry disubstituted phenanthroline **7** originated in all the cases a catalytic system of poor activity and devoid of enantiodifferentiating ability.

Catalyst concentration.

The dependences of the catalytic activity and stereoselectivity on the concentration of the catalyst are clearly apparent from the selected results summarized in Table 2. Since the initial concentration of acetophenone has been kept constant to $1.6.10^{-1}$ M throughout all the catalytic runs, the catalyst concentration is expressed as well by the substrate-to-Rhodium ratio [S]/[Rh] which is the parameter used in the text.

With both ligands, a decrease in the concentration of the catalytic precursor results in an increase of both the specific rate and the asymmetric induction. This fact indicates that the more active catalytic species is at the same time the more stereoselective and that its relative concentration in solution increases as the total Rhodium concentration decreases.

TABLE 2

REDUCTION OF ACETOPHENONE CATALYZED BY $[Rh(Hex)Cl]_2$ AND 3-ALKYLSUBSTITUTEDPHENANTHROLINES **3b** AND **3c**. ([S] = $1.6x10^{-1}$ M; [KOH] = $1.92x10^{-3}$ M; [Phen]/[Rh] = 2)

Run	[S]/[Rh]	Phen	Conv.(%)	Time(m)	r(c/h)	e.e.(%)
1	200	**3b**	94 (95)	5 (10)	2250	4.0
2	500	**3b**	95	10	2850	18.5
3	1000	**3b**	84 (89)	10 (23)	5040	25.0
4	2000	**3b**	61 (87)	10 (90)	7320	28.0
5[a]	2000	**3b**	72 (89)	10 (40)	8640	30.0
6	200	**3c**	90 (96)	5 (10)	2160	36.0
7[b]	200	**3c**	92	60	184[c]	57.8
8	500	**3c**	97	10	2900	57.5
9	1000	**3c**	96	10	5750	61.5
10	2000	**3c**	68 (90)	10 (45)	8150	60.5

a) [Phen]/[Rh] = 4 b) $[Rh(Cod)Cl]_2$ as catalytic precursor. c) Calculated on the total reaction time.

Ligand concentration.

The effect of addition of increasing amounts of ligand at constant catalyst concentration has been thoroughly examined (Table 3). A close analogy with the trend recorded in the transfer hydrogenation of 4-*t*.butylcyclohexanone with $[Rh(Hex)Cl]_2$/4,7-dimethylphenanthroline[7] is noticed. Operating at [S]/[Rh] = 2000 with Hex as procatalyst and **3c** as ligand, both the catalytic activity and the stereoselectivity jump up abruptly as the [Phen]/[Rh] ratio increases from 1 to 1.5, then they steadily improve upon further increases up to a ratio of 4, where the optimum conditions are attained. The same trend is observed with ligand **3b** and with the Cod procatalyst, although in the last case the effect is less spectacular. Noticeably, ligand **3b** provides a 34.5% e.e. with Cod as procatalyst (run 8). This is an appreciable improvement of the best value obtained with this ligand in our previous work[3] (31%). These data provide evidence that more than one phenanthroline is coordinated to

the metal in the most active catalyst and point out that the presence of free ligand has a beneficial effect on the stereoselectivity.

Other parameters.

Only minor differences in rate and enantioselectivity were observed on varying the concentration of KOH between $1.92.10^{-3}$ and $2.4.10^{-4}$ M, corresponding to a KOH/Rh ratio of 24 and 3.0, respectively. In all the catalytic experiments the KOH concentration was kept within these limits. Lowering the reaction temperature to 60°C resulted in a sharp decrease of the rate with no beneficial effect on the stereoselectivity.

TABLE 3

REDUCTION OF ACETOPHENONE CATALYZED BY $[Rh(Diol)Cl]_2$ AND 3-ALKYLSUBSTITUTED PHENANTHROLINES ([Rh] = 8 x 10-5 M; [S]/[Rh] = 2000; [KOH]/[Rh] = 24)

Run	Diol	Phen	Phen/Rh	Conv.(%)	Time(m)	r(c/h)	e.e.(%)
1	Hex	**3c**	1.0	80	480	575	10.5
2	Hex	**3c**	1.5	92	90	7450	56.5
3	Hex	**3c**	2.0	90	45	8150	60.5
4	Hex	**3c**	4.0	94	30	9900	62.0
5	Hex	**3b**	2.0	87	90	7320	28.0
6	Hex	**3b**	4.0	89	40	8640	30.0
7[a]	Cod	**3b**	2.0	66	420	47[b]	31.5
8[a]	Cod	**3b**	4.0	74	210	105[b]	34.5

a) [S]/[Rh] = 500 b) Calculated on the total reaction time.

The body of the results reported above clearly indicates that more than one catalytic species is formed when $[Rh(Diol)Cl]_2$ is combined in solution with a chiral phenanthroline. From the data of Tables 2 and 3 a Rhodium(I) complex containing two moles of phenanthroline coordinated to the metal can be assumed as the most active and stereoselective catalyst. The inverse dependence of the catalytic activity on the Rhodium concentration (Table 2) points out the presence of a fast equilibrium between this derivative and other catalytic species, one or more, that contain only one mole of ligand per Rhodium.These catalysts should be less active and less, or not at all, stereoselective.

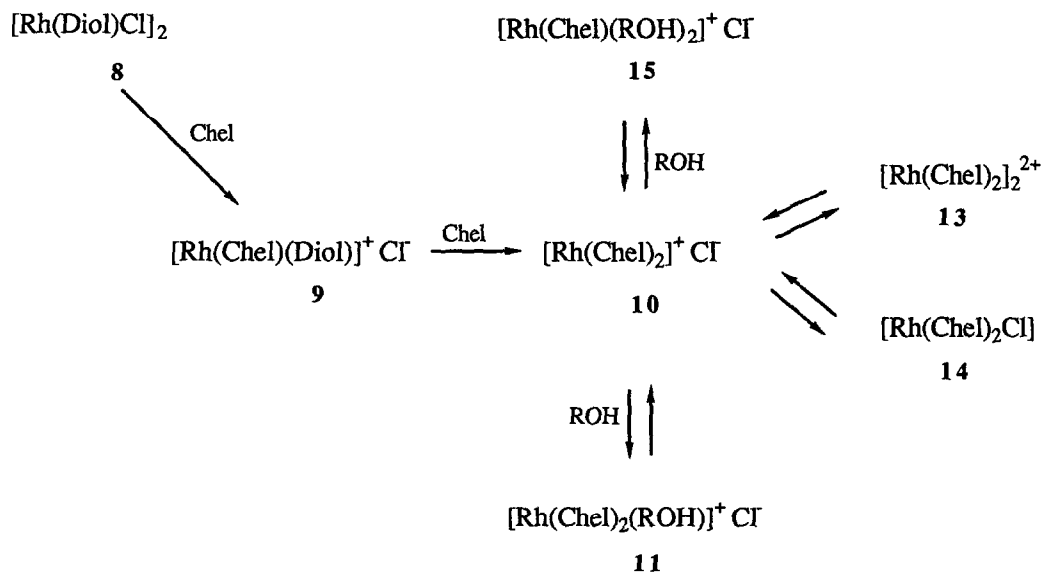
Further support to this assumption comes from the different behavior of the two catalytic precursors Cod and Hex (Table 1). Chelate nitrogen ligands (chel) like 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) readily react with $[Rh(Diol)Cl]_2$ affording the corresponding orange-red square planar cationic complexes[8] $[RhChel(Diol)]^+Cl^-$ **9**. When chel is phen, the Cod derivative shows λ_{max} 476 nm (ε 10940). 3-mono- and 3,8-di- alkylphenanthrolines react in the same way as judged by the absorption spectra of the Cod adducts of **3b**

and **7**, λ_{max} 474 nm (ε 15500) and λ_{max} 471 nm (ε 19730), respectively. Thus, differently from 2,9-dimethylphenantroline that affords a yellow pentacoordinate species [RhChel(Cod)Cl][9], it seems that one or two alkylsubstituents in the 3- or 3,8- positions do not interfere with the normal coordination of the phenanthroline ligand and that a planar geometry around the Rhodium atom can be equally attained.

In the presence of excess nitrogen ligand, the Cod derivatives **9** react sluggishly, whereas the Hex derivatives undergo a ready displacement of the olefin[10] affording the corresponding bischelate derivatives $[Rh(Chel)_2]^+Cl^-$ **10**. Such a compound, characterized by a deep violet color and by an extreme sensitivity to molecular oxygen[11], is in our opinion the species that is primarily responsible for the high catalytic activity and stereoselectivity observed. Its concentration, and hence the catalytic activity, is higher when starting from Hex rather than from Cod. Conversely, a higher concentration of free ligand is available for **10** when starting from Cod and hence a higher stereoselectivity is obtained.

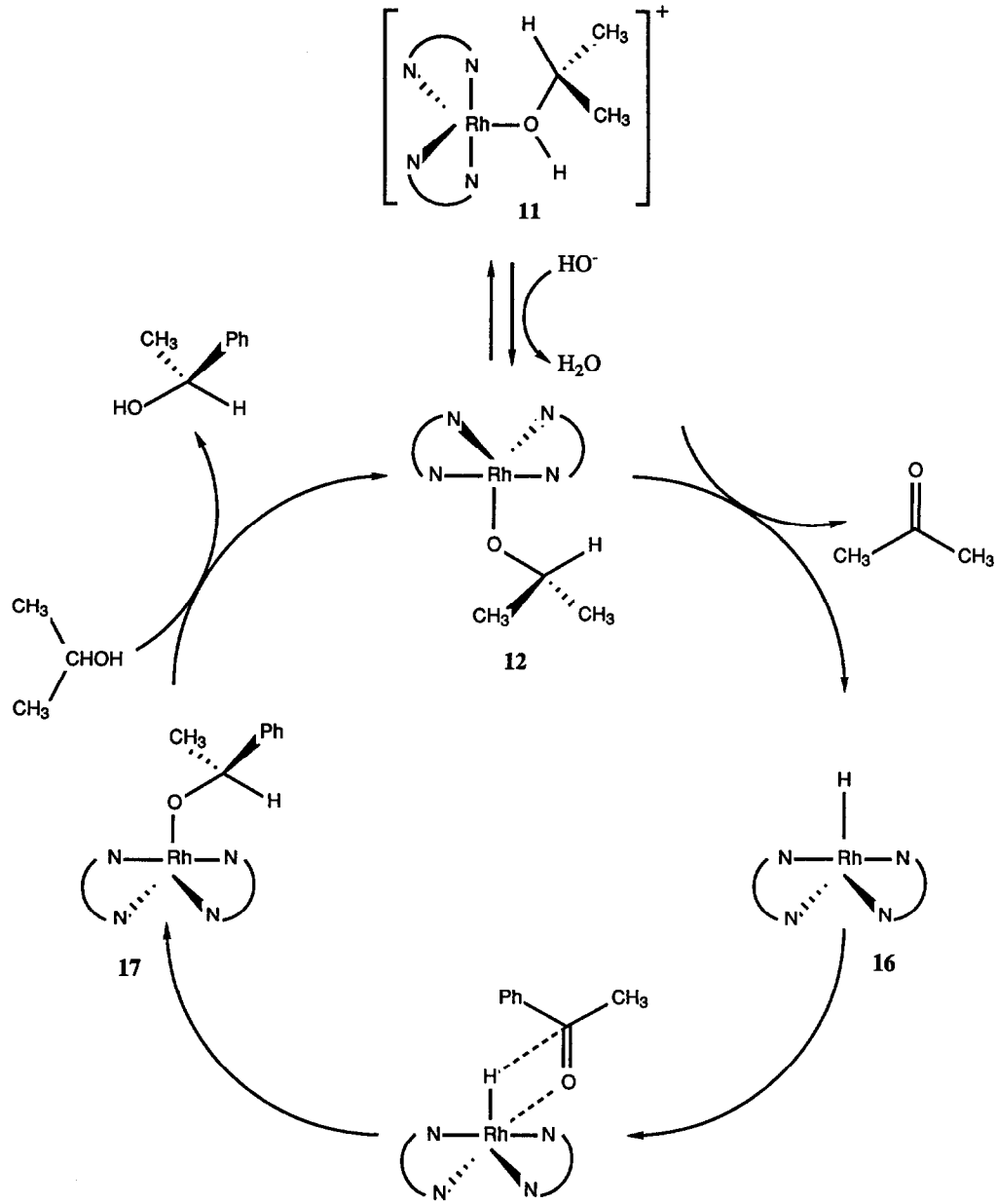
In 2-propanol solution complex **10** is involved in several equilibria which are modelled according to Creutz results[11] in Scheme 3. Activation of **10** for catalysis can reasonably involve the easy formation of the solvato complex **11** followed by proton abstraction to afford a neutral pentacoordinate alkoxy derivative **12** (see Scheme 4). This species should initiate the catalytic cycle of the reaction.

SCHEME 3



This activation path, that may account for the necessity of a base and of a preactivation protocol in the catalytic experiments, is contrasted by some competitive reactions like dimerization of **10** to **13** and

SCHEME 4



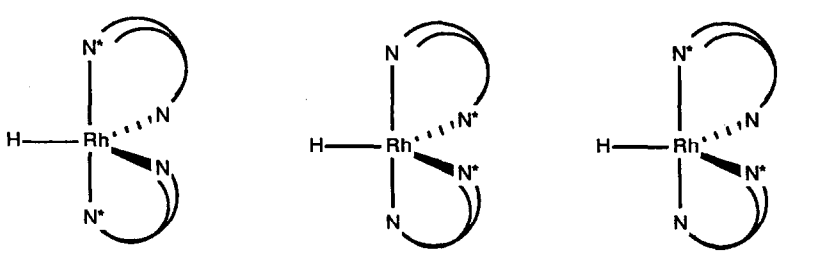
coordination of the external chloride to afford the neutral pentacoordinate complex **14**. Dissociation of one mole of phen to a solvato derivative **15** can also occur. Compounds **13** and **14** are inactive as catalysts and thus the amount of Rhodium available for catalysis is regulated by the position of these equilibria that are shifted towards **10** as the total Rhodium concentration is lowered. The species **15** should be a fairly active, but poorly stereodifferentiating catalyst. According to the data of Tables 2 and 3, the extent of its contribution to the final result can be reduced both upon increasing the [phen]/[Rh] ratio and again upon decreasing the Rhodium concentration.

A catalytic cycle for the transfer hydrogenation of acetophenone starting from compound **12** can be realized as reported in Scheme 4. Hydride abstraction from the 2-propoxy ligand should give the pentacoordinated Rhodium hydride **16** that, in the following stereodetermining step, should preferentialy add to the Re face of acetophenone to afford the (S)-alkoxy derivative **17**. Displacement of 1-phenylethanol by 2-propanol would then restore the starting situation affording again the intermediate **12**.

The hydride **16** is the key intermediate of this mechanistic picture and the species responsible for the stereoricognitive process. The high dilution and the high turnover precluded us to obtain any direct evidence of its presence during the catalysis, but its partecipation seems quite reasonable and finds support in some recent papers dealing with strictly related [Rh(bipy)$_2$H]. Its formation in protonated form upon reaction of [Rh(bipy)$_2$]$^+$Cl$^-$ with hydrogen in ethanol has been reported[11] and its possible role in the water gas shift reaction has been discussed[12]. More recently[13], evidences for its presence as the major species during the catalytic ethanol dehydrogenation promoted by [Rh(bipy)2]$^+$Cl$^-$ in the presence of NaOH have been produced. Actually, dehydrogenation of 2-propanol occurred to some extent in our system when acetophenone was absent.

Due to electronic and in particular steric reasons, the pentacoordinated hydride **16** should assume very likely a trigonal bipyramidal geometry. Taking into account that the two nitrogens of a monosubstituted phenanthroline are not equivalent, three isomeric structures are possible in this case (Fig. 1), in each of which the phen ligands are assembled around the metal in a chiral arrangement like two blades of a propeller around their axis (the Rh-H bond).

FIG. 1



N* = substituted ring.

This situation, that makes chiral the Rhodium atom too, can be compared as well to the very beginning of a double helix structure with the metal lying on the axis. Spontaneous self-assembly of polypyridine ligands

in mono-[14] or bis-[15] helicate structures has been reported and polybipyridine[16] and bisphenanthroline[17] derivatives are known to bind metals in chiral double helix disposition.

As it seems reasonable that equivalent nitrogens are accommodated in equivalent coordination sites, the formation of the species **C** seems quite unlikely and the hydride **16** should have the structure **A** or **B**. Noticeably, both these provide a C_2 symmetry around the Rhodium and the favorable effect of this fact on asymmetric reactions is well recognized[18]. Thus, the dramatic amplification of the chiral information of the alkyl substituent in remote position obtained through the chiral assembly of the two phen ligands and the presence of a C_2 axis may well account for the high and otherwise inexplicable stereoselectivity observed in the transfer hydrogenation.

Within the frame of this hypothesis, we may speculate that with 3,8-disubstituted phenanthroline **7** the bischelate derivative **10** should become unstable with respect to the monochelate **15** owing to increase of steric hindrance in the trigonal plane. This fact may account for the sharp decrease of the catalytic activity and the lack of stereoselectivity.

At present we have no substantial argument as to choice which between **A** and **B** is the real catalyst. Although computer aided molecular modelling seems to point out a slight preference for the apical disposititon of the substituted phenanthroline nitrogens, we are inclined to consider both the species as active and probably competitive catalysts in our conditions

EXPERIMENTAL

Melting points were determined on a Büchi melting point apparatus and are uncorrected. GLC Analyses were performed on a Hewlett Packard 5890A instrument equipped with a 30 m SP 1000 or SP 2100 capillary columns. ^1H NMR Spectra were recorded on a Varian VXR 300 spectrometer at 300 MHz in deuterochloroform solution with tetramethylsilane as internal standard (δ=0). Optical rotations were determined with a Perkin Elmer 241 polarimeter. Elemental analyses were performed with a Perkin Elmer Elemental Analyzer 240B.

Commercial chemical reagents were used as received. (+)-(S)-2-Methylene-3-methylpentanal **2b**, $(\alpha)_D^{25}$ + 29.8 (neat; l=1), was prepared from (-)-(S)-2-methyl-1-butanol (Fluka; 96% optical purity) as described[19]. (+)-(S)-2-Methylene-3,4,4-trimethylpentanal **2c**, $(\alpha)_D^{25}$ +75.8 (neat; l=0.1), was obtained by Mannich reaction[20] from (-)-(R)-3,4,4-trimethylpentanal prepared in 65% yield from (+)-(R)-3,4,4-trimethylpentanoic acid of 92% optical purity[6]. Propan-2-ol and butan-2-ol (Carlo Erba) were distilled from CaO and stored under an inert atmosphere. Acetophenone (Riedel) was washed with a 5% aqueous KOH solution, dried (Na_2SO_4), distilled under reduced pressure and stored under argon. The Rhodium(I)-diolefin complexes were synthesized according to literature procedures[21].

Preparation of (-)-(S)-3-(1,2,2-trimethylpropyl)-1,10-phenanthroline 3c.

(+)-(S)-2-Methylene-3,4,4-trimethylpentanal **2c** (1.51 g; 10.7 mmol) was slowly added to a mixture of 8-aminoquinoline **1** (1.23 g; 8.6 mmol) in 85% phosphoric acid (7.5 ml) containing arsenic anhydride (1.53 g), stirred at 110°C. The reaction mixture was stirred 13 h at 120°C and then was poured onto crushed ice. The aqueous solution was extracted with ether, then was made alkaline with 10% NaOH and extracted with methylene chloride. The dichloromethane solution was dried (Na_2SO_4) and, after removal of the solvent, the residue was distilled under reduced pressure (240-250°C at 10 Pa) and the distillate was flash-cromatographed with a 1/1 mixture of ethyl acetate -petroleum ether. Crystallization from ether-hexane afforded pure **3c**: 0.52 g (23% yield); m.p. 138-140°C; $[\alpha]_D^{25}$ -7.4 (c=1; EtOH 95%); ^1H NMR: 9.13 (1H, dd, 9H), 8.99 (1H, d, 2H), 8.18 (1H, dd, 7H), 7.95 (1H, d, 4H), 7.72 (2H, s, 5H and 6H), 7.55 (1H, dd, 8H), 2.84 (1H, q), 1.39 (3H, d), 0.91 (9H, s). (Found: C, 81.64; H, 7.81; N, 10.48. $C_{18}H_{20}N_2$ requires: C, 81.78; H, 7.63; N, 10.60).

According to the same procedure, 3-isopropyl-1,10-phenanthroline **3a** was prepared in 25% yield from 2-methylene-3-methylbutanal **2a**: m.p. 83-4°C (ether); b.p. 230°C/10 Pa; ^1H NMR: 9.12 (1H, dd, 9H), 9.05 (1H, d, 2H), 8.17 (1H, dd, 7H), 7.97 (1H, d, 4H), 7.72 (2H, s, 5H and 6H), 7.53 (1H, dd, 8H), 3.18 (1H, m), 1.38 (6H, d). (Found: C, 80.85; H, 6.51; N, 12.88. $C_{15}H_{14}N_2$ requires: C, 81.05; H, 6.35; N, 12.60).

Preparation of (+)-(S)-3-sec.butyl-8-nitroquinoline 5.

(+)-(S)-2-Methylene-3-methylpentanal **2b** (4 g; 35.6 mmol) was slowly added to a solution of 2-nitroaniline **4** (4.92 g; 35.6 mmol) and arsenic anhydride (5.82 g) in 85% phosphoric acid (31.5 ml) stirred at 120°C. The reaction mixture was mantained 37 h at 120°C and then poured onto crushed ice.The aqueous solution was extracted with ether, then was made alkaline with 20% NaOH and extracted with methylene chloride. The dichloromethane solution was dried (Na_2SO_4) and, after removal of the solvent, the residue was distilled under reduced pressure affording the pure product **5**: 2 g (24% yield); b.p. 220-230°C at 10 Pa ; $[\alpha]_D^{25}$ +24.6 (c=1; EtOH 95%).^1H NMR: 8.95 (1H, s, 2H), 8.00 (2H, m, 5H and 7H), 7.59 (2H, m, 4H and 6H), 2.88 (1H, m), 1.75 (2H, m), 1.37 (3H, d), 0.88 (3H, t). (Found: C, 68.11; H, 6.35; N, 11.94. $C_{13}H_{14}N_2O_2$ requires: C,67.81; H, 6.13, N, 12.17).

Preparation of (+)-(S)-3-sec.butyl-8-aminoquinoline 6.

A solution of (+)-(S)-3-*sec*.butyl-8-nitroquinoline **5** (2g; 8.7 mmol) in methanol (40 ml) was hydrogenated under atmospheric pressure at 25°C in the presence of 10% Pd/C (140 mg). After the theoretical amount of hydrogen was absorbed (3 h), the suspension was filtered, the filtrate was evaporated and the residue was distilled under reduced pressure affording the pure product **6**: 1.55 g (89% yield); b.p. 175°C/10 Pa; $[\alpha]_D^{25}$ +27.1 (c=1; EtOH 95%). ^1H NMR: 8.62 (1H, s, 2H), 7.80 (1H, s, 4H), 7.28 (1H, q, 6H), 7.16 (1H, d, 7H), 6.85 (1H, d, 5H), 2.78 (1H, m), 1.70 (2H, m), 1.33 (3H, d), 0.86 (3H, t). (Found: C, 78.15; H, 7.91; N, 13.72. $C_{13}H_{16}N_2$ requires: C, 77.96; H, 8.05; N, 13.99).

Preparation of (+)-(S,S)-3,8-di-sec.butyl-1,10-phenanthroline 7.

(+)-(S)-2-Methylene-3-methylpentanal **2b** (0.87 g; 7.75mmol) was slowly added to a mixture of (+)-(S)-3-*sec*.butyl-8-aminoquinoline **6** (1.55 g; 7.7 mmol) in 85% phosphoric acid (6.8 ml) containing arsenic anhydride (1.26 g) stirred at 110°C. The reaction mixture was stirred at 120°C 20 h and then was poured onto crushed ice. The aqueous solution was extracted with ether, then was made alkaline with 10% NaOH and extracted with methylene chloride. The dichloromethane solution was dried (Na_2SO_4) and, after removal of the solvent, the residue was distilled under reduced pressure (250-260°C at 10 Pa) and the distillate was flash-cromatographed (petroleum ether-ethyl acetate 2:1). Crystallyzation from ether-hexane afforded pure **7**: 0.6 g (27% yield); $[\alpha]_D^{25}$ +40.2 (c=1; EtOH 95%). ^{1}H NMR: 9.03 (2H, s, 2H and 9H), 8.00 (2H, s, 4H and 7H), 7.73 (2H, s, 5H and 6H), 2.90 (2H, m), 2.78 (4H,m), 1.41 (6H, d), 0.87 (6H, t). (Found: C, 82.04; H, 8.41; N, 9.79. $C_{20}H_{24}N_2$ requires: C, 82.15; H, 8.27; N, 9.58).

Catalytic transfer hydrogenation of acetophenone.

Appropriate amounts of the required phenathroline and of the catalyst precursor were added to 45 ml of propan-2-ol in a three-necked flask. The solution was deareated by heating under reflux in an argon stream for 30 min. The deareated substrate, dissolved in 5 ml of propan-2-ol, was added to the boiling solution from a dropping funnel thermostated at 60°C. Appropriate amounts of a deareated solution of KOH was then added and the progress of the reaction was monitored by GLC. At the end of the reaction, the solution was neutralized (AcOH) and the solvent was evaporated. The residue was taken up with ether and the resulting solution was extracted with 10% aqueous HCl to recover the chiral ligand. Methyl phenyl carbinol was quantitatively recovered by distillation under reduced pressure and its enantiomeric excess was determined by GLC of the corresponding *t*.butylurethane on a 50m Chirasil-L-Val capillary column (Alltech) according to a published methodology[22].

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