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The aminophosphine-phosphinites and related ligands: synthesis, coordination chemistry and enantioselective catalysis[1]

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[1] Dedicated to the memory of Professor Francis Petit

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Abstract

The synthesis and coordination chemistry of aminophosphine-phosphinites (AMPP) and closely related ligands is reviewed. Asymmetric catalytic reactions involving organometallic-AMPP complexes are presented. Examples of enantioselective C–C bond formation in the presence of nickel- (dienes and diene-olefins dimerization, allylic substitution) and palladium-AMPP catalysts (nucleophilic addition to allylic substrates), hydroformylation based on platinum and rhodium complexes, rhodium-based hydrosilylation, hydrogenation of C=C and C=O bonds in the presence of rhodium and ruthenium complexes and homo Diels-Alder catalyzed by cobalt species are presented.

Keywords: Aminophosphine-phosphinites; Asymmetric catalysis; Asymmetric C–C formation; Asymmetric hydroformylation; Asymmetric hydrogenation; Asymmetric hydrosilylation; Chiral diphosphines; Cobalt; Nickel; Palladium; Platinum; Rhodium; Ruthenium

1. Introduction

The discovery of highly selective and efficient catalysts for synthetically useful reactions constitutes a central challenge in organic chemistry. As such, asymmetric catalysis can be considered as an ideal method for synthesizing optically active compounds [1–3]. There are various possibilities to achieve such chiral catalytic systems (organic compounds, enzymes and antibodies, inorganic compounds). Nonetheless, the use of chiral organometallic complexes as homogeneous stereoselective catalysts is a most attractive strategy because it allows the access to large quantities of optically active compounds using only small amounts of optically active catalysts. The multiplication of the chiral information involved can make enantioselective catalysis competitive with enzymatic routes with respect to the industrial production of optically active organic derivatives. Therefore, over the last three decades, enantioselective catalysis pervaded numerous selective organic transformations [4–8]. Actually, the transition metal complexes act as templates that regulate organic reactions taking place in the coordination sphere.

Such an approach has seen tremendous development over the decades after the first example of homogeneous enantioselective catalysis i.e. cyclopropanation of styrene by decomposition of ethyl diazoacetate in the presence of chiral Schiff base-Cu(II) as reported by Nozaki and Noyori (ee < 10%) [9]. Afterwards, the discovery of the phosphine-Rh(I) catalysed asymmetric hydrogenation of dehydro amino acids [10–13] and phosphine-Ni-based olefin codimerization [14,15] opened the door to highly enantioselective catalysis. Today, spectacular enantioselectivities have been reached in numerous reactions leading to well-known enantioselective catalyses such as hydroformylation, cyclopropanation, allylic alkylation, organometallic addition to aldehydes, olefin isomerization, aldol-type reactions, Diels–Alder reactions, and so forth [4–8,16,17] allowing the formation of chiral C–H, C–C, C–O, C–Si, C–N bonds. These enantioselective processes are particularly important in the pharmaceutical, agrochemical, flavour, and fragrance industries because of the necessity to have access sometimes to enantiopure derivatives, especially when only one of the enantiomers is responsible for the desired biological activity, the other being poison-

ous or inducing opposed side effects. An example of the dramatic consequence of chirality mismatching was demonstrated by the tragedy resulting from the use of the tranquilliser thalidomide. The efficiency of asymmetric homogeneous catalysis with chiral organometallic compounds can now be conducted on such large scales with a sufficiently high substrate to catalyst ratio and high concentrations that industrial applications appeared and several optically active compounds have been produced via asymmetric catalysis (L-DOPA, L-menthol and carbapenems) [18–22].

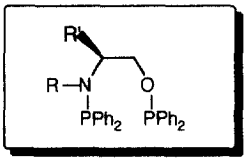
Generally, all the asymmetric catalysts present an active site for the chemical transformation located in a chiral environment usually provided by a chiral ligand bound to the metallic center. Thereby, it is clear that the course of the metal-catalysed reaction can be effectively controlled by the chiral ligands. As a matter of fact, by designing properly the ligand, the reactivity and the selectivity of a catalyst can be adjusted to a specific requirement and, consequently, the design and the synthesis of suitable ligands is of prime importance. The outcome of extensive research carried out in that area during the past three decades has been the preparation of a rapidly growing number of chiral ligands which allow high enantioselective catalytic processes, most of them being chiral chelating bisphosphines [16,17,23,24]. The most successful use of these ligands is the enantioselective hydrogenation of various functions such as C=C, C=O, C=N. Some relevant examples of chiral bisphosphines are DIOP, DIPAMP, BPPFA, BPPM, BINAP, BIPHEMP, and DUPHOS [4–8,16,17,23,24].

In the early 1980s, within a tight collaboration with Professors Buono and Peiffer in Marseille, we and others introduced at the same time the synthesis of new chiral diphosphine ligands based on aminoalcohols as the source of chirality [25–27]. We anticipated that such ligands, the aminophosphine-phosphinites further abbreviated AMPP, would behave as chelating ligands allowing a good stereocontrol when associated to a transition metal and applied in catalytic processes. In fact, the first AMPP ligands were used successfully in asymmetric hydrogenation of dehydro amino acids [25–27]. Further developments followed on the basis of both the access to new such type of ligands as well as their application to other enantioselective catalytic processes. In this account, we cover the literature that appeared so far on the synthesis of the aminophosphine-phosphinites and closely related optically active diphosphines and their corresponding chiral precatalysts as well as their use in asymmetric transformations.

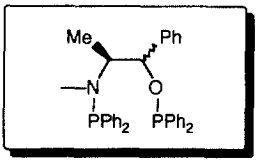
2. AMP, AMPP and BAMP ligands

Amino(do)phosphine-phosphinite ligands exhibit a dissymmetric functionality due to the presence of phosphorus moieties at both the nitrogen and oxygen atoms. The variety of this hybrid ligands arises from the nature of the substituents at the phosphorus atoms as well as of the nature of the chiral backbone. To date, more than 70 AMPP ligands have been synthesized starting from about 30 different chiral precursors (Scheme 1). In this review, we will present also closely related ligands, i.e. amino-phosphinites (AMP) and bis(aminophosphanes) (BAMP).

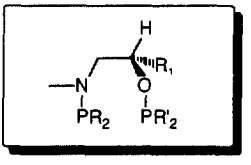
AMPP ligands ex-amino alcohols



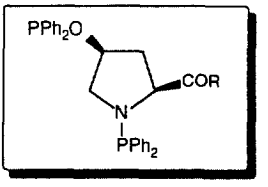
R = Me	R' = Me	AlaNOP
R = Me	R' = iPr	ValNOP
R = Me	R' = (*S*)-CH(Me)Et	IleuNOP
R = Me	R' = $CHCH_2(CH_3)_2$	LeuNOP
R = Me	R' = Ph	PheGlyNOP
R = Me	R' = CH_2Ph	PheNOP
R = Et	R' = Me	NEt-AlaNOP
R = Et	R' = Et	Butaphos*



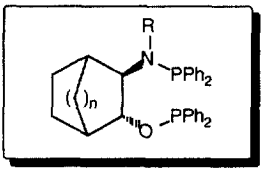
(-)-(1*R*,2*S*)	Ephos
(+)-(1*S*,2*S*)	Ψ-Ephos



R = R' = Ph, R_1 = Ph	isoPheGlyNOP
R, R' = Cp, Cy, Ph; R_1 = Me	Cp,Cp-isoAlaNOP
	Cy,Cy-isoAlaNOP
	Cy,Cp-isoAlaNOP
	Cp,Cy-isoAlaNOP
	Ph,Cp-isoAlaNOP

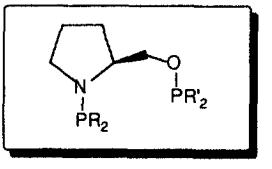


R = OEt	E-ProNOP
R = $O(CH_2)_2OEt$	E,E-ProNOP
R = NHBu	Bu-ProNOP
R = OEt, and $P(iPr)_2$	iPr-E-ProNOP



n = 0, R = H	AC-PONP
n = 0, R = Me	MAC-PONP
n = 1, R = Me	

(Döbler, Pracejus, 1987)



R, R' = Me, iPr, Cp, Cy, Ph, Nm (α-naphtyl)methyl

	Ph,Cy-ProNOP
	Cy,Ph-ProNOP
ProNOP*	Ph,iPr-ProNOP
Me-ProNOP	iPr,Ph-ProNOP
iPr-ProNOP	Ph,Cp-ProNOP
Cp-ProNOP	Cp,Ph-ProNOP
Cy-ProNOP	iPr,Cp-ProNOP
Nm-ProNOP	Cp,iPr-ProNOP
	Cy,Cp-ProNOP
	Cp,Cy-ProNOP

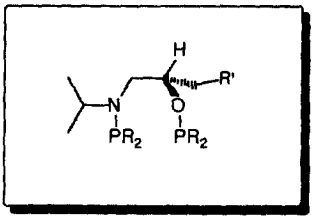
** (Cesarotti, 1982, PROLOPHOS)*

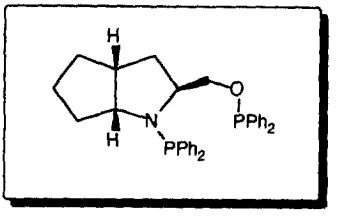
Scheme 1. Examples of aminophosphine-phosphinite and related ligands.

2.1. *Accessibility to organic chiral precursors*

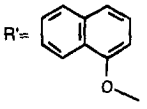
Amino alcohols are the precursors of choice for the synthesis of AMP and AMPP ligands. A large variety of these molecules is easily and cheaply attainable from natural proteinogenic amino acids, which have formed the historical basis of AMPP

Scheme 1 (continued)

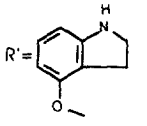




"Condensed ProNOP"
(Krause, 1995)

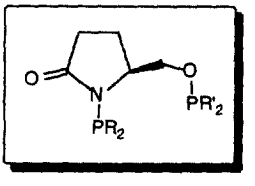


R = Ph Propraphos
R = Cy Cy,Cy-Propraphos
(Krause, 1989)

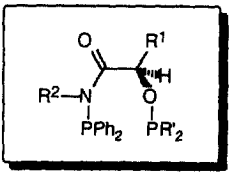


R = Ph Pindophos
(Krause, 1996)

AMPP ligands ex-amido alcohols



R, R' = Ph, Cp, Cy

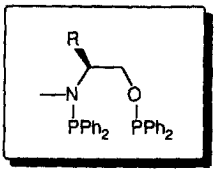


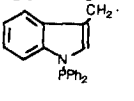
R' =Ph, Cp or Cy

Ph-oxoProNOP
Cp,Cp-oxoProNOP
Cy,Cy-oxoProNOP
Cy,Cp-oxoProNOP
Cp,Ph-oxoProNOP

R^1 = Me, R^2 = Me Ph,,R'-MeLactaNOP
R^1 = Ph , R^2 = Me Ph,R'-MeMandelNOP
R^1 = Ph, R^2 = Bz Ph,R'-BzMandelNOP

Potentialy tricoordinating AMPP ligands



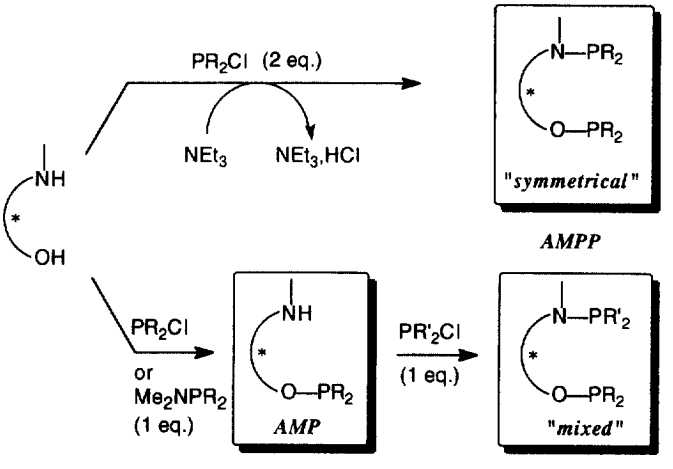
R = (*R*)-CH(Me)($OPPh_2$) ThreoNOOP
R = (*S*)-CH(Ph)($OPPh_2$) PheSerNOOP
R = $(CH_2)_2$-$OPPh_2$ AspNOOP
R = $(CH_2)_3$-$OPPh_2$ GluNOOP
R =  TryNNOP

Scheme 1. (*continued*)

and the informative acronyms used for their nomenclature [28]. Thus, a number of ligands such as for instance the so-called AlaNOP, ValNOP, ProNOP, etc., together with potentially tricoordinating ligands derived from functionalized amino acids such as ThreoNOOP, were developed (Scheme 1). Also, natural amino alcohols (in particular ephedrine at the origin of the EPHOS (AMPP) and EPHOS-NH (AMP) ligands) and other naturally important precursors (hydroxyproline, lactic acid, etc.) were used. Pracejus, Döbler and Krause in Rostock have developed AMPP ligands from purely synthetic amino alcohols (amino-2-cyclohexanol derivatives, propranolol, etc.) [29,30]. Amido alcohols, which are closely related precursors, have also been used to prepare amidophosphine-phosphinites. The former include various α-hydroxyamides as well as 5-oxoprolinol, easily obtained from cheap pyroglutamic acid, and which leads to oxoProNOP type ligands. On the other hand, diamines are at the origin of the BAMP ligands, in particular the ProNNP derivatives which are prepared from (*S*)-(anilinomethyl)pyrrolidine, a diamine easily available from natural proline.

2.2. *Preparation of AMP, AMPP and BAMP ligands*

The general synthetic scheme of AMP, AMPP and BAMP ligands is based on the nucleophilic attack of an hydroxy and/or a secondary amino or amido function of the chiral organic precursor onto a chlorophosphine in the presence of a tertiary amine (Scheme 2). Using this principle, one can prepare, in a one or a two-step synthesis, either so-called "symmetrical" or "mixed" AMPP and BAMP, which bear, respectively, the same or different substituents at the phosphorus moieties. The intermediary product of the reaction performed in the presence of one mol equivalent of a chlorophosphine is an amino-phosphinite (AMP); the latter, such as the outstanding EPHOS-NH ligand, can be isolated in good yield and further used in some specific catalytic reactions (see Section 3).



Scheme 2. Synthesis of AMPP-type ligands.

The optimal reaction conditions for the synthesis of AMP, AMPP and BAMP ligands depend on the nature of the chlorophosphine–organic precursor couple. For obvious electronic reasons, PPh_2Cl is more reactive towards a nucleophile than chlorodialkylphosphines (PR_2Cl, R = Me, *i*Pr, cyclopentyl (Cp), cyclohexyl (Cy), etc.). Also, an amine is generally more nucleophilic than an amide. Consequently, the reaction of an amino alcohol with PPh_2Cl proceeds most often at room temperature in a THF–NEt_3 mixture, while it is generally necessary to heat at reflux this mixture for the phosphinylation of an amido alcohol with a chlorodialkylphosphine. In some cases, this procedure proved inefficient, in particular for the preparation of some BAMP chelates due to the non reactivity of the -NHPh residue towards PR_2Cl (R = alkyl). It was then necessary to deprotonate first the diamino precursor with BuLi before reaction with PR_2Cl [31]. After optimization, pure AMPP and BAMP are usually isolated in 70–90% yields [32,33].

The numerous combinations between different phosphorus moieties allow the preparation of a large variety of AMPP ligands, and to a lesser extent of BAMP ligands, with adjustable electronic and steric properties. The synthetic scheme of AMPP and BAMP which combines easiness and versatility awards to this type of ligands major advantages over the other classes of chiral phosphorus ligands. Obviously, the other key points that must be taken into account are the interest of these ligands in coordination chemistry as well as their performance in transition metal-catalysed processes, and this is discussed in the following paragraphs.

3. Nickel–AMPP complexes and related catalysis

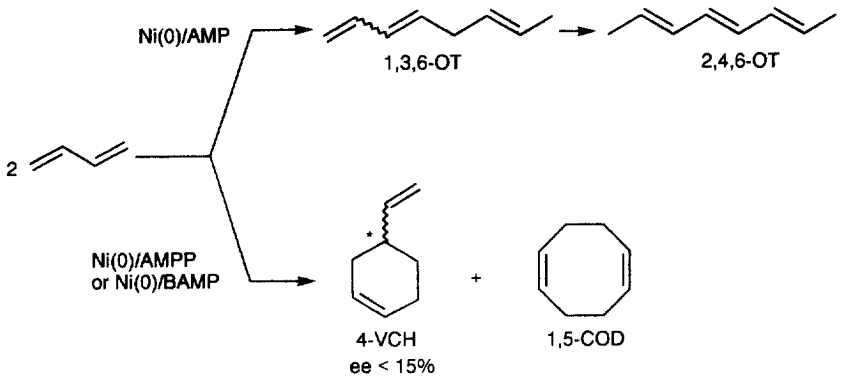
Over the last decades, much attention has been devoted to selective carbon–carbon bond forming reactions in the area of transition metal catalysed organic syntheses. In this context, nickel catalysts have shown high performances in the reactions of dienes dimerization and diene-olefins codimerization [34,35]. AMP, AMPP and BAMP ligands were evaluated in such reactions and have shown typical chemo and regioselectivities. More recently, BAMP–nickel complexes have also shown to be efficient in the asymmetric alkylation reaction of allylic acetates with dimethyl malonate.

The nickel catalysts were prepared in situ by mixing the zerovalent nickel complex $Ni(COD)_2$ with one or two equivalents of the appropriate ligand. In a few cases, zerovalent nickel catalysts were obtained through reduction of nickel salts by an alkyl or alkoxydialkylaluminium in the presence of the ligand.

3.1. Dienes dimerization

During the dimerization of butadiene, the highly selective formation of linear dimers was observed with the AMP ligands and cyclic dimers with AMPP and BAMP ligands (Scheme 3).

In the case of the linear butadiene dimerization, the $Ni(COD)_2$–(1*R*,2*S*)-Ephos-NH catalytic system has been found to be the most active ever described with a



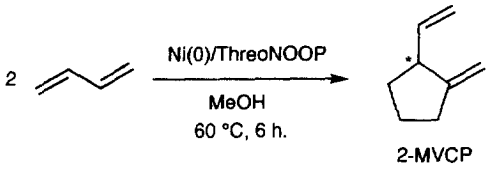
Scheme 3. Nickel ctalysed dimerization of butadiene.

turnover number (TN) up to 5000, affording almost exclusively octa-1,3,6-trienes, before the occurrence of an isomerization process leading to octa-2,4,6-trienes [36,37]. It has to be noted that no cocatalyst was added to the reaction mixture contrary to the Heimbach or Pittman systems [38,39] in which a large excess of morpholine or alcohol was introduced as a proton donor reagent. In fact, the AMP skeleton combines the two properties required by this reaction: at least one phosphinylated P–O moiety on one side of the chain and a proton in close proximity with the metal center provided by the pendant N–H group at the other side. In order to prove its contribution, labelled experiments were performed with butadiene on Ni(0)-Ephos-ND, which gave octa-1,3,6-trienes deuterated on the terminal methyl group, that is $CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2D$ [36].

In the presence of bidentate ligands, cyclic dimers were formed selectively (Scheme 3) [40]. More recently, a high 4-vinylcyclohexene/cycloocta-1,5-diene ratio (80/20) has been obtained with the bisaminophosphane and particularly with the Ni(0)–(*S*)-ProNNP system [41]. The main feature observed in this reaction was that, upon increasing the ligand/nickel ratio from 1 to 2, a selectivity into 4-VCH up to 99% has been reached. Nevertheless, whatever the ligand and the ligand/metal ratio, the optical yield remained low (ee < 15%).

When the reaction was performed in the presence of methanol, 2-methylenevinylcyclopentane (2-MVCP) could also be obtained as the major product with some ligands [42]. After optimization of the reaction conditions using the experimental research methodology [43], the Ni(0)–ThreoNOOP–MeOH catalytic system has shown to be one of the most efficient investigated with a 70% selectivity in 2-MVCP [44] (Scheme 4). Nevertheless, no enantiomeric excess has been determined. Aminophosphinite and aminodiphosphinite ligands have also been used in the presence of Ni(0)–MeOH catalytic system and gave rise to octa-1,3,7-trienes and 2-MVCP preferentially [42].

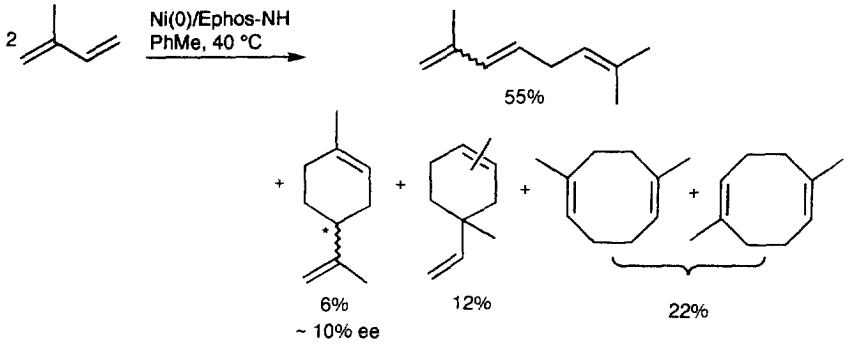
The catalytic system $Ni(COD)_2$–(1*R*,2*S*)-Ephos-NH was further evaluated with a large variety of substituted dienes. As a matter of fact, linear dimerization of substituted and functionalized dienes is of great interest for organic synthesis since



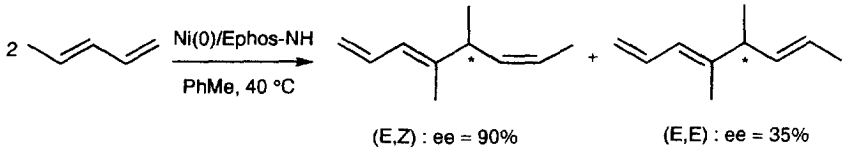
Scheme 4. Cyclic dimerization of butadiene.

it provides a useful tool for the synthesis of terpene derivatives. Among alkyl substituted dienes, isoprene and piperylene were dimerized in the presence of nickel catalysts [36,37] (Schemes 5 and 6). In the case of isoprene, both cyclic and linear dimerizations occurred and the catalytic activity decreased greatly as compared to butadiene. Moreover, the linear products arise unfortunately exclusively from a tail-to-tail linkage whereas natural terpenes are expected from a head-to-tail coupling. On the other hand, piperylene was much more reactive than its isomer and only linear dimers are produced with a remarkable selectivity into head-to-head linkage. The latter are optically active and 90% and 35% enantiomeric excesses were obtained, respectively, for the (E,Z) and (E,E) isomers.

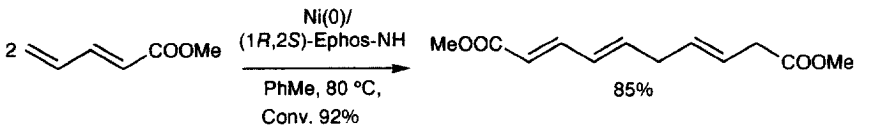
During the dimerization of functionalized dienes in the presence of $Ni(COD)_2$–(1*R*,2*S*)-Ephos-NH, only dienic esters reacted. Actually, no reaction occurred with other substrates bearing electrodonating groups such as NEt_2, OMe, $OSiMe_3$ and OAc instead of the ester function [45]. Interestingly, whatever the starting ester, only linear products were formed regioselectively. A good activity was observed with methyl penta-2,4-dienoate with an exclusive tail-to-tail linkage



Scheme 5. Nickel catalysed dimerization of isoprene.



Scheme 6. Nickel catalysed dimerization of piperylene.

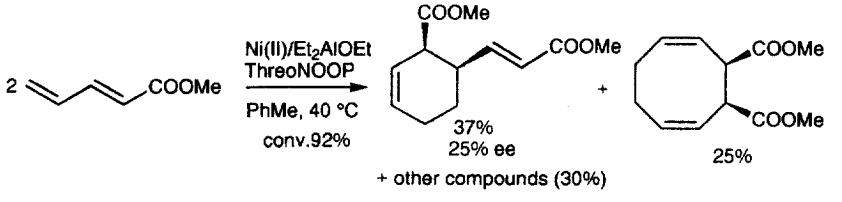


Scheme 7. Nickel catalysed dimerization of a functionalized diene.

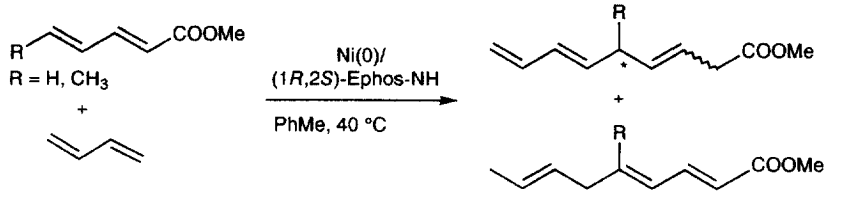
(Scheme 7). In the case of methyl sorbate, the activity was lower and the dimers were formed with a head-to-head linkage. Unfortunately, all attempts to determine the optical yield failed. The cyclodimerization of methyl penta-2,4-dienoate was also investigated with the catalytic system: $Ni(acac)_2$–Et_2AlOEt–L-ThreoNOOP (Scheme 8) [46]. A 92% conversion was obtained and the main products were cyclohexenic compounds with an enantiomeric excess of 25% into the major diastereomer.

3.2. *Diene-olefin codimerization*

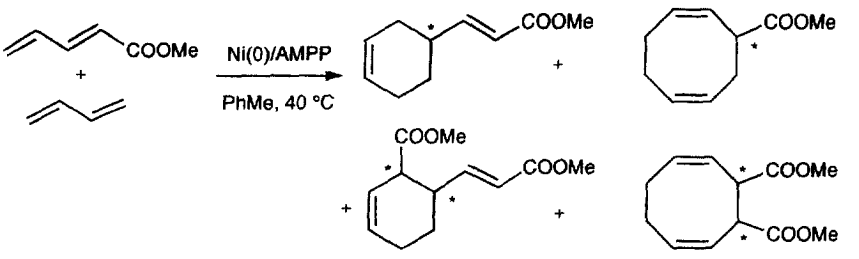
Further studies have been performed to apply these catalytic systems to cross-coupling reactions between different dienes. As in the case of cyclodimerization, only dienic esters reacted with butadiene. According to the ligand, linear or cyclic codimers were obtained. Thus, with the Ni(0)–Ephos-NH monophosphine based system, linear trienic esters have been prepared by reaction of butadiene with methyl penta-2,4-dienoate or methyl sorbate (Scheme 9) [47]. In the presence of bidentate AMPP ligands, chiral cyclocodimers were formed (Scheme 10) [48]. Butadiene/methyl penta-2,4-dienoate cyclocodimerization gave rise to vinylcyclohexenic and octadienic esters, the latter being the major products. However, cyclodimers, arising from homocyclodimerization of butadiene, were formed at the mean time. In contrast, during butadiene-methyl sorbate reaction, cyclooctadienic esters were



Scheme 8. Asymmetric dimerization of a functionalized diene.



Scheme 9. Nickel catalysed codimerization.

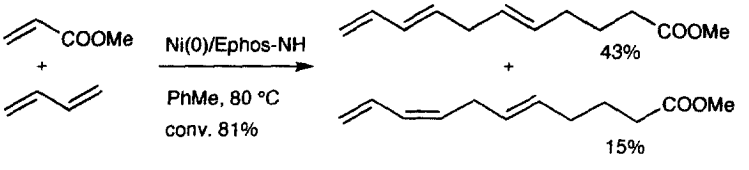


Scheme 10. Nickel catalysed cyclocodimerization.

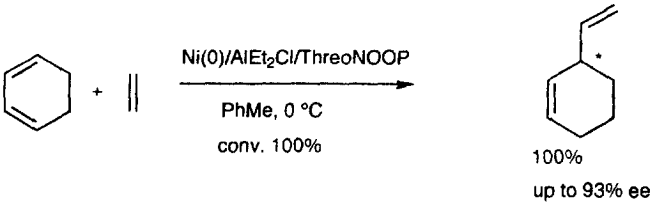
formed exclusively. In the latter, once more, a dimerization of butadiene took place concomitantly leading to cyclic dimers.

The methyl acrylate–butadiene codimerization has also been achieved with the Ni(0)–(1*R*,2*S*)-Ephos-NH catalytic system giving rise to new functionalized linear polyenes (Scheme 11) [49]. Octa-1,3,6-trienes cannot be avoided due to the high activity of this system towards linear butadiene dimerization. It has to be noticed that the cooligomers have different structures from those reported in the literature for this kind of reaction [50]. This is due again to the particular structure of the aminophosphinite ligand in which the NH moiety is directly involved in the catalytic cycle as it has been shown with labelled experiments.

The asymmetric hydrovinylation of cyclohexa-1,3-diene has been performed on $Ni(COD)_2$–$AlEt_2Cl$–AMPP or aminophosphine system (Scheme 12) [51,52]. Such catalysts were very efficient even at very low temperature. As an example, the tridentate (2*R*,3*R*)-threoNOOP ligand was one of the most enantioselective, giving quantitatively (+)-(*S*)-3-vinylcyclohexene with up to 93% ee when the reaction was carried out at −30 °C. It has also to be noticed that the reaction must be stopped just after ethylene consumption in order to avoid the isomerization of the hydrovinyl-



Scheme 11. Linear nickel-based cooligomerization.



Scheme 12. Nickel catalysed asymmetric hydrovinylation.

ation product into ethylidene cyclohexene that takes place after completion of the codimerization with AMPP based catalysts.

3.3. Alkylation of allylic acetates with stabilized nucleophiles

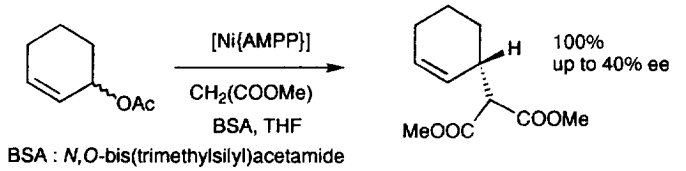
For the formation of C–C bonds, very few studies report the nucleophilic substitution reactions of allylic compounds on nickel catalysts because of the low activity of these systems in comparison with palladium catalysts [53]. Recently, the alkylation of a variety of allylic acetates with a stabilized nucleophile in presence of a BAMP–Ni(0) system gave rise to much more efficient catalysts than other usual diphosphines [54]. From an asymmetry point of view, this system has been used in the reaction of 3-acetoxycyclohexene with dimethylmalonate (Scheme 13): this is the first example of a nickel catalysed asymmetric alkylation with a stabilized nucleophile. Moreover, it proves to be the most efficient in terms of activity and remains quite competitive with the outstanding palladium/ligand systems for the enantioselectivity although the enantiomeric excess remains rather low (ee < 40%) [55].

4. Palladium–AMPP complexes and related catalysis

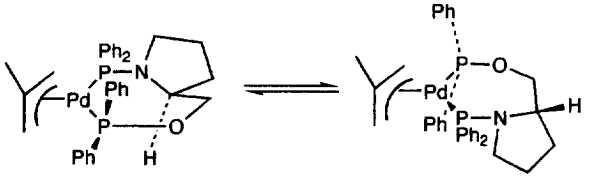
Only a few reports describe the synthesis of palladium–AMPP complexes and their related catalysis. Thus, only $[Pd(allyl)\{(S)\text{-ProNOP}\}]^+X^-$ ($X = BF_4$, PF_6) and $PdCl_2\{AMPP\}$ complexes have been described and applied in asymmetric allylation reactions.

4.1. Synthesis and characterization of Pd–AMPP complexes

The chiral complexes $[Pd(\eta^3\text{–}CH_2\text{–}CMe\text{–}CH_2)\{(S)\text{-ProNOP}\}]^+X^-$ ($X = BF_4$, PF_6) were prepared through reaction of the ligand with $[Pd(\eta^3\text{–}CH_2\text{–}CHMe\text{–}CH_2)]^+X^-$ at $-78\ ^\circ C$ [56,57]. The stereochemistry and the dynamic behaviour of such complexes have been studied essentially by NMR spectroscopy. Thus, it has been shown that the complexes exist in solution in two diastereomeric forms in equilibrium (2.5/1) (Scheme 14). This study has been further extended to analogous complexes bearing *meso* prochiral allyls (η^3–RCH–CH–CHR) where R = Me or Ph [58]. These complexes might exist as eight diastereomers, but the ^{31}P NMR spectra have revealed that in the former only two isomers are present and



Scheme 13. Nickel catalysed asymmetric allylic alkylation.



Scheme 14. Diastereomeric palladium {ProNOP} complexes.

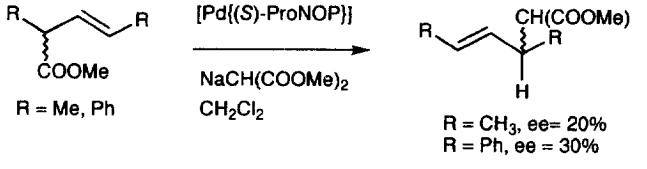
in the latter two species represent about 90% of the total amount. For both complexes a complete NMR study has shown that the allylic substituents are in a *syn* position and that the two isomers differ in allylic orientation leading to the observed chirality.

$PdCl_2${AMPP} complexes have been prepared by an exchange reaction between $(CH_3CN)_2PdCl_2$ and AMPP ligands in THF [59].

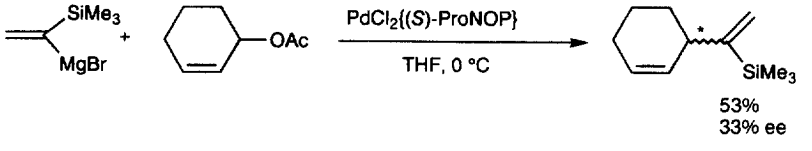
4.2. Palladium–AMPP catalysis

The palladium complexes $Pd(\eta^3\text{–}RCH\text{–}CH\text{–}CHR)\{(S)\text{–ProNOP}\}^+X^-$ catalyse the addition of soft carbon nucleophiles to allylic substrates. When racemic (E)-3-acetoxy-1,3-dimethylprop-1-ene or (E)-acetoxy-1,3-diphenyl-prop-1-ene are allowed to react with an excess of sodium dimethylmalonate in the presence of the allyl complexes, dimethyl or diphenyl pent-3-en-2-yl-malonate are formed quantitatively with 20% and 30% enantiomeric excess, respectively (Scheme 15) [58].

The first example of a palladium catalysed asymmetric coupling of a silylated organomagnesium compound with an allylic acetate has been described in the presence of $PdCl_2${AMPP} (Scheme 16). For instance, 1-trimethylsilyl vinyl magnesium bromide and 3-cyclohexenyl acetate gave rise to 3-(1-trimethylsilyl vinyl)cyclohexene with an ee up to 33% when the ligand was (*S*)-ProNOP [59].



Scheme 15. Palladium catalysed allylic substitution.

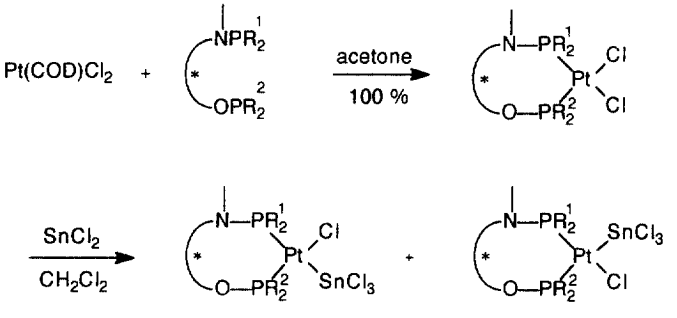


Scheme 16. Palladium catalysed allylic substitution.

5. Platinum–AMPP complexes and related catalysis

Optically active platinum complexes of general formula $PtCl_2\{AMPP\}$ were prepared in high yields through reaction of the corresponding aminophosphine-phosphinite ligands with either Zeise's salt $K[Pt(C_2H_4)Cl_3]$ or $Pt(COD)Cl_2$ [60–62] (Scheme 17). Contrary to the free ligands which are quite air sensitive, platinum complexes $PtCl_2\{AMPP\}$ are stable off-white solids which can be stored in air for long periods of time. These complexes showed typical ^{31}P NMR spectra consisting of two sets of doublets of similar intensity due to the two phosphorus atoms ($J(P(O),P(N)) \sim 10$ Hz) and two doublets of doublets constituting the ^{195}Pt satellites ($J(Pt,P(N))$, $J(Pt,P(O))$ 3800–4000 Hz) [61]. The crystal structures of $PtCl_2\{(S)$-Ph,Ph-ProNOP$\}$ and $PtCl_2\{(S)$-Ph,Cy-ProNOP$\}$ have been determined [61,63]. In both complexes, the platinum atom has a *cis* square planar coordination with angular distortions due to steric factors. Most interestingly, the replacement of the phenyl rings at the P(O) moiety by cyclohexyl substituents induces a drastic change in the conformation of the seven-membered metallacycle, thus resulting through a torsion effect, in a different orientation of the phenyl rings bound to P(N). Namely, in the {(*S*)-Ph,Ph-ProNOP}–Pt complex the latter are unsymmetrically displaced from each side of the mean square plane, whilst in the {(*S*)-Ph,Cy-ProNOP}–Pt complex both phenyl rings exhibit rather similar displacements and face/edge exposure.

The insertion reaction of stannous chloride into the Pt–Cl bond of complexes $PtCl_2\{AMPP\}$ takes place readily at room temperature in chlorinated solvents yielding the corresponding $PtCl(SnCl_3)\{AMPP\}$ complexes (Scheme 17) [63]. Due to the functional P(N)/P(O) dissymmetry of the AMPP ligands, the formation of two isomeric complexes in which the trichlorostannato ligand is located either *trans* to the P(N) moiety or *trans* to the P(O) moiety was observed using ^{31}P NMR spectroscopy. The relative ratios of the two isomeric complexes in the final reaction mixtures varied from 100/0 up to 55/45 according to the nature of the substituents at the P(N) and P(O) moieties of the chelating phosphorus ligand. It was assumed that the regioselectivity of the insertion of stannous chloride into the Pt–Cl bond of $PtCl_2\{AMPP\}$ is controlled by the relative electron density of the two phosphorus



Scheme 17. Synthesis of platinum complexes.

atoms in the AMPP, leading to different *trans* effects onto the Pt–Cl bonds to be broken. As a matter of fact, stannous chloride inserts generally rather selectively into the Pt–Cl bond *trans* to the electron rich P(N) residue, but when the original higher electron density of the P(N) atom versus the P(O) atom is significantly balanced by the electron-withdrawing phenyl groups at P(N) and the electron-donating alkyl groups at P(O), a mixture of *trans*-P(N) and *trans*-P(O) insertion complexes was obtained.

The $PtCl_2${AMPP} complexes, in combination with $SnCl_2 \cdot 2H_2O$, were evaluated as catalytic precursors in the asymmetric hydroformylation of styrene into 2-phenylpropanal (Scheme 18) [60,61].

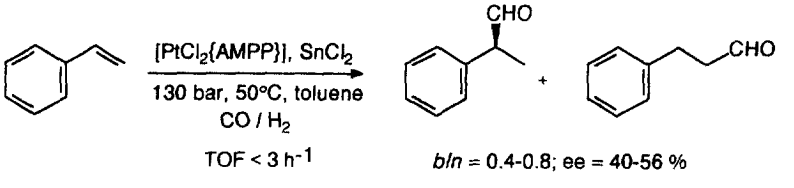
Reactions proceeded quite slowly (100 turnovers in 15–200 h) and afforded modest branched/normal (*b/n*) ratios (0.4–1.1) and enantiomeric excesses (up to 56%). The results obtained with various ligands derived from (*S*)-prolinol suggest that the catalytic activity of the Pt–AMPP complexes is mainly affected by the aminophosphine moiety of the ligand, and highest catalytic activities were observed with *N*-diphenylphosphino substituents. This trend could be connected to the aforementioned apparent relation between the electron density onto the P(N) atom and the relative amount of *trans*-P(N) insertion complex $PtCl(SnCl_3)${AMPP} (see earlier). On the other side, catalytic results suggest that the enantioselectivity depends on the nature of the phosphinite part as the best ee's were systematically obtained with dicyclohexylphosphinoxy substituents.

6. Rhodium–AMPP complexes and related catalysis

6.1. Synthesis of cationic and neutral Rh–AMPP complexes

Cationic Rh–AMPP complexes have been prepared either by the method of Schrock and Osborn using the $[Rh(COD)Cl]_2$–$NaClO_4$ combination or directly by displacing one of the COD ligands in $[Rh(COD)_2]X$ ($X = ClO_4$, BF_4) by the appropriate ligand. Both methods have been largely employed with a wide variety of amino(do)phosphine-phosphinite ligands to produce in good yields [Rh(COD){AMPP}]X type complexes which were further used in asymmetric hydrogenation of dehydroaminoacids (see Section 6.3). The latter are air-stable compounds and the crystal structure of two of them has been determined (see Section 6.2).

A common way to prepare neutral Rh–AMPP complexes is through displacement



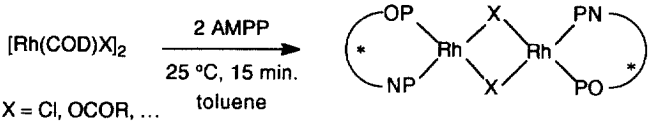
Scheme 18. Platinum catalysed asymmetric hydroformylation.

of the COD ligand in $[Rh(COD)X]_2$ precursors (X=Cl, OCOR) by the AMPP ligand. Thus, treatment of $[Rh(COD)X]_2$ with two equivalents of AMPP ligands in toluene at room temperature afforded complexes $[Rh\{AMPP\}X]_2$ as red–orange solids in nearly quantitative yields (Scheme 19) [32,33]. The conservation of the dinuclear structure in the solid state through chloro-bridging was established by mass spectrometry as well as by a X-ray diffraction study (see Section 6.2). Mononuclear neutral Rh–AMPP complexes could be attained in different ways. Thus, $Rh(\eta^5\text{-}C_5H_5)\{(S)\text{-Cy,Cy-ProNOP}\}$ was prepared in 93% yield by splitting of the corresponding dinuclear chlororhodium complex $[Rh\{AMPP\}X]_2$ with sodium cyclopentadienide. The acetylacetonato complex Rh(acac){(*S*)-Cy,Cy-ProNOP} was obtained in 86% yield through COD displacement in Rh(acac)(COD). Also, a transmetallation process between an intermediary Cu–AMPP complex (easily obtained by mixing CuCl with the AMPP ligand) and $[Rh(COD)Cl]_2$ has allowed the preparation of 18-electrons mononuclear chlororhodium complexes such as Rh(COD)(Propraphos)Cl [64].

6.2. *NMR and crystallographic features of Rh–AMPP complexes*

The $^{31}P\{^1H\}$ NMR spectra of neutral and cationic complexes exhibited the eight-line AB parts of ABX ($X=^{103}Rh$) spin systems, due to the non-equivalence of the phosphorus atoms. Typical values in cationic complexes [Rh(COD){AMPP}]X follow [65]: $\delta(P(O))=110$–120 ppm, $\delta(P(N))=80$–96 ppm, $J(P\text{–}P)=17$–30 Hz, $J(Rh\text{–}P(O))=170$ ppm, $J(Rh\text{–}P(N))=159$–167 Hz. Interestingly, variable temperature ^{31}P NMR studies carried out on toluene solutions of dinuclear complexes of the type $[Rh\{AMPP\}Cl]_2$ showed the existence of a dynamic phenomenon and the coexistence of two yet unidentified species could be observed at low temperature (<290 K). This dynamic phenomenon was not observed for mononuclear species such as Rh(acac){(*S*)-Cy,Cy-ProNOP} in the temperature range 250–350 K [32].

The crystal structure of two cationic complexes, $[Rh(COD)\{(R)\text{-Ph,Ph-PheNOP}\}]^+$ [66] and $[Rh(COD)\{(S)\text{-Ph,Ph-ProNOP}\}]^+$ [67], and of two neutral complexes, Rh(acac){(*S*)-Cy,Cy-ProNOP} [32] and the dimeric $[Rh\{(S)\text{-Ph,Ph-MandelNOP}\}Cl]_2$ [33], has been determined. In all cases, the rhodium atom has an almost perfect square-planar coordination typical of 16-electron complexes. An interesting feature in view of asymmetric catalysis lies in the conformation of the seven-membered metallacycle. All the above complexes adopted a distorted λ boat-type conformation with the oxygen atom in the mean plane P(N)–Rh–P(O), except Rh(acac){(*S*)-Cy,Cy-ProNOP} in which the nitrogen atom lies in the mean plane RhP_2. This fact suggests that a number of similar

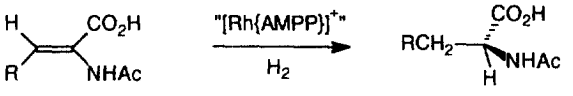


Scheme 19. Synthesis of rhodium {AMPP} complexes.

Table 1
Enantioselective hydrogenation of dehydroaminoacids using Rh^+–AMPP catalysts[a]

Ligand	R	Solvent	TOF (min^{-1})	ee (%)	Ref.
(*S*)-ProNOP	H	EtOH	nd	74 (*S*)	[25,65,66]
	Ph	EtOH	21	86 (*S*)	[65–67,69]
(1*R*,2*S*)-EE-ProNOP	H	EtOH	nd	92 (*R*)	[65,66]
(1*R*,2*S*)-EPHOS	Ph	MeOH	nd	12 (*R*)	[25,27]
	Ph	dioxane	nd	80 (*R*)	[27]
(1*R*,2*R*)-EPHOS	Ph	MeOH	nd	9 (*R*)	[27]
(1*S*,2*S*)-EPHOS	H	EtOH	nd	13 (*S*)	[25,65,66]
(1*R*,2*R*)-MAC-PONP	H	EtOH	>25	97 (*S*)	[29,30]
	*i*Pr	MeOH	>50	96 (*S*)	[29,30]
	Ph	iPrOH	18	95 (*S*)	[29,30]
(*S*)-Propraphos	Ph	MeOH	15	88 (*R*)	[64,70]
(*S*)-PindophosH	Ph	MeOH	143	91 (*S*)	[70]

[a] All the ligands bear PPh_2 substituents at their N and O atoms. 20–25 °C; 1 atm H_2; S/Rh = 100–2000. nd: not determined.



Scheme 20. Asymmetric hydrogenation of dehydroaminoacid derivatives.

conformational energy minima related to seven-ring chelates with either nitrogen or oxygen in the plane RhP_2, are readily accessible to the aminophosphine phosphinite family. This point has been discussed in detail by Pavlov at al. [66] with the aim to forecast the absolute configuration of the prevailing enantiomer in asymmetric hydrogenation of C=C bonds.

6.3. *Asymmetric hydrogenation of C=C bonds*

All the groups involved in AMPP chemistry since 1982 have naturally directed their catalytic applications towards asymmetric hydrogenation of functionalized olefins, particularly that of dehydroaminoacids, which is nowadays a basic reaction in fine chemical synthesis. The reactions were typically performed in the presence of cationic rhodium catalysts; no significant differences in the catalytic performances could be observed upon the way of preparation, and most of the work in this area referred to in situ generated Rh–AMPP catalysts.

Among the numerous catalysts investigated, good results were rapidly obtained using proline and ephedrine-derived AMPP ligands [25,27,68,65,69,67,70]. From that pioneering work, several other AMPP were designed, affording enantiomeric excesses up to 97% and high activities at ambient temperature under 1 atm of H_2. Typical results obtained on simple dehydroaminoacid derivatives are quoted in Table 1 (Scheme 20).

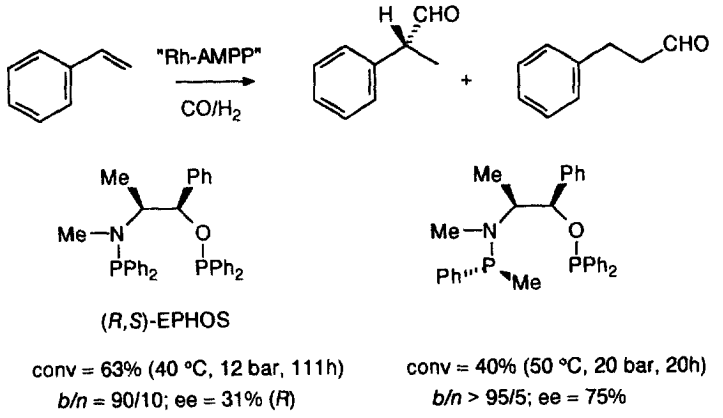
Some general trends deduced from experimental results are: (i) the better ability in terms of catalytic activity and enantioselectivity of diphenylphoshino substituted ligands over AMPP bearing alkyl or cycloalkyl substituents at their phosphorus moieties; (ii) the critical influence of the chiral skeleton of the starting aminoalcohol such as, for instance, the absolute configuration in Ephos type ligands; (iii) the strong influence of the solvent on catalytic activity and enantioselectivity, although best results are systematically obtained in polar solvents. Krause et al. have used an efficient Rh–AMPP hydrogenation system, i.e. Rh^+-propraphos, to prepare unusual aminoacids in high yields and ee ranging from 70% to 95% [71–78]. Also, modest to good results could be obtained on inactivated olefinic substrates such as α-acetoxystyrene (24% ee [27]), itaconic acid (64% ee, [27,67]) or dimethyl itaconate (up to 80% [79]).

On the other hand, several spectroscopic and kinetic studies were conducted with the aim to get a better insight in the mechanistic pathway. In particular, it was shown using ^{31}P NMR that variation at the nitrogen substituent in the aminophosphine-phosphinite moiety of the rhodium catalyst causes a change in the concentration of the catalyst–substrate complexes [79]. Nevertheless, the concrete geometry of these intermediates controlling the predominating steric pathway of the asymmetric hydrogenation is still unclear, essentially because of the very high conformational flexibility of the seven-membered chelates (see Section 6.2). Moreover, electronic effects must undoubtedly be taken into account [80].

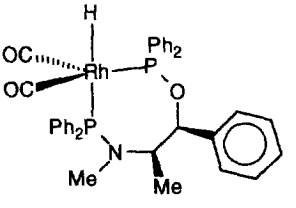
6.4. *Asymmetric hydroformylation of C=C bonds*

Several aminophosphine phosphinite rhodium systems were investigated for the hydroformylation of styrene [81]. Among these ligands, (1*S*,2*R*)-EPHOS was applied in the presence of classical neutral rhodium precursors and electrogenerated rhodium catalysts. The results, albeit modest nowadays when compared with the highly efficient Takaya's BINAPHOS and Biphemphos systems [82], were strikingly dependent on the nature of the catalyst precursor and on the reaction conditions applied. Namely, replacing classical catalyst precursors by electrogenerated rhodium species or using $Rh_4(CO)_{12}$ resulted in a significant increase of the enantioselectivity from 18% to 31% ee (Scheme 21). The (*S*,*S*) diastereomeric EPHOS ligand was much less efficient as it gave hydratropaldehyde of opposite configuration in 7% ee with a lower activity. Recently, new AMPP ligands bearing a chiral phosphorus atom on the N atom were built from (1*R*,2*S*)-(−)-ephedrine and were evaluated in the rhodium-catalysed hydroformylation of styrene [83,84]. Enantioselectivities up to 77% ee and high regioselectivities (>97%) into 2-phenylpropanal were obtained under mild conditions, that gives a new interest for AMPP in hydroformylation.

An interesting feature brought by Rh–AMPP systems arose from the spectroscopic detection of catalytic intermediates. Namely, the ^1H and ^{31}P NMR analysis of a hydridorhodium complex generated from $[Rh(\mu\text{-}CO)(CO)\{(1S,2R)\text{-EPHOS}\}]_2$ and a 1:1 mixture of H_2 and CO (1 atm) suggested a trigonal bipyramidal structure as shown in Scheme 22 [81]. A similar geometry was found for the complex $HRh(CO)_2\{(S,R)\text{-BINAPHOS}\}$ formed under the same oxo conditions [82]. In both



Scheme 21. Rhodium catalysed asymmetric hydroformylation.



Scheme 22. Proposed hydroformylation catalytic intermediate.

EPHOS and BINAPHOS hydridorhodium complexes, the aminophosphine phosphinite and the phosphine phosphite adopt equatorial-axial coordination to the rhodium centre, respectively. Very recently, a high-pressure NMR study of a chiral at phosphorus AMPP–Rh–hydrido complex corroborated such a conformation around the metallic center [83,84]. The highly dissymmetric structures around rhodium was pointed out to be the most important factor to achieve high enantioselectivities and to generate a single catalytic species [81,83,84].

6.5. *Asymmetric hydrosilylation of C=C and C=O bonds*

Asymmetric hydrosilylation provides an alternative route to hydrogenation for the preparation of chiral amines and alcohols. Early attempts in this way using neutral Rh–AMPP catalyst precursors have led to modest ee's [85,86], although comparable with those obtained with the best systems at this time such as DIOP. Thus, the reduction of the Schiff base $Ph(CH_3)C{=}NCH_2Ph$ with diphenylsilane in the presence of in situ generated "RhCl{AMPP}" complexes led after hydrolysis to *N*-benzyl-α-phenylethylamine in 40–60% yield and enantioselectivities up to 30% ee (ValNOP) [85]. On the other hand, the same catalytic systems promote the hydrosilylation of acetophenone into 2-phenylethanol in nearly quantitative yields and in up to 26% ee (E-ProNOP, 43% ee using the bulky α-naphtylphenylsilane) [86].

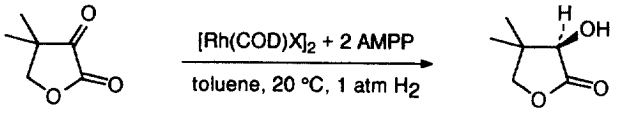
Enantioselectivities were strongly dependent on the structure of the chiral skeleton of the AMPP ligand, and a defined system exhibited variable performance for the reduction of C=C and C=O bonds, so that each case required appropriate optimization.

6.6. *Asymmetric hydrogenation of C=O bonds*

The synthesis of chiral functionalized alcohols through catalytic hydrogenation of keto compounds in the presence of Rh–AMPP complexes has been a major goal of our group in the last decade. Basic development of Rh–AMPP catalysts was performed using dihydro-4,4-dimethyl-2,3-furandione (ketopantolactone) as a model substrate, that leads to pantolactone, a key-intermediate in the synthesis of pantothenic acid and B vitamins (Scheme 23).

Early work has established the superior ability both in terms of activity and enantioselectivity of neutral complexes over cationic precursors [28,65]. Accordingly, catalytic reactions are best conducted using equally either preformed or in situ generated $[Rh\{AMPP\}X]_2$ precursors (X = halogen, OCOR) in apolar solvents such as toluene [87–91]. Also, it appeared that, in contrast with the enantioselective hydrogenation of C=C bonds, so-called "basic" AMPP ligands bearing alkyl and above all cycloalkyl substituents at their phosphorus moieties are much more efficient than diphenylphosphino substituted ligands [87–91]. While the latter required 50 atm and 50 °C to get acceptable rates for the hydrogenation affording even though poor results, the former yield highly active and enantioselective catalytic species since 1 atm and 20 °C are proper conditions. The performance of representative Rh–AMPP systems are summarized in Table 2.

Some interesting results could be obtained using *amino*phosphine-phosphinites, especially isoAlaNOP type ligands (Table 2). As a matter of fact, the dinuclear chlororhodium complex of (*S*)-Cp,Cp-isoAlaNOP afforded (*S*)-pantolactone in 89% ee with high catalytic activities (TOF at 50% conversion at room temperature up to 850 h^{-1}). Interestingly, the corresponding (*S*)-Ph,Cp-isoAlaNOP rhodium complex yielded the (*R*)-enantiomer in 81% ee. It is noteworthy that a similar inversion of the configuration of the hydrogenated product of *N*-benzyl benzoylformamide was also observed with the same complexes [32]. However, the best performance, i.e. TOF's up to 3300 h^{-1} at room temperature under 1 atm of H_2 and enantioselectivities up to 99%, were obtained with systems involving *amido*phosphine-phosphinites derived from oxoprolinol (Table 2) [33]. Whatever the type of AMPP used, catalytic activities and enantioselectivities depended strongly on the nature of the substituents on phosphorus as well as on the nature of the non chiral ligands. The



Scheme 23. Rhodium-based asymmetric hydrogenation of ketopantolactone.

Table 2
Enantioselective hydrogenation of ketopantolactone using neutral "Rh{AMPP}X" catalysts[a]

Chiral ligand	X	$t_{1/2}^{b}$ (min)	ee[c] (%, conf)	Ref.
(*S*)-Cy,Cy-ProNOP	Cl	27	47 (*R*)	[32,87–91]
(*S*)-Cy,Cy-ProNOP	$\eta^5-C_5H_5^c$	16	20 (*R*)	[32,87–91]
(*S*)-Cy,Cy-ProNOP	acac	120	34 (*R*)	[32,87–91]
(*S*)-Cp,Cp-ProNOP	Cl	19	76 (*R*)	[32,87–91]
(*S*)-*i*Pr,*i*Pr-ProNOP	Cl	19	56 (*R*)	[32,87–91]
(*S*)-Cp,Cp-isoAlaNOP	Cl	7.5	89 (*S*)	[32,87–91]
(*S*)-Ph,Cp-isoAlaNOP	Cl	nd[d]	81 (*R*)	[32,87–91]
(*S*)-Cy,Cy-oxoProNOP	Cl	58	96.6 (*R*)	[33,87–91]
(*S*)-Cy,Cy-oxoProNOP	CF_3CO_2	<2	97.7 (*R*)	[33,87–91]
(*S*)-Cp,Cp-oxoProNOP	I	17	98 (*R*)	[33,87–91]
(*S*)-Cp,Cp-oxoProNOP	CF_3CO_2	1.8	98.7 (*R*)	[33,87–91]

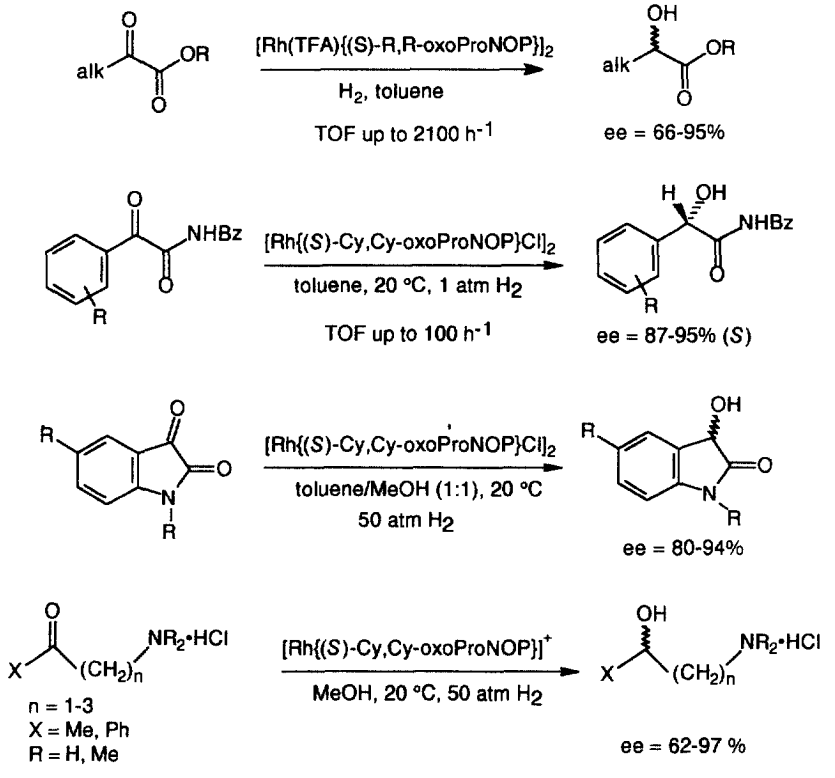
[a]20 °C, 1 atm H_2, substrate/Rh = 200, toluene; Cp = cyclopentyl; Cy = cyclohexyl.
[b]Time for 50% conversion.
[c]T = 70°C.
[d]Not determined.

results of several studies indicated that both the catalytic activity and the enantioselectivity of $[RhX\{AMPP\}]_2$ complexes are mainly governed by the P(N) moiety of the ligand and that the trifluoroacetato moiety is the most efficient non chiral ligand for the hydrogenation of ketopantolactone.

These catalysts were applied in the enantioselective hydrogenation of several α-keto esters, α-keto amides and α, β, and γ-aminoketones (Scheme 24) [92–94]. Trifluoroacetato-Rh–AMPP catalytic precursors promoted the rapid, efficient synthesis of aliphatic α-hydroxy esters in moderate to high enantioselectivities (66–95% ee), contrary to most of the aromatic α-hydroxy esters (8–81% ee). Best enantioselectivities for α-hydroxy amides like *N*-benzylmandelamide derivatives (85–95% ee) and dioxindoles (hydrogenation products of isatine derivatives, 80–94% ee) were obtained with chloro-Rh–AMPP precursors. On the other hand, chloro-, trifluoroacetato- and cationic Rh–AMPP precursors proved to be equivalent in terms of enantioselectivity (up to 97% ee) for the hydrogenation of α-aminoketones [94]. Interestingly, the cationic rhodium catalyst are also quite enantioselective for the hydrogenation of β- and γ-aminoketones [94].

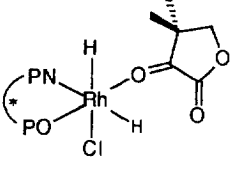
The last example of Rh–AMPP based catalysis is the hydrogenation of the C=N bonds in the pyrazine ring of the vitamin folic acid which has been carried out diastereoselectively with silica gel supported Rh–ProNOP and oxoProNOP precatalysts (27–31.7%) [95].

The mechanism of rhodium-catalysed hydrogenation of keto compounds is much less documented than that of olefins. Chelation of α-keto amides onto the rhodium center of cationic catalytic species has been proposed from spectroscopic investigations with cationic rhodium complexes and *N*-benzylphenylglyoxamide [94,96]. However, all attempts from our and other groups have failed up to now to isolate or even identify catalytic intermediates formed from neutral rhodium complexes and



Scheme 24. Rhodium catalysed asymmetric hydrogenation of functionalized ketones.

various keto derivatives. Experimental observations from Rh–AMPP-catalysed hydrogenations in toluene suggested that, contrary to α-keto amides, α-keto esters do not chelate onto the rhodium centre, probably because of the lower coordinating ability of alkoxycarbonyl versus amido groups, and that in such circumstances the asymmetric induction is mainly controlled by the steric hindrance around the C=O function [89]. Molecular modelling, in conjunction with extended Hückel analysis, conducted on putative dihydrido rhodium intermediates (Scheme 25) showed that the hydride *trans* to the N-PR_2 part of the bidentate ligand is more likely to react with the coordinated substrate ketone [97]. This approach can correctly predict the chiral configuration of the product alcohol in a number of cases (in particular the



Scheme 25. Postulated catalytic intermediate.

aforementioned reversal in the absolute configuration upon the nature of the N–PR_2 moiety in isoAlaNOP ligands; Table 2 [32]), but tends to over-predict the observed chiral purity.

7. Ruthenium–AMPP complexes and related catalysis

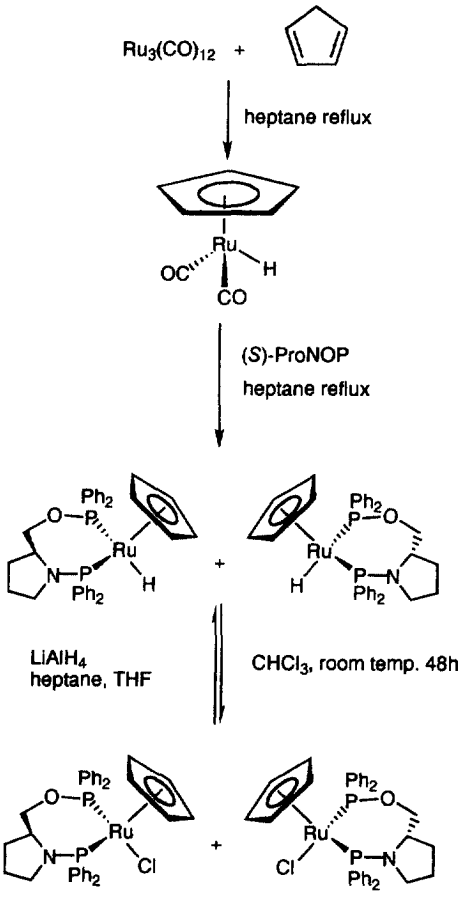
The above results demonstrate that Rh–AMPP catalysts provide very efficient catalysts which show often high to almost complete enantioselectivities for the hydrogenation of various functionalized ketones. Interestingly also, over the last decade, there has been rapidly growing interest in the syntheses and applications of ruthenium(II) complexes bearing chiral atropisomeric diphosphines based on binaphtyl, biphenyl and bisphospholane backbones [4–8,98–100]. In order to compare the easily accessible AMPP ligands to atropisomeric diphosphines and Ru(II){AMPP} complexes to Rh(I){AMPP} complexes, we and others explored the synthesis and application of AMPP ruthenium complexes.

7.1. Synthesis of neutral and cationic chiral Ru(II)–AMPP complexes

Cyclopentadienyl–ruthenium complexes have been synthesized starting from $Ru_3(CO)_{12}$ by CO substitution as described in Scheme 26 [101]. The resulting hydride complex [Ru(η^5-C_5H_5){(*S*)-ProNOP}H] could be converted into the corresponding chloro complex [Ru(η^5-C_5H_5){(*S*)-ProNOP}Cl] in the presence of chloroform (Scheme 26). The reverse reaction occurred when the chloro complex was reduced with $LiAlH_4$. The corresponding bromo and iodo compounds were obtained through a halide exchange reaction in the presence of a large excess of NaBr and NaI, respectively, producing [Ru(η^5-C_5H_5){(*S*)-ProNOP}X] (X = Br, I) complexes as mixture of diastereomers resulting from the chirality at ruthenium [102]. All the transformations occurred unambiguously with retention of configuration at the ruthenium atom.

Cationic arene ruthenium–AMPP complexes were synthesized through a two-step procedure [103]. In the first step, $[RuX_2(arene)]_2$ (arene = benzene or *p*-cymene) was reacted in THF with the appropriate AMPP ligand leading to the monodentate AMPP–Ru complexes RuX_2(arene){AMPP} (Scheme 27). In the case of (*S*)-Ph,Ph-ProNOP, a by-product (10%) corresponding to a PN monodentate AMPP complex has also been observed by ^{31}P NMR (Scheme 27). For the second step, the monodentate complex was dissolved in the appropriate solvent (CH_3CN or isopropanol) which, through chelation of the diphosphine, led to the bidentate complexes [RuCl(C_6H_6){(*S*)-Cy,Cy-ProNOP}]Cl, [RuCl(C_6H_6){(*S*)-Ph,Ph-ProNOP}]Cl and [RuI(*p*-cymene){(*S*)-Ph,Ph-ProNOP}]I as mixture of diastereomers resulting from enantiomeric configurations at the ruthenium atom. However, such a methodology did not work equally well for a general preparation of cationic ruthenium–AMPP complexes. In fact, this two-step synthesis applied to (*S*)-Ph,Ph-oxoProNOP failed to give the cationic complex.

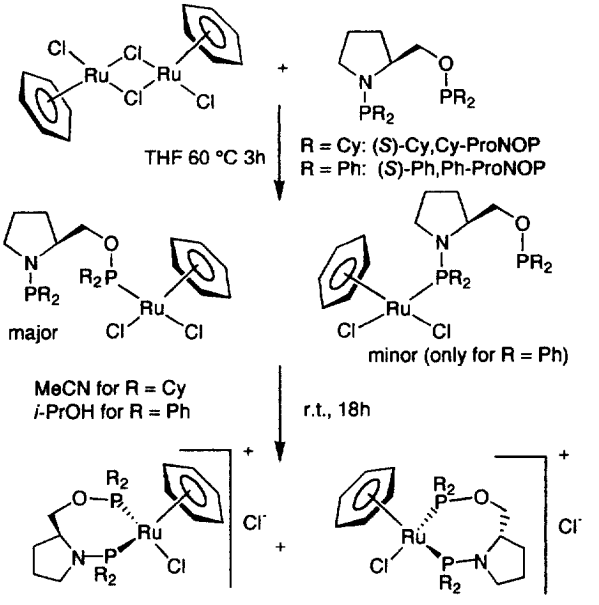
The allyl complexes Ru{AMPP}(2-methylallyl)$_2$ were synthesized through reac-



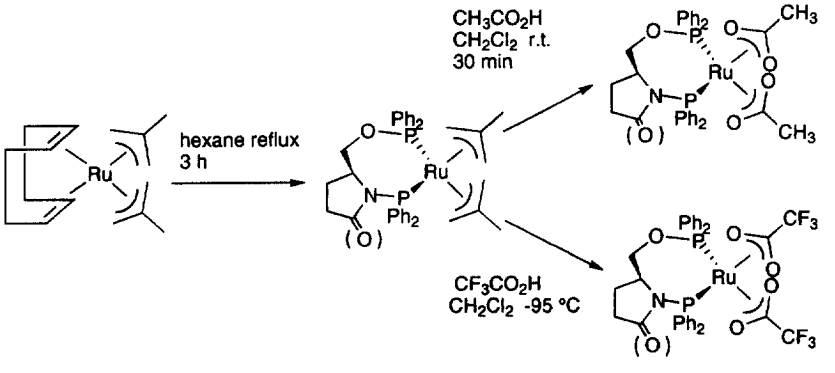
Scheme 26. Synthesis of neutral ruthenium {AMPP} complexes.

tion of Ru(COD)(2-methylallyl)$_2$ and the AMPP (*S*)-Ph,Ph-ProNOP or (*S*)-Ph,Ph-oxoProNOP in hexane at reflux (Scheme 28) [104,105]. The expected neutral complexes Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$ and Ru{(*S*)-Ph,Ph-oxoProNOP}(2-methylallyl)$_2$ precipitated over the course of the reaction as yellow powders. The existence of diastereomers was attributed to the relative *cisoid* or *transoid* configurations of the two allylic ligands coordinated to the ruthenium [104,105]. Interestingly, a solution prepared with the single crystal of one of the two diastereomers of Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$, which has been characterized by X-ray crystallography, showed clearly the presence of the two starting isomers when analysed by ^{31}P NMR spectroscopy [104,105]. This indicates that complex Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$ was rather fluxional in solution through isomerization of the allyl ligands.

The complexes Ru{(*S*)-Cy,Cy-ProNOP}$(OCOCH_3)_2$ and Ru{(*S*)-Cy,Cy-ProNOP}$(OCOCF_3)_2$ were obtained as mixture of diastereomers from reaction of



Scheme 27. Synthesis of cationic ruthenium complexes.



Scheme 28. Synthesis of carboxylate ruthenium complexes.

$Ru(COD)(OCOCH_3)_2$ and $Ru_2(COD)_2(OCOCF_3)_4$, respectively, with (*S*)-Cy, Cy-ProNOP [104,105]. On the other hand, acetato complexes were synthesized from reaction, in dichloromethane, of Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$ or Ru{(*S*)-Ph,Ph-oxoProNOP}(2-methylallyl)$_2$ with four equivalents of glacial acetic acid (Scheme 28). Thus, Ru{(*S*)-Ph,Ph-ProNOP}$(OCOCH_3)_2$ was obtained as mixture of diastereomers and Ru{(*S*)-Ph,Ph-oxoProNOP}$(OCOCH_3)_2$ as a single species.

Finally, the two methylallyl complexes Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$ and Ru{(*S*)-Ph,Ph-oxoProNOP}(2-methylallyl)$_2$ reacted with trifluoroacetic acid

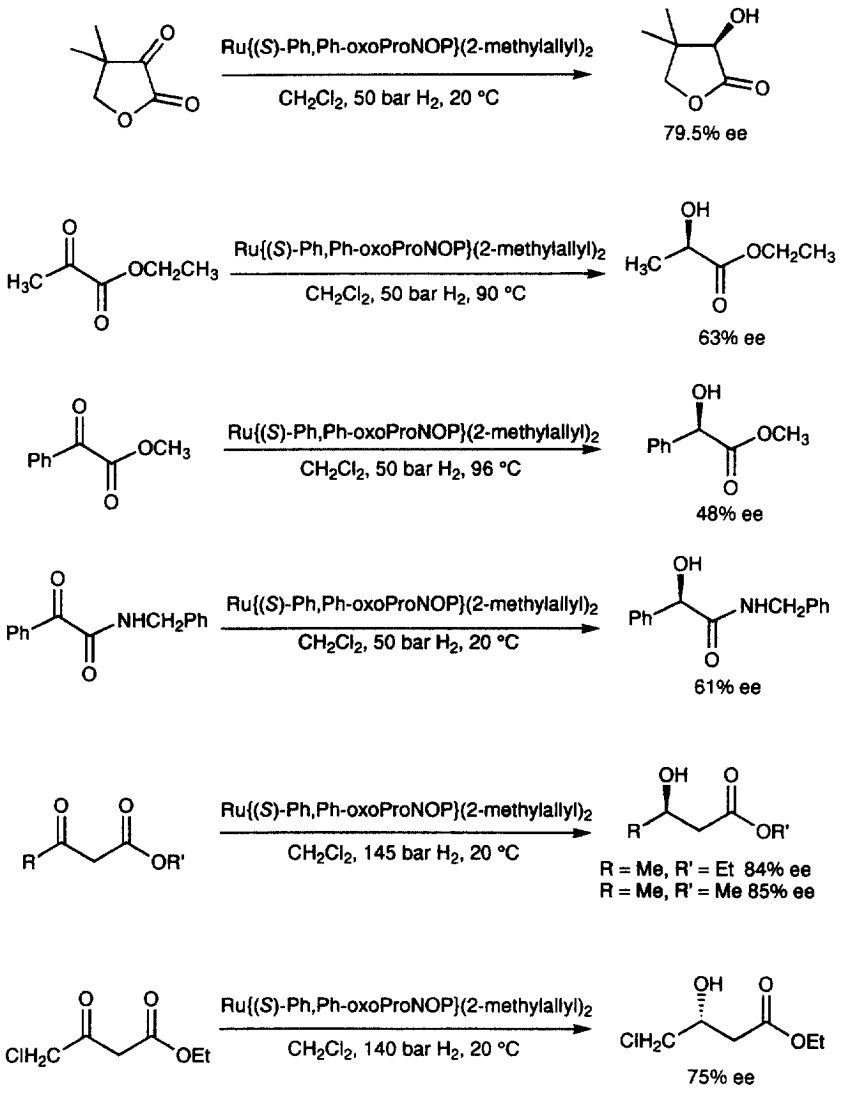
at −95 °C producing the trifluoroacetato complexes Ru{(*S*)-Ph,Ph-ProNOP}$(OCOCF_3)_2$ and Ru{(*S*)-Ph,Ph-ProNOP}$(OCOCF_3)_2$, respectively (Scheme 28) [104,105].

7.2. *Ruthenium-based asymmetric hydrogenation and mechanistic considerations*

The above complexes were applied in the asymmetric hydrogenation of diversely α-functionalized ketones (for example dihydro-4,4-dimethyl-2,3-furandione (KPL), ethylpyruvate (EP), methylbenzoylformate, ethyl-(2-thiophene)glyoxylate, and *N*-benzylbenzoylformamide) and β-ketoesters (ethylacetoacetate, methylacetoacetate, and ethyl-4-chloroacetoacetate) [103–106], leading to the corresponding chiral hydroxy compounds (Scheme 29).

Generally, α-substituted ketoesters were hydrogenated under 50 bar of hydrogen and at room temperature. For α-ketoesters, enantiomeric excesses observed for the hydrogenation with cationic and neutral ruthenium precursors of (*S*)-Cy,Cy-ProNOP were very low (<6% ee). It appeared that ruthenium complexes bearing PPh_2 substituted AMPP ligands produce more enantioselective catalysts. This is in sharp contrast with what is usually observed with rhodium based catalysts where the best substituents are PCy_2 or PCp_2. Also, all complexes bearing the (*S*)-Ph,Ph-oxo-ProNOP diphosphine provided unambiguously the more enantioselective catalysts (Table 3) (Scheme 29). Thus, the highest ee was 79.5% for the α-substituted ketone dihydro-4,4-dimethyl-2,3-furandione. Interestingly, we observed also that acetato and trifluoroacetato based catalyst precursors bearing the same AMPP led to similar results (approximately 65% ee). Catalytic hydrogenations of others α-ketoesters lead to more moderate ee's (11–63%). If generally an increase of temperature induces a decrease of the enantioselectivity, for two substrates, i.e. ethylpyruvate and methylbenzoylformate, the opposite was observed (Table 3). The involvement of different mechanistic pathways has been suggested in relation with the applied temperature.

β-ketoesters are better substrates with respect to enantioselectivity for the hydrogenation in the presence of ruthenium AMPP catalysts (75–85% ee) (Scheme 29) [106]. However, the reactions had to be carried out under more drastic conditions, namely under higher hydrogen pressure to get acceptable conversions (generally 145 bar). In fact, an increase of temperature was beneficial to the rate, but detrimental to the enantioselectivity. Even if slightly less selective, the complexes bearing carboxylates lead always to higher hydrogenation rates than the corresponding allylic precursors. For example, Ru{(*S*)-Ph,Ph-ProNOP}$(OCOCF_3)_2$ led to total conversion for the hydrogenation of ethylacetoacetate (74% ee) while in the same reaction conditions Ru{(*S*)-Ph,Ph-oxoProNOP}$(2\text{-methylallyl})_2$ gave only 52% conversion (85% ee) (145 bar H_2, 20 °C). The chelation of β-ketoesters was evidenced by the reversal of the configuration of the major enantiomer formed during the asymmetric hydrogenation ethyl-4-chloroacetoacetate [106]. As a matter of fact, the competitive directing effects between the ester and the chloride sites in that substrate is in favour of the chelation through the chloride leading to the observed reversal of configuration.



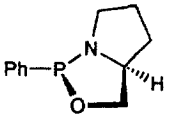
Scheme 29. Ruthenium catalysed asymmetric hydrogenation of functionalized ketones.

Interestingly, when mixing Ru{(*S*)-Ph,Ph-ProNOP}(2-methylallyl)$_2$ with H_2 (50 bar) in CH_2Cl_2 without substrate, we were able to detect three hydride species by ^1H NMR, two of them being in an exchange mode at room temperature [105]. Moreover, using the mixture generated for the NMR study for the hydrogenation of dihydro-4,4-dimethyl-2,3-furandione, we observed that the catalytic activity and enantioselectivity were identical to those of the starting precursor. These results are consistent with a possible mechanism involving monohydrido ruthenium catalysts [105].

Table 3
Asymmetric hydrogenation of α-functionalized ketones in the presence of ruthenium catalyst precursors[a]

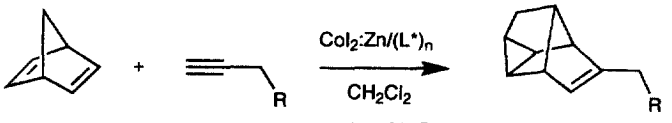
Substrate	Complex	Temp. (°C)	React. time (h)	Conversion (%)	ee (%) (Conf.)
KPL	$[RuCl(C_6H_6)\{(S)\text{-Ph,Ph-ProNOP}\}]Cl$	20	17	47	41 (*R*)
	$Ru\{(S)\text{-Ph,Ph-ProNOP}\}(2\text{-methylallyl})_2$	20	65	95	40 (*R*)
	$Ru\{(S)\text{-Ph,Ph-oxoProNOP}\}(2\text{-methylallyl})_2$	20	65	100	79.5 (*R*)
	$Ru\{(S)\text{-Ph,Ph-oxoProNOP}\}(OCOCH_3)_2$	20	15	32	65 (*R*)
	$Ru\{(S)\text{-Ph,Ph-ProNOP}\}(OCOCF_3)_2$	20	17	27	62 (*R*)
EP	$Ru\{(S)\text{-Ph,Ph-oxoProNOP}\}(2\text{-methylallyl})_2$	20	60	72	11 (*S*)
		60	15	46	44 (*R*)
		90	16	100	63 (*R*)

[a]Hydrogenation reactions were carried out in a stainless-steel autoclave under 50 bar of H_2 in the presence of 0.05 mol of substrate in deoxygenated CH_2Cl_2 (15 ml); substrate/Ru = 150/1.



(2R,4S)-2-phenyl-1,3,2-oxazaphospholidine

Scheme 30. Monophosphine ligand.



R = Ph, *n*-Bu, OH, OBn, OAc, OCO*t*Bu, CH_2OH, CH_2OMe, CH_2OAc, Pr

Scheme 31. Cobalt catalysed Diels Alder reaction.

8. Cobalt–AMPP based catalysis

For a final example of application of aminophosphine-phosphinite ligands, two AMPPs i.e. (*S*)-ValNOP and (*S*)-ProNOP (the proliNOP acronym is used in the paper) as well as an oxazaphospholidine derived from prolinol (Scheme 30) have been applied in the homo Diels–Alder reaction between norbornadiene and acetylenic compounds [107].

In the presence of CoI_2:Zn catalytic systems, deltacyclenes are produced with high enantioselectivities (up to 97% ee) and in good yields (Scheme 31). The catalytic systems are very sensitive to the anhydrous character of the cobalt species, the coordinating hability of the solvent, and the presence and position of the functionalized groups of the acetylenes.

Recently, the study has been extended to various propargylic derivatives

(Scheme 31) [108]. The yields and enantioselectivities are greatly dependant on the nature of the acetylenic compounds and on the reaction conditions.

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