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Reactivity of Chiral Oxazaphospholidines on Activated Halide Compounds : Synthesis and Coordination Studies of Chiral Hybrid Phosphine-Phosphine Oxide Ligands

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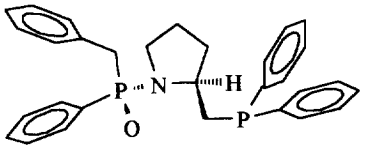
Abstract: The Michaelis Arbuzov reaction between the enantiopure 2-phenyl-1,3,2-oxazaphospholidine **1** and different activated halide compounds **2** afforded with total diastereoselectivity chiral phosphinamides **3**. Oxazaphospholidine **1** reacted with α-haloacetophenones **4a-c** to give both chiral Michaelis Arbuzov products **5** and a mixture of diastereomers **6**:**7** as the Perkow products. New hybrid phosphine-phosphine oxide ligands were easily obtained from phosphinamides **3**, bearing chirality on the carbon chain and the phosphine oxide moiety (BPPO), or on the carbon chain and the two different phosphorus centers (**8** and **9**). The coordination chemistry of ligand BPPO has been studied, with transition metals and Lewis Acids. © 1997 Elsevier Science Ltd.

INTRODUCTION

In recent years there has been great interest in the preparation of optically active phosphorus compounds used as ligands of transition metal catalysts in enantioselective reactions[1]. Recently, it was reported that hybrid phosphine-phosphine oxide ligands such as $Ph_2P(CH_2)_nP(O)Ph_2$ can behave as mono or bidentate ligands[2]. In complexes with this type of ligand, there is a strong bonding between the soft transition metal and the soft phosphine, and a weaker bonding with the harder phosphine oxide in bidentate complexes. Moreover, the two different binding sites are each capable of coordinating different types of metal : a strong bonding between a soft metal centre (low valent transition metal) and the soft phosphine, and a complexation of a hard metal (alkali and alkaline earth metal cations) or Lewis acids by the harder phosphine oxide[3]. This type of heterotopic ligand could play a crucial role in catalytic reactions such as allylic alkylation, hydroformylation or cross-coupling[4]. We previously reported[5] the enantioselective synthesis of a new chiral phosphine-phosphine oxide ligand, (*Rp*)-benzylphenyl[2-(*S*)-diphenylphosphinomethylpyrrolidin-1-yl]phosphine oxide (structure of BPPO, scheme 1).



BPPO

Scheme 1

The key step of this synthesis was the formation of a chiral phosphine oxide compound, *via* an enantioselective Michaelis-Arbuzov reaction by using a chiral oxazaphospholidine. The scope and limitations of this reaction are studied on different activated halide compounds, such as allylic bromides, halogenated esters

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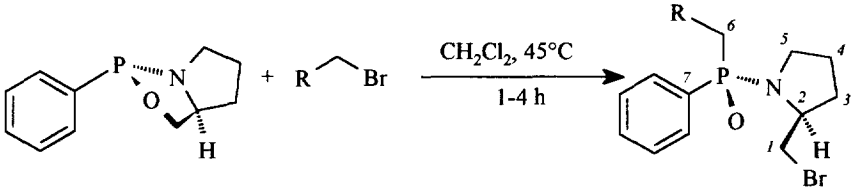
and ketones. An application to the synthesis of chiral hybrid ligands bearing chirality on two different phosphorus centers is proposed, and the coordination ability of this type of ligand is explored.

MICHAELIS-ARBUZOV REACTIONS OF 2-PHENYL-1,3,2-OXAZAPHOSPHOLIDINE

The reaction of an alkylhalide with a tricoordinated organophosphorus compound bearing at least one alkoxy group is known as the Michaelis-Arbuzov reaction. Since its discovery by Michaelis in 1898[6], and its generalisation by Arbuzov[7], this reaction has been extensively applied to the synthesis of various organophosphorus compounds[8].

In the following part of this study, only 2-phenyl-1,3,2-oxazaphospholidine **1**, prepared from (*S*)-(+)-prolinol, was utilised as a tricoordinated phosphorus compound to avoid stereoselective ring extension of the bromomethylpyrrolidine to bromopiperidine previously reported by Hammer *et al.*[9] and observed by us with phosphinamides[5]. In order to complement previous results observed with benzylbromide[5], we have reacted 2-phenyl-1,3,2-oxazaphospholidine **1** with different classes of alkyl halides such as allylic bromides, α-halogenoesters and α-halogenoketones. Methylenecarboxyphosphinamides obtained from α-bromoesters lead to attractive compounds since the carbonyl group acts as an additional chelating center with respect to the metal or Lewis acid.



1

2a, R= Ph
2b, R= $CH{=}CH_2$
2c, R= $CH{=}CH\text{-}CH_3$
2d, R= $CO_2\text{-}CH_3$
2e, R= $CO_2\text{-}C(CH_3)_3$
2f, R= $CO_2\text{-}CH_2\text{-}Ph$

3a
3b
3c
3d
3e
3f

Scheme 2

We have unambiguously demonstrated[5] that the reaction between **1** and benzylbromide **2a** proceeds with total diastereoselectivity and retention of configuration at the phosphorus atom. It was expected that the stereochemical integrity at phosphorus would be maintained for all the halogenated substrates leading to the chiral phosphinamide compounds **3b-3f**. For example, condensation of **1** with allylic bromide leads to the formation of a single diastereomeric compound within 4 hours in refluxing dichloromethane.

Under the same reaction conditions, crotylbromide **2c** reacts with **1** (reaction time : 3 hours), to yield phosphinamide **3c** as a single diastereomer. ^1H and ^{31}P NMR analyses revealed that the methylene unit was bonded to the phosphorus atom and the double bond remained in its *E* configuration. The substitution reaction does not proceed according to a S_N' process, since there is no amount of this type of substitution product. Generalisation using other alkylbromides with no unsaturation such as 1,2-dibromoethane requires more harsh conditions, leading to subsequent degradation of starting material and tetracoordinated phosphorus compounds (consecutive reactions), since the nucleophilic attack of **1** is slower than with unsaturated allylic bromides **2b** and **2c**.

Table 1 : Michaelis-Arbuzov Reactions between **1** and Alkylbromides **2a-c** and α-Bromoesters **2d-f**

Entry	Reactant	Time (h)	Product	Yield **3** (%)	δ ^{31}P **3** (ppm)	$[\alpha]_D^{20}$ **3**
1	**2a**	3	**3a**	92	31.4	+2.5 (*c* 1.0 CH_2Cl_2)
2	**2b**	5	**3b**	63	31.6	-21.0 (*c* 1.0 CH_3COCH_3)
3	**2c**	5	**3c**	83	32.3	-34.5 (*c* 1.0 CH_3COCH_3)
4	**2d**	1	**3d**	75	26.5	-11.3 (*c* 1.0 CH_2Cl_2)
5	**2e**	1	**3e**	67	27.0	-20.3 (*c* 1.0 CH_3COCH_3)
6	**2f**	2	**3f**	51	26.8	-25.3 (*c* 1.0 CH_3COCH_3)

In refluxing dichloromethane, α-halogenoesters such as methyl, *tert*-butyl and benzyl α-bromoacetates, **2d**, **2e** and **2f** respectively, react within 2 hours with oxazaphospholidine **1**. Monitoring the reaction course by ^{31}P NMR, indicated, in all the cases, total conversion of **1**, and formation of a single phosphinamide **3**.

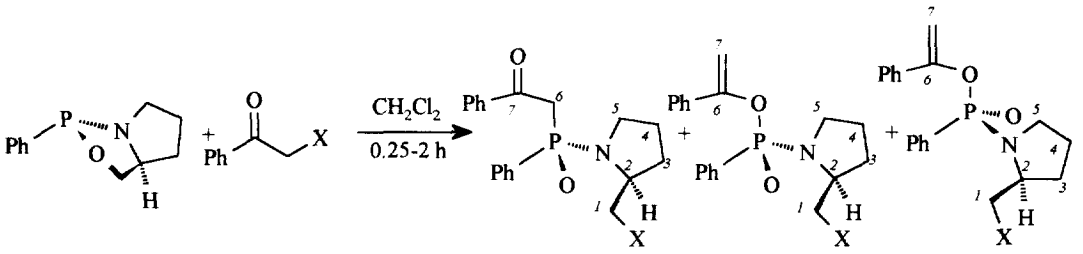
With α-halogenoesters **2d-f**, reaction times are shorter than with allylic halides. These enhanced rates reflect stabilization of the S_N2 transition state through overlap between the adjacent π orbitals of the carbonyl and the p-type orbital which develops at the α-carbon in the transition state[10].

PERKOW REACTIONS OF 2-PHENYL-1,3,2-OXAZAPHOSPHOLIDINE

Trialkylphosphites react with α-halocarbonyl compounds to give a β-ketophosphonate or a vinylphosphate, or a mixture of both. The reactions of a wide variety of trivalent phosphorus compounds bearing at least one alkoxy group with α-halocarbonyl reagents have been shown to give vinyl pentavalent phosphorus products, and the reaction is now referred to as the Perkow reaction[11]. With trialkylphosphite several factors (solvent, temperature, and nature of the halogen) influence the product ratio ketophosphonate/vinylphosphate. Generally the more electronegative halogen atom favours the formation of vinylphosphate. As shown in scheme 3 and in table 2, α-halogenoacetophenone **4** reacts quantitatively with oxazaphospholidine **1** under the previously described conditions, leading to a mixture of tetracoordinated phosphorus compounds : ketophosphinamide **5** in which the configuration at the phosphorus atom is retained (Michaelis-Arbuzov product), and two vinylphosphonamide diastereomers **6** and **7** differing by the absolute configuration at the phosphorus atom (Perkow products) [12].

With α-chloroacetophenone **4a**, only vinylphosphonamide diastereomers **6a** and **7a** are obtained in 90% yield. These diastereomers cannot be separated using classical chromatography methods. With α-bromoacetophenone **4b**, three tetracoordinated organophosphorus compounds **5b**, **6b** and **7b** are rapidly formed in a 43/6/51 ratio (δ ^{31}P : 27.0 ; 17.7 ; 17.2 ppm respectively). Compound **5b** was separated from the two diastereomeric vinylphosphonamides **6b** and **7b** by Medium Pressure Liquid Chromatography (MPLC) on silica gel, and identified as a ketophosphinamide by the typical $^2J_{P-H}$ value of the methylene (-CH_2-CO) group. The vinylphosphonamide diastereomers could not be separated. Surprisingly, when the reaction was performed

from 0 to 25°C, the distribution of the three adducts **5b**, **6b** and **7b** remained the same. With α-iodoacetophenone **4c**, oxazaphospholidine **1** reacts readily even at room temperature in less than 15 minutes. Two diastereomeric vinylphosphonamides, **6c** and **7c**, are obtained in an equimolar ratio. The distribution we observed between products **5**, resulting from a Michaelis-Arbuzov reaction, and adducts **6** and **7**, resulting from a Perkow reaction between **1** and an α-halogenated ketone **4**, is in agreement with those previously reported with achiral phosphorus compounds[13]. With a chlorine atom, adducts are essentially Perkow adducts, while with a bromine atom, a mixture of adducts is obtained.



1 **4a**, X=Cl; **4b**, X=Br; **4c**, X=I → **5a**, **5b**, **5c** → **6a and 7a**, **6b and 7b**, **6c and 7c**

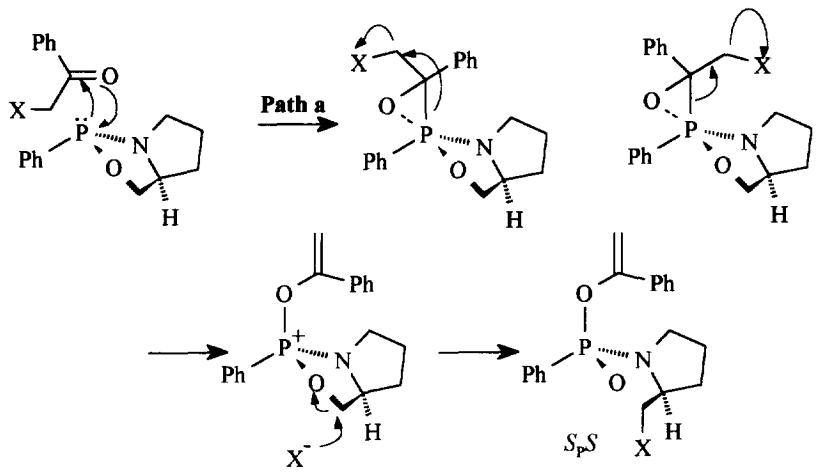
Scheme 3

Table 2 : Perkow Reaction between **1** and α-Haloketones **4a-c**

Entry	Reactant	Time (h)	Yield (%)	Adducts	δ ^{31}P (ppm)	Ratio
1	**4a**	1	90	**6a**	17.7	7
				7a	17.3	3
2	**4b**	1	67	**5b**	27.0	4
				6b	17.7	1
				7b	17.2	5
3	**4c**	2	51	**6c**	17.7	1
				7c	17.2	1

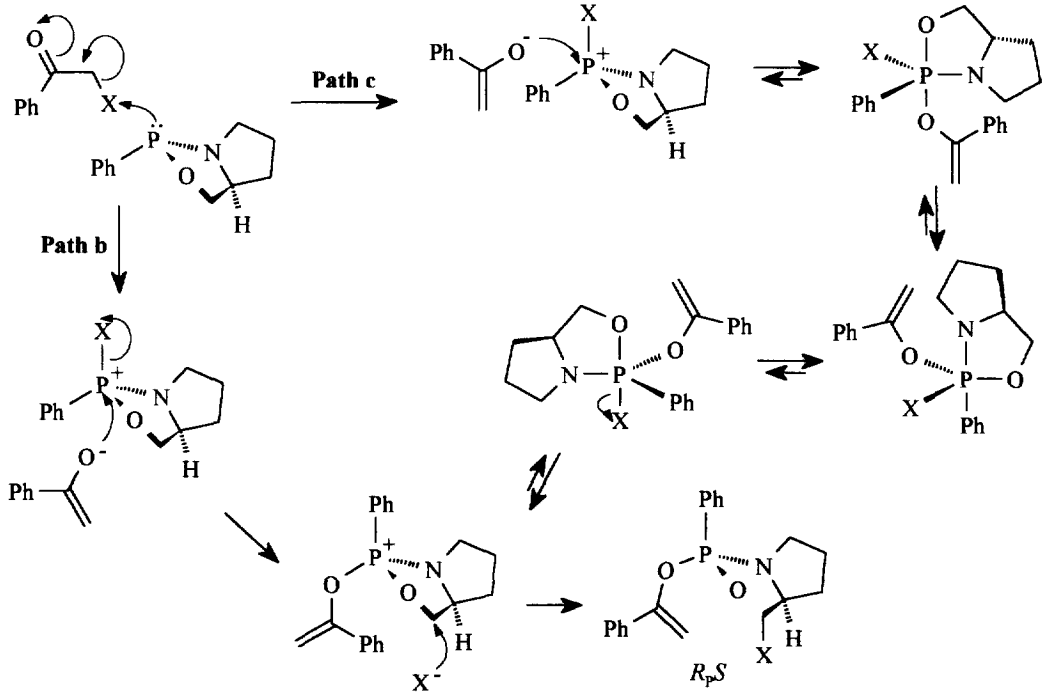
It is interesting to note that, as for the formation of ketophosphonium, there is retention of configuration at the phosphorus atom in **5b**. For the Perkow reaction on oxazaphospholidine **1** there is either retention or inversion of configuration at the phosphorus atom, leading to a diastereomeric mixture of **6** and **7**. Many different mechanisms have been proposed for the Perkow reaction. One of the more plausible proceeds with : (i) a nucleophilic attack of the phosphorus atom lone pair onto the carbonyl group, leading to a pentacoordinated intermediate including a three-membered ring; (ii) a subsequent cleavage of the C-P bond with expulsion of the halogen atom affording an enolalkoxyphosphonium salt, which is then converted to an enolphosphonate *via* a Michaelis-Arbuzov cleavage of the alkoxy group by the halide ion.

Scheme 4 (Path a) illustrates this mechanism for the reaction of **1** with α-haloacetophenone. The two diastereomers do not result from a preferential attack of compound **1** on one of the enantiofaces of the carbonyl group, but this epimerisation depends upon the extent of involvement of pentacoordinated intermediates and resultant pseudorotation. However the formation of the stereochemically rigid spirophosphorane due to the constrained structure of the oxazaphospholidine and oxaphosphirane rings and the relative apicophilicity of the ligands could lead to the retention of the phosphorus atom configuration.



Scheme 4

A way to interpret the inversion of the phosphorus atom is to consider the ability of **1** to attack the halogen atom (Paths b and c, scheme 5) to give a halogenophosphonium enolate ion pair, which then interacts to give O-phosphonylation. The inversion of configuration at the phosphorus atom can proceed by direct in-line substitution (Path b, scheme 5), or by a trigonal bipyramidal mechanism involving pseudorotations[14] (Path c, scheme 5).



Scheme 5

The use of a chiral tricoordinated compound can be conclusive concerning the mechanism of the Perkow reaction. Unfortunately for the moment the absolute configuration of the main compounds **6** and **7** cannot be determined, neither by sequences of reactions leading to a chiral organophosphorus compound with well-known absolute configuration, or by obtaining a suitable crystal for X-ray studies.

However we can note that the observed diastereoselectivity between **6** and **7** depends upon the relative importance of the different mechanistic pathway varying with the nature of the halogen atom (Cl : 42%; Br : 79%; I : 0%).

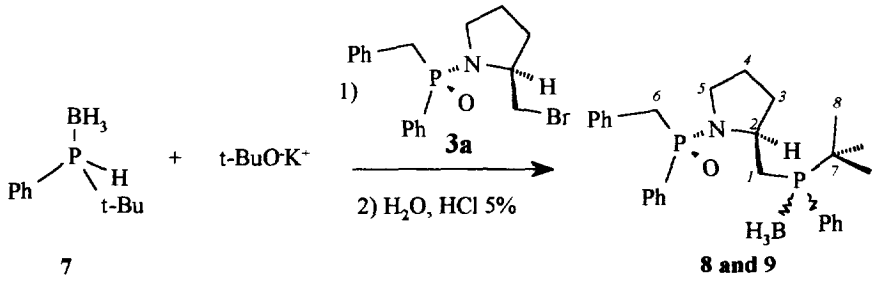
CHIRAL PHOSPHINE-PHOSPHINE OXIDE LIGANDS

We previously reported[5] the enantioselective synthesis of a new chiral phosphine-phosphine oxide ligand, (*RP*)-benzylphenyl[2-(*S*)-diphenylphosphinomethylpyrrolidin-1-yl]-phosphine oxide (BPPO), by substitution of the bromine atom in compound **3a** with diphenylphosphide.

Chiral hybrid ligands bearing chirality on two different phosphorus centers can be easily obtained according to this methodology, using chiral phosphide-borane complexes, instead of lithium diphenylphosphide. The pioneering work of Imamoto concerning the stability and the reactivity of phosphine-borane complexes[15] with respect to phosphines[16], has demonstrated their potential as intermediates in the synthesis of phosphine ligands. The potential of phosphide-borane complexes prepared from reductive cleavage of phosphinite-borane complexes or abstraction of a proton from phosphine-borane complexes bearing at least one P-H bond, as nucleophiles has been widely demonstrated.

Unfortunately, obtaining a chiral phosphine-borane from an optically active phosphinite-borane, or from resolution of racemic phosphine-borane complexes on semi-preparative cyclodextrin columns, gave unsatisfactory results for a multi grams synthesis.

(±)-*t*-Butylphenylphosphine-borane **7** prepared in good yields according to a described method[16a], was reacted with 1.1 eq. of *t*-BuOK in THF at -30°C to afford quantitatively potassium *t*-butylphenylphosphine-borane. Subsequent addition of **3a** at the same temperature leads to the formation of two diastereomeric compounds in a 67/33 ratio (Scheme 6). The two expected epimers **8** and **9** were separated by column chromatography on silica gel, and their structures were confirmed by standard ^1H-^1H and ^1H-^{13}C NMR correlations.



7 **8 and 9**

Scheme 6

Since separate recrystallisations of the two diastereomeric complexes **8** and **9** did not afford suitable crystals for X-ray investigations, the absolute configuration of each of the phosphorus atoms bonded to borane were not determined. Nucleophilic substitution of **7** on **3a** proceeds with total consumption of each reactant.

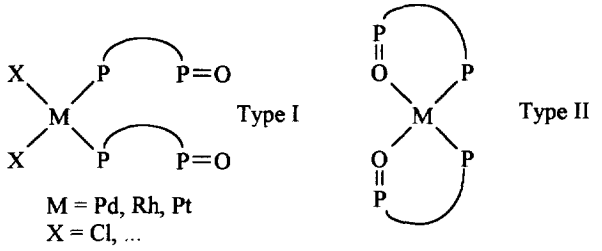
Quenching the reaction course at 50% of conversion and subsequent separation of the mixture, afforded **8** and **9** in the same 67/33 distribution and recovery of starting materials **3a** and **7**. Remaining **7** has no optical activity, demonstrating that there is no kinetic resolution in this process. Racemisation of optically active *t*-butylphenylphosphine-borane in the presence of *t*-BuOK was extremely fast at room temperature : enantioenriched mixtures lead to racemic mixtures in less than one hour.

The free optically pure phosphine can be obtained by decomplexation of the phosphine-borane complex in the presence of an excess of amine. Moreover, the use of DABCO allowed the "*in-situ*" preparation of phosphines without a further isolation step[17], increasing interest in air-stable phosphine-borane complexes.

We have demonstrated in the first part of this work that chiral oxazaphospholidines are interesting chirons for the synthesis of potential chiral phosphine-phosphine oxide ligands by a Michaelis-Arbuzov reaction. To illustrate the coordination ability of these new ligands we have studied the coordination of ligand BPPO with different transition metal complexes and Lewis acids.

COMPLEXATION

This type of phosphine-phosphine oxide ligand is able to coordinate transition metals in a monodentate fashion through the P atom (Type I, scheme 7), or as a bidentate P,P=O chelate (Type II, scheme 7). In this work, both behaviours were observed, depending on the metal, and the type of complex (neutral or cationic).



Scheme 7

Several air-stable complexes **10-13** and **15-18** were easily prepared. The mono- and bidentate modes of coordination of the ligand BPPO, by its PPh_2 and P=O groups to the metal were determined by several spectroscopic observations :

i) The $^{31}P-\{^1H\}$ resonance at low field from the chemical shift of the uncoordinated phosphorus group. Chemical shift differences between "free" ligand BPPO (δPPh_2 = -20.5 ppm; $\delta P{=}O$ = +32.7 ppm) and coordinated phosphine or phosphine-oxide group were unambiguous :

$$16.3 \leq \Delta\delta\ PPh_2 \leq 40.4 \text{ ppm and } 10.7 \leq \Delta\delta P{=}O \leq 16.7 \text{ ppm.}$$

ii) The measurement of the coupling constants $^1J_{P\text{-}M}$ and $^3J_{P\text{-}M\text{-}O=P}$ between the metal and the phosphorus group.

iii) The P=O stretching frequency of the free ligand ($\nu P{=}O$ = 1200 cm^{-1}) shifts to lower frequencies depending on the nature of the metal.

Spectroscopic data for complexes **10-18** of BPPO with various transition metals such as rhodium(I), tungsten(0), palladium(II) and platinum(II) are displayed in Table 3 :

Table 3 : ^{31}P - $\{^1H\}$ NMR and Infrared Data of Complexes with Ligand BPPO

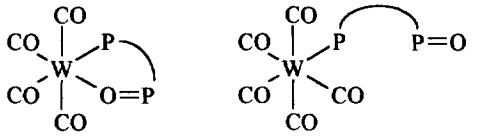
	Complex	δ PPh_2 ppm	δP=O ppm	Δδ PPh_2[a] ppm	ΔδP=O[a] ppm	$^1J_{M-P}$ Hz	IR νP=O cm^{-1}
10	$[Rh(COD)(BPPO)]^+, BF_4^-$	+ 19.9	+ 48.4	+ 40.4	+ 15.7	152	1160
11a	$[W(BPPO)(CO)_4]$	+ 10.3	+ 45.6	+ 30.8	+ 12.9	227	1165
11b[b]	$[W(BPPO)(CO)_5]$	+ 2.4	+ 29.1	+ 22.9	- 3.6	237	-
12	$[PdCl_2(BPPO)_2]$	+ 10.1	+ 31.2	+ 30.6	- 1.5	-	1200
13	$[Pd(BPPO)_2]^{2+}, 2BF_4^-$	+ 30.7	+ 49.4	+ 51.2	+ 16.7	-	1100
14[b]	$[Pd(\eta^3\text{-}C_6H_9)(BPPO)]^+, BF_4^-$	+ 13.9	+ 45.2	+ 34.4	+ 12.9	-	-
15	$[PtCl_2(BPPO)_2]$	+ 0.9	+ 31.0	+ 21.4	- 1.7	3645	1185-1200
16	$[Pt(BPPO)_2]^{2+}, 2BF_4^-$	- 4.2	+ 52.4	+ 16.3	+ 19.4	4025	< 1160
17	$[PtCl_2(BPPO)_2TiCl_4]$	+ 3.7	+ 43.4	+ 24.2	+ 10.7	3738	1100
18	$[PtCl_2(BPPO)_2nBu_2SnCl_2]$	+ 1.8	+ 32.6	+ 22.3	- 0.1	3673	1155

(a) Chemical shift differences between complexed and "free" ligand (δPPh_2= -20.5 ppm; δP=O = +32.7 ppm).

(b) Observed by ^{31}P NMR, not isolated.

Complex **10** was obtained by an exchange reaction with 1 equivalent of ligand BPPO and 0.5 mole equivalent of $[RhCl(COD)]_2$ followed by treatment with $AgBF_4$. Although the structure of this cationic complex is not yet elucidated, it was found that BPPO behaves as a bidentate ligand. Thus, analysis of the ^{31}P-$\{^1H\}$ NMR spectra showed clearly P-P and P-Rh coupling constants ($^1J_{P\text{-}Rh}$ = 152 Hz; $^2J_{P=O\text{-}Rh}$ = 3.5 Hz; $^3J_{P=O\text{-}Rh\text{-}P}$ = 3.5 Hz) proving the bidentate mode of coordination of the ligand. These values of $^1J_{P\text{-}Rh}$ and $^3J_{P=O\text{-}Rh\text{-}P}$ are in accordance with those reported elsewhere[18].

Complex **11** was synthesised by mixing 1 mole equivalent of ligand BPPO and 1 mole equivalent of $[W(CO)_6]$ but was obtained as a mixture of two different complexes **11a** and **11b** in a ratio estimated to be 75/25 by integration of the corresponding signals in the ^{31}P-$\{^1H\}$ NMR spectrum. Only the major product **11a** was isolated by column chromatography. All attempts to obtain single crystals suitable for X-ray diffraction analysis have failed. ^{31}P NMR analysis of pure complex **11a** indicated that the PPh_2 group was ligated to the tungsten atom, with a coupling constant $^1J_{P\text{-}W}$ = 227 Hz and that phosphine oxide group was also coordinated to the metal (δP=O = +45.6 ppm, νP=O = 1165 cm^{-1}). ^{31}P-$\{^1H\}$ NMR spectra of the mixture **11a/11b** showed that ligand BPPO acts as a monodentate ligand in the non isolated complex **11b**: $^1J_{P\text{-}W}$ = 237 Hz, δP=O = +29.1 ppm (Scheme 8).



11a **11b**

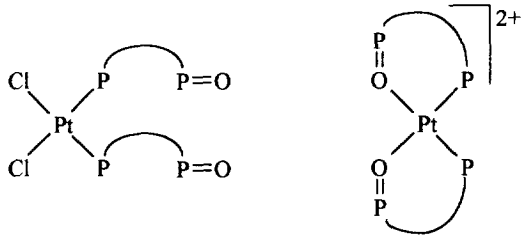
Scheme 8

Complex **12** $[PdCl_2(BPPO)_2]$ was prepared in 95% chemical yield by mixing 1 mole- equivalent of dichlorobis(acetonitrile)palladium and 2 equivalents of ligand BPPO. Analysis of this complex by $^{31}P-\{^1H\}$ NMR spectroscopy revealed that the ligand acts as a monodentate ligand (there was no change in chemical shift and stretching frequency of the P=O group).

On the other hand, treatment of complex **12** with $AgBF_4$ led to the formation of a cationic complex $[Pd(BPPO)_2]^{2+}$, 2 BF_4^- **13,** where BPPO behaves as a bidentate ligand with a large enhancement in the chemical shift of the P=O group : $\delta_{P=O}$ = +49.4 ppm and a coupling constant $^3J_{P=O-Pd-P}$ = 4 Hz.

A π-allylic cationic complex $[Pd(\eta^3-C_6H_9)(BPPO)]^+$, BF_4^- **14** has been prepared according to Åkermark's method[19] but cannot be isolated. Nevertheless, the $^{31}P-\{^1H\}$ NMR analysis of the crude reaction product showed the bidentate mode of coordination of ligand BPPO.

Addition of 2 mole-equivalents of ligand BPPO to a $CHCl_3$ solution of $[PtCl_2(COD)]$ afforded $[PtCl_2(BPPO)_2]$ complex **15** in quantitative chemical yield. When only 1 mole-equivalent of ligand BPPO was added to $[PtCl_2(COD)]$, complex $[PtCl_2(BPPO)_2]$ was present in solution. Addition of a second mole equivalent caused no further change in the $^{31}P-\{^1H\}$ NMR spectrum, indicating that with 1 mole equivalent of this ligand only 50% of the $[PtCl_2(COD)]$ had reacted. The high value of $^1J_{P-Pt}$ = 3645 Hz indicated that in complex **15** both phosphorus atoms are in the *cis* conformation, with the P-atom *trans* to a hard donor such as Cl^-[20] (Scheme 9).

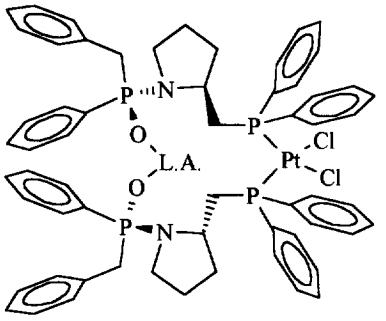


15 **16**

Scheme 9

Addition of $AgBF_4$ led to the formation of a cationic bis chelate complex **16,** where BPPO behaves as a bidentate ligand : $\delta_{P=O}$ = +52.4 ppm, and $\nu_{P=O}$ = 1160 cm^{-1}. $^{31}P-\{^1H\}$ NMR spectroscopic equivalency of the two PPh_2 groups at δ = - 4.2 ppm can be in accordance with a chelate structure in which both P^{III} atoms are in a *cis* configuration, with the P-atom *trans* to a hard donor (P=O) as revealed by the high value of $^1J_{P-Pt}$ = 4025 Hz.

Due to the ability of the P=O group of the ligand BPPO to be "free" in the $[PtCl_2(BPPO)_2]$ complex, compound **15** seemed to be a suitable starting material for the synthesis of bimetallic complexes in which the phosphine moiety is ligated to the platinum while the P=O group is coordinated with another metal, for example a Lewis Acid. Such complexes were easy to obtain, mixing $[PtCl_2(BPPO)_2]$ and $TiCl_4$ or nBu_2SnCl_2 in dichloromethane solution. After drying, bimetallic complexes were obtained (Scheme 10). In both cases **17** and **18,** the phosphine group remained bonded to the platinum atom (δ_P = +3.7 and +1.8 ppm with $^1J_{P-Pt}$ = 3738 and 3673 Hz respectively). In complex **17,** the P=O coordination was achieved by $TiCl_4$ as shown by ^{31}P NMR spectroscopy. On the other hand, the P=O coordination by nBu_2SnCl_2 in complex **18** was confirmed by the highfield shift of the ^{119}Sn NMR signal (δ_{Sn} = - 32.3 ppm) whereas the ^{31}P NMR signals were little affected. The geometry of the complexes is assumed to be *cis*, due to the high values of $^1J_{P-Pt}$ (3738 and 3673 Hz).



17 : L.A. = $TiCl_4$
18 : L.A. = nBu_2SnCl_2

Scheme 10

In this work, it has been established that ligand BPPO acts generally as a monodentate ligand in neutral metallic complexes, and as a bidentate ligand in cationic metal complexes. Moreover, bimetallic complexes[21] containing a transition metal and a Lewis Acid have been prepared from a $[PtCl_2(BPPO)_2]$ complex. The structure of these complexes could not yet be established unequivocally; work is in progress to obtain monocrystals of such complexes suitable for X-ray diffraction analysis. The potential of such complexes, involving two different metals, is obvious and they could be of a great interest in catalytic reactions such as cross coupling or hydroformylation.

GENERAL CONCLUSION

Reactivity of enantiopure 2-phenyl-1,3,2-oxazaphospholidine **1** with halide compounds was explored. The Michaelis Arbuzov reaction with benzylbromide **2a**, allylbromides **2b-c** and α-bromoesters **2d-f** gave rise to chiral (*Rp*)-phosphinamides **3a-f**. With α-haloacetophenones **4a-c**, we obtained both a chiral ketophosphinamide **5**, resulting from a Michaelis Arbuzov reaction, and a mixture of vinylphosphonamide diastereomers **6** and **7**, resulting from the Perkow reaction. The products ratio **5**/(**6**,**7**) was very dependent on the nature of the halide.

We have developed a stereoselective synthesis of chiral phosphine-phosphine oxide ligands, *via* a substitution reaction of the bromine atom of compound **3a** by diphenylphosphide, giving (*Rp*)-benzylphenyl[2-(*S*)-diphenylphosphinomethylpyrrolidin-1-yl]-phosphine oxide (BPPO), and by (±)-t-butylphenylphosphide-borane complex, leading to chiral diastereomer ligands **8** and **9**.

The coordination chemistry of ligand BPPO has been studied. Different transition metal complexes were obtained in which BPPO behaved as a monodentate ligand : $[W(BPPO)(CO)_5]$ **11b**, $[PdCl_2(BPPO)_2]$ **12**, $[PtCl_2(BPPO)_2]$ **15**; and as bidentate ligand : $[Rh(COD)(BPPO)]^+$, BF_4^- **10**, $[W(BPPO)(CO)_4]$ **11a**, $[Pd(BPPO)_2]^{2+}$, $2BF_4^-$ **13**, $[Pd(\eta^3\text{-}C_6H_9)(BPPO)]^+$, BF_4^- **14**, $[Pt(BPPO)_2]^{2+}$, $2BF_4^-$ **16**. It was demonstrated that BPPO was applicable to the synthesis of heterobimetallic complexes : $[PtCl_2(BPPO)_2TiCl_4]$ **17** and $[PtCl_2(BPPO)_2nBu_2SnCl_2]$ **18**.

Results on the enantioselective catalytic reactions involving these ligands will be reported in due course.

EXPERIMENTAL SECTION

All syntheses were carried out under nitrogen using N_2/vacuum lines, and Schlenk tube techniques. All solvents were purified by classical methods [22], and degassed with N_2 before use. Ligand (*RP*)-benzylphenyl[2-(*S*)-diphenylphosphinomethyl pyrrolidin-1-yl] phosphine oxide (BPPO) was prepared using a previously described method[5].

All the transition metal complexes $[RhCl(COD)]_2$[23], $[PdCl_2(CH_3CN)_2]$[24], $[PtCl_2(COD)]$[25] were prepared according to published procedures except for $[W(CO)_6]$ which was purchased from Aldrich.

NMR spectra were recorded as CD_2Cl_2 or $CDCl_3$ solutions on AC 100 or AC 200 Bruker spectrometers; ^1H at 100.13 MHz (or 200.26 MHz; $Si(CH_3)_4$ as internal reference); ^{13}C at 25.18 MHz (or 50.36 MHz; $Si(CH_3)_4$ as internal reference); ^{31}P-{^1H} at 40.5 MHz (H_3PO_4 85% as external reference); ^{119}Sn-{^1H} at 37.3 MHz ($SnMe_4$ as external reference).

Infrared spectra were recorded as Nujol mulls, on a Perkin Elmer 298 spectrometer (range 4000-600 cm^{-1}).

Column chromatographies were performed using Silica gel 60 (70-230 Mesh), purchased from Merck.

General procedure for the Michaelis-Arbuzov and the Perkow reactions:

A 50 mL three-necked, round bottom flask, was equipped with a magnetic stirring bar, a nitrogen inlet adapter, a reflux condenser fitted with an oil bubbler, and a pressure-equalizing funnel. To a solution of 2-phenyl-1,3,2-oxazaphospholidine (0.518g, 2.50 mmol) in 15 mL of degassed CH_2Cl_2, alkyl- or allyl halide (2.50 mmol) in 10 mL of degassed CH_2Cl_2 was added. The mixture was heated to 45°C, and the reaction was monitored by ^{31}P NMR spectroscopy. After the indicated time (tables 1 and 2), the solvent was removed by rotary evaporation. The crude product was purified in most cases by column chromatography.

Reaction of **1** with **2a** :

*(R_P)-benzylphenyl- [(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide **3a***

Crude compound **3a** was washed with dry pentane, and obtained as a white powder (0.870g, yield = 92%, mp = 128°C).

IR (KBr) : ν (cm^{-1}) 3057, 3012 (C_{sp^2}-H); 2971, 2873 (C_{sp^3}-H); 1610, 1595 (C=C); 1435 (P-Phenyl); 1195 (P=O); 748, 695 (arom. monosubst.). **^1H NMR** ($CDCl_3$) : δ (ppm) 1.70-2.11 (m, $2H_3$+$2H_4$); 2.83-3.52 (m, $2H_6$+$2H_5$+$2H_1$); 3.15-3.82 (m, H_2); 7.11 (s, $5H_{arom}$); 7.19-7.82 (m, $5H_{arom}$). **^{13}C NMR** ($CDCl_3$) :δ (ppm) 24.6 (d, $^3J_{PC}$=5.8 Hz, C_4); 30.67 (d, $^3J_{PC}$=5.3 Hz, C_3); 36.4 (d, $^3J_{PC}$=2.0 Hz, C_1); 36.6 (d, $^1J_{PC}$=85.0 Hz, C_6); 47.9 (d, $^2J_{PC}$=2.8 Hz, C_5); 58.8 (d, $^2J_{PC}$=2.0 Hz, C_2); 126.6-131.8 ($10C_{arom}$). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 31.4. $[\alpha]_{589}^{20}$ = +2.5 (*c* = 1.0 ; CH_2Cl_2). **Anal.** calculated for $C_{18}H_{21}NOPBr$: C, 57.16; H, 5.60; N, 3.70. found: C, 56.54; H, 5.38; N, 3.41.

The synthesis of **3a** can be carried out on a large scale : 30 mmole (7.79g, yield = 98%).

Reaction of **1** with **2b** :

*(R_P)-Allylphenyl[(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide **3b***

The dark yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 15 g; eluent acetone; 24 fractions of 15 mL). After concentration, **3b** was obtained as a colourless oil (0.517g, yield = 63%).

IR (neat) : ν (cm^{-1}) 3057, 3012 (C_{sp^2}-H); 2971, 2873 (C_{sp^3}-H); 1637, 1592 (C=C); 1438 (P-Phenyl); 1118 (P=O); 748 (arom. monosubst.). **^1H NMR** ($CDCl_3$) : δ (ppm) 1.70-2.14 (m, $2H_3$+$2H_4$); 2.83 (m, $2H_6$); 3.31-

3.39 (m, H_1+2H_5); 3.55 (dd, ^3J=0.9 Hz, ^3J=3.6 Hz, H_1); 3.89 (m, H_2); 5.03 (m, =CH_2); 5.84 (m, =CH-); 7.41-7.76 (m, 5H_{arom}). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.6 (d, $^3J_{PC}$=5.8 Hz, C_4); 30.7 (d, $^3J_{PC}$=4.6 Hz, C_3); 35.3 (d, $^1J_{PC}$=88.6 Hz, C_6); 36.6 (d, $^3J_{PC}$=2.6 Hz, C_1); 47.9 (C_5); 58.8 (C_2); 120.3 (d, $^3J_{PC}$=13.0 Hz,C<u>H</u>=CH_2); 127.5 (d, $^3J_{PC}$=8.6 Hz, CH=C<u>H</u>$_2$); 128.4-132.3 (5C_{10-12}). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 31.6 ppm. $[\alpha]_{589}^{20}$ = -21.0 (*c* = 1.0 ; CH_3COCH_3). **Anal.** calculated for $C_{14}H_{19}NOPBr$: C, 51.24; H, 5.84; N, 4.27. found: C, 51.38; H, 5.97; N, 4.14.

Reaction of **1** with **2c** :

(R_p)-(E-but-2-enyl)phenyl[(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide 3c

The brown oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL). After concentration, **3c** was obtained as a colourless oil (0.710g, yield = 83%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1591 (C=C); 1438 (P-Phenyl); 1197 (P=O); 745 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.75 (m, CH_3); 1.80-2.12 (m, 2H_3+2H_4), 2.72 (m, 2H_6); 3.31-3.39 (m, H_1+2H_5); 3.57 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_1); 3.93 (m, H_2); 5.42-5.51 (m, 2H, -CH=); 7.2-7.8 (m, 5H_{arom}). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 17.7 (d, $^4J_{PC}$=2.2 Hz, CH_3); 24.2 (d, $^3J_{PC}$=4.9 Hz, C_4); 30.4 (d, $^3J_{PC}$=5.3 Hz, C_3); 33.5 (d, $^1J_{PC}$=89.6 Hz, C_6); 36.2 (d unresolved, C_1); 47.5 (d, $^2J_{PC}$=2.4 Hz, C_5); 58.5 (d, $^2J_{PC}$=1.5 Hz, C_2); 118.9 (P-CH_2-C<u>H</u>=); 119.3 (CH_3-C<u>H</u>=); 127.9-131.6 (5C_{arom}); 131.5 (d, $^1J_{PC}$=120.0 Hz, C_7). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 32.3. $[\alpha]_{589}^{20}$ = -34.5 (*c* = 1.0 ; CH_3COCH_3). **Anal.** calculated for $C_{15}H_{21}NOPBr$: C, 52.65; H, 6.19; N, 4.09. found: C, 52.78; H, 6.07; N, 3.98.

Reaction of **1** with **2d** :

(R_p)-(Carbomethoxymethyl)phenyl[(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide 3d

The dark yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL). After concentration, **3d** was obtained as a colourless oil (0.676g, yield = 75%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1740 (C=O); 1590 (C=C); 1440 (P-Phenyl); 1220 (P=O); 1120 (C-O); 745, 695 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.6-2.1 (m, 2H_3+2H_4); 3.2 (m, 2H_5+2H_6); 3.6 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_2); 3.7 (s, CH_3); 4.2 (m, 2H_1); 7.2-8.0 (m, 5H_{arom}). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.7 (d, $^3J_{PC}$=6.4 Hz, C_4); 30.8 (d, $^3J_{PC}$=5.6 Hz, C_3); 36.2 (C_1); 37.8 (d, $^1J_{PC}$=80.6 Hz, C_6); 48.0 (d, $^2J_{PC}$=3.0 Hz, C_5); 52.5 (CH_3); 59.1 (d, $^2J_{PC}$=2.7 Hz, C_2); 128.5-132.5 (6C_{arom}); 166.7 (d, $^2J_{PC}$=5.2 Hz, -CO_2-). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 26.5. $[\alpha]_{589}^{20}$ = -11.3 (*c* = 1.0; CH_2Cl_2). **Anal.** calculated for $C_{14}H_{19}NO_3PBr$: C, 46.69; H, 5.32; N, 3.89. found: C, 46.48; H, 5.47; N, 3.82.

Reaction of **1** with **2e** :

(R_p)-(Carbo-tertio-butoxymethyl)phenyl- [(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide 3e

The yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL). After concentration, **3e** was obtained as a colourless oil (0.674g, yield = 67%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1591 (C=C); 1438 (P-Phenyl); 1197 (P=O); 745 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.3 (s, 9H, CH_3); 1.9 (m, 2H_3+2H_4); 3.2 (m, 2H_5+2H_6); 3.6 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_2); 4.2 (m, 2H_1); 7.2-8.0 (m, 5H_{arom}). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.4 (d, $^3J_{CP}$=6.3 Hz, C_4); 27.6 (3 CH_3); 30.6 (d, $^3J_{CP}$=5.4 Hz, C_3); 36.0 (d, $^3J_{CP}$=2.5 Hz, C_1); 38.9 (d, $^1J_{CP}$=81.1 Hz, C_6); 47.8 (d, $^2J_{CP}$=2.8 Hz, C_5); 58.9 (d, $^2J_{CP}$=2.5 Hz, C_2); 81.7 (-C(<u>C</u>H_3)$_3$); 131.0 (d, $^1J_{CP}$=125.6 Hz, C_7); 128.1-132.1 (5$C_{arom.}$); 164.9 (d, $^2J_{CP}$=5.2 Hz, -CO_2-). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 26.8. $[\alpha]_{589}^{20}$ = -25.3

(c = 10.0 ; CH_3COCH_3). **Anal.** calculated for $C_{17}H_{25}NO_3PBr$: C, 50.76; H, 6.26; N, 3.48. found: C, 50.57; H, 6.39; N, 3.53.

Reaction of **1** with **2f** :

*(R_P)-(Carbobenzyloxymethyl)phenyl[(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide **3f***

The yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone/pentane : 60/40; 12 fractions of 15 mL, then 24 fractions of 30 mL). After concentration, **3f** was obtained as a colourless oil (0.556g, yield = 51%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1740 (C=O); 1591 (C=C); 1440 (P-Phenyl); 1197 (P=O); 1120 (C-O); 745 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.6-2.1 (m, $2H_3$+$2H_4$); 3.2 (m, $2H_5$+$2H_6$); 3.6 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_2); 4.2 (s, -CH_2-); 4.2 (m, $2H_1$); 7.2-8.0 (m, $10H_{arom}$). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 21.4 (d, $^3J_{CP}$=6.7 Hz, C_4); 30.6 (d, $^3J_{CP}$=7.5 Hz, C_3); 36.0 (C_1); 37.7 (d, $^1J_{CP}$=86.2, C_6); 47.7 (C_5); 59.0 (d, $^2J_{CP}$=2.8 Hz, C_2); 67.1 (-CH_2-O); 128.3-135.0 ($10C_{arom.}$); 165.8 $^3J_{CP}$ = 5.2 Hz, -CO_2-). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 27.0. $[\alpha]_{589}^{20}$ = - 20.3 (c = 1.0 ; CH_3COCH_3). **Anal.** calculated for $C_{20}H_{23}NO_3PBr$: C, 55.06; H, 5.31; N, 3.21. found: C, 55.22; H, 5.42; N, 3.14.

Reaction of **1** with **4a** :

*(1'-Phenylvinyloxy)phenyl[(S)-2-chloromethylpyrrolidin-1-yl]phosphine oxide **6a** and **7a***

The dark yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL). After concentration, a mixture of **6a** and **7a** (75/25) was obtained as a colourless oil (0.371g, yield = 41%; d.e. = 50%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1591, 1645 (C=C); 1439 (P-Phenyl); 1173 (P=O); 745, 638 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.4-2.0 (m, $2H_3$+$2H_4$); 2.8-3.1 (m, $2H_5$); 3.4 (m, H_1); 3.6 (m, H_1); 5.1 (m, H_7); 5.3 (m, H_7); 6.7-7.9 (m, $10H_{arom}$). **major compound : ^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.7 (d, $^3J_{CP}$=7.8 Hz, C_3); 29.4 (d, $^3J_{CP}$=7.5 Hz, C_4); 47.4 (d, $^2J_{CP}$=8.0 Hz, C_5); 47.5 (C_1); 59.2 (d, $^2J_{CP}$=5.1 Hz, C_2); 97.7 (d, $^3J_{CP}$=4.6 Hz, C_7); 126.8 (d, $^2J_{CP}$=13.5 Hz, C_6); 124.8-133.0 ($10C_{arom.}$); 134.8 (d, $^3J_{CP}$=0.9 Hz, C_{arom}-C_6); 151.5 (d, $^1J_{CP}$=80.8 Hz, C_{arom}-P). **minor compound : ^{13}C NMR** ($CDCl_3$) : δ (ppm) 25.0 (d, $^3J_{CP}$=7.8 Hz, C_3); 29.1 (d, $^3J_{CP}$=7.5 Hz, C_4); 59.9 (d, $^2J_{CP}$=3.5 Hz, C_2); 96.9 (d, $^3J_{CP}$=4.6 Hz, C_7). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 17.7 (75%); 17.2 (25%).

Reaction of **1** with **4b** :

*(R_P)-(2'-Oxo-2'-phenylethyl)phenyl[(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide **5b***

Compound **5b** was obtained as a colourless oil (0.437g, yield = 43%)(see **6b** and **7b**).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1590, 1645 (C=C); 1438 (P-Phenyl); 1171 (P=O); 745, 638 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.5-2.1 (m, $2H_3$+$2H_4$+H_6); 2.9-3.3 (m, H_6+$2H_5$); 3.5 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_2); 3.8-4.2 (m, $2H_1$); 6.7-8.2 (m, $10H_{arom}$).**^{13}C NMR** ($CDCl_3$) : δ (ppm) 21.4 (d, $^3J_{CP}$=6.5 Hz, C_4); 24.6 (d, $^3J_{CP}$=6.7 Hz, C_3); 36.3 (C_1); 42.0 (d, $^1J_{CP}$=76.8 Hz, C_6); 48.0 (C_5); 59.1 (d, $^2J_{CP}$=2.8 Hz, C_2); 125.2-133.4 ($12C_{arom.}$); 173.6 (d, $^2J_{CP}$=16.1 Hz, C_7). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 27.0. $[\alpha]_{589}^{20}$ = -0.3 (c = 10.0 ; CH_3COCH_3). **Anal.** calculated for $C_{19}H_{21}NO_2PBr$: C, 56.17; H, 5.21; N, 3.45. found: C, 56.20; H, 5.16; N, 3.48.

(1'-Phenylvinyloxy)pheny [(S)-2-bromomethylpyrrolidin-1-yl]phosphine oxide ***6b*** *and* ***7b***

The dark yellow oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL) where compound **5b** was separated from the two other compounds **6b** and **7b**.. After concentration, a mixture of **6b** and **7b** (87/13) was obtained as a colourless oil (0.579g, overall yield = 57%, d.e. = 74%).

IR (neat) : ν (cm^{-1}) 3056 (C_{sp^2}-H); 2967, 2875 (C_{sp^3}-H); 1590, 1645 (C=C); 1438 (P-Phenyl); 1171 (P=O); 745, 638 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.3 (t, ^3J=7.5 Hz, H_3); 1.5-2.2 (m, H_3+$2H_4$); 3.1-3.2 (m, H_5); 3.3 (m, ^3J=9.5 Hz, H_5); 3.7 (dd, ^3J=9.6 Hz, ^3J=3.2 Hz, H_2); 3.9-4.1 (m, ^3J=3.2 Hz, H_1); 4.2 (m, ^1J=15.1 Hz, ^3J=7.3 Hz, H_1); 5.2 (m, H_7); 5.4 (m, H_7); 6.9-8.0 (m, $10H_{arom}$). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.5 (d, $^3J_{CP}$=7.5 Hz, C_3); 30.3 (d, $^3J_{CP}$=7.5 Hz, C_4); 37.0 (C_1); 47.4 (d, $^2J_{CP}$=4.8 Hz, C_5); 59.0 (d, $^2J_{CP}$=5.0 Hz, C_2); 97.7 (d, $^3J_{CP}$=4.8 Hz, C_7); 126.8 (d, $^2J_{CP}$=13.5 Hz, C_6); 124.8-135.1 ($10C_{arom.}$); 134.8 (d, $^3J_{CP}$=0.9 Hz, C_{arom}-C_6); 151.5 (d, $^1J_{CP}$=80.8 Hz, C_{arom}-P). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 17.7 (87%); 17.2 (13%).

Reaction of **1** with **4e** :

(1'-Phenylvinyloxy)pheny[(S)-2-iodomethylpyrrolidin-1-yl]phosphine oxide ***6c*** *et* ***7c***

The dark brown oil obtained was purified by column chromatography on silicagel (SiO_2 : 35 g; eluent acetone; 24 fractions of 30 mL). After concentration, a mixture of **6c** and **7c** (51/49) was obtained as a colourless oil (0.465g, yield = 41%; d.e. = 50%). These compounds are not stable under usual conditions and rapidly decompose to various tetracoordinated phosphorus compounds.

IR (neat) : ν (cm^{-1}) 3055 (C_{sp^2}-H); 2968, 2876 (C_{sp^3}-H); 1590, 1645 (C=C); 1437 (P-Phenyl); 1171 (P=O); 745, 638 (arom. monosubst.). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 1.54-1.98 (m, $2H_3$+$2H_4$); 2.78-3.15 (m, $2H_5$); 3.37 (dd, ^3J=0.9 Hz, ^3J=2.5 Hz, H_2); 3.59 (m, H_1); 3.88 (m, H_1); 6.25 (d, ^3J=2.0 Hz, H_7); 2.26 (d, ^3J=2.0 Hz, H_7); 7.15-7.65 (m, $10H_{arom}$). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 22.7 (s, C_4); 23.7 (s, C_3); 24.6 (C_1); 47.9 (C_5); 58.6 (d, $^2J_{CP}$=2.8 Hz, C_2); 59.4 (d, $^2J_{CP}$=5.0 Hz, C_2);104.1 (d, $^3J_{CP}$=4.8 Hz, C_7); 106.7 (d, $^2J_{CP}$=13.5 Hz, C_6); 127.1-132.3 ($11C_{arom.}$); 151.5 (d, $^1J_{CP}$=80.8 Hz, C_{arom}-P). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 17.7 ppm (51%); 17.2 ppm (49%).

Synthesis of hybrid ligands **8** and **9**

tertio-butylphenylphosphine-borane complex and corresponding lithium phosphide

were prepared using the procedure described by Imamoto[16h].

(R_P)-Benzylphenyl[(S)-2-((tert-butyl)phenylphosphinomethyl)pyrrolidin-1-yl]phosphine oxide ***8*** *(1st diastereomer*

To a solution of 9.45 g (25 mmol) phosphine oxide **3a** in THF (50 mL) cooled at -30°C, was added *tert*-butylphenylphosphide in THF (10 mL) portionwise. The mixture was stirred at -30°C for 2 h, then for 12 h at room temperature. Then degassed water (40 mL) was added carefully, the two phases were decanted, the aqueous phase was extracted twice with degassed CH_2Cl_2 (15 mL). The organic phases were mixed, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The two diastereomers were separated by column chromatography on silicagel (SiO_2 : 35 g ; eluent benzene/ethyl acetate ; 12 fractions of 10 mL, 12 fractions of 30 mL). After removal of the solvent, the product **8** was both obtained as colourless oil. Subsequent recrystallisation in degassed benzene leads to a white solid (6.56g, yield : 55%, mp = 65°C).

IR (KBr) : ν (cm^{-1})1200 (P=O). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 0.98 (d, $^3J_{CP}$=13.8 Hz, $9H_8$); 1.15-1.32 (m, $2H_4$); 1.40 (m, H-B); 1.56-1.68 (m, H_{3a}); 2.22 (m, H-B); 2.69 (m, H-B); 3.04-3.07 (m, H_{3b}+$2H_5$); 3.17 (dd,

^2J=14.4 Hz, , $^2J_{CP}$=16.2 Hz, H_{6a}); 2.99 ($^2J_{CP}$ and ^2J=14.4 Hz, H_{6b}); 3.52 (m, H_2); 7.04-7.95 (m, $15H_{arom}$). **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.62 (s, C_4); 24.70 (s, $3C_8$); 23.9 (d, $^1J_{CP}$=30.2 Hz, C_1); 28.75 (d, $^1J_{CPB}$=33.2 Hz, C_7); 32.62 (d, $^3J_{CP}$=7.0 Hz, C_3); 36.29 (d, $^1J_{CP}$=84.6 Hz, C_6); 49.90 (d, $^2J_{CP}$=4.0 Hz, C_5); 54.90 (s, C_2); 125.11-134.92 ($18C_{arom}$). **^{31}P NMR** ($CDCl_3$) : δ (ppm) - 22.51 to -29.13 (m, P-B); 30.28 (s, P=O). **^{11}B NMR** ($CDCl_3$) : δ (ppm) -41.1. $[\alpha]_{589}^{20}$ = -41.1 (*c*=1.0 ; CH_2Cl_2).

(R_P)-Benzylphenyl[(S)-2-((tert-butyl)phenylphosphinomethyl)pyrrolidin-1-yl]phosphine oxide ***9*** *(2nd diastereomer)*

After concentration, the minor compound was obtained as a colourless oil. Subsequent recrystallisation in a cyclohexane/benzene mixture 50/50 furnished a white solid. (4.18g, yield : 35%, mp = 74°C).

IR (KBr) : ν (cm^{-1}) 1200 (P=O). **^{1}H NMR** ($CDCl_3$) : δ (ppm) 0.92 (d, $^3J_{CP}$=13.9 Hz, $9H_8$); 1.29 (m, H_{3a}); 1.67-1.72 (m, H_{3b}+$2H_4$); 2.05 (dt, $^1J_{CP}$=14.6 Hz, ^2J=12.1 Hz, H_{1a}); 2.28 (dt, $^1J_{CP}$=2.8 Hz, , ^2J=12.1 Hz, H_{1a}); 3.19 (m, H_{5b}); 3.34 ($^2J_{CP}$ et ^2J=14.1 Hz, H_{6a}); 3.41 (m, H_{5b}); 3.52 (dd, $^2J_{CP}$=17.3 Hz, ^2J=14.4 Hz, H_{6b}); 4.07 (m, H_2); 7.13-7.69 (m, $15H_{arom}$) **^{13}C NMR** ($CDCl_3$) : δ (ppm) 24.65 (d, $^3J_{CP}$=7.0 Hz, C_4); 25.23 (s, $3C_8$); 25.67 (d, $^3J_{CPB}$=27.2 Hz, C_1); 29.46 (d, $^1J_{CPB}$=34.2 Hz, C_7); 32.25 (d, $^3J_{CP}$=7.0 Hz, C_3); 36.63 (d, $^1J_{CPO}$=85.5 Hz, C_6); 46.95 (s, C_5); 56.02 (d, $^3J_{CP}$=6.0 Hz, C_2); 126.56-133.22 ($18C_{arom}$). **^{31}P NMR** ($CDCl_3$) : δ (ppm) - 22.32 to -27.53 (m, P-B); 30.04 (s, P=O). **^{11}B NMR** ($CDCl_3$) : δ (ppm) -41.9. $[\alpha]_{589}^{20}$ = -41.1 (*c*=1.0 ; CH_2Cl_2).

Preparation of BPPO complexes

$[Rh(COD)(BPPO)]^+$, BF_4^- ***10***

Bis[chloro(cycloocta-1,5-diene)rhodium] ($[RhCl(COD)]_2$, 0.1 g, 0.2 mmol) and ligand BPPO (0.193 g, 0.4 mmol) were stirred at room temperature in methanol (3 mL) for 30 min. Silver tetrafluoroborate (0.08 g, 0.41 mmol) in water (1 mL) was then added. After stirring for 1 h, the complex is filtered off, and dried *in vacuo*. The crude solid was then recrystallized from ethanol, leading to a yellow powder of $[Rh(COD)(BPPO)]^+$, BF_4^- (0.250g, yield = 80%, mp = 138°C dec.).

IR (Nujol) : ν (cm^{-1}) 1160 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 19.9 (dd, $^1J_{P\text{-}Rh}$=151.7 Hz, $^3J_{P\text{-}Rh\text{-}O=P}$=3.5 Hz, PPh_3); 48.4 (t, $^2J_{P=O\text{-}Rh}$=3.5 Hz, $^3J_{P=0\text{-}Rh\text{-}P}$=3.5 Hz, P=O).

$[W(BPPO)(CO)_4]$ ***11a***

A solution of $[W(CO)_6]$ (0.173 g, 0.49 mmol) and ligand BPPO (0.237 g, 0.49 mmol) in toluene (10 mL) was refluxed overnight. After evaporation and drying, a crude solid was obtained as a mixture of two complexes (as shown by ^{31}P NMR spectroscopy). The major product **11a** was isolated by column chromatography on silica-gel (20g, eluent dichloromethane) as a gold yellow powder (0.115g, yield = 30%, mp = 165-170°C dec.). In $[W(BPPO)(CO)_4]$ **11a**, the coordination of ligand BPPO was achieved by both phosphine and phosphine oxide moieties. The minor product was characterised in the mixture as $[W(BPPO)(CO)_5]$ complex **11b** where only the PPh_2 group was coordinated to the metal.

IR (Nujol) : ν (cm^{-1}) 1165 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 2.4 (s with 2 satellites, $^1J_{P\text{-}W}$=237 Hz, PPh_3); 45.6 (P=O).

11b : **^{31}P NMR** ($CDCl_3$) : δ (ppm) 10.3 (s with 2 satellites, $^1J_{P\text{-}W}$=227 Hz, PPh_3); 29.13 (P=O).

$[PdCl_2(BPPO)_2]$ ***12***

To a suspension of $[PdCl_2(CH_3CN)_2]$ (0.259 g, 1 mmol) in tetrahydrofurane (50 mL), ligand BPPO (0.968 g, 2 mmol) was added and the mixture stirred for 30 min. After evaporation and drying *in vacuo*, $[PdCl_2(BPPO)_2]$ complex was obtained as a powder (1.087g, yield = 95%, mp = 180°C dec.).

IR (Nujol) : ν (cm^{-1}) 1200 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 10.1 (PPh_3); 31.2 (P=O).

$[Pd(BPPO)_2]^{2+}$, 2 BF_4^- ***13***

A solution of $[PdCl_2(BPPO)_2]$ (0.183 g, 0.16 mmol) in dichloromethane (10 mL) was treated with a solution of $AgBF_4$ (0.0626 g, 0.32 mmol) in anhydrous methanol (5 mL), and the mixture was stirred for 1 h. The precipitate was filtered off and the filtrate dried *in vacuo*. The cationic complex $[Pd(BPPO)_2]^{2+}$, $2BF_4^-$ was obtained as a yellow powder (0.180g, yield = 90%, mp = 164-166°C dec.).

IR (Nujol) : ν (cm^{-1}) 1100 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 30.7 (d, $^3J_{P\text{-}Pd\text{-}O=P}$=4.0 Hz, PPh_3); 49.4 (d, $^3J_{P=O\text{-}Pd\text{-}P}$=4.0 Hz, P=O).

$[Pd(\eta^3\text{-}C_6H_9)(BPPO)]^+$, BF_4^- ***14***

$[Pd(\eta^3\text{-}C_6H_9)Cl]$ complex was synthesised according to Trost's method[26] and transformed into the corresponding cationic complex $[Pd(\eta^3\text{-}C_6H_9)(CH_3CN)_2]^+$, BF_4^- by the pathway developed by Åkermark[19]. A dichloromethane solution (3 mL) of this cationic complex (0.2 g, 0.56 mmol) was cooled to -20°C and a solution of ligand BPPO (0.155 g, 0.32 mmol) in dichloromethane (5 mL) was added. After 15 min stirring, solvent was removed *in vacuo* at 0°C. The solid was dried and washed with diethyl ether. The complex was characterised by ^{31}P NMR spectroscopy, but was unstable in solution and decayed during attempts of recrystallization.

^{31}P NMR ($CDCl_3$) : δ (ppm) 13.9 (d, $^3J_{P\text{-}Pd\text{-}O=P}$=29.0 Hz, PPh_3); 45.2 (m, P=O).

$[PtCl_2(BPPO)_2]$ ***15***

To a suspension of $[PtCl_2(COD)]$ (0.163 g, 0.435 mmol) in $CHCl_3$ (5 mL), a solution of ligand BPPO (0.42 g, 0.87 mmol) in chloroform (5 mL) was added and the mixture stirred for 15 min. After evaporation and drying *in vacuo*, $[PtCl_2(BPPO)_2]$ complex was obtained as a powder (0.536g, quantitative yield, mp = 180°C dec.).

IR (Nujol) : ν (cm^{-1}) 1185-1200 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 0.9 (s with 2 satellites, $^1J_{P\text{-}Pt}$=3645 Hz, PPh_3); 31.0 (P=O).

$[Pt(BPPO)_2]^{2+}$, 2 BF_4^- ***16***

A solution of $[PtCl_2(BPPO)_2]$ (0.197 g, 0.16 mmol) in dichloromethane (10 mL) was treated with a solution of $AgBF_4$ (0.0626 g, 0.32 mmol) in anhydrous methanol (5 mL) and the mixture stirred for 1 h. The precipitate was filtered off, and the filtrate dried *in vacuo*. The cationic complex was obtained as a powder (0.192g, yield = 90%, mp = 155-160°C dec.).

IR (Nujol) : ν (cm^{-1}) <1160 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) -4.2 (s with 2 satellites, $^1J_{P\text{-}Pt}$=4025 Hz, PPh_3); 52.4 (P=O).

Bimetallic complexes of ligand BPPO with Platinum and Lewis Acids

To a solution of $[PtCl_2(BPPO)_2]$ (0.1 g, 0.081 mmol) in dichloromethane (10 mL) was added 1 equivalent of $TiCl_4$ (0.0154 g, 0.081 mmol) {respectively nBu_2SnCl_2 (0.0246 g, 0.081 mmol)}. After stirring for 15 min, dichloromethane was removed, and the complex dried *in vacuo*. Yields were quantitative.

$[PtCl_2(BPPO)_2(TiCl_4)]$ **17** (0.115g, mp = 170°C dec).

IR (Nujol) : ν (cm^{-1}) 1100 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 3.7 (s with 2 satellites, $^1J_{P\text{-}Pt}$=3738 Hz, PPh_3); 43.4 (P=O).

$[PtCl_2(BPPO)_2(nBu_2SnCl_2)]$ **18** (0.124g, mp = 175°C dec).

IR (Nujol) : ν (cm^{-1}) 1155 (P=O). **^{31}P NMR** ($CDCl_3$) : δ (ppm) 1.8 (s with 2 satellites, $^1J_{P\text{-}Pt}$=3673 Hz, PPh_3); 32.6 (P=O). **^{119}Sn NMR** ($CDCl_3$) : δ (ppm) -32.3.

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