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Effects of the electronic properties of chiral chelating diphosphines in stereoselective Diels–Alder cycloaddition reactions promoted by their transition metals complexes

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Abstract

The Pd(II) and Pt(II) complexes (perchlorates and hexafluoroantimoniates, respectively) of a series of C_2 symmetric biheteroaromatic diphosphines differing in their electronic properties at phosphorus have been tested as catalysts in [4 + 2]-cycloaddition reactions of cyclopentadiene and *N*-2-alkenoyl-1,3-oxazolidine-2-ones. The best stereoselection results were obtained with the complexes produced from electron-rich ligands, which were found to give also the kinetically most active catalysts. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Stereoselective Diels–Alder reaction catalyzed by complexes of trivalent aluminum, boron and transition metals with chiral modifiers represents a very efficient tool to contemporarily generate up to four contiguous stereocenters under very mild experimental conditions. Activation of the dienophilic counterpart generally develops trough a Lewis type acid–base face-selective interaction between a carbonyl function present on the reactant and the chiral catalytic complex [1].

Several classes of chiral promoters have been tested in different types of Diels–Alder reactions in order to select the most efficient ones from the point of view of stereoselection capacity and catalytic efficiency. It was found that oxygenated chelating functions, like those present in BINOL [2], in 3,3′-diaryl-BINOL [3] and in tartrate derivatives [4], give very high enantiomeric and diastereomeric excesses in some reference reactions, even though metal coordination at nitrogen was found equally efficient in ligands difunctionalized with chiral oxazoline units [5].

The utilization of chiral diphosphine ligands has been rather poorly considered in the past, probably because preliminary results with DIOP and CHIRAPHOS [6] were found rather unpromising.

Very recently, highly satisfactory results were obtained with BINAP as ligand of Pd(II) and Pt(II) in cycloaddition reactions between cyclopentadiene and *N*-alkenoyl-1,3-oxazolidin-2-ones **1a–c** which are in standard use for the evaluation of the stereoselection capacity of all new ligands presented in the chemical literature (Scheme 1) [7].

In a few cases, enantiomeric excesses up to 99% were found, even though cases of quite low stereoselectivity are reported. The nature of the counterion seems to play a crucial role on this respect, since the best results were obtained with perchlorate and hexafluoroantimonate ions, while the worst data (less than 5% enantiomeric excesses) were found with chloride ion. A

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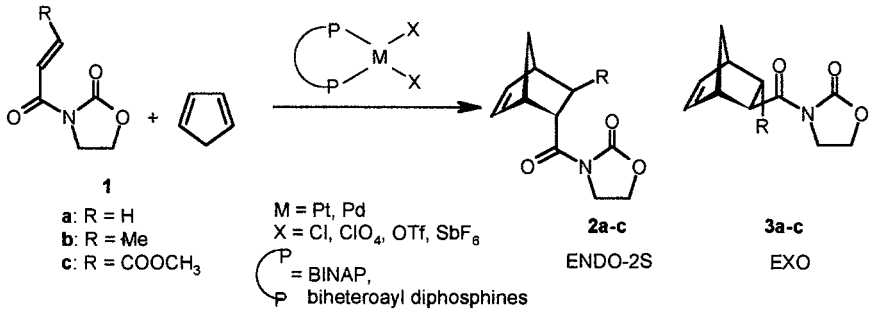


Scheme 1.

possible interpretation of these extraordinary effects is based on the consideration that the large electronic availability of BINAP weakens Lewis acidity of the metal center in the complex, thus lowering its capacity to associate to the dienophile. Hard anions restitute the metal the electronic deficiency necessary to effectively interact with the dienophilic species.

Since we have synthesized in the past few years a wide and homogeneous series of chiral C_2 symmetric diphosphines, characterized by a biheteroaromatic atropisomeric backbone [8] displaying different electronic properties at their phosphorus atoms, we considered to test them as ligands of palladium(II) and platinum(II) in the standard cycloaddition reactions reported above.

The diphosphines currently available in an enantiopure state are reported in Plate 1, each one associated with its own acronym and oxidative potential value, $E°$ (V). This parameter, determined by voltammetry, is that we have selected to quantitatively evaluate the electronic availability at phosphorus of chelating diphosphine ligands [8b].

Investigation of the influence of the electronic properties of phosphorus of diphosphine ligands on the exit of reaction catalyzed by their transition metal complexes is a challenging point in homogeneous catalysis research, since it is known that each reaction and substrate require that metal and ligand be tailored according to their requirements. We have recently given evidence that catalysts prepared from electron-rich diphosphines (*N*-Me-2-BINP, [9] tetraMe-BITIOP, [8c] *N*-MOM-2-BINP [9]) are nearly two order of magnitude more active than those resulting from electron-poor systems (BITIANP, BISCAP) in the hydrogenation of the ketonic function of β-oxoesters. In the case of acetoacetic ester we found a linear relationship between $E°$ and the logarithm of the rate constant [9]. An opposite situation was found in the inter- [10] and intra-molecular [11] Heck reaction, where the Pd(0) complexes produced by electron-poor diphosphines (BITIANP) were found to produce faster kinetics than those found when electron-rich ligands (tetraMe-BITIOP, BINAP) were used. In some cases, however, fast kinetics were found to work against stereoselectivity [11]. We were convinced that electron-poor diphosphines could be, at least in principle, more active than the electron-rich ones since their scarce donation ability could leave a higher Lewis acid character on the metal, thus favoring the coordination of the catalyst to the dienophile. In this light we planned to add to the series of biheteroaromatic diphosphines a new term, namely the 2,2′-bis(dicyclohexylphosphino)-1,1′-bibenzimidazole (**4**, Cy-BIMIP), probably displaying electronic and steric properties quite different from those exhibited by the corresponding diphenylsubstituted ligand BIMIP (Plate 2).

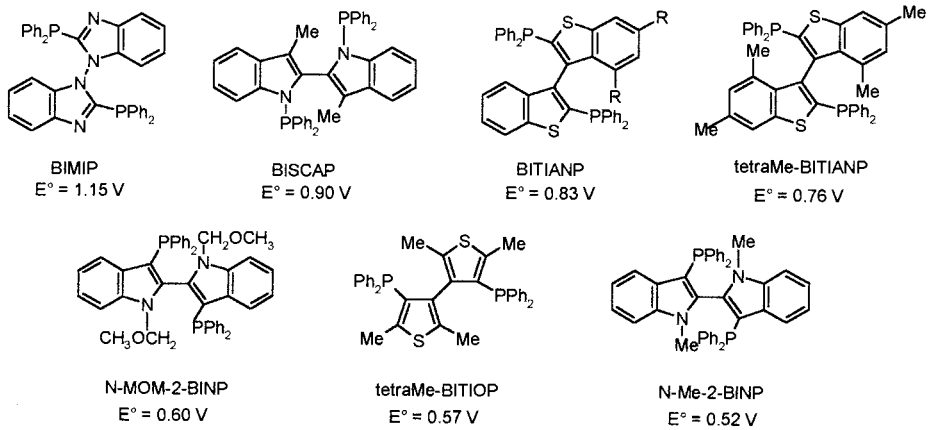
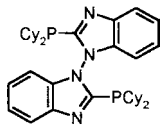


Plate 1.



4 Cy-BIMIP

Plate 2.

2. Results and discussion

The synthesis of Cy-BIMIP (**4**) was achieved in good yields by quenching the dianion of 1,1′-bibenzimidazole with chloro-dicyclohexylphosphine.

Voltammetry of Cy-BIMIP (Fig. 1) showed an oxidation peak at 1.0 V (vs. Ag/Ag^+), 0.15 V less than BIMIP, as expected by considering that the former carries dialkylsubstituted phosphine groups, while the latter is a triaryldiphosphine.

It is interesting to note that the $E°$ value found for diphosphine **4**, bearing the cyclohexyl disubstituted phosphane groups is only slightly lower than that of the corresponding diphenyl substituted ligand, BIMIP. It is evident that the heteroaromatic rings of the backbone influence the electronic properties of the phosphane groups much more efficiently than the non stereogenic substituents. A similar behavior was also found in the case of C_1 symmetric diphosphanes [12]. A possible interpretation of these findings involves conformational effects which allow the phosphorus lone pairs to align and overlap the π system of the biheteroaromatic rings,

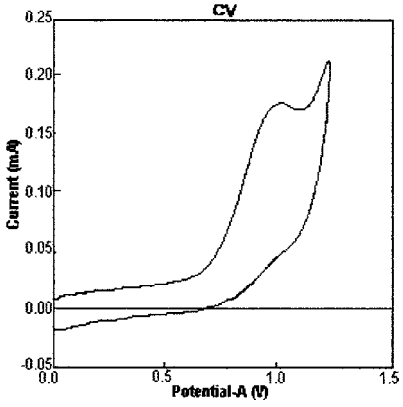
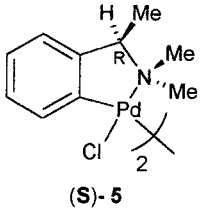


Fig. 1. Voltammetry of 2,2′-bis(dicyclohexylphosphino)-1,1′-bibenzimidazole (**4**) (Cy-BIMIP).



(S)- 5

Plate 3.

thus inhibiting any conjugative interaction with the other substituents at phosphorus. Their influence would be limited to inductive effects only and would be, by consequence, rather modest.

The preparation of enantiopure diphosphines generally follows two main known strategies. In the case of electron-rich diphosphines, the resolution process is performed at level of phosphine-oxides and is based on fractional crystallization of their diastereomeric adducts with chiral acids. Alkaline decomplexation of the adducts affords enantiopure phosphine-oxides, which are reduced to phosphines with trichlorosilane. *N*-Me-2-BINP, [9] tetraMe-BITIOP, [8c] *N*-MOM-2-BINP, [9] tetraMe-BITIANP [8a] and BITIANP [8a] were easily obtained in an enantiopure state according to this methodology.

In the case of electron-poor systems, resolution can be performed by fractional crystallization of the diastereomeric complexes obtained by reaction of racemic diphosphines with a chiral enantiopure aminopalladium complex, generally the di-μ-cloro-bis-[(*R*/*S*) - *N*,*N* - dimethyl(α - methylbenzyl)aminato - C^2N]-palladium (II) (**5**) which can be easily prepared from *N*,*N*-dimethyl-1-phenyl-ethylamine, [13] commercially available in both enantiopure forms (Plate 3).

In the present case we utilized a technique, previously successfully experimented for resolution of BIMIP, [14] which combines kinetic resolution and fractional crystallization. If a fourth of a mole of the resolving reagent, prepared from *R*-(+)-*N*,*N*-dimethyl-1-phenyl-ethylamine, is used per mole of racemic (±)-**4**, both a 15% diastereomeric excess in the complexed and a 15% enantiomeric excess in the uncomplexed diphosphine are obtained. Once this unbalanced state is reached, it was easy to obtain the levorotatory antipode (−)-**4** in an enantiopure state by fractional crystallization of the free phosphine from toluene in a 6% isolation yield. Cleavage of the complex with sodium cyanide, purification by chromatography, followed by repeated crystallization of the product from toluene gave enantiopure (+)-**4** in an about 8% overall yield. Repetition of this procedure allowed total resolution of the racemate.

The enantiomeric purity of (+)- and (−)-**4** was checked by chiral HPLC and confirmed by the ^{31}P-NMR spectra of their complexes with enantiopure (*R*)- and (*S*)-**5**, respectively (Fig. 2). These spectra, when compared with those obtained from racemic (±)-**4**, which are very complex probably because some antipodal interactions are active in solution when both diastereoisomers are present, clearly demonstrate that the samples are constituted by only one diastereoisomer.

The investigation of stereoselection ability and catalytic activity of the metal complexes prepared from biheteroaromatic diphosphines was focused on the reac-

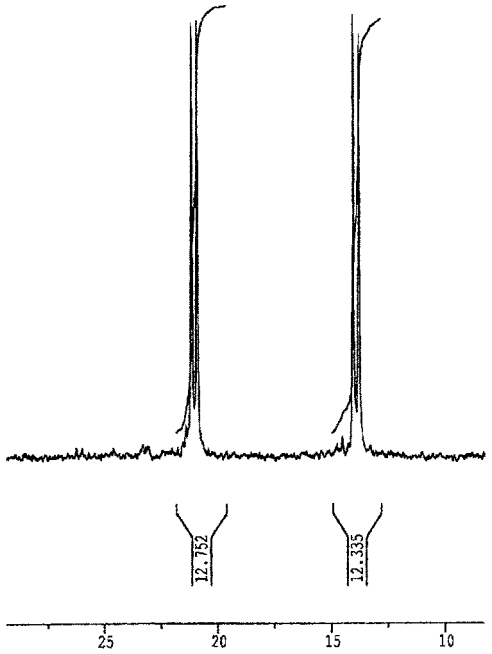


Fig. 2. ^{31}P-NMR spectrum ($CDCl_3$) of the complex of (−)-CyBIMIP and (*R*)-**5**.

tions described in Scheme 1, in particular on the cycloaddition of cyclopentadiene and the *N*-acryloyl- and *N*-[(*E*)-2-butenoyl]-1,3-oxazolidin-2-ones (**1a**) and (**1b**).

The former reaction was found to be rather fast even in the absence of metal complexes. Kinetic ^{1}H-NMR experiments demonstrated that the uncatalyzed reaction follows a first order kinetic in the dienophile, with a rate constant $= 2.6 \times 10^{-4}$ s^{-1} at 25 °C. Thus, the uncatalyzed non stereoselective reaction highly competes with the catalyzed stereoselective process at this temperature, with detrimental effects on final diastereo- and enantiomeric excesses. The uncatalyzed reaction is progressively inhibited by lowering the reaction temperature; it is very slow at −40 °C and nearly completely stopped at −60 °C.

Table 1 reports the diastereo- and enantio-selection data obtained in the reaction of **1a** and cyclopentadiene in the presence of the Pd(II) complexes of different biheteroaromatic diphosphines at −40 and −60 °C. The experiments were carried out in parallel with the analogous complex obtained from BINAP.

The catalysts were prepared from bis(acetonitrile) Pd(II) chloride and the ligand (1% excess) in dichloromethane solution at 25 °C. Removal of the solvent gave a solid complex which was used in a crude state. The chloride- perchlorate anion exchange was performed in situ with silver perchlorate.

The data reported in the table demonstrate that:

1. The uncatalyzed non-stereoselective reaction is still active at −40 °C, since stereoselectivity increases by further lowering the temperature to −60 °C.
2. Electron-rich biheteroaromatic diphosphines give catalysts with a high stereoselection ability, while meager diastereomeric and enantiomeric excesses follow the use of electron-poor ligands.
3. Also from the kinetic point, electron-rich diphosphines give more active catalysts than electron-poor diphosphines, as demonstrated by the observation that the metal complexes prepared from electron-poor BIMIP and CyBIMIP do not drive the reaction to completion, even after prolonged times at −40 °C.
4. Scarce stereoselectivity and poor kinetics are interdependent phenomena. The stereoisomeric excesses are negatively affected by low catalytic activity, since it makes the uncatalyzed non-stereoselective reaction to be competitive with the catalyzed stereoselective process.

The reaction of cyclopentadiene and *N*-(2-butenoyl)-2-oxazolidinone (**1b**) is very slow at room temperature in the absence of efficient promoters. The Pt(II) complexes of electron-rich diphosphines, with hexafluoroan-

Table 1
Reactions of cyclopentadiene and *N*-acryloyl-1,3-oxazolidin-2-one (**1a**) in the presence of Pd(II) complexes (perchlorates) of biheteroaromatic diphosphines and BINAP in dichloromethane

Diphosphine ligand [a]	*E*° (V)	*T* (°C)	Time (h)	Conv. (%)	de (%) [b]	ee (%) [c]	Abs. conf. [d]
(−)-*S*-*N*-Me-2-BINP	0.52	−40	15	100	87	91	*R*
(+)-*S*-tetraMe-BITIOP	0.57	"	15	100	81	90	*R*
(+)-*R*-BINAP	0.63	"	15	100	86	89	*S*
(−)-*S*-BITIANP	0.83	"	15	100	82	72	*R*
(+)-Cy-BIMIP	1.00	"	110	50	85	20	*R*
(−)-*R*-BIMIP	1.15	"	40	60	59	48	*S*
(−)-*S*-*N*-Me-2-BINP	0.52	−60	112	100	92	96	*R*
(+)-*S*-tetraMe-BITIOP	0.57	"	112	100	84	94	*R*
(+)-*R*-BINAP	0.63	"	112	100	90	99.7	*S*

[a] Dienophile **1a**–catalyst molar ratio: 10. Cyclopentadiene–dienophile **1a** molar ratio: 5.
[b] Evaluated by ^{1}H-NMR and HPLC; the *endo* diastereoisomer **2a** prevails on the *exo* diastereoisomer **3a** in all the cases.
[c] Evaluated by chiral HPLC (Chiracel OD; eluant:hexane–*iso*-propanol, 85:15).
[d] Referred to the stereocenter in position 2 of the endo diastereoisomer **2a**.

Table 2
Reactions of cyclopentadiene and *N*-[(*E*)-2-butenoyl]-1,3-oxazolidin-2-one **1b** in the presence of Pt(II) complexes of biheteroaromatic diphosphines and BINAP (hexafluoroantimoniates) in dichloromethane at 0 °C

Diphosphine ligand [a]	*E*° (V)	Time (h)	Conv. (%)	de (%) [b]	ee (%)[c]
(−)-*S*-*N*-Me-2-BINP	0.52	160	45	72	75
(−)-*R*-tetraMe-BITIOP	0.57	160	40	75	58
(+)-*R*-BINAP	0.63	160	40	71	73

[a] Dienophile **1b**–catalyst molar ratio: 5. Cyclopentadiene–dienophile **1b** molar ratio: 10.
[b] Evaluated by HPLC and ^{1}H-NMR spectroscopy; the *endo* diastereoisomer **2b** prevails on the *exo* diastereoisomer **3b** in all the cases.
[c] Evaluated by ^{1}H-NMR spectroscopy with Eu(III)tris[3-heptafluoropropylhidroxymethylene-(+)camphorato] as a shift reagent in $CDCl_3$.

timoniate as anion, were found active catalysts for this reaction. They were prepared according to the methodology described before for the synthesis of the Pt(II) complexes. Table 2 reports the satisfactory diastereo- and enantio-selection data obtained in the reaction of **1b** and cyclopentadiene in the presence of the Pd(II) complexes (hexafluoroantimoniates) of *N*-Me-2-BINP and tetraMe-BITIOP at 25 °C. The analogous complex prepared from BINAP was used as reference catalyst.

3. Conclusions

The data reported in this paper give some useful indications for the choice of the most efficient diphosphine ligands to apply in [4 + 2] cycloaddition reactions: they should possess large electronic availability at phosphorus. The bond between the metal and electron-poor phosphine groups is probably too loose to maintain the dienophyle and the chiral ligand at the correct distance to allow the latter to perform an efficient face selection on the double bond.

This indication is similar to that we had in the hydrogenation of β-oxoesters where we were able to find a quantitative relationship between the rate constant and the electrochemical oxidative potential of the free diphosphine employed to prepare the catalyst [9]. It is opposite, as anticipated, to the requirements of inter- and intramolecular Heck reaction needing electron-poor diphosphines to develop efficient kinetics [10,11].

4. Experimental

Chiral HPLC analyses were performed with a DAICEL CHIRACEL OD column (210 nm). Electrochemical experiments were performed in a three-electrode cell at 25 °C under nitrogen. The working electrode was a platinum microelectrode (0.003 cm^2); the counter electrode was platinum; the reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs. SCE). The voltammetric apparatus (Amel, Italy) included a 551 potentiostat modulated by a 568 programmable function generator. Diphosphine **4** concentration was 10^{-3} M in acetonitrile; scan rate: 50 mV s^{-1}; 0.1 M tetrabutylammonium perchlorate was the supporting electrolyte.

4.1. Reagents

Acetonitrile for voltammetric measurements was distilled twice over phosphorus pentoxide and once over calcium hydride. Tetraethylammonium perchlorate was dried at 70 °C before use. $(MeCN)_2PdCl_2$ is commercially available, while $(EtCN)_2PtCl_2$ was prepared according to the literature [15]. *N*-acriloyl-1,3-oxazolidin-2-one (**1a**) and *N*-[(*E*)-2-butenoyl]-1,3-oxazolidin-2-one (**1b**) were prepared according to literature methods [4]. Cyclopentadiene was freshly prepared by distillation of dicyclopentadiene before the cycloaddition. Methylene dichloride for cycloaddition reactions was distilled over phosphorus pentoxide and degassed with argon. $AgClO_4$ and $AgSbF_6$ were dried under vacuum before use for 1 h. All reactions and manipulations were performed using standard Schlenk techniques.

4.2. (±)-2,2′-Bis(dicyclohexyphosphino)-1,1′-bibenzimidazole (±)-(4)

A 1.6 M buthyllitium solution in hexane (13 ml, 20.8 mm) is dropped into a stirred solution of 1,1′-bibenzimidazole [8b] (2.4 g, 10.3 mm) and *N*,*N*,*N*′,*N*′-tetramethylendiamine (3.2 ml) in dry THF (50 ml) at − 55 °C under nitrogen. Temperature is left to raise 0 °C and maintained during the addition of chloro-dicyclohexylphosphine (5 g, 21.5 mm). The mixture is left to stand for 16 h. Solvent is removed under reduced pressure and the residue treated with water and methylene dichloride to afford (±)-**4** as a solid (3.5 g) which was purified by treatment with warm EtOAc under nitrogen and then crystallized from toluene (20 ml) (3.41 g, yield: 58%); m.p. 291–294 °C. ^{31}P-NMR ($CDCl_3$): − 21,4 (s). ^{1}H-NMR: 0.9–2.6 (44H, m, 4 cyclohexyl); 6.82 (2H, d); 7.2 (2H, t); 7.35 (2H, t); 7.97 (2H, d); MS *m*/*z* 626 (M^+).

4.3. Resolution of (±)-2,2′-bis(dicyclohexyphosphino)-1,1′-bibenzimidazole (±)-(4)

A solution of di-μ-chloro-bis[(*R*)-dimethyl(α-methylbenzyl)aminato-2-C,N]dipalladium (II) (*R*)-(**5**) (0.79 g, 1.4 mmol) in benzene (15 ml) was added to a solution of (±)-(**4**) (3.41 g, 5.4 mmol) in benzene (100 ml). The resulting suspension was filtered and the filtrate kept in the dark for 20 h, then evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column using an EtOAc–methylene dichloride (9:1) mixture as eluant. The first fractions eluted were evaporated to dryness to give enantiomerically enriched (−)-(**4**) (1.27 g, $[\alpha]_D^{23} = -26$, $c = 0.49$, toluene) which was crystallized from toluene (15 ml) to give some racemic (±)-(**4**) (1.09 g). Removal of the solvent from the mother liquors gave a residue (0.062 g) which was crystallized from toluene (6 ml) to give enantiopure (−)-(**4**) (0.046 g, m.p. 320–325 °C (dec.), $[\alpha]_D^{23} = -176$, $c = 0.5$, toluene). The final fractions eluted were evaporated to dryness to give the diastereomerically enriched complex between (+)-(**4**) and (*R*)-**5** (1.66 g). The complex was dissolved in methylene dichloride (45 ml) and a solution of NaCN (7.5 g) in water (45 ml) was added under nitrogen atmosphere. The mixture was stirred for 15 h, then the organic layer was dried and evaporated to dryness under reduced pressure to give a residue which was chromatographed on a silica gel column using an EtOAc–methylene dichloride, 9:1 mixture as eluant. The first fractions eluted were evaporated to dryness to give enantiomerically enriched (+)-(**4**) (0.86 g, $[\alpha]_D^{23} = +42$, $c = 0.5$, toluene) which was crystallized from toluene (15 ml) to give some **4** in a nearly racemic form (0.53 g, $[\alpha]_D^{23} = +1.5$, $c = 0.5$, toluene). Removal of the solvent from the mother liquors gave a residue (0.115 g) which was crystallized twice from toluene (5 and 3 ml) to give enantiopure (+)-(**4**) (0.070 g, $[\alpha]_D^{23} = +182$, $c = 0.5$, toluene).

4.4. Preparation of the palladium(II) and platinum(II) dichlorocomplexes: general procedure

A solution of $(MeCN)_2PdCl_2$ or $(EtCN)_2PtCl_2$ (one equivalent) in methylene dichloride was added to a solution of the diphosphine (1.01 equivalents) in methylene dichloride under argon atmosphere. The mixture was stirred at room temperature (r.t.) for 24 h, then the solvent was removed under reduced pressure to give a dichlorocomplex which was employed in the cycloaddition reaction without any further purification. Chemical shifts of the ^{31}P-NMR ($CDCl_3$) of the complexes are reported below: (BIMIP)$PdCl_2$: $\delta = 13$; (Cy-BIMIP)-$PdCl_2$: $\delta = 33.1$; 29.8; (BITIANP)$PdCl_2$: $\delta = 19.3$; (BINAP)$PdCl_2$: $\delta = 29.8$; (tetraMe-BITIOP)$PdCl_2$: $\delta = 25.7$; (*N*-Me-2-BINP) $PdCl_2$: $\delta = 20.5$; (tetraMe-BITIOP)$PtCl_2$: $\delta = 6.5$ (s + satellite d, $J = 3640$ Hz); (BINAP) $PtCl_2$: $\delta = 10.5$ (s + satellite d, $J = 3660$ Hz).

4.5. Cycloaddition reactions

The cycloaddition reaction of **1a** and cyclopentadiene in the presence of (tetraMe-BITIOP)$Pd(ClO_4)_2$ is described herein as a general procedure.

A solution of (tetraMe-BITIOP)$PdCl_2$ (0.016 g, 0,021 mmol) in methylene dichloride (1 ml) was added to $AgClO_4$ (0.008 g, 0.019 mmol) and the mixture was stirred at r.t. for 1 h. A solution of **1a** (0.029 g, 0.206 mmol) in methylene dichloride (1 ml) was added and the resulting solution was cooled at −40/−60 °C in a cryostat, then cyclopentadiene (85 μl, 1.03 mmol) was introduced. The progress of the reaction was monitored by TLC [eluant: C_6H_{12}–ethyl acetate, 3:2]. Solvent and cyclopentadiene were removed in vacuo and residue was treated with a C_6H_{12}–EtOAc 1:1 solution and the resulting suspension was filtered through a silica gel column. The fractions containing the cycloaddition products were combined and submitted to chiral HPLC analysis, after removal of the solvent.

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