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# Review on asymmetric cycloaddition reactions at phosphorus (III) atom

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**Dedicated to Professor Yulia H. Budnikova in recognition of her scientific contributions to the fields of organic chemistry, electrochemistry and catalysis**

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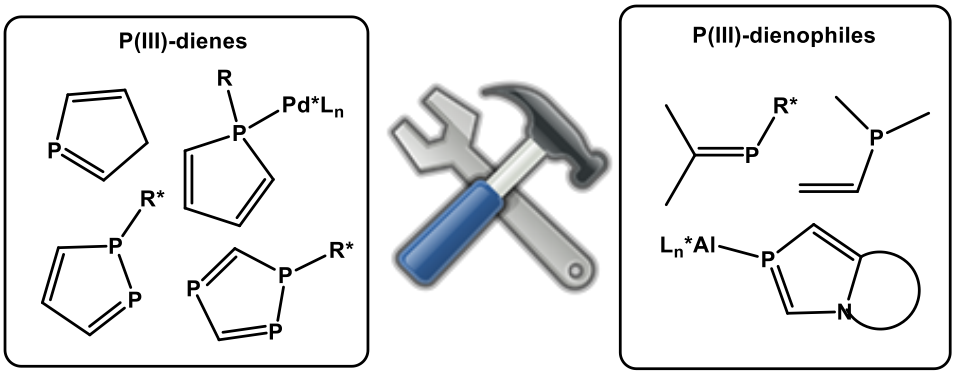
## Abstract

The asymmetric hetero-Diels-Alder reactions are one of the most powerful methods for the construction of optically active mono- and polycyclic heterocycles with extensive synthetic applications. At the present time the phospha-Diels-Alder reactions still received much less attention, despite its potential utility to obtain *P*-chiral cyclic phosphines for use in asymmetric homogeneous catalysis. This review is a comprehensive account of asymmetric cycloaddition reactions including trivalent phosphorus atom in phosphalkenes, phospholes, heterophospholes and other *P*(III) species as prochiral motif. This original synthetic strategy is of interest for the synthesis of polycyclic and caged *P*-chiral phosphines and subsequent ligand design for asymmetric catalysis.

***Asymmetric cycloaddition reactions at P(III)***




**Keywords:** asymmetric cycloaddition reaction, chiral phosphine, *P*-stereogenic phosphine, *P*-chiral, phosphorus heterocycle, asymmetric catalysis.

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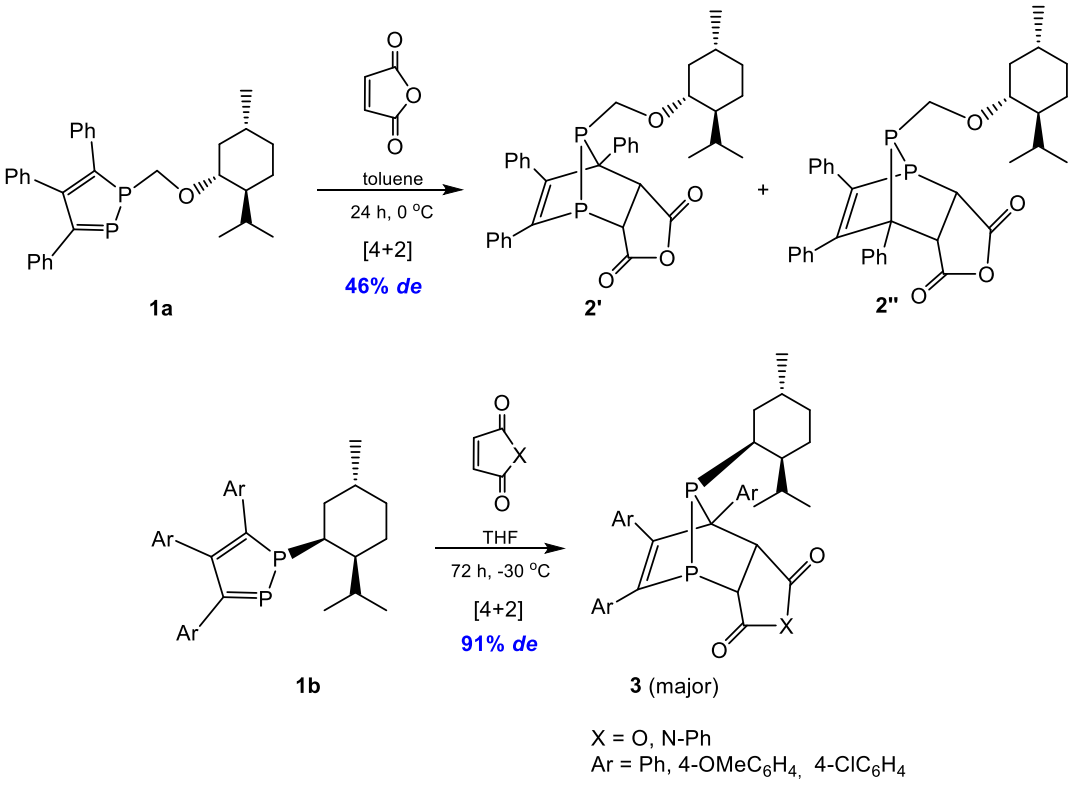
## 1. Introduction

The asymmetric hetero-Diels-Alder reactions are one of the most powerful methods for the construction of optically active six-membered mono- and polycyclic heterocycles, with extensive synthetic applications in natural or unnatural compounds with a wide range of biological activity.[1-3] The simultaneous formation of two carbon-carbon or carbon-heteroatom bonds leads to the creation of up to four stereogenic centers in a single step from achiral dienophiles and dienes, making this one of the most fascinating and elegant methods in asymmetric organic synthesis. At the same time, compared to the asymmetric carbo-, oxa-, and aza-Diels-Alder reactions, the phospha-Diels-Alder version still received much less attention, despite its potential utility to obtain *P*-chiral cyclic phosphines for use in asymmetric homogeneous catalysis[4-6] and as novel drugs.[7-8] In the last decade the scope of this reaction has been extended to phosphorus (III) compounds, in spite of the low availability of a P=C bond compared to a C=C bond.

## 2. Asymmetric Cycloaddition Reactions with Chiral Dienes

The planarity and high reactivity of 1,2-diphospholes[9-10] allow to control the stereoselectivity in cycloaddition reactions using the principle of diastereotopic face differentiation by employing a P=C double bond as prochiral motif. The formation of two diastereomers was clearly observed in the [4+2] cycloaddition reaction of 1-((1*R*,2*S*,5*R*)-menthyl)oxymethyl-1,2-diphosphole (**1a**) as chiral diene with non-chiral maleic anhydride (Scheme 1). During the reaction in the temperature range from –30 °C to +60 °C a small diastereomeric excess of **2`** and **2``** (30-46% *de*) was observed.[11] At the same time, asymmetric Diels-Alder reactions of 1-(+)-neomenthyl-3,4,5-triaryl-1,2-diphosphole (**1b**) with maleic acid derivatives proceeded with higher diastereoselectivity (up to 91% *de*) and results in the corresponding enantiopure 1,7-diphosphanorbornenes **3** after recrystallization.[12-14] An analysis of the structure of 1-(+)-neomenthyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (**1b**) indicated that steric shielding of one side by the bulky isopropyl group causes a preferential approach of the dienophile from the opposite side resulting in one attractive and one repulsive pathway of the [4+2] cycloaddition reaction. This study approves that getting closer of the chiral inductor with the dienic system of 1,2-diphospholes leads to an increase of stereochemical outcome (*de*) of hetero-Diels-Alder reaction.

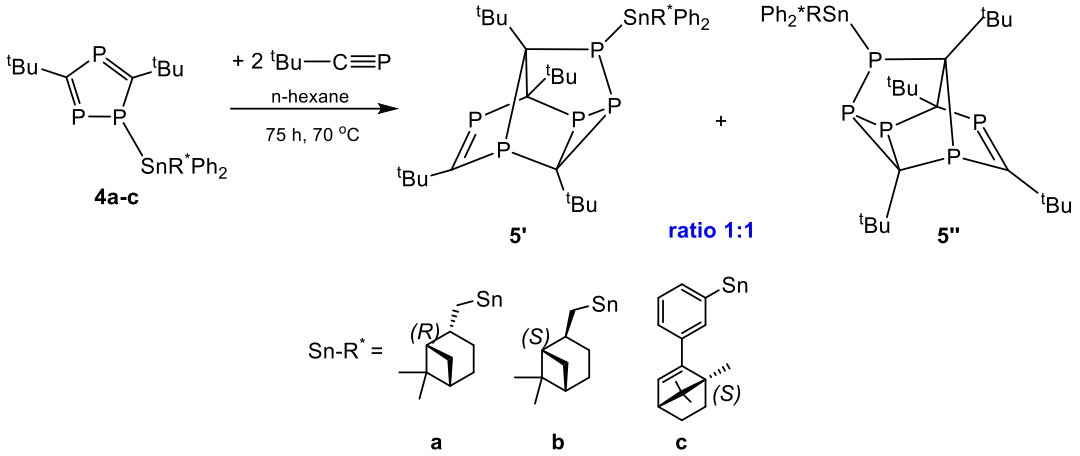



**Scheme 1**. [4+2] Cycloaddition reactions of chiral 1-alkyl-1,2-diphospholes **1** with maleic acid derivatives.

The catalytic activity and induction of enantioselectivity for the prepared enantiopure phosphines **3** with a rigid [2.2.1] phosphabicyclic structure, namely 1,7-diphosphanorbornenes, were evaluated in Pd-catalyzed asymmetric allylic substitution (25% *ee*) and phosphine-catalyzed [3+2] organocatalytic cyclization of allenes with activated alkenes (68% *ee*).[15] Later it was shown that selective oxidation of the bridgehead phosphorus atom in 1,7-diphosphanorbornenes **3** allowed increasing the enantioselectivity of allylic alkylation from 14% to 63% *ee*.[16]

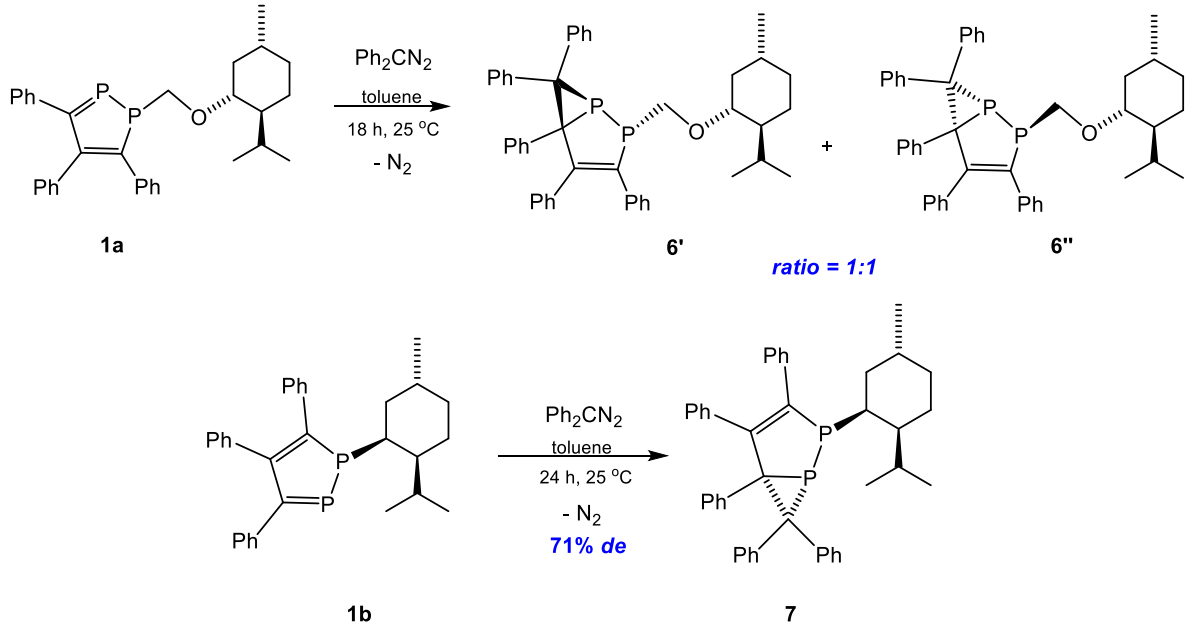
An effective cycloaddition reaction of diastereomeric (R*)diphenyltin-3,5-di(*tert*-butyl)-1,2,4-triphosphole derivatives **4a-c** (R* = (-)-*cis*-myrtanyl (**4a**), (-)-*trans*-myrtanyl (**4b**), *m*-(2-bornyl-2-ene)phenyl (**4c**)) with two equivalents of *tert*-butylphosphaalkyne led to 1:1 mixtures of diastereomeric stannylated pentaphosphadeltacyclene derivatives **5`** and **5``** with seven stereogenic centers in the cage unit (Scheme 2). The (-)-*cis*-myrtanyl derivative **5a** was separated into its diastereomers, and destannylation of diastereisomer led to the P-H cage compounds as a pure enantiomer.[17]




**Scheme 2**. Cycloaddition reaction of chiral 1,2,4-triphospholes **4a-c** with *tert*-butylphosphaalkyne.

The asymmetric version of 1,3-dipolar cycloaddition reactions is one of the most powerful tools for the construction of enantiomerically pure heterocycles for agrochemistry and drug discovery.[18-19] Up to 4 stereocenters can be created in a stereoselective manner in one single step. Diastereoselective 1,3-dipolar cycloaddition reaction of 1-alkyl-1,2-diphospholes **1** with a chiral substituent at *P*-atom with diphenyldiazomethane was used as a new way for selective synthesis of *P*-chiral bicyclic phosphiranes. The formation of two diastereomers in 1:1 ratio was observed in the 1,3-dipolar cycloaddition of 1-((1*R*,2*S*,5*R*)-menthyl)oxymethyl-1,2-diphosphole (**1a**) with diphenyldiazomethane, while the reaction between 1-(+)-neomenthyl-1,2-diphosphole (**1b**) and diphenyldiazomethane proceeded with better 71% *de* (Scheme 3). Enantiopure 2-(+)-neomenthyl-3,4,5,6,6-pentaphenyl-1,2-diphosphabicyclo[3.1.0]hex-3-ene (**7**) was obtained by crystallization.[20]



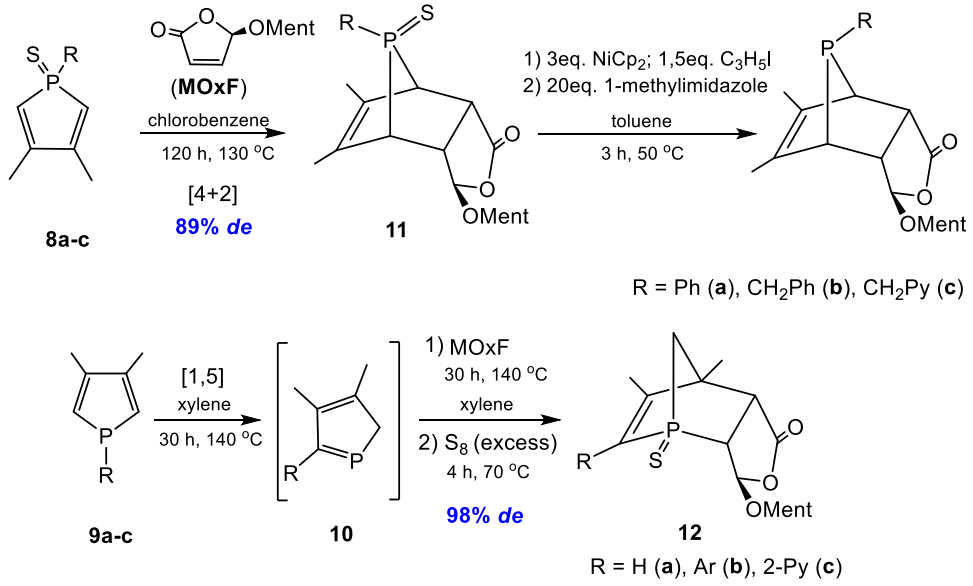

**Scheme 3**. Reaction of chiral 3,4,5-triphenyl-1-alkyl-1,2-diphospholes **1** with diphenyldiazomethane.

This study proved that the closest combination of a chiral auxiliary with the >C=P– group of 1,2-diphospholes facilities stereoselective 1,3-dipolar cycloaddition reactions, which is important for further developments of asymmetric cycloaddition reactions for synthesis of chiral *P*-stereogenic phosphines.

## 3. Asymmetric Cycloaddition Reactions with Chiral Dienophiles

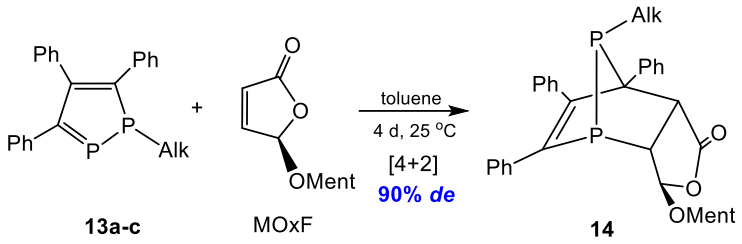
The principle of stereotopic face differentiation was successfully applied to P=C bond of 1-mono- and 1,2-diphospholes and became a powerful synthetic tool for highly selective and efficient synthesis of *P*-chiral phosphines from readily available starting materials. An efficient and highly stereoselective asymmetric Diels–Alder reactions of 1*H*- **8**, **9** and 2*H*-monophospholes **10** with the chiral dienophile (5*R*)-(*l*-menthyloxy)-(5*H*)-furanone (MOxF) allowed to generate multiple stereogenic centers resulting in *P*-chiral 7-phosphanorbornenes[21] **11** and 1-phosphanorbornenes **12** (Scheme 4).[22] The observed reaction pathway has been supported by theoretical calculations showing that the cycloaddition reaction between 2*H*-phosphole **10** and MOxF is of normal electron demand.[23] The [4+2] cycloaddition products were converted to their air stable sulfur derivatives, which were isolated and the *endo*- and *exo*-isomers were separated by column chromatography. The phosphorus atom in the obtained cycloadducts **11** and **12** was easily desulfurized to give the corresponding *P*(III)-species, which were further functionalized and yielded different bidentate phosphines.




**Scheme 4**. Asymmetric Diels–Alder reactions of 1*H*- and 2*H*-phospholes **8**-**10** with the (5*R*)-(*l*-menthyloxy)-(5*H*)-furanone (MOxF).

An asymmetric [4+2] cycloaddition reaction with chiral dienophile was also successfully applied to 3,4,5-triphenyl-1-alkyl-1,2-diphospholes **13** which then involved into the highly stereoselective Diels–Alder reaction with MOxF giving *P*-chiral *anti-endo*-1,7-diphosphanorbornenes **14** with 80-90% *de* (Scheme 5).




**13a-c** MOxF **14**

Alk = i-Pr (**a**), Pr (**b**), i-Bu (**c**)

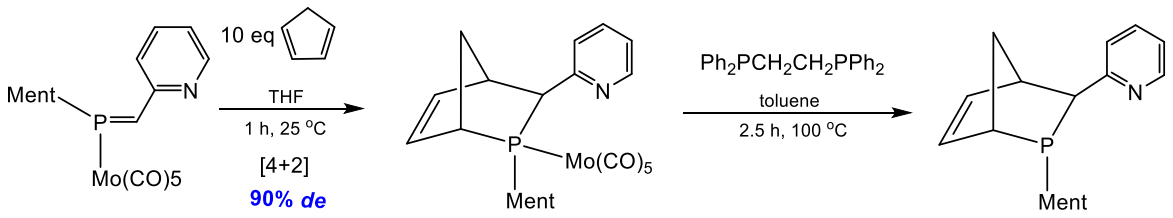
**Scheme 5**. Asymmetric [4+2] reaction of 1-alkyl-1,2-diphospholes **13** with MOxF.

In both cases the observed selectivity was explained by the transition state showing one attractive and three repulsive interactions. Firstly, the attractive *endo* orientation of the transition state in [4+2] cycloaddition reactions is well known due to secondary orbital interactions of the HOMO (diene) and LUMO (dienophile).[24-25] Secondly, the sterically shielding *l*-menthyloxy group (OMent) of MOxF protects one side of the molecule from being attacked by 1-mono- and 1,2-diphospholes, and a *Re*-face addition of the dienophile is expected for the cycloaddition reaction.[26] The above-mentioned interactions cause very good diastereoselectivity in a single concerted step and yield mainly one polycyclic rigid structure out of eight possible stereoisomers.

The use of **14** as ligand in the Pd-catalyzed asymmetric allylic alkylation of cinnamyl acetate with cyclic ethyl 2-oxocyclohexane-1-carboxylate and ethyl 2-oxocyclopentane-1-carboxylate provided up to 52% and 47% *ee*, respectively.[27]

## 4. Metal-mediated Asymmetric Cycloaddition Reactions

Cycloaddition reaction of prochiral phosphaalkene complex **15** was used in the synthesis of optically active phosphines. A two-step procedure was devised for the conversion of $[MentPH_2]Mo(CO)_5$ (where Ment = (1*R*,2*S*,5*R*)-menthyl) into optically pure 2-menthyl-2-phospha-5-norbornene **16**. The phosphaalkene complex 2-PyCH=P(Ment*)$Mo(CO)_5$ **15** reacted with cyclopentadiene to give **16** with 90% *de*. The decomplexation of the resulting molybdenum complex **16** was carried out by heating with diphosphorus chelating ligand and led to **17** (Scheme 6).[28]



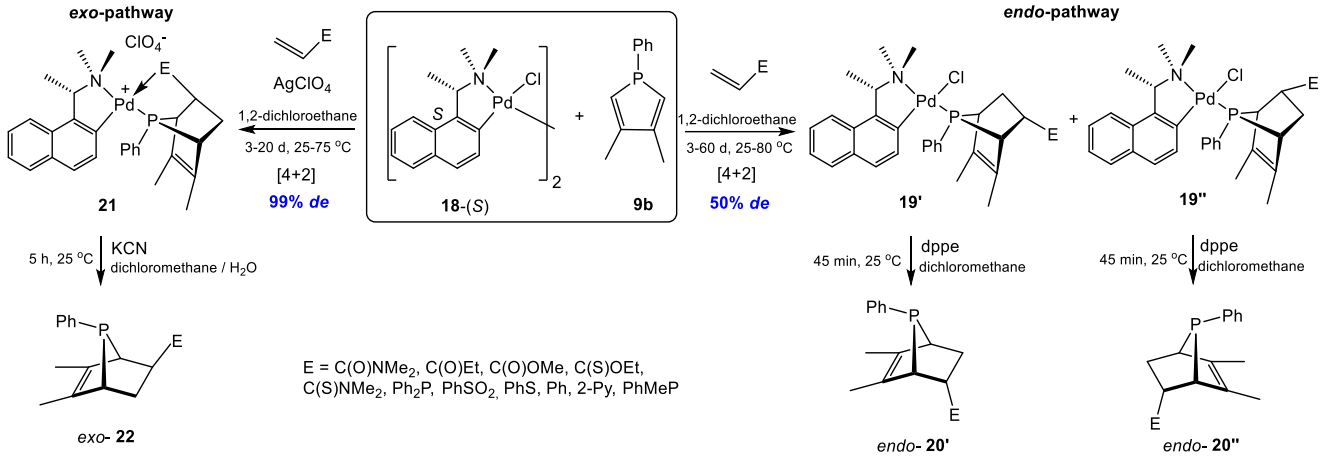

**15** **16** **17**

**Scheme 6**. Use of prochiral phosphaalkene complex **15** in the synthesis of optically active phosphine **17**.

The Diels–Alder reaction of phospholes with various dienophiles in the coordination sphere of chiral Pd-complexes was proposed as a method for the synthesis of chiral phosphines.[29] The chiral (*S*)-*ortho*-(1-dimethylaminoethyl)-naphthalene palladium (**18**) was complexed with 3,4-dimethyl-1-phenylphosphole (**9b**), and then involved into the Diels–Alder reaction with various dienophiles (*N*,*N*-dimethylacrylamide,

diphenylvinylphospine, styrene, and others) to result in diastereoisomers of *endo*-amidophosphanorbornene complexes **19**. It should be noted that [4+2] cycloaddition reactions of 1*H*-monophospholes **9** in the coordination sphere of Pd-complexes **18** proceeds under milder conditions (25-80 °C) compared to uncoordinated 1*H*-monophospholes (140-150 °C). The stereoselectivity of the reaction was moderate (up to 50% *de*), but diastereoisomers were easily separated by chromatography or recrystallization to yield a library of enantiopure bicyclic cage phosphines **20** with 40-85% yields after decomplexation with KCN (Scheme 7, right).

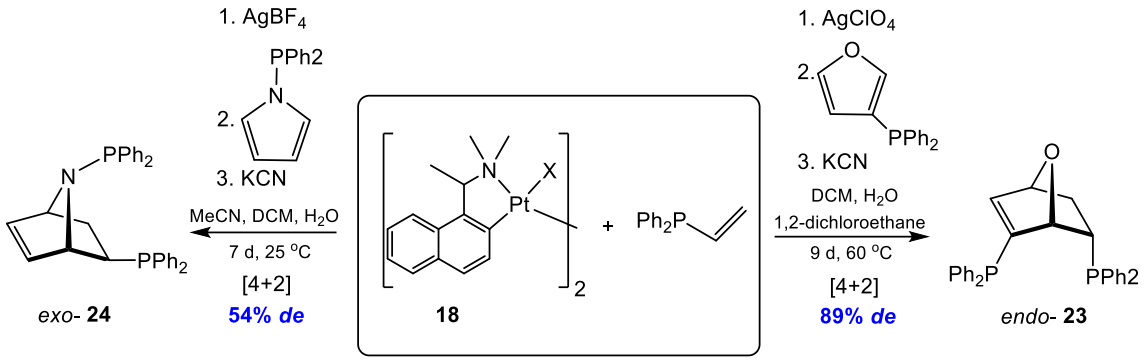



**Scheme 7**. Asymmetric [4+2] cycloaddition reaction on (*S*)-*ortho*-(-(1-dimethylaminoethyl)-naphthalene palladium template **18**.

It was shown that the stereochemical course of the [4+2] cycloaddition depends on the presence of silver perchlorate or tetrafluoroborate in the reaction medium.[30] Therefore, it is possible to select either the *exo*- or the *endo*-cycloaddition reaction pathways by controlling the number of coordination sites on the *ortho*-Pd naphthylamine template **18**. In the *endo*-cycloaddition pathway, the kinetically stable chloro-ligand is coordinated to the neutral template, but in the *exo*-cycloaddition pathway, the kinetically labile perchlorato ligand forms a cationic intermediate, which coordinates simultaneously onto the chiral template during the course of cycloaddition reaction. Therefore, the reaction of **18** with 3,4-dimethyl-1-phenylphosphole (**9b**) in the presence of $AgClO_4$ led to the formation of only one enantiopure cycloaddition products **21** and phosphines *exo*-**22** with 99% *de* (Scheme 7, left).[31]

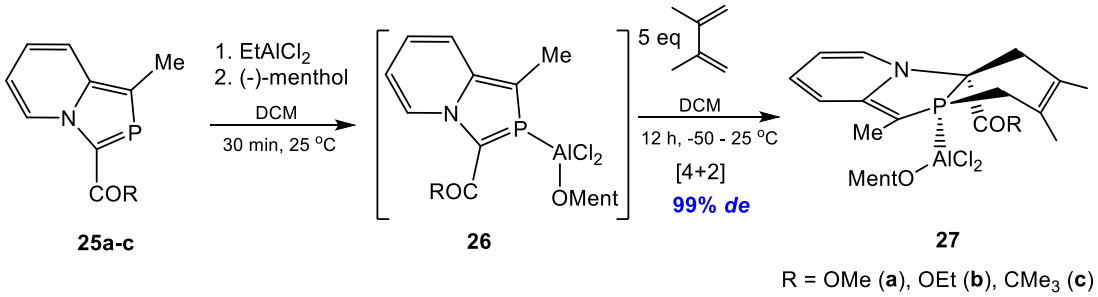
Using the same methodology the asymmetric Diels–Alder reaction between diphenylvinylphosphine and *N*-diphenylphosphinopyrrole or 3-diphenylphosphinofurane on the Pt-(1-dimethylaminoethyl)-naphthalene or Pt-(*R*)-(1-dimethylaminoethyl)-naphthalene template **18** resulted in the formation of dicyclic diphosphines **23**, **24** with 54-89% *de*, which were obtained as enantiomerically pure crystalline compounds in good yields (Scheme 8).[32-33]




**Scheme 8**. The asymmetric Diels–Alder reactions between diphenylvinylphosphine and *N*-diphenylphosphinopyrrole or 3-diphenylphosphinofuran.

The >C=P– functionality in 2-phosphaindolizines **25** was activated by coordinating the phosphorus atom to the Al(OMent)$Cl_2$ moiety when it reacts with 2,3-dimethylbutadiene with complete diastereoselectivity (Scheme 9). Computational calculations of the model [4+2] cycloaddition reactions of (3-methoxycarbonyl-1-methyl-2-phosphaindolizine-η$^1$-*P*)-Al(OMent)$Cl_2$ (**26a**) with 1,3-butadiene revealed that the *Re*-face is sterically hindered, and consequently, attack of the diene occurs preferentially from the *Si*-face.[34]




**Scheme 9**. Diels–Alder reaction of 2-phosphaindolizine-η$^1$-*P*-aluminium(O-menthoxy) dichlorides **26** with 2,3-dimethylbutadiene.

## Conclusions

The principle of diastereotopic face differentiation by employing a P=C double bond of phosphalkenes, phospholes, heterophospholes and other *P*(III) species as prochiral motif in [4+2] cycloaddition reactions was successfully used in the synthesis of *P*-chiral polycyclic phosphines. Although first results reveal moderate yield and enantioselectivity in asymmetric catalysis, the original synthetic strategy for these new enantiopure *P*-chiral ligands are of interest for the synthesis of polycyclic and caged chiral phosphines and subsequent ligand design for asymmetric catalysis. Related 1-phosphanorbornenes have shown excellent results in asymmetric transition metal catalysis and organocatalysis (*ee* values are of 90-99%).[35-40] The use of such rigid polycyclic phosphines provides fixed *P*-chirality by a non-racemizable chiral phosphorus center, whose geometry precludes any loss of enantiomeric purity during catalysis or the associated recycling processes.[41-43]

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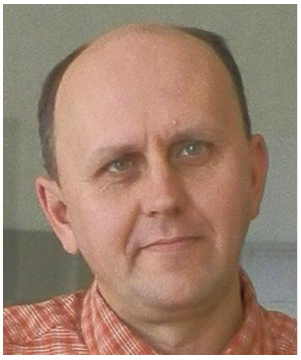

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