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Communication

Metal effects on the asymmetric syntheses of chiral P–N bidentate ligands

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ABSTRACT

The organoplatinum complex containing ortho-metalated (*S*)-[1-(dimethylamino)ethyl]naphthalene as the chiral auxiliary has been used to promote the asymmetric cycloaddition reactions between 3,4-dimethyl-1-phenyl phosphole and (*E*)-1-phenyl-3-pyridin-2-yl-2-propenone or (*E*)-1-methyl-3-pyridin-2- yl-2-propenoate in high selectivity under mild condition. However, the corresponding palladium complex didn't show similar reactivity. This Diels–Alder reaction generated five new stereogenic centers in a single step. The naphthylamine auxiliary could be removed chemoselectively from the template products by treatment with concentrated hydrochloric acid to form the corresponding dichloro platinum complexes [(P–N)$PtCl_2$]. The molecular structure and absolute configuration of the major dichloro platinum complex have been resolved by single-crystal X-ray diffraction. Finally, the enantiomerically pure P–N ligands can be readily liberated from the corresponding dichloro platinum complexes as air-sensitive solids by treatment with aqueous potassium cyanide in quantitative yield.

1. Introduction

Optically active P–N bidentate ligands, which possess a combination of soft π–acceptor phosphorus and hard σ–donor nitrogen, have long been considered as very useful compounds for metal-based homogeneous asymmetric catalysis reactions [1–8]. For example, Zhang et al. have used the newly designed chiral P–N bidentate ligands (Mor-DalPhos) and gold(I) complexes to prepare a series of 2,4-disubstituted oxazoles *via* [3 + 2] annulations between readily available terminal alkynes and aromatic/alkenic carboxamides under mild conditions [9]. Quite recently these P–N bidentate ligands have also been successfully applied in the enantioselective intramolecular cyclopropanation [10].

There are two main methods to prepare the chiral P–N bidentate ligands. The classical resolution is converting the racemic mixtures into a pair of diastereomers by reaction with an optically pure reagent. The original racemic mixture cannot be separated directly, but the diastereomers could be separated by chromatography or fractional crystallization since the physical properties of the diastereomers are different. When monodentates or other resolving agents are involved, however, the resolution process could become rather tedious and inefficient. Furthermore, separation of diastereomers is a prerequisite when the target ligand contains more than one stereogenic centre. Another method is asymmetric synthesis. For instance Noyori and co-workers reported the synthesis of MAP-type P–N heterobidentate ligand from the chiral starting material (*R*)-binol in 7 steps [11]. Subsequently Hiemstra and Maarseveen et al. have prepared the similar binol-derived MAP-type P–N bidentate ligand *via* the Staudinger reaction in 4 steps [12]. However the total yield of the above-mentioned reactions is relatively low.

Our group has previously used the chiral ortho-metalated-amine palladium complexes to prepare a series of functionalized chiral phosphines such as P–P, P–As, P–N bidentate ligands *via* asymmetric hydrophosphination and hydroamination [13–18]. For example the organopalladium complex containing ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reactions of diphenylphosphine with (*E*)-1-phenyl-

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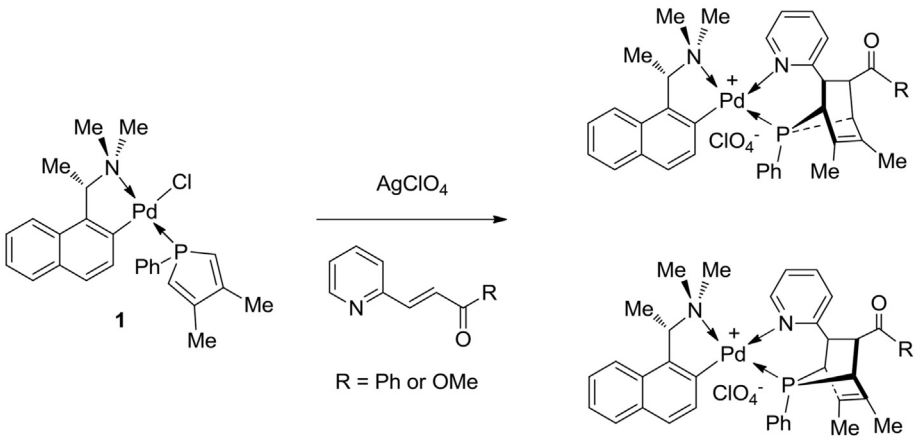


Scheme 1. Asymmetric Diels-Alder reaction promoted by chiral palladium template.

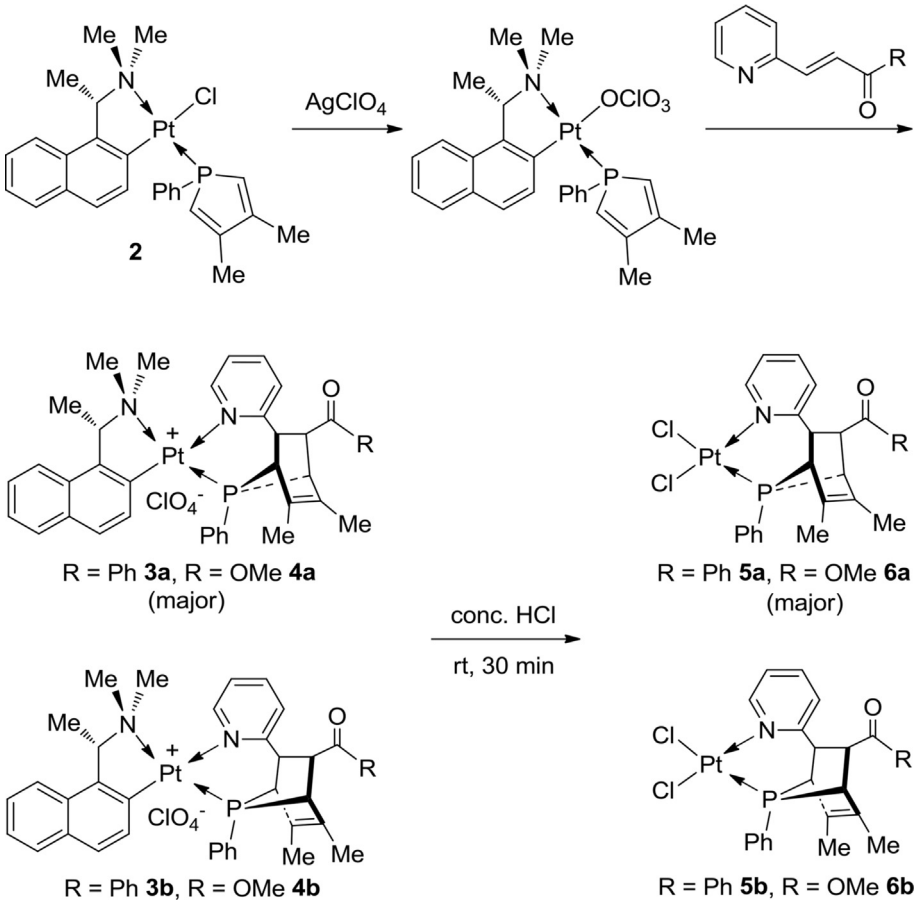
3-pyridin-2-yl-2-propenone/(*E*)-1-methyl-3-pyridin-2-yl-2-propenoate in high selectivity under mild conditions [19].

The asymmetric Diels–Alder reaction is one of the well-known reactions with high efficiency for the construction of chiral six-membered ring [20–22]. The ability of this reaction inwhich the formation of two carbon–carbon bonds lead to the creation of up to four chiral centres in a single step from the achiral dienes and dienophiles makes it one of the most elegant methods in asymmetric organic synthesis. Herein we reported the syntheses of two new novel chiral P–N bidentate ligands *via* the asymmetric Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole and (*E*)-1-phenyl-3-pyridin-2-yl-2-propenone/(*E*)-1-methyl-3-pyridin-2-yl-2-propenoate and found that the metal ion has a considerable effect on the reactivity and selectivity.

2. Results and discussion

2.1. Asymmetric cycloaddition reactions between DMPP and (E)-1-phenyl-3- pyridin-2-yl-2-propenone/(E)-1-methyl-3-pyridin-2-yl-2-propenoate promoted by chiral metal template

In the absence of a metal ion, no reaction was observed between



Scheme 2. Asymmetric Diels-Alder reaction promoted by chiral platinum template.