

# Organic Compounds Incorporating Low-Coordinate Phosphorus-Carbon Double Bonds : Synthesis, Transition Metal Complexes, and Catalytic Application

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## 論 文 内 容 要 旨

### Introduction

The coordination chemistry of low-coordinate phosphorus compounds is of particular interest because of their unique electronic properties. The coordinative behaviour of these compounds differs markedly from common tertiary phosphines and from diimine ligands, despite the presence of structural similarities. An illustrative example of  $sp^2$  hybridized phosphorus compounds are the 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutenes, abbreviated as DPCB. In addition to possessing a lone pair of electrons on each phosphorus which can act as a  $\pi$ -donor, they also possess low-lying  $\pi^*$  orbitals which are strong  $\pi$ -acceptors towards transition metals. Furthermore, extended conjugation allows for a considerable degree of tunability, that is to say, the electronic

characteristics of functional groups distant from the active site can have a considerable influence on the chemistry of the metal center. These properties lead to unique coordination properties and have been applied to the development of unusual complexes and new catalytic systems.

#### Chapter 1. An Efficient Preparation of 3,4-Diphosphinidenecyclobutenes

Until recently, the preparation of DPCB analogues was conducted using one of two related synthetic protocols. Although both have proven useful, both require the use of moisture sensitive intermediates, are operationally tedious, and generate large amounts of chemical waste. A new synthetic method found by lithiation of TMS ether **B** followed by treatment with an appropriate quantity of dibromoethane could lead to condensation and cyclization leading to DPCB as the major product. (Schemes 1, 2) This protocol is efficient, operationally simple, and provides DPCB compounds in good overall yields.

#### Chapter 2. Synthesis and Catalytic Properties of Cationic Rhodium(I) and Palladium(II) Complexes Bearing Diphosphinidenecyclobutene Ligands

The unique electronic structure of low-coordinate phosphorus compounds has led to considerable interest in their coordination chemistry. In efforts to further explore the coordination behavior of these ligands and the reactivity of the resulting complexes, a series of cationic rhodium(I) and dicationic palladium(II) complexes bearing DPCB ligands was prepared and evaluated. (Figure 1) The respective complexes were prepared via ligand exchange. (Schemes 3-5) The catalytic activity of the complexes was evaluated in the hydroamidation of  $\alpha,\beta$ -unsaturated ketones, a synthetically useful reaction that is known to be acid catalyzed. (Scheme 6) The catalytic performance of **1a** was examined for a variety of structurally diverse enones.

#### Chapter 3. Application of Diphosphinidenecyclobutene Ligands towards Palladium Catalyzed Cross coupling Reactions: Cross coupling of Aryl Bromides with Organostannanes and Cyanation of Aryl Bromides

Transition metal catalyzed Stille cross-coupling reactions are a well-established method for the formation of C-C bonds between  $sp^2$  hybridized carbons. The effectiveness of DPCB complexes in this reaction well demonstrates the unique electronic properties of phosphathenes. After optimization of reaction conditions, it was found that favorable results were obtained by the reaction of 4-bromoanisole with 1.1 equivalents of tributyl(vinyl)tin in the presence of 2 equivalents of CsF and 2 mol% of DPCB/Pd(OAc)<sub>2</sub> in 2 mL of dioxane at 100°C. (Scheme 7) A variety of aryl bromide and tin substrates gave the corresponding coupling product in good to excellent yields.

Benzonitriles are frequently encountered in organic chemistry, appearing in a variety of useful compounds. Furthermore, the cyano group provides a useful synthetic intermediate, being easily transformed into other functionalities. In addition to other synthetic methods, palladium-catalyzed cyanation has been investigated as a route to aromatic nitriles. The catalyst system was evaluated against a broad range of substrates exhibiting a wide functional-group tolerance. (Scheme 8) The excellent conversion of 1-bromo-4-nitrobenzene was particularly gratifying. In comparison, identical reaction conditions employing PPh<sub>3</sub> or dppf as ligand as opposed to DPCB provided 45% and 46% conversion of the nitro-arene, respectively. The high reactivity of sterically congested 2,4,6-trimethylphenyl bromide was a pleasant surprise, giving the cyanation product in 83% yield.

#### Chapter 4. Solid-supported Diphosphinidene-cyclobutene as a Solid-phase Catalyst: Direct Allylation of Aniline with Allyl Alcohol

The immobilization of homogeneous catalysts has been demonstrated to be an effective approach towards the construction of useful catalytic systems. Immobilized catalyst and reagent systems can offer several key advantages, one being the relative ease of separation of the immobilized component from the reaction mixture. In addition to affecting procedural aspects of a reaction, the polymer matrix can form a unique microenvironment with respect to the reactants having pronounced influence on the course of the reaction.

Immobilized ligand was constructed from PS-PEG-Br (TentaGel S-Br, 0.25 mmol Br/g, Rapp Polymere GmbH) via an ether linkage by first swelling the solid support in dimethylformamide, then adding hydroxylated DPCB and an excess of potassium carbonate. The suspension was mechanically shaken at ambient temperature for 48 hours, then shaken at 50 °C for an additional 48 hours. (Figure 2) A  $\pi$ -allyl palladium complex of the supported ligand was prepared by swelling the resin in dichloromethane followed by treatment with  $[\text{Pd}(\pi\text{-allyl})(\mu\text{-Cl})_2]$ . Subsequent treatment with silver triflate followed by repeated washes with dichloromethane provided the immobilized catalyst. (Figure 3)

Direct allylation of aniline was chosen as a test case for the immobilized ligand. (Scheme 9) It has been previously reported that a catalyst system utilizing a  $(\pi\text{-allyl})\text{Pd}$  complex of methoxy DPCB facilitated direct elaboration of aniline with allyl alcohols. In the present study, the resin was found to catalyze the allylation of aniline at room temperature in toluene with a 0.1 mmol% catalyst load. Yields calculated from aniline were typically around 64% with the remaining material being comprised of roughly equal quantities of starting material and diallylated aniline. Reactions were complete within 3 hours and the resin remained active for about 5 runs before showing signs of lost activity.

#### Chapter 5. Novel Ferrocene Derived Phosphaethene Compounds: Synthesis, Complexes, and Catalysis

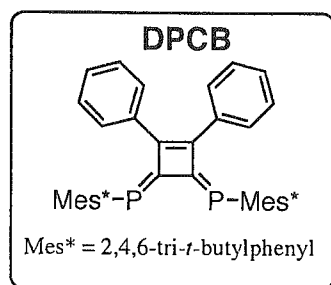
The use of ferrocenyl phosphine ligands in coordination chemistry has been well studied and applications towards catalysis are numerous. With the aim of discovering a ligand suitable for catalytic applications, a number of ferrocene-derived phosphaethenes were prepared. The first was compound **2**, a 1,1'-disubstituted compound structurally related to dppf and was prepared from the corresponding bis-aldehyde by means of a phospha-Peterson reaction. In hopes to prepare a chiral ligand, the chemistry of (dimethylaminomethyl)ferrocene was explored. It has been well established that *N,N*-dimethyl-1-ferrocenylethylamine can be ortholithated and functionalized in an enantioselective manner. Due to the high cost of the chiral amine, exploratory reactions were performed with the readily available achiral analogue. Ortholithiation followed by formylation proved to be straightforward as well as elaboration of the resulting aldehyde via phospha-Peterson reaction to give the desired phosphaethene **3**. Attention was then turned towards a mixed donor ferrocene derivative which contains both an  $\text{sp}^2$  and an  $\text{sp}^3$  hybridized phosphorus. Compound **4** was prepared from a known aldehyde via phospha-Peterson reaction in good yield.

A variety of transition metal complexes were prepared and characterized, several of which are shown here. Complex **5**, a dichloro platinum complex, was prepared by ligand exchange with an appropriate substrate. Dinuclear rhodium complex **6** was also prepared. A dimethyl platinum complex, **7**, was prepared from the requisite precursors to give a highly crystalline red solid. The dicationic mixed donor complex **8** was prepared via ligand exchange to give the desired complex as a purple amorphous solid.

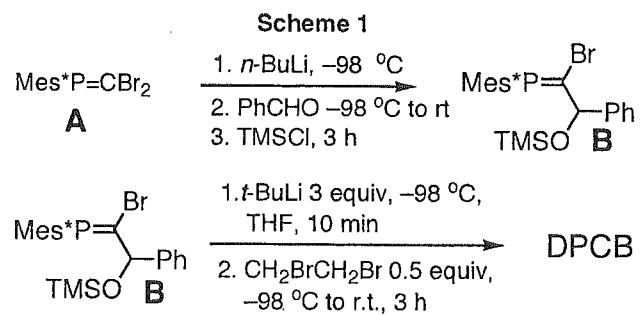
The dicationic palladium complex was evaluated for catalytic activity in the hydroamidation of cyclohexenone with benzyl carbamate. (Scheme 6) The complex was found to be active at 1 mol% giving complete conversion as

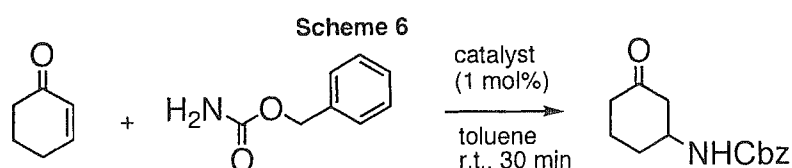
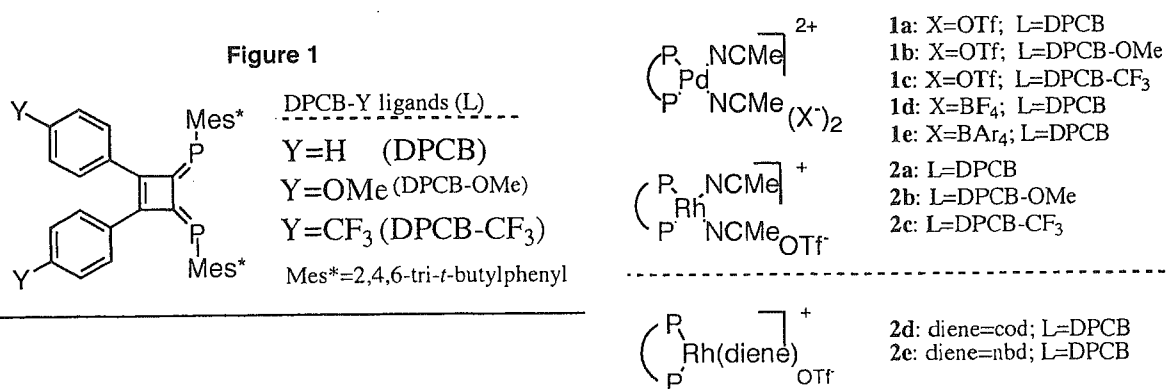
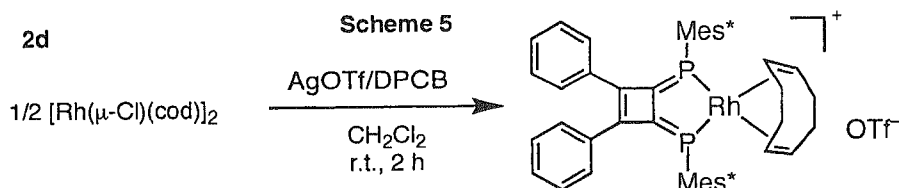
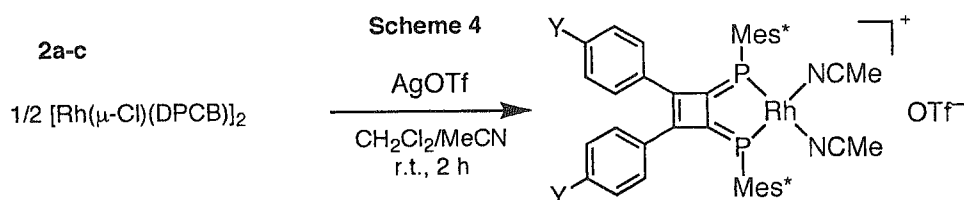
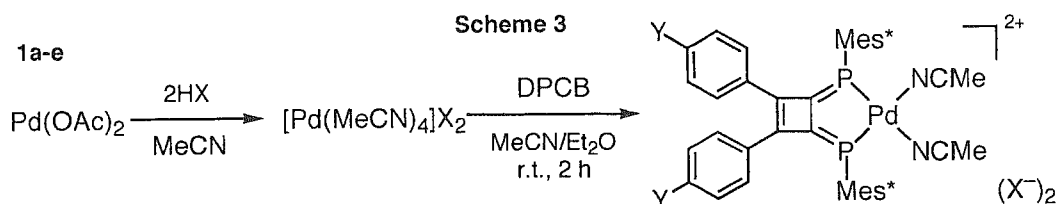
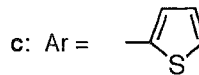
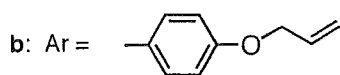
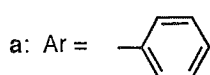
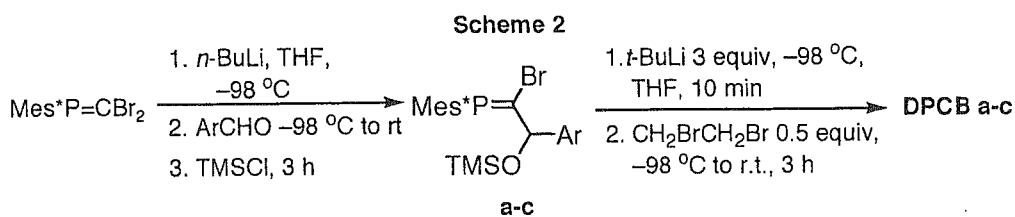
determined by both GC and HNMR in 2 hours. Modest enantioselectivity was observed with the target molecule being produced in 64% isolated yield and 20% enantiomeric excess. A  $\pi$ -allyl palladium complex **9** was also prepared and evaluated in the catalytic hydroamination of dienes and the direct allylation of aniline. The hydroamination reaction was found to proceed in 20% ee.

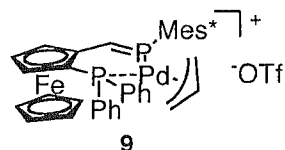
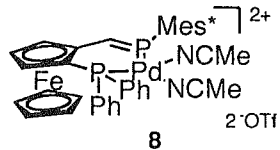
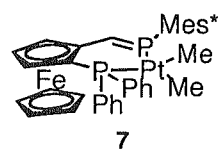
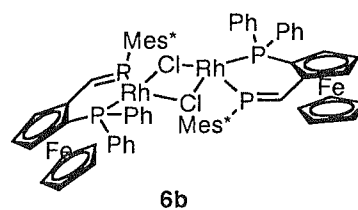
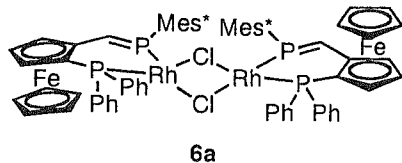
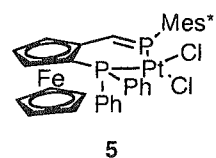
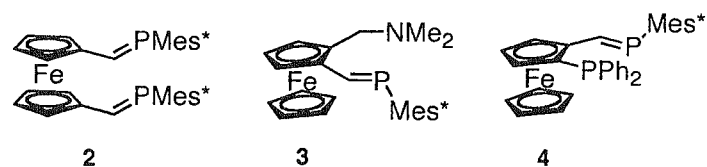
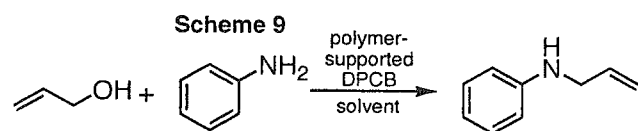
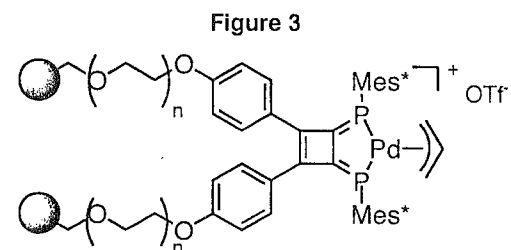
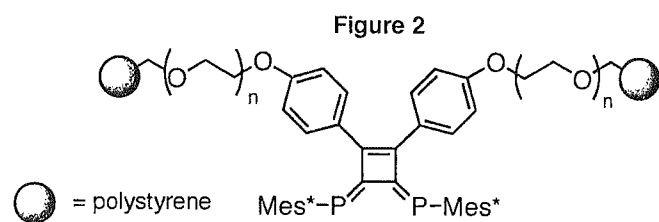
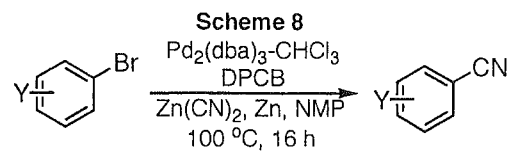
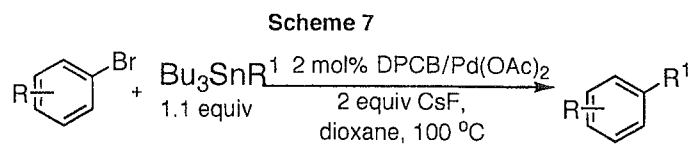
diagrams



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## 論文審査の結果の要旨

本論文は、 $sp^2$  混成型リン原子を有する特異な構造の配位子である、3,4-ジホスフィニデンシクロブテン（以下、DPCBと略す）配位子およびその各種遷移金属錯体の合成および性質に関する研究成果をまとめたものである。 $sp^2$  混成型リン原子を有する化合物（低配位リン化合物）は、通常不安定な化学種であるが、かさ高い置換基を用いることにより安定化される。このため、通常の $sp^3$  混成型リン原子を有する配位子と較べると応用面での研究は限られていた。このような背景からRader Scott Jensen は、DPCB配位子の基礎的・応用的な研究を含めた総合的な研究を行った。

まず、新規な合成法により、1,2-ビス[(4-アシルオキシ)フェニル]DPCB誘導体などを効率的に合成した。代表的なDPCB誘導体についてはパラジウムあるいはロジウム錯体へと誘導し、X線結晶構造解析等により、構造に関する知見を得た。

さらに、DPCB錯体を用いる幾つかの触媒反応について検討した。即ち、まずMichael付加型のヒドロアミド化反応への応用について検討した。さらに、Stilleクロスカップリングや芳香族シアノ化反応についても検討した。これらの反応においてはDPCB触媒は有効に働いていることがわかった。これはリン・炭素二重結合の $\pi$ -受容性が大きいためであると考えられ、従来型にはない特色を有する配位子および錯体触媒であることがわかった。また、ポリマー担持DPCB( $\pi$ -アシルパラジウム)錯体触媒を合成し、この固定化触媒がアニリンのアリル化反応に有効であり、また繰り返し利用することができることも証明した。

続いて、面不斉を有する新規ホスファエテン型配位子についても検討した。即ち、幾つかの不斉フェロセニルホスファエテンを合成しその錯体が、Michael付加型のヒドロアミド化反応において不斉触媒として機能することを証明した。

これらの成果は、著者が自立して研究を行うに必要な高度の研究能力と学識を有することを示している。したがって、Rader Scott Jensen 提出の博士論文は博士（理学）の学位論文として合格と認める。