



## Construction of optically active multimetallic systems of rhodium(I), palladium(II), and ruthenium(II) with a P-chiral tetraphosphine ligand

Keiji Yashio, Masatoshi Kawahata, Hiroshi Danjo\*, Kentaro Yamaguchi\*, Masaharu Nakamura, Tsuneo Imamoto

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan  
International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan  
Department of Chemistry, Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

### ARTICLE INFO

#### Article history:

Received 5 September 2008  
Received in revised form 2 October 2008  
Accepted 7 October 2008  
Available online 17 October 2008

#### Keywords:

P-chiral phosphines  
Tetraphosphines  
Bimetallic complexes  
Heterometallic complexes

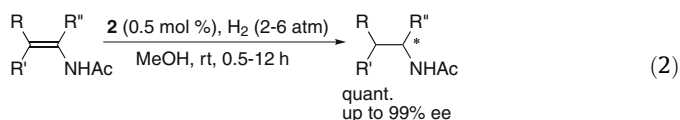
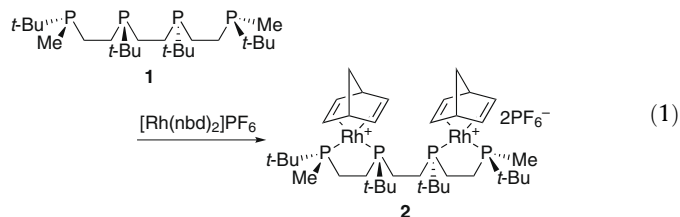
### ABSTRACT

The treatment of optically P-chiral tetraphosphine, (3*S*,6*R*,9*R*,12*S*)-6,9-di-*tert*-butyl-2,2,3,12,13,13-hexamethyl-3,6,9,12-tetraphosphatetradecane (**1**), with rhodium(I), palladium(II), and ruthenium(II) complex precursors led to the selective formation of mono-, di-, or trinuclear homo- or heterometallic complexes, [Rh(**1**)SbF<sub>6</sub>] (4), [{Rh(nbd)}<sub>2</sub>(**1**)](SbF<sub>6</sub>)<sub>2</sub> (3), [{Pd(η<sup>3</sup>-allyl)}<sub>2</sub>(**1**)](SbF<sub>6</sub>)<sub>2</sub> (5), [{RuCl(η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)}<sub>2</sub>(**1**)] (6), and [{RuCl<sub>2</sub>(η<sup>6</sup>-benzene)}<sub>2</sub>(PdCl<sub>2</sub>)(**1**)] (8). These complexes were characterized by NMR and X-ray crystallographic analysis.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Transition metal-catalyzed asymmetric transformation processes are recognized as one of the most important strategies for the production of optically active fine chemicals [1]. Recently, increasing attention has been given to the application of multimetallic catalysis in these asymmetric syntheses, and there have been several important reports of Lewis acid catalysis [2,3]. On the other hand, only a limited number of reports are available regarding transition metal catalysis [4,5]. If the catalytic functions of various transition metals could be integrated in a single catalyst, it would be possible to realize the new catalytic processes. In our previous research, we prepared P-chiral tetraphosphine **1** and applied to transition metal catalysis [6]. Tetraphosphine **1** coordinated to two rhodium atoms to form homobimetallic complex **2** (Eq. (1)). It also exhibited high enantioinduction ability in the asymmetric hydrogenation of various enamides (Eq. (2))



In this case, each rhodium center in the complex acted independently as a single catalyst and gave almost the same performance as a rhodium(I) complex of (*S,S*)-1,2-bis(*tert*-butyl(methyl)phosphino)ethane (abbreviated to *t*-Bu-BisP<sup>\*</sup>) [7]. Although high enantioselectivity and reactivity were maintained in comparison with the *t*-Bu-BisP<sup>\*</sup> complex, we could not find any new reactivity and selectivity based on the cooperation between two metal centers. Given this background, we planned to design and prepare various types of homo- and heterobimetallic complexes of a P-chiral tetraphosphine in order to realize cooperative asymmetric transition metal catalysis. Herein we describe the selective preparation of various transition metal complexes of P-chiral tetraphosphine **1**, and their crystal structures [8]. As shown in Fig. 1, tetraphosphine **1** was selectively converted into mono-, di-, and trimetallic structures by

\* Corresponding authors. Address: Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan. Tel.: +81 87 894 5111; fax: +81 87 894 0181 (H. Danjo).  
E-mail address: danjo@kph.bunri-u.ac.jp (H. Danjo).

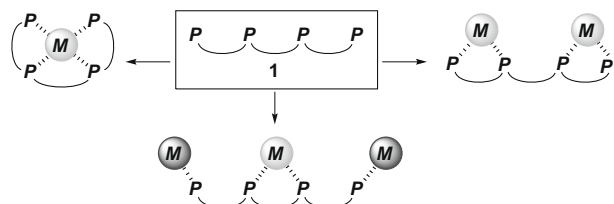


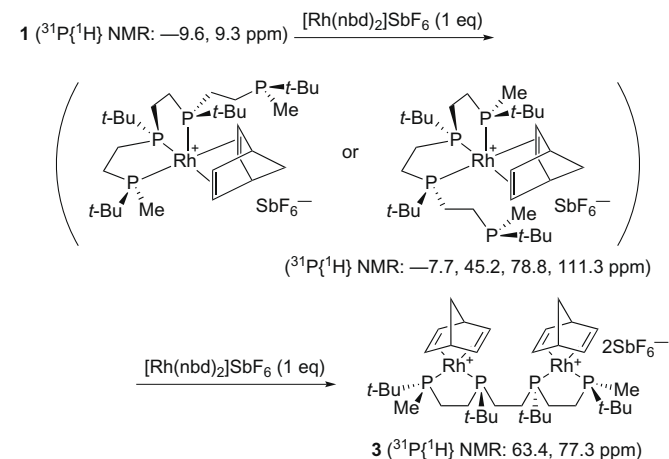
Fig. 1. Three coordination modes of tetraphosphine **1**.

treatment with the metal complex precursors having an appropriate number of free coordination sites.

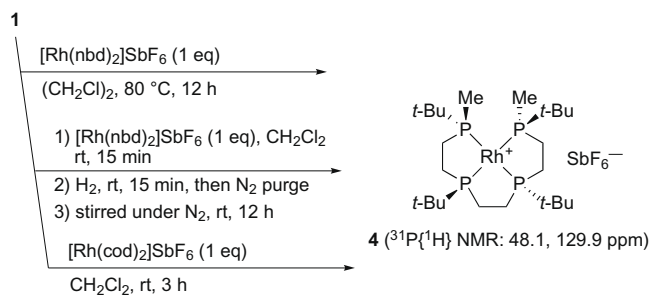
## 2. Results and discussion

The complexation of P-chiral tetraphosphine **1** with rhodium(I) was carried out with [Rh(diene)<sub>2</sub>] type precursors. When 2 equiv. of [Rh(nbd)<sub>2</sub>]SbF<sub>6</sub> was employed, the complexation took place smoothly in dichloromethane at room temperature, and dirhodium complex **3** was obtained as the sole product (Scheme 1). The complexation using 1 equiv. of [Rh(nbd)<sub>2</sub>]SbF<sub>6</sub> was also conducted and its reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR. The intensities of the signals at −9.6 and 9.3 ppm, which were ascribed to **1**, decreased gradually and new signals at −7.7 ppm (d, <sup>3</sup>J<sub>P-P</sub> = 30 Hz), 45.2 ppm (dt, <sup>2+3</sup>J<sub>P-P</sub> = 22 Hz, J<sub>P-Rh</sub> = 113 Hz), 78.8 ppm (dq, <sup>2+3</sup>J<sub>P-P</sub> = 26 Hz, J<sub>P-Rh</sub> = 130 Hz), and 111.3 ppm (dt, <sup>2+3</sup>J<sub>P-P</sub> = 24 Hz, J<sub>P-Rh</sub> = 126 Hz) appeared within 15 min. No signals assigned to dirhodium(I) complex **3** could be detected during this transformation process. The large coupling constants of the three signals at 45.2, 78.8, and 111.3 ppm (J<sub>P-Rh</sub> = 113–130 Hz) indicate that the three phosphino groups of the tetraphosphine **1** coordinate to the rhodium center in the facial manner to form an 18-electron pentacoordinated rhodium(I) complex shown in Scheme 1, in which two possible structures can be drawn for the monorhodium(I) intermediate complex. In each case, one norbornadiene ligand would stay on the rhodium(I) center and occupy two equatorial coordination sites adjacent to each other. By P–P homodecoupling experiment, it was found that the phosphorus atoms at −7.7 and 78.8 ppm coupled to each other. The addition of 1 equiv. of [Rh(nbd)<sub>2</sub>]SbF<sub>6</sub> to this solution led to the rapid formation of dirhodium(I) complex **3**.

A different coordination mode was observed when the complexation of **1** with 1 equiv. of [Rh(nbd)<sub>2</sub>]SbF<sub>6</sub> was carried out at 80 °C in dichloroethane (Scheme 2). In this case, <sup>31</sup>P NMR signals of **1** disappeared completely and two quartets of doublets newly appeared at 48.1 and 129.9 ppm. The same signals were found



Scheme 1. Formation of dirhodium complex **3**.



Scheme 2. Formation of complex **4**.

when dirhodium complex **3** was treated with free tetraphosphine **1** under hydrogen atmosphere, and the signal at *m/z* = 569, which corresponded to (**1** + Rh), was observed in ESI-MS measurement. This implies that all norbornadiene ligands are dissociated from the rhodium center, and the four phosphino groups of **1** fully coordinate to the same rhodium center to form complex **4** [9]. Use of 1 equiv. of [Rh(cod)<sub>2</sub>]SbF<sub>6</sub> as a rhodium(I) precursor also gave the same complex. Because of weak coordination, cyclooctadiene ligands could be dissociated from the rhodium centers even at ambient temperature. This led to the exclusive formation of **4**, and only trace amounts of the corresponding dinuclear-complex like **3** were detected even when 2 equiv. of [Rh(cod)<sub>2</sub>]SbF<sub>6</sub> was employed. This contrasts the predominant formation of dirhodium complex **3** from [Rh(nbd)<sub>2</sub>]SbF<sub>6</sub>. The structure of complex **4** was unequivocally determined by X-ray crystallographic analysis, as shown in Fig. 2. Tetraphosphine **1** coordinates quadridentatively to the Rh center to form distorted square planar complex **4** in which all *tert*-butyl groups are located at quasi axial positions. According to <sup>31</sup>P{<sup>1</sup>H} NMR measurement, it was found that the four phosphorus atoms of **4** were magnetically inequivalent and gave the second order multiplet signals corresponds to AA'BB'X spin system (Fig. 3) [8j].

The complexation of **1** with other transition metals exhibiting various coordination patterns was investigated in order to construct various multimetallic systems. Similar to dirhodium complex **2**, dipalladium complex **5** was readily formed when **1** was treated with 2 equiv. of [Pd(η<sup>3</sup>-allyl)(cod)]SbF<sub>6</sub>. Diruthenium complex **6** was also prepared by using [RuCl(η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)(cod)] (Scheme 3). These three types of complexation have unambiguously occurred because of the simple coordination mode of the precursors; after the removal of diene ligand, [Rh(nbd)]PF<sub>6</sub>, [Pd(η<sup>3</sup>-allyl)]SbF<sub>6</sub>, and [RuCl(η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)] would have two coordination sites at *cis* position. The crystal structures of the homobimetallic complexes **2**, **5**, and **6** are shown in Fig. 4. In all three cases, the two metals in five-membered chelate rings are oriented in almost the same direction (“*cis*”-conformation). This fact points to the possibility of developing cooperative dual catalysts for various

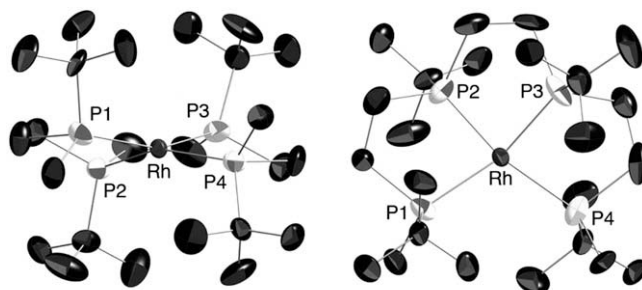


Fig. 2. ORTEP drawings of **4** (front and top views). Ellipsoids are at 50% probability. Hydrogen atoms and SbF<sub>6</sub><sup>−</sup> are omitted for clarity.

Download English Version:

<https://daneshyari.com/en/article/1327805>

Download Persian Version:

<https://daneshyari.com/article/1327805>

[Daneshyari.com](https://daneshyari.com)