JOURNAL OF THE CHINESE CHEMICAL SOCIETY

For information on submission of manuscripts & publication, visit us at http://chemistry.org.tw/public_jour.php

中國化學會

EDITORIAL BOARD

P. O. Box 1-18, Nankang
Taipei 115, Taiwan
Tel: +886-2-3366-8206
Fax: +886-2-2364-8940
Email: jccs@chem.sinica.edu.tw

Instructions on Galleyproof

Please proof-read the typewritten manuscript and make the corrections with the following instructions.

1. **Use red ink to indicate the corrections in the margins of the galley proof and scan it to us (*.PDF file) or write us where are the modifications in the WORD (*.doc).**

2. All the accepted manuscripts have been reviewed by English editor and the Editorial Office has made the changes as indicated by English reviewer.

3. Do not erase or obliterate type; instead, strike one line through the copy to be deleted and write the change in the margin.

4. Clarify complicated corrections by rewriting the entire phrase or sentence in the margin.

5. Check all text, data, and references against the original manuscript. Pay particular attention to equations; formulas; tables; captions; spelling of proper names; and numbering of equations, illustrations, tables, and references.

6. The printing of all graphics is generally black-and-white.

7. Be sure of the type of the manuscript: "Note" or "Communication" will be marked in the left-above side of the first page. As to "Article", it will be blank.

8. **Return any corrections immediately (within 24 hours, two days) by email or your paper will be published as it is in the proof.**

With many thanks for your help and cooperation,

Sincerely yours,

Yu Wang

Yu Wang
Editor-in-Chief

Proof-read Signature:

Date:

(return this page to JCCS)

（**Continue on Page 2 for the guide on how to prepare a running title**）

A running title, appearing in the left-upper side of each page, is strongly recommended in less than 50 letters. It is a short but clear sub-title to let readers grab the essence of your endeavors.

J. Chin. Chem. Soc., Vol. 56, No. 4, 2009 **1**

A running title with 50 letters is strongly recommended.

The Nitrogen-Assisted Triphenylphosphine Displacement of 3-Hydroxypyridine and 3-Aminopyridine Ligands in Palladium(II) Complexes: Crystal Structures of $[Pd(PPh_3)Br]_2\{\mu,\eta^2\text{-}C_5H_3N(OH)\}_2$ and $[Pd(PPh_3)Br]_2\{\mu,\eta^2\text{-}C_5H_3N(NH_2)\}_2$

Kuang-Hway Yih[a]* (易光輝), Hsiao-Fen Wang[b] (王曉芬), Keh-Feng Huang[b] (黃克峰),
Chang-Chi Kwan[b] (官常慶) and Gene-Hsiang Lee[c] (李錦祥)
[a]*Department of Applied Cosmetology, Hungkuang University Shalu, Taichung 433, Taiwan, R.O.C.*
[b]*Department of Applied Cosmetology, Providence University Shalu, Taichung 433, Taiwan, R.O.C.*
[c]*Instrumentation Center, College of Science, National Taiwan University, Taipei 106, Taiwan, R.O.C.*

Treatment of $Pd(PPh_3)_4$ with 2-bromo-3-hydroxypyridine $[C_5H_3N(OH)Br]$ and 3-amino-2-bromopyridine $[C_5H_3N(NH_2)Br]$ in dichloromethane at ambient temperature cause the oxidative addition reaction to produce the palladium complex $[Pd(PPh_3)_2\{\eta^1\text{-}C_5H_3N(OH)\}(Br)]$, **2** and $[Pd(PPh_3)_2\{\eta^1\text{-}C_5H_3N(NH_2)\}(Br)]$, **3**, by substituting two triphenylphosphine ligands, respectively. In dichloromethane solution of complexes **2** and **3** at ambient temperature for 3 days, it undergo displacement of the triphenylphosphine ligand to form the dipalladium complexes $[Pd(PPh_3)Br]_2\{\mu,\eta^2\text{-}C_5H_3N(OH)\}_2$, **4** and $[Pd(PPh_3)Br]_2\{\mu,\eta^2\text{-}C_5H_3N(NH_2)\}_2$, **5**, in which the two 3-hydroxypyridine and 3-aminopyridine ligands coordinated through carbon to one metal center and bridging the other metal through nitrogen atom, respectively. Complexes **4** and **5** are characterized by X-ray diffraction analyses.

Keywords: 2-Bromo-3-hydroxypyridine; 3-Amino-2-bromopyridine; Palladium; Dipalladium; Nitrogen-assisted; X-ray diffraction.

INTRODUCTION

Palladium complexes catalyzed forming C-C bond process are the most important reactions in organic synthesis.[1] Intramolecular reductive elimination of Pd-N binuclear complex[2] $[Pd(\mu\text{-}C_9H_6N)(\mu\text{-dppm})]_2(Cl)_2$ yielding organic compound 2,2′-biquinoline and complex $[Pd_2Cl_2(dppm)_2]$ has been reported. A. Beeby[3] reported a pyridyl-bridged palladium complex as an effective precatalyst for the Suzuki cross-coupling reactions of a variety organoboronic acids and aryl bromides. The catalytic activity of dipalladium complex $[PdBr_2(Bh_2\text{-bimy})]_2$ in aqueous Suzuki-Miyaura cross-coupling reactions were studied by Huynh.[4] The palladacycle[5] complex $\{Pd[P(o\text{-}C_6H_4CH_2)Ph_2]\}_2(\mu\text{-}OAc)_2$ is a high efficient catalyst precursor for the coupling of aryl boronic acids and aryl halides. Complex $[(LPdCl_2)_2]$[6] (L = *N*,*N*′-bis(2,2-diethoxyethyl)imidazolium) exhibited excellent catalytic activity in Heck reaction.

Recently we reported syntheses, reactivities, inter- and intramolecular dissociation, and crystal structures of Pd complexes containing thiocarbamoyl,[7] oxythiocarbonyl,[8] thiazolinyl,[9] and methylpyridine[10] moieties. These ligands induced forming binuclear complexes in which those were assisted by nitrogen or sulfur atom.

In order to obtain a better understanding of how these ligands interact with the metal center and the following study for applying in organic synthesis, we report the synthesis and crystal structures of dipalladium complexes including the 3-hydroxypyridine and 3-aminopyridine containing ligands in this paper.

RESULTS AND DISCUSSION

Treatment of $Pd(PPh_3)_4$, **1** with 2-bromo-3-hydroxypyridine $[C_5H_3N(OH)Br]$ and 3-amino-2-bromopyridine $[C_5H_3N(NH_2)Br]$, in dichloromethane at ambient temperature yield the colorless complexes $[Pd(PPh_3)_2\{\eta^1\text{-}C_5H_3N(OH)\}(Br)]$, **2** and $[Pd(PPh_3)_2\{\eta^1\text{-}C_5H_3N(NH_2)\}(Br)]$, **3**, with 92 and 91% isolated yield, respectively (Scheme I). The air-stable colorless compounds **2** and **3** are soluble in dichloromethane and acetonitrile, slightly soluble in methanol, and insoluble in diethyl ether and *n*-hexane. By con-