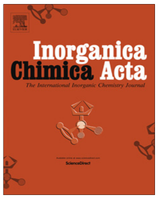
Inorganica Chimica Acta 471 (2018) 355–363

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Research paper

# Synthesis of O,N,O—P multidentate ligands and the formation of early–late heterobimetallic complexes

Noriyuki Suzuki *, Satoru Yoneyama, Keisuke Shiba, Takeshi Hasegawa, Yoshiro Masuyama

*Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan*

ARTICLE INFO

*Article history:*
Received 19 August 2017
Received in revised form 12 November 2017
Accepted 15 November 2017
Available online 21 November 2017

*Keywords:*
Heterobimetallic complex
Niobium
Palladium
Multidentate ligand

ABSTRACT

A multidentate O,N,O—P ligand **4** designed for early–late heterobimetallic (ELHB) complexes was synthesized. The ligand **4** has an O,N,O-tridentate ligand moiety and a triarylphosphine group. The O,N,O-moiety based on lutidine scaffold selectively coordinated to early transition metals such as titanium and niobium in the reaction with the corresponding metal alkoxides to form mononuclear complexes. Coordination of the triarylphosphine moiety to the niobium atom was negligible in the Nb-ONO—P complex according to $^{31}$P NMR spectroscopy, whereas a part of the phosphorus atom coordinated to the titanium atom in the Ti-ONO—P complex. Addition of $[PdCl(\pi\text{-allyl})]_2$ or $[RhCl(cod)]_2$ to the Nb-ONO—P complex gave rise to the formation of ELHB complexes. Thus, the one-pot preparation of ELHB complexes was achieved by simple procedure.

## 1. Introduction

Cooperative effects of early and late transition metals in catalytic reactions have received much attention because they could be utilized to achieve novel, highly selective synthetic reactions. Early–late heterobimetallic (ELHB) complexes must be one of the most promising ways to realize synergy effects. There are many reports on the synthesis of ELHB complexes [1–25]. There are also many examples of successful cooperative effects resulting from two metals in a heterobimetallic complex in catalytic reactions [9,14,17,26–39].

It has been demonstrated that novel catalytic reactions can be accomplished by using well designed ligands. For example, the interaction between the ligand and the substrate can control the conformation where the metal center selectively activates the specific position of the substrate [29–32,40–51].

Thus, for ELHB complexes, ligand design is very important to realize the cooperative effects. The ligand should be designed so that the two metals are located at an appropriate distance from each other. Multidentate ligands are useful for constructing ELHB complexes, although they have to coordinate to two different metal atoms selectively [19]. Some of ELHB complexes, however, involves tedious preparative methods and suffers from low selectivity and low yields. Although many ELHB complexes can be synthesized in a straightforward fashion, simple protocols should be still pursued. Hence, the development of simple protocols for preparation of ELHB complexes is considered important. The one-pot synthesis of ELHB complexes must be convenient, particularly with regard to practical usage for catalytic reactions.

We previously reported on the preparation of multidentate O,N,O—N,N ligands **1** and selective formation of titanium-palladium complexes **3** (Scheme 1) [52]. We employed O,N,O-tridentate ligands that have a lutidine scaffold to construct the Ti-coordinated moiety [53,54–63].

We found that titanium tetraisopropoxide $[Ti(O\textit{i}\text{-}Pr)_4]$ selectively reacted with the O,N,O-tridentate ligands **1** to form the titanium complex **2** at room temperature (rt) due to the oxophilicity of the early transition metal. Simply adding bis(benzonitrile)palladium dichloride to a solution of **2** resulted in the quantitative formation of **3** at ambient temperature. The di(pyridin-2-yl)methyl group, a bidentate ancillary nitrogen ligand, in **1** selectively coordinated to palladium by exchanging with benzonitrile. However, to date, our attempts to synthesize ELHB complexes with other late transition metals such as Ni and Rh have been unsuccessful. We postulated that one possible reason for this problem is the coordination of the pyridyl group on the side arm to the Ti atom in **2**.

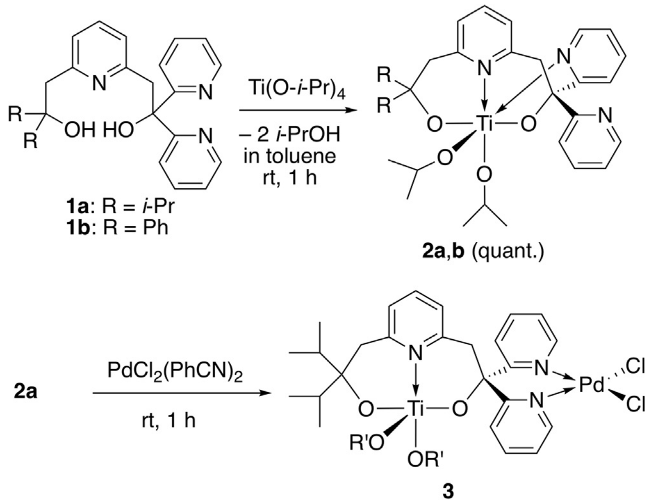
Thus, we next designed multidentate ligands **4** that possess a phosphine moiety, because triarylphosphine is widely used, in many catalytic reactions, as ancillary ligand with various late transition metals. Here we report on the synthesis of O,N,O—P multidentate ligands **4** and the preparation of Nb–Pd and Nb–Rh complexes using the ligand (Fig. 1) [64–80].

Attempts to use them in catalytic reactions are also described.

---

* Corresponding author.
*E-mail address:* norisuzuki@sophia.ac.jp (N. Suzuki).

https://doi.org/10.1016/j.ica.2017.11.027
0020-1693/© 2017 Elsevier B.V. All rights reserved.



**Scheme 1.** The O,N,O—N,N multidentate ligands **1** and Ti-Pd heterobimetallic complexes.

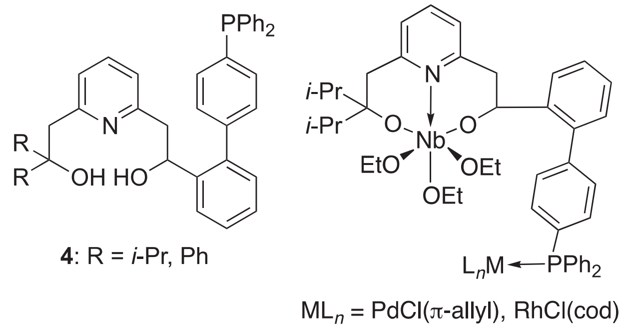


**Fig. 1.** The O,N,O—P multidentate ligands **4** and its ELHB complexes.

## 2. Results and discussion

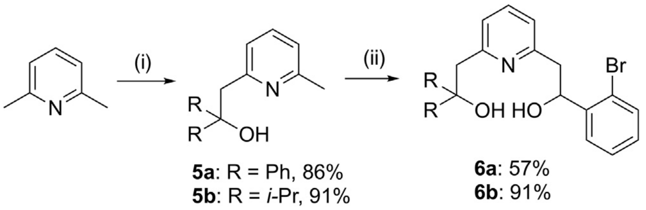
### 2.1. Preparation of O,N,O—P ligands

In this study, we decided to use a monodentate phosphine ligand as an ancillary ligand for late transition metals. In solution, a monodentate ligand bound to the O,N,O-complex would be in an equilibrium between coordination to the metal to form an ELHB complex and dissociation. We envisioned that the formation of heterobimetallic complexes in solution with monodentate ligand moiety might be effective for catalytic reactions. We employed a benzene ring as a spacer to install a phosphine ligand.

In the previous studies, the O,N,O-tridentate ligands **1** were prepared from 2,6-lutidine [55,56,60,81].

We now adopted the same methodology to synthesize O,N,O—P multidentate ligand **4** bearing a phosphine ligand on one of the alkoxide arms. Mono-ols **5a** and **5b** were prepared from 2,6-lutidine by lithiation and subsequent reactions with the corresponding ketones. The mono-ols **5** were again treated with two equiv of *n*-butyllithium, and then reacted with 2-bromobenzaldehyde to afford the diols **6** (Scheme 2).

On the other hand, phosphine oxide **7** was prepared from *p*-dibromobenzene via stepwise phosphination and borylation followed by oxidation (Scheme 3). Finally, Suzuki-Miyaura coupling between **6** and **7** afforded **8**, and subsequent reduction of **8** with phenylsilane gave the O,N,O—P ligand **4** (Scheme 4). $^{31}$P NMR spectroscopy of the phosphine oxide **8** showed single signal at 30 ppm, which is characteristic for aryl phosphine oxide.



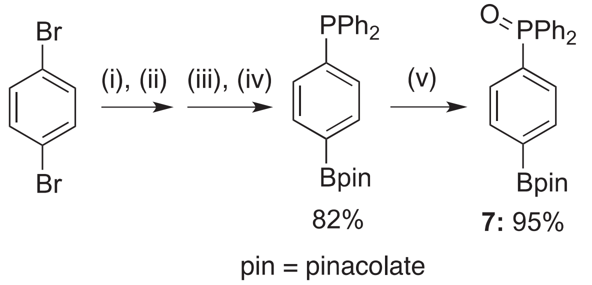
**Scheme 2.** Preparation of the O,N,O-tridentate ligand scaffold **6**. (i) 1 eq *n*-BuLi at −78 °C, 2.5 h, then 1 eq $R_2C{=}O$, rt, overnight in THF; (ii) 2 eq *n*-BuLi, −78 °C to −20 °C, 5 h, then 1.2 eq 2-bromobenzaldehyde, −78 °C to rt, 2 h.

The O,N,O—P ligands **4** showed single signal at −6 ppm showing triarylphosphine(III) character. The molecular structure of **4b** was determined by X-ray diffraction study. It clearly showed that triarylphosphine moiety was bound to the O,N,O-ligand part (Fig. 2).

### 2.2. Preparation of titanium and niobium complexes of 4

We previously reported that the [ONO—NN]Ti(OR)$_2$ complexes **2** were obtained from the ligand **1** and Ti(O*i*-Pr)$_4$ by alcohol exchange reactions [52]. In the present study we added Ti(O*i*-Pr)$_4$ to the benzene solution of **4** (Scheme 5). We employed **4b** because **4a** was less soluble in common organic solvents. The benzene solution was stirred for 1 h at rt, and volatiles were removed in vacuo. $^1$H NMR spectroscopy of the residue suggested the quantitative formation **9** [82]. Two isopropoxy groups were observed, and one of the methylene signals of **4b** shifted downfield significantly. Signals of the pyridine ring shifted upfield. These changes in the chemical shifts were similar to those observed in the reaction between the ligand **1** and Ti(O*i*-Pr)$_4$. Two septets assignable to methine proton of isopropoxy groups were observed at 5.03 and 5.18 ppm. Besides, there found a broad signal at 4.52 ppm, implying that free isopropanol coordinates to the titanium atom to form six-coordinated complex. Two diastereomeric configuration are possible owing to the presence of chiral carbon, and interchange between these two in solution might cause broadening the methine signals. We also carried out the reaction of niobium(V) ethoxide, Nb(OEt)$_5$, and **4b**. The $^1$H NMR spectra of the reaction mixture suggested the formation of the Nb complex **10**. Liberated ethanol was observed, and inequivalent ethoxy groups were also found. The signals of the O,N,O—pyridine shifted similarly to the Ti case. In $^{31}$P NMR spectroscopy of **9** and **10**, a major signal appeared at −5 ppm indicating that most of the phosphorus atoms have no interaction with the metal. A minor signal was observed at 27 ppm. The integration ratios of the major and minor signals were 74/26 in **9** and 91/9 in **10**.

The $^{31}$P NMR of the phosphine oxide **8** appeared at 30 ppm. Thus, it is likely that these signals represent the oxidized species



**Scheme 3.** Preparation of phosphine oxide **7**. (i) 1 eq *n*-BuLi, −78 °C, 1 h; (ii) 1 eq Ph$_2$PCl, −78 °C, 2 h, then rt 1 h; (iii) 1.1 eq *n*-BuLi, −78 °C, 1 h; (iv) 1.3 eq *i*-PrOBpin, −78 °C, 0.5 h, then rt, 2.5 h in THF; (v) FeCl$_3$·6H$_2$O 10 mol%, KSCN 30 mol%, O$_2$, 80 °C, 22 h in CH$_3$CN.