

Synthesis and reactions of heterodinuclear organopalladium complex having an unsymmetrical PN ligand

Nobuyuki Komine, Susumu Tsutsuminai, Masafumi Hirano, Sanshiro Komiya *

Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan

Received 1 February 2007; received in revised form 20 April 2007; accepted 20 April 2007
Available online 25 April 2007

This paper is dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Novel heterodinuclear organopalladium complexes having an unsymmetrical PN ligand ($\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P}$) RPd-ML_n ($\text{ML}_n = \text{Co}(\text{CO})_4$; R = Me (**2a**), Ph (**2b**), $\text{ML}_n = \text{MoCp}(\text{CO})_3$; R = Ph (**3b**)) are synthesized by metathetical reactions of $\text{PdRX}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ (X = I, NO_3) with $\text{Na}^+[\text{ML}_n]^-$. Reversible dissociation of the Pd–N bond in **3b** is revealed by variable temperature NMR studies. Reactions of **2a** and **2b** with CO yield corresponding acyl complexes ($\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P}$)(RCO) $\text{Pd-Co}(\text{CO})_4$ (R = Me (**5a**), Ph (**5b**)). Rate of CO insertion for **2a** and **2b** is significantly faster than those for mononuclear methylpalladium complex, $\text{PdMeI}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ (**1a**), and methylpalladium–cobalt complex with a 1,2-bis(diphenylphosphino)ethane (dppe) ligand, $(\text{dppe-}\kappa^2\text{P,P}')\text{MePd-Co}(\text{CO})_4$ (**6a**). **5a** smoothly reacts with nucleophiles such as diethylamine, methanol and benzenethiol to give corresponding amide, ester and thioester, respectively. These reactions of **5a** are also significantly faster than those of corresponding mononuclear analogues and the similar heterodinuclear complexes with symmetrical bidentate ligands such as 1,2-bis(diphenylphosphino)ethane or *N,N,N',N'*-tetramethylethylenediamine ligand.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Heterodinuclear organopalladium complex; Unsymmetrical PN ligand; CO insertion

1. Introduction

Heterodinuclear organometallic complexes are expected to show cooperative effects of different metal centers [1]. We previously reported synthesis of heterodinuclear organoplatinum or -palladium complexes with a symmetrical bidentate ligand such as 1,5-cyclooctadiene (cod), 1,2-bis(diphenylphosphino)ethane (dppe), *N,N,N',N'*-tetramethylethylenediamine (tmeda), 2,2'-bipyridine (bpy), and 1,10-phenanthroline (phen), $\text{L}_2\text{RM-M'L}'_n$ (M = Pt, Pd; M' = Mo, W, Mn, Re, Fe, Co; R = Me, Et, CH_2CMe_3 , Ph, COMe, CPh, H; $\text{L}_2 = \text{cod}$, dppe, tmeda, bpy, phen; $\text{L}' = \text{CO}$, Cp) [2]. They show unique reactions such as organic group transfer between different metal centers

[2a,2c,2d,2h,2k,2o], significant acceleration of β -H elimination [2f,2i], and enhanced CO insertion reactions [2g,2j]. On the other hand, introduction of an unsymmetrical PN ligand into organometallic complex is expected to give higher selectivity and activity, because PN chelating ligand may provide a preferential vacant coordination site on metal center due to facile dissociation of the nitrogen atom. We recently reported synthesis of heterodinuclear organoplatinum complex having a hemilabile ligand and reactions of heterodinuclear methylplatinum–molybdenum derivative, $(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})\text{MePt-MoCp}(\text{CO})_3$ with dimethyl acetylenedicarboxylate to give novel μ -platinacyclobutenone complexes $(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})\text{MePt}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C}(\text{O})\text{C}_2(\text{CO}_2\text{Me})_2\}\text{MoCp}(\mu\text{-CO})(\text{CO})$ [3]. In this work, we investigated the synthesis and reactions of novel heterodinuclear organopalladium complexes having an unsymmetrical PN ligand.

* Corresponding author.

E-mail address: komiya@cc.tuat.ac.jp (S. Komiya).

2. Results and discussion

2.1. Synthesis of heterodinuclear organopalladium–cobalt (or –molybdenum) complexes

A series of novel heterodinuclear organopalladium–cobalt (or –molybdenum) complexes having an unsymmetrical PN ligand were prepared by the metathetical reaction of $\text{PdRX}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ ($\text{R} = \text{Me, Ph}$; $\text{X} = \text{I, NO}_3$) with corresponding carbonyl metallates such as $\text{Na}^+[\text{MoCp}(\text{CO})_3]^-$ [4] and $\text{Na}^+[\text{Co}(\text{CO})_4]^-$ [5]. Starting complexes $\text{PdRI}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ ($\text{R} = \text{Me}$ (**1a**), Ph (**1b**)) were prepared by the oxidative addition of methyl or phenyl iodide to $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ [6] ($\text{dba} = \text{dibenzylideneacetone}$) in the presence of 2-(diphenylphosphino)triethylamine [7] in 46% and 14% yield, respectively (Eq. (1)). These novel organopalladium complexes having an unsymmetrical PN ligand (**1a,b**) were characterized by NMR and IR spectroscopies and elemental analysis. Selected IR and NMR data of newly prepared compounds, **1a** and **1b**, are summarized in

Table 1. The molecular structure of **1a** was determined by single crystal X-ray structure analysis, and the ORTEP drawing of **1a** is depicted in Fig. 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1a** shows a singlet at δ 42.4. In the ^1H NMR of **1a**, the methylene protons of the NCH_2CH_3 moiety appear as two doublets of quartets at δ 3.05 and 3.40, indicating that these methylene protons are diastereotopic. This fact is an indication of rigid coordination of both nitrogen and phosphorus atoms to the Pd center. The Pd–Me resonance is observed at δ 0.65 as a doublet with a small $^3J_{\text{PH}}$ value 3.9 Hz, suggesting that the Me ligand locates in the *cis* position to the phosphorus atom. This structural feature may be due to difference of relative *trans* influence of the coordinating atoms, where ligands having strong *trans* influence (Me and P) disfavor mutually *trans* positions to each other. Thus, the starting complex $\text{PdMeI}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ (**1a**) in solution as well as in solid state has a square planar geometry depicted in Eq. (1). Analogous spectroscopic data are also obtained for $\text{PdPhI}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ (**1b**).

Table 1

Selected IR and NMR data of mononuclear palladium complex, $\text{PdRI}(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})$ and heterodinuclear organopalladium–cobalt(or –molybdenum) complexes, $(\text{Et}_2\text{NC}_2\text{H}_4\text{PPh}_2\text{-}\kappa^2\text{N,P})\text{RPd-ML}_n$ ($\text{ML}_n = \text{Co}(\text{CO})_4, \text{MoCp}(\text{CO})_3$)

Complex	IR (νCO , cm^{-1}) ^a	^1H NMR (ppm, rt)		^{31}P NMR (ppm, rt)
		R	NCH_2CH_3	
1a ^b		0.65 (d, $^3J_{\text{PH}} = 3.9$ Hz, 3H, CH_3)	1.20 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, NCH_2CH_3) 3.05 (dq, $^2J_{\text{HH}} = 13.0$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2H, NCH_2CH_3) 3.40 (dq, $^2J_{\text{HH}} = 13.0$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2H, NCH_2CH_3)	42.4 (s)
1b ^c		6.5–6.7 (m, 3H, <i>m</i> - and <i>p</i> - C_6H_5) 6.93 (m, 2H, <i>o</i> - C_6H_5)	1.36 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H, NCH_2CH_3) 3.19 (dq, $^2J_{\text{HH}} = 13.8$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 2H, NCH_2CH_3) 3.45 (dq, $^2J_{\text{HH}} = 13.8$ Hz, $^3J_{\text{HH}} = 7.0$ Hz, 2H, NCH_2CH_3)	32.6 (s)
2a ^d	1866 (s) 1935 (s) 2014 (s)	0.95 (d, $^3J_{\text{PH}} = 4.8$ Hz, 3H, CH_3)	0.80 (t, $^3J_{\text{HH}} = 7.2$ Hz, 6H, NCH_2CH_3) 2.72 (dq, $^2J_{\text{HH}} = 14.4$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2H, NCH_2CH_3) 3.10 (dq, $^2J_{\text{HH}} = 14.4$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2H, NCH_2CH_3)	32.7 (s)
2b ^d	1876 (s) 1901 (s) 1961 (s) 2024 (s)	6.6–6.7 (m, 3H, <i>m</i> - and <i>p</i> - C_6H_5) 6.96 (brs, 2H, <i>o</i> - C_6H_5)	0.86 (t, $^3J_{\text{HH}} = 6.6$ Hz, 6H, NCH_2CH_3) 2.84 (br, 2H, NCH_2CH_3) 3.12 (br, 2H, NCH_2CH_3)	22.6 (s)
3b ^b	1789 (s) 1886 (s)	6.5–6.6 (m, 3H, <i>m</i> - and <i>p</i> - C_6H_5) 6.97 (d, $^3J_{\text{HH}} = 7.8$ Hz, 2H, <i>o</i> - C_6H_5)	1.19 (t, $^3J_{\text{HH}} = 6.9$ Hz, 6H, NCH_2CH_3) 3.2 (br, 4H, NCH_2CH_3)	23.9 (s)
5a ^e	1686 (s) 1875 (s) 1912 (s) 1945 (s) 2020 (s)	1.99 (s, 3H, COCH_3)	1.78 (t, $^3J_{\text{HH}} = 6.9$ Hz, 6H, NCH_2CH_3) 2.99 (br, 4H, NCH_2CH_3)	14.2 (s)
5b ^e	1645 (m) 1890 (s) 1932 (s) 1952 (s) 2027 (m)	7.0–7.3 (m, 5H, COC_6H_5)	1.25 (t, 6H, $^3J_{\text{HH}} = 7.2$ Hz, NCH_2CH_3) 3.1 (br, 4H, NCH_2CH_3)	14.6 (s)

^a IR spectra were measured by KBr pellet method.

^b NMR spectra were measured in acetone- d_6 .

^c In CDCl_3 .

^d In C_6D_6 .

^e In CD_2Cl_2 .

Download English Version:

<https://daneshyari.com/en/article/1328202>

Download Persian Version:

<https://daneshyari.com/article/1328202>

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