Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 691 (2006) 4012–4020
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Rhodium(I) complexes containing a bulky pyridinyl N-heterocyclic carbene ligand: Preparation and reactivity

Chao-Yu Wang, Yi-Hong Liu, Shei-Ming Peng, Shiuh-Tzung Liu *

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, ROC

Received 25 March 2006; received in revised form 1 June 2006; accepted 2 June 2006
Available online 15 June 2006

Abstract

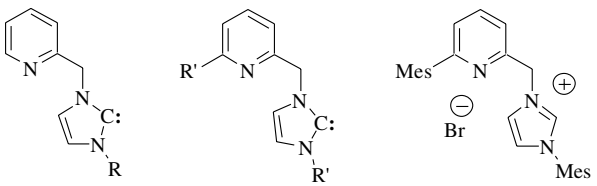
Coordination chemistry of a new pyridine imidazole-2-ylidene ligand (pyN^C) system with sterically hindered substituents toward rhodium(I) metal ions has been investigated. The rhodium complex [(pyN^C)RhCl(COD)] (COD = 1,5-cyclooctadiene) was prepared via the transmetallation from the silver complex $[(C\text{-pyN^C})_2Ag]AgI_2$. Upon the abstraction of chloride, the pyridinyl nitrogen coordinated to the metal center and formed $[(C,N\text{-pyN^C})Rh(COD)]BF_4$ with the chelation of pyN^C. The pyridinyl nitrogen donor was found to be labile and could be replaced by various donors such as phosphine, azide and halides. Substitution of COD by various donors does not proceed except strong π-acid ligands such as CO and $P(OCH_3)_3$. However, the chelation of pyN^C was replaced by the bisphosphine (P∼P) to form $[(P{\sim}P)_2Rh]BF_4$, which was subsequently oxidized to yield $[(P{\sim}P)_2Rh(O_2)]BF_4$.

Keywords: Carbene; Rhodium; Substitution; Coordination

1. Introduction

Since the stable diaminocarbene was first isolated by Arduengo [1], the chemistry involving this type of carbenes has been attracted considerable attention [2–13]. These carbenes are considered as an important class of ligands with strong basicity and good σ-donating properties. Thus, transition metal complexes containing N-heterocyclic carbene moiety were found to be thermally stable and less sensitive toward dioxygen as compared to those with phosphine ligands [7].

Regarding chelate-carbene ligands, quite a few heterofunctionalized diaminocarbene ligands are known [10–12]. Amongst, Cavell and coworkers have demonstrated that the chelation effect of the pyridinyl imidazole-2-ylidene ligand **1** toward palladium ions is due to the presence of a strong coordinating pyridinyl donor [9]. Furthermore, the carbene ligand with a steric bulky substituent on the imidazole ring makes the coordination environment more versatile [9,10]. It has been shown that Rh(I) complexes with a bulky carbene moiety underwent C–H activation on the substituent of ligand itself to form a Rh(III) species [9]. However, bidentate ligands with sterically hindered groups on both pyridine and imidazole rings such as **2** have less examined [9]. In view of these background, studies on the synthesis of pyridinyl-carbene precursor **3**, preparation of the corresponding rhodium complexes and their reactivities toward various donors were investigated.



1 **2** **3**

* Corresponding author. Tel.: +886 2 2366 0352; fax: +886 2 2363 6359.
E-mail address: stliu@ntu.edu.tw (S.-T. Liu).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.06.004

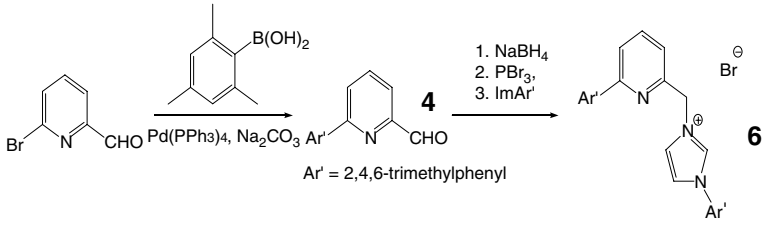
2. Results and discussion

2.1. Synthesis of ligands and silver complexes

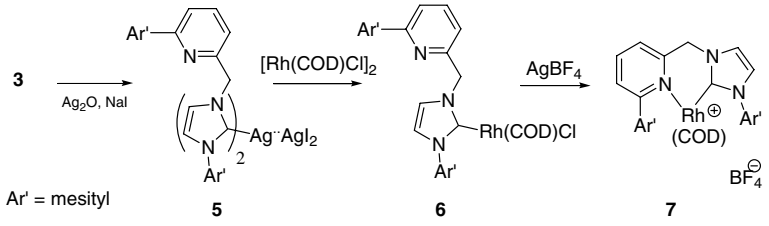
The synthetic approach leading to pyridinyl-imidazolium salt **3** is shown in Scheme 1. Mesityl substituted pyridine-aldehyde **4** was prepared in 90% yield from the coupling of mesitylboronic acid with 6-bromopyridine-2-carbaldehyde in the presence of $Pd(PPh_3)_4$ as the catalyst. Subsequent functional groups transformation provided the desired imidazolium salt **3** with mesityl substituents. The imidazolium salt **3** as well as the intermediates leading to it were characterized by both spectroscopic and elemental analyses.

Deprotonation of imidazolium salt **3** with *n*-BuLi to produce the corresponding carbene (denoted as pyN^C) did not succeed presumably due to the interference of the deprotonation of benzylic methylene protons [9]. Alternatively the carbene transfer method was employed to prepare the desired metal complexes (Scheme 2) [8,14]. First the imidazolium salt **3** was converted into the silver carbene complex **5** [15]. In comparison with the related species, this reaction took much longer reaction time for completion, indicating that the bulky substituents readily slowed down the formation of carbene complexes. Characterization of this silver carbene complex was based on both spectroscopic data and elemental analysis. $^{13}C\{^1H\}$ NMR spectrum of the silver complex showed a characteristic shift for $Ag–C_{(carbene)}$ at δ 183.5, which was assigned to the 2*C*-imidazol-2-ylidene(carbene) carbon [16]. From the observation of $m/z = 897.4$ (^{107}Ag) and 899.5 (^{109}Ag) on the FABMass spectrum clearly illustrated the formation of Ag(I) bis(carbene) complex, which had the same stoichiometry as those reported species [15]. Elemental analysis of the complex also suggested the formula of (*C*-pyN^C)$_2$Ag$^{\cdot\cdot}$AgI$_2$, but the crystallization of the complex in CH_2Cl_2/hexane gave the X-ray suitable crystals in the formula of (*C*-pyN^C)$_2$AgI, a substitution of $[AgI_2]^-$ by the iodide anion.

Fig. 1 displays the ORTEP plot of the silver carbene complex (*C*-pyN^C)$_2$AgI. The angle of C(1)–Ag–C(28) [160.7(2)°] is much deviated from the linear geometry, which is smaller than those of the reported species such as [1,3-dimesityl(imidazol-2-ylidene)]$_2$Ag$^+$ [176.3(2)°] [15].



Scheme 1. Ligand preparation.



Scheme 2. Preparation of rhodium carbene complexes.

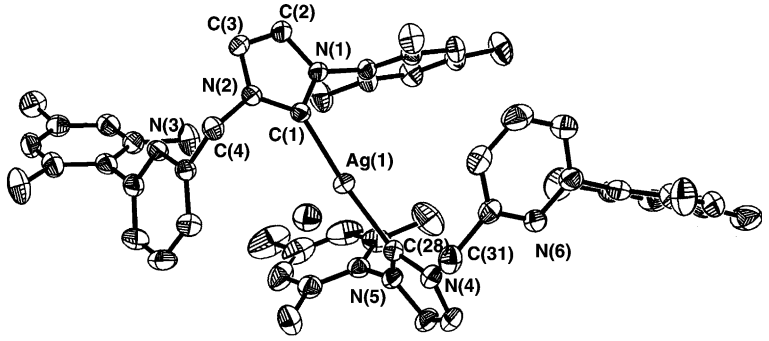


Fig. 1. ORTEP plot of (*C*-pyN^C)$_2$AgI. (30% probability ellipsoids). Ag(1)–C(1) 2.108(4) Å, Ag(1)–C(28) 2.117(4) Å, C(1)–Ag(1)–C(28) 160.7(2)°.