

Synthesis, structure, and catalytic properties of palladium complexes containing bis(phosphino)-amine ligands



Khodayar Gholivand^{a,*}, Mohammad Kahnouji^a, Reza Latifi^b, Farzaneh T. Fadaei^c, Akram Gholami^a, Kurt J. Schenk^c

^a Department of Chemistry, Faculty of Science, Tarbiat Modares University, Tehran, Iran

^b Department of Chemistry, 107 Physical Science Building, Oklahoma State University, Stillwater, 74078 OK, United States

^c École Polytechnique Fédérale de Lausanne, CCC-IPSB, Le Cubotron Dorigny, 1015 Lausanne, Switzerland

ARTICLE INFO

Article history:

Received 15 December 2015

Received in revised form 3 April 2016

Accepted 5 April 2016

Available online 16 April 2016

Keywords:

Palladium complexes

X-ray crystallography

Heck coupling reactions

ABSTRACT

Two *N,N*-bis(diphenylphosphino)-amine ligands [amine = 4-aminomorpholine (**L**₁) or 1-amino-4-methylpiperazine (**L**₂)] and their Pd(II) complexes were synthesised and characterised by IR and NMR spectroscopies. The structures of ligand **L**₁ and both complexes **C**₁ and **C**₂ were determined by X-ray crystallography. The catalytic activity of **C**₁ and **C**₂ in the Heck coupling reactions was assessed. The effect of parameters such as palladium source, solvent, base and reaction time on the conversion was investigated to obtain the optimum conditions for the reaction.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Phosphorus (III) ligands are capable of stabilising transition metals in low valence, especially with electron-rich transition metals [1–7]. This capacity has, in recent years, spurred researchers to focus on the synthesis and characterisation of new phosphorus (III) ligands for various applications such as metal-catalysed reactions [3,8–12].

Palladium complexes containing aminophosphine ligands serve as highly active catalysts and have become one of the most popular organometallics used in organic synthesis [13]. In particular, these complexes proved to be the catalysts of choice for the reaction of arylchlorides with arylboronic acid (the Suzuki reaction) or with alkenes (the Heck reaction) as well as for the formation of C–C bonds through cross-coupling [14,15].

Bis(phosphino)amines, RN(PR₂)₂, present a different coordination behaviour if the donor–acceptor properties are altered by incorporating a substituent in the ligand backbone [16–21,3,8,22–25]. Preparative routes enable access to various structural modifications via simple P–N bond formation [26–32]. In comparison to a P–C–P linkage, the P–N–P skeletons possess a wider versatility. Indeed, a small alteration of the substituents on both P and N centres gives rise to changes in the P–N–P angle and the conformation around the P-centres. In turn, this can cause

significant changes of the coordination behaviour and the structural properties of the resulting complexes, allowing the synthesis of a wide range of new compounds by the reaction of bis(phosphino)amines with transition metals [33–35].

In this paper, we report the preparation of two bis(phosphino)-amine ligands and their Pd(II) complexes. All the compounds were characterised by IR, NMR spectroscopies. The structures of the ligand **L**₁ and the complexes **C**₁ and **C**₂ were determined by X-ray crystallography. The complexes turned out to be useful pre-catalyst in the Heck cross-coupling reactions. The effect of various parameters such as palladium source, solvent, base and reaction time on the conversion was investigated and the optimum conditions for the reaction were obtained.

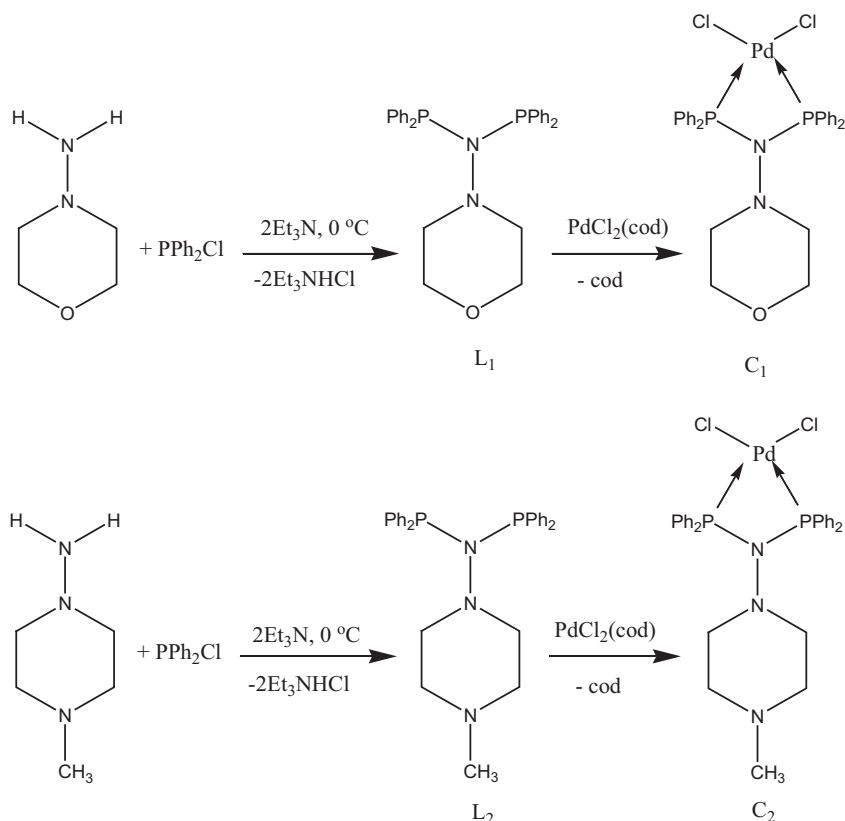
2. Results and discussion

2.1. Synthesis of ligands and complexes

The new *N,N*-bis(diphenylphosphino)-amine ligands, where amine = 4-aminomorpholine (in **L**₁) or 1-amino-4-methylpiperazine (in **L**₂), were prepared via aminolysis of the corresponding amine with two equivalents of Ph₂PCl in the presence of triethylamine in dichloromethane solution at 0 °C (Scheme 1). Compounds **L**₁ and **L**₂ were isolated as white and air-stable solids in high yields (75% and 70%, respectively) under anaerobic conditions. The reaction of **L**₁ and **L**₂ with [Pd(COD)Cl₂] finally gives the corresponding Pd(II) complexes in high yields (ca. 87%).

* Corresponding author.

E-mail address: gholi_kh@modares.ac.ir (K. Gholivand).



Scheme 1. Synthesis of ligands **L₁** and **L₂** and their complexes.

Table 1
Crystal data and structure refinement for **L₁**, **C₁** and **C₂**.

Compound	L₁	C₁	C₂
Empirical formula	C ₂₈ H ₂₈ N ₂ O P ₂	C ₂₈ H ₂₈ Cl ₂ N ₂ O P ₂ Pd	C ₂₉ H ₃₂ Cl ₂ N ₃ P ₂ Pd, Cl
Formula weight	470.46	647.76	697.26
Wavelength (Å)	0.6934	0.71073	0.71073
T (K)	100	296	296
Crystal system	Orthorhombic	monoclinic	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁
a (Å)	7.228(1)	9.6622(2)	10.429(2)
b (Å)	10.373(1)	16.1186(4)	14.353(3)
c (Å)	32.078(3)	17.8554(4)	20.105(4)
α (°)	90	90	90
β (°)	90	95.722(1)	90
γ (°)	90	90	90
V (Å ³)	2405.1(5)	2766.97(11)	3009.5(10)
Z	4	4	4
Density [g/cm ³]	1.299	1.555	1.539
μ [mm ⁻¹]	0.205	1.004	1.014
F(000)	992	1312	1416
θ Min, Max [Deg]	2.06, 33.13	1.7, 27.4	1.7, 28.3
Crystal size [mm]	0.20 × 0.15 × 0.10	0.15 × 0.15 × 0.15	0.10 × 0.10 × 0.30
Index ranges	-11 ≤ h ≤ 11, -15 ≤ k ≤ 15, -48 ≤ l ≤ 48	-15 ≤ h ≤ 15, -21 ≤ k ≤ 21, -29 ≤ l ≤ 29	-13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -19 ≤ l ≤ 26
Reflections collected	58459	31238	23878
R _{int} [%]	0.0429	0.0348	0.0598
Data/restraints/parameters	8879/0/298	6286/192/380	7420/1/347
Goodness-of-fit (GOF) on F ²	1.050	1.286	1.023
R ₁ [I > 2 σ(I)]	0.0256	0.0444	0.0366
wR ₂ [I > 2 σ(I)]	0.0729	0.1141	0.0621
Largest difference peak/hole (e/Å ³)	0.312 and -0.249	0.786 and -1.316	0.564 and -0.409
Observed data [I > 2.0 σ(I)]	8808	5909	6500

Download English Version:

<https://daneshyari.com/en/article/1306375>

Download Persian Version:

<https://daneshyari.com/article/1306375>

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