Journal of Organometallic Chemistry 802 (2016) 39–48

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

(Ferrocenylpyrazolyl)palladium(II) complexes: Syntheses, characterization and rearrangement in solution

Collins Obuah, James Darkwa*

Department of Chemistry, University of Johannesburg, Auckland Park Kingsway Campus, Auckland Park 2006, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form
22 October 2015
Accepted 3 November 2015
Available online 17 November 2015

Keywords:
Ferrocenylprazolyl
Palladium complexes
Ethylene
Carbon monoxide
Copolymerization

ABSTRACT

Reactions of **L1**-**L6** (3-ferrocenylpyrazolyle (**L1**), 3-ferrocenyl-5-methylpyrazolyle (**L2**) 3-ferrocenylpyrazolyl-methylenepyridine (**L3**) and 3-ferrocenyl-5-methylpyrazolylmethylene-pyridine (**L4**), 3-ferrocenylpyrazolylethylamine (**L5**) and 3-ferrocenyl-5-methylpyrazolylethyl-amine (**L6**)) with [PdCl(Me) (cod)] formed the mononuclear complexes [PdCl(Me) (κ^1-**L1**)$_2$] (**1**), [PdCl(Me) (κ^1-**L2**)$_2$] (**2**), [PdCl(Me) (κ^2-**L3**)] (**3**), [PdCl(Me) (κ^2-**L4**)] (**4**), [PdCl(Me) (κ^2-**L5**)] (**5**) and [PdCl(Me) (κ^2-**L6**)] (**6**). Reactions of **1**–**6** with the halide abstractor, Na[BAr$_4$], (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$), led to the formation of the salts, [PdMe(NCMe) (κ^1-**L1**)$_2$][BAr$_4$] (**7**), [PdMe(NCMe) (κ^1-**L2**)$_2$][BAr$_4$] (**8**), [PdMe(NCMe) (κ^2-**L3**)][BAr$_4$] (**9**), [PdMe(NCMe) (κ^2-**L4**)][BAr$_4$] (**10**), [PdMe(NCMe) (κ^2-**L5**)][BAr$_4$] (**11**), [PdMe(NCMe) (κ^2-**L6**)][BAr$_4$] (**12**) respectively. However, when **3** or **4** was reacted with of Na[BAr$_4$] and a slight excess of methyl acrylate, the products were surprisingly the bis(ligand)palladium complexes [Pd(κ^2-**L3**)$_2$][BAr$_4$]$_2$ (**13**) and [Pd(κ^2-**L4**)$_2$][BAr$_4$]$_2$ (**14**) instead of the expected acylpalladium chelate complexes ([(κ^2-**L**)Pd{(CH$_2$)$_2$C(O)OMe}][BAr$_4$]).

Complexes **1**–**6**, activated with Na[BAr$_4$], and pre-activated complexes **7**–**12** at 10 bar of ethylene and 30 bar of carbon monoxide produced polyketones, albeit with low activity (*ca.* 1.00 g.mmol^{-1}Pd.h^{-1}); with the active catalysts rearranging to mainly bis(pyrazolyl)palladium complexes similar to **13** and **14**.

1. Introduction

Nitrogen-donor palladium complexes have been used extensively in catalysis partly due to their electrophilic metal centres which enable them to form relatively strong Pd–H and Pd–C bonds. Palladium also allows easy access to 0 and + 2 oxidation states in which the palladium centre initiate reactions, such as oxidative-addition, transmetallation and reductive-elimination processes [1].

Since the seminal work by Brookhart and co-workers [2], nitrogen-donor palladium complexes as catalysts have received considerable attention because these catalysts are very active in the production of polyolefins and are tolerant to polar monomers. In particular the use of α-diimine ligands to prepare nickel and palladium catalysts have dominated this area of research [3]. One unique advantage of α-diimine ligands is their ability to form air and heat stable cationic chelating acylpalladium complexes when (α-diimine)palladium chloromethyl complexes are reacted with methylacrylate and NaBAr$_4$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) [4]. This reaction produces the cationic species, [(N^N)Pd{(CH$_2$)$_2$C(O)OMe}]$^+$, which is essentially the active catalysts when these chelating acylpalladium complexes are used in the polymerisation of ethylene [5]. In this form the oxophilicity of the palladium centre is reduced; enabling such cationic species to catalyse the copolymerisation of ethylene with a variety of polar-functional olefins.

Despite the attributes of (α-diimine)acylpalladium cationic species narrated above, there are instances where these cationic species decompose even under mild conditions *via* pathways that are not completely understood; leading to the formation of palladium black [6]. Brookhart and co-workers have suggested that increasing the steric bulk of the α-diimine ligand in the (α-diimine) acylpalladium cationic species could enhance their stability. This had led to several modifications of the α-diimine ligand, especially the aniline part of the ligand and such modifications have also improved the catalytic activity of (α-diimine)palladium complexes as ethylene polymerization catalysts significantly [7].

Despite the attributes of (α-diimine)acylpalladium cationic species narrated above, there are instances where these cationic species decompose even under mild conditions *via* pathways that

* Corresponding author.
E-mail address: jdarkwa@uj.ac.za (J. Darkwa).

http://dx.doi.org/10.1016/j.jorganchem.2015.11.003
0022-328X/

are not completely understood; leading to the formation of palladium black [6]. Brookhart and co-workers have suggested that increasing the steric bulk of the α-diimine ligand in the (α-diimine) acylpalladium cationic species could enhance their stability. This has led to several modifications of the α-diimine ligand, especially the aniline part of the ligand and resulting also in improved catalytic activity of (α-diimine) palladium complexes as ethylene polymerization catalysts significantly [7].

Following the success of α-diimine ligands in producing good and relatively stable palladium ethylene oligomerisation and polymerization catalysts, other bidentate nitrogen-donor palladium catalysts with ligands, such as 1,4-diazabutadiene, 2,2′-dipyridyl and 1,10-phenanthroline, have been investigated as catalysts for ethylene reactions [8]. Similar to (α-diimine)palladium catalysts, catalytic activity of these nitrogen-donor palladium complexes are influenced by the electronic property and steric bulk of the nitrogen-donor ligands. So a good balance between these two factors is crucial in producing an active and stable catalyst.

We have used ferrocenyl units to provide steric bulk in a mix of pyridine and pyrazole or amine and pyrazole to prepare a series of (ferrocenylpyrazolylmethylenepyridine)palladium or (ferrocenylpyrazolylethylamine)palladium chlorormethyl complexes and attempted to use these palladium complexes to produce (pyrazolyl) acylpalladium cation species (complex A, Fig. 1) similar to the cationic species reported by Brookhart and co-workers (Fig. 1). Although we were able to prepare acylpalladium cations with our ligands, these acylpalladium complexes were not very stable. In this report we provide some valuable insights into the decomposition that these acylpalladium cations undergo.

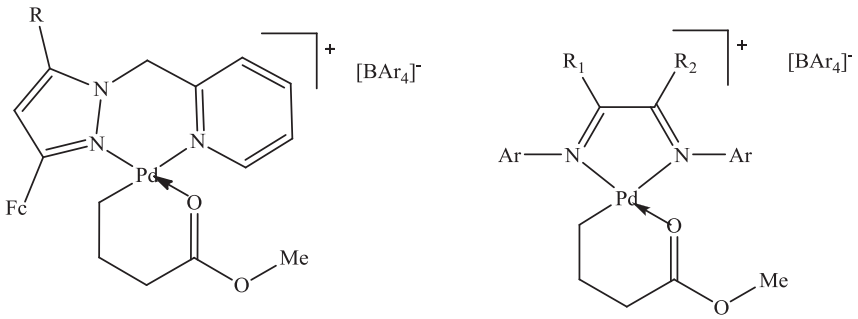
2. Results and discussions

2.1. Syntheses and characterisation of palladium complexes 1–14

The syntheses of compounds **L1**–**L6** were performed as reported in the literature [9–11]. The reaction of **L1** and **L2** with [PdClMe(cod)] were carried out in a 2:1 ratio; whilst the reactions of **L3**–**L6** were in a 1:1 ratio to produce complexes **1**–**6** (Scheme 1). All the palladium complexes were isolated as air stable orange (**1** and **2**) or yellow (**3**–**6**) solids. On reacting **1**–**6** with Na[BAr_4] in the presence of acetonitrile in a 1:1 mol ratio, complexes **7**–**12** could be isolated as foamy or crispy orange solids (Scheme 2). However, on reacting **3** or **4** with Na[BAr_4] and a slight excess of methylacrylate, intended to produce the acylpalladium cationic compound **A** in Fig. 1, we instead isolated the [bis(3-ferrocenylpyrazolyl-methylenepyridine)palladium][BAr_4] (**13**) and [bis(3-ferrocenyl-5-methyl-pyrazolyl-methylenepyridine)palladium][BAr_4] (**14**) salts in Scheme 3.

All new palladium complexes (**1**–**14**) were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analyses; and in selected cases by single crystal X-ray crystallography. The ^{1}H NMR spectra of **1**–**6** showed characteristics of their corresponding ligands but with downfield shifts. Whereas the ^{1}H NMR spectra of complexes **3**–**6** showed the presence of two structural isomers for each of these compounds, the ^{1}H NMR spectra of **1** and **2** did not show features that would indicate the presence of isomers (Fig. S1). For example ^{1}H NMR spectrum of complex **4** (Fig. S2) shows peaks for the isomer as four set of peaks in the 7.00–9.30 ppm region for the four pyridinyl protons. In addition the at 6.21 ppm is assigned to the pyrazolyl proton, the peaks at 4.40 ppm and 4.37 ppm are the protons on the substituted cyclopentadienyl ring of the ferrocenyl group and the peak at 4.04 ppm is assigned to the unsubstituted cyclopentadienyl of the ferrocenyl group. Lastly, methyl protons on the pyrazolyl unit and the methyl group bonded to the palladium appear in the spectrum at 2.52 ppm and 0.61 ppm respectively. These peaks indicate the presence of a major product while lower intensity peaks in the spectrum are indicative of the presence of a minor product.

Further evidence of the presence of isomers of **4** could be found in the low temperature ^{1}H NMR spectrum of **4** (Fig. S2) at −50 °C where the linker protons are observed. However, these protons were not seen when the spectrum was run at room temperature. We have recently observed linker protons in a low temperature spectrum for [{2,(3,5-ditert-butylpyrazol-1-yl)ethyl}pyridine-2ylmethyleneiminemethylpalldium][BAr_4] [12]. The spectrum of **4** has two sets of doublets at 5.18 and 6.05 ppm and 5.42 and 5.90 ppm, for the two sets of CH_2 linkers in each isomer. We label these two isomers as **4a** and **4b**; and based on the electron-donor ability of the ferrocenyl moiety in the ligand, assign the more abundant isomer as **4a**. This is the isomer that crystallised and whose solid state structure was determined by crystallography (Fig. 2). We recently reported the synthesis and characterisation of these ligands, including the crystal structures of **L3** and **L4** [9,10] that support our assignment of **4** exhibiting structural isomers with **4a** as the major isomer. Indeed the structure of **4a** in this report was found to be that proposed in Scheme 1. Furthermore, both isomers would have the chloro ligand bonded to the palladium *trans* to the pyridyl nitrogen as observed in a report on the structure of [(pyrazolylpyridyl)chloromethylpalladium] [13], where the chloro group is *trans* to the pyridyl nitrogen. It is worth noting that two other isomers for complexes **3**–**12** are possible; namely the geometrical isomer where the chloro ligand for **3**–**6** or the NCMe ligand for **7**–**12** bonded to palladium is either *trans* to the pyridinyl nitrogen or *trans* to the pyrazolyl nitrogen. We do not see evidence of such isomers from the NMR spectra of these complexes.



Complex A

Brookhart complex

Fig. 1. Acylpalladium chelate compounds.