Inorganica Chimica Acta 442 (2016) 24–29

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Synthesis, properties and group 10 metal complexes of a bis(dipyridylphosphinomethyl)phenyl pincer ligand

Teresa F. Vaughan, John L. Spencer *

School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

ARTICLE INFO

Article history:
Received 6 September 2015
Received in revised form 16 November 2015
Accepted 17 November 2015
Available online 2 December 2015

Keywords:
Pyridylphosphine
Pincer
Phosphine selenide
Platinum(II) complexes
Palladium(II) complexes

ABSTRACT

The synthesis, properties and coordination behaviour of the bis(dipyridylphosphinomethyl)phenyl pincer ligand 1,3-$C_6H_4(CH_2PPy_2)_2$ (Py = 2-pyridyl) are reported. The basicity of the phosphorus atoms in the ligand is explored through the synthesis of the phosphine selenide and a protonation study. The $^1J_{PSe}$ value of 742 Hz indicates that this ligand is less basic than PPh_3 and the protonation study confirms the nitrogen atoms are more basic than the phosphorus atoms. Protonation of the ligand also renders it water-soluble. The ligand reacts with [PtXY(hex)] (X = Y = Me; X = Cl Y = Me, hex = hexa-1,5-diene) at 50 °C to give pincer [PtX(PCP)] complexes (X = Me, Cl). In contrast, when reaction with [PtXY(hex)] (X = Y = Me, Cl; X = Cl Y = Me) occurs at ambient temperature, dimeric complexes of the type [PtXY(μ-PP)]$_2$ are observed in the NMR spectra. The presence of a methyl ligand appears to facilitate metalation: when there is no methyl ligand present formation of the platinum pincer complex does not occur even after prolonged thermolysis. However, reaction with [$PdCl_2(MeCN)_2$] proceeds readily at 50 °C from the dimer to the [PdCl(PCP)] complex.

1. Introduction

Polydentate ligands containing phosphorus and nitrogen donor atoms continue to attract attention due to their diverse coordination chemistry. One of the important features of *P,N* ligands is their ability to stabilise metals in a range of oxidation states and geometries. The phosphorus donor is considered to be a soft Lewis base and can stabilise soft Lewis acids, such as metal centres in low oxidation states. In contrast, nitrogen donors are hard ligands and therefore are better ligands for hard metal centres like those high oxidation states [1]. Thus this hard/soft combination can lead to selective binding to metal ions of different types [2] and the potential for hemilability [3].

Tertiary phosphines with pyridyl substituents (pyridylphosphines) are among the most widely studied *P,N* ligands and are attractive ligands for coordination chemistry [4–6]. They have been important in the development of water-soluble catalysts [7] and their silver(I) and gold(I) complexes have proven useful in inorganic medicinal chemistry [8]. While pyridylphosphines of the type $PPh_{3-n}Py_n$ have been extensively studied, pyridyl*di*phosphines have received far less attention [4–6]. There are two distinct types of pyridyldiphosphines: those with the pyridyl ring as part of the ligand backbone, such as type I in Fig. 1, and those with pyridyl rings as substituents on the phosphorus atoms, type II.

While type I ligands have been found to act as pincer ligands forming complexes that are catalytically active in a range of reactions [9,10], ligands of type II have received far less attention. In particular pincer type ligands with pyridyl substituents on the phosphorus donor atoms have not been reported.

Pincer ligands refer to tridentate chelating ligands which usually coordinate to metal centres in a meridional fashion. There has been a large variety of structures reported. Pincer ligands are often named based on the ligating atoms present. Thus the type I ligand in Fig. 1 would be referred to as a PNP ligand. A major reason why pincer ligands receive so much attention is due to the high catalytic activity of their complexes. For example, palladium complexes of pincer ligands have been shown to be active catalysts in a range of reactions [11]. In particular, pincer complexes have been found to be highly active catalysts for Heck and Suzuki cross-coupling reactions. One of the reasons these complexes are attractive catalysts is because they show high thermal stability. This is a consequence of the rigid tridentate coordination typically forming two five-membered rings [11].

Herein, we report the synthesis, properties and coordination chemistry, with platinum(II) and palladium(II), of the bis(dipyridylphosphinomethyl)phenyl pincer ligand 1,3-$C_6H_4(CH_2PPy_2)_2$ (**1**) (Py = 2-pyridyl).

---

* Corresponding author. Tel.: +64 4 463 5119.
E-mail address: john.spencer@vuw.ac.nz (J.L. Spencer).

http://dx.doi.org/10.1016/j.ica.2015.11.018

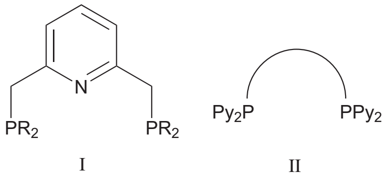


Fig. 1. Types of pyridyldiphosphines.

2. Results and discussion

2.1. Ligand synthesis and properties

The synthesis of 2-pyridylphosphines usually involves lithiation of 2-bromopyridine and subsequent reaction with a chlorophosphine. For example, tris(2-pyridyl)phosphine is synthesised *via* the reaction of 2-pyridyllithium with phosphorus trichloride and the most widely used pyridyldiphosphine, 1,2-bis(di-2-pyridylphosphino)ethane, is formed when 2-pyridyllithium is reacted with 1,2-bis(dichlorophosphino)ethane [12]. However, the disadvantage of this methodology is the use of chlorophosphine reagents which often require a complicated multi-step synthesis or, when commercially available, are expensive.

Given this, the new ligand **1** was synthesised using an adaptation of the alternative method reported by Berners-Price et al. [12]. Reaction of dibromo-*m*-xylene with two equivalents of lithium bis(2-pyridyl)phosphide, generated *in situ* from the reaction of tris(2-pyridyl)phosphine with a lithium dispersion, gave ligand **1** (Scheme 1). Ligand **1** was isolated as a pale yellow solid after the 2,2′-bipyridine formed as a byproduct in this reaction was removed *via* sublimation [13].

While the presence of the pyridyl rings in ligand **1** did not render the ligand water-soluble, when the pyridyl nitrogens were protonated through reaction with $HCl_{(aq)}$ the resulting protonated ligand was soluble in water.

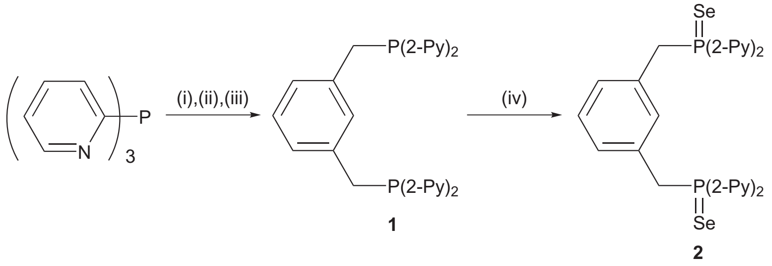
When ligand **1** was reacted with 1–6 equivalents of the strong acid $H_2C(SO_2CF_3)_2$ the pyridyl nitrogen atoms were protonated before the phosphorus atoms in **1**. In the ^{31}P NMR spectra of the reactions of compound **1** with one to four equivalents of acid the signal of the product appeared between −24.5 and −22.5 ppm. Usually when a phosphorus atom is protonated to form a phosphonium ion the signal in the ^{31}P NMR spectrum shifts downfield [14–17]. However, the shift observed in these reactions was in the opposite direction, which suggests that the proton was not bound to the phosphorus but rather to the nitrogen atoms. Infrared spectroscopy (IR) was used to confirm that the protons were bound to the nitrogens in these reactions. In the IR spectra, recorded of the products of the reactions of one and four equivalents of $H_2C(SO_2CF_3)_2$ with **1**, N–H stretches were observed at 3081 and 3100 cm^{-1} and the ν(C=N) stretching vibration had shifted to 1607 cm^{-1} compared to 1580 cm^{-1} in the free ligand. A shift of 10–30 cm^{-1} of the ν(C=N) stretching vibration to higher frequencies has been reported to be indicative of protonation of the nitrogen in a pyridyl ring [18] or coordination of a metal to the nitrogen atom [2,19]. Thus the shift of the C=N stretch could be concluded to indicate that the proton was bound to the nitrogen. In the reaction with six equivalents of acid N–H stretches and C=N stretches consistent with the nitrogen atoms being protonated were observed at 3100 and 1606 cm^{-1} as well as P–H stretches at 2361 and 2363 cm^{-1} in the IR spectrum. This confirmed that reaction with six equivalents of $H_2C(SO_2CF_3)_2$ protonated all of the nitrogen and phosphorus atoms in ligand **1**.

This reactivity meant that the proton basicity of the phosphorus in **1** could not be investigated through direct titration. Instead, the basicity of the phosphine was explored indirectly through the synthesis of a phosphine selenide. The measurement of $^1J_{PSe}$ has been found to be a reliable method to probe the basicity of a phosphine and is particularly useful for determining the basicity of heteroatom-containing phosphines for which direct titration is not possible [20,21]. It has been established that the larger the value of $^1J_{PSe}$ the greater the ‘s’ character of the phosphorus lone pair, meaning that phosphines with electron-withdrawing substituents will have larger $^1J_{PSe}$ values than electron-rich phosphines [22]. For example the phosphine selenides of PMe_3 and PPh_3 have $^1J_{PSe}$ values of 684 and 732 Hz respectively [22,23]. The reaction between ligand **1** and excess elemental selenium was complete after refluxing overnight in chloroform. The ^{31}P NMR spectrum of the phosphine selenide product **2** (Scheme 1) showed a singlet at 34.0 ppm with a $^1J_{PSe}$ value of 742 Hz. Given this it was concluded that ligand **1** was slightly less basic than PPh_3 and that 2-pyridyl substituents are more electron withdrawing than phenyl groups.

2.2. Platinum(II) and palladium(II) complexes

The reaction of ligand **1** with dimethyl(hexa-1,5-diene)platinum at 50 °C for 16 h led to the formation of the [PtMe(PCP)] complex **3** (Scheme 2). The ^{31}P NMR spectrum of complex **3** consisted of a singlet at 38.3 ppm with platinum-195 satellites, $^1J_{PtP} = 2969$ Hz. In the ^{1}H NMR spectrum of **3** the signal for the methylene protons appeared as a virtual triplet at 4.46 ppm ($^2J_{PH} + {}^4J_{PH} = 5.9$ Hz). This triplet is characteristic of complexes of this type with strong phosphorus–phosphorus coupling between *trans* phosphorus donor atoms that are magnetically equivalent [24]. This was consistent with the NMR data of the analogous diphenylphosphino pincer complex [25]. The signal for the methyl ligand in the ^{1}H NMR spectrum appeared as a singlet at 0.48 ppm with ^{195}Pt satellites, $^2J_{PtH} = 75$ Hz.

When ligand **1** was reacted with chloromethyl(hexa-1,5-diene)platinum under the same conditions as above, the [PtCl(PCP)] complex **4** was formed (Scheme 2). The signal in the ^{31}P NMR spectrum of **4** was very similar to that of **3**, appearing as a singlet at 38.0 ppm with $^1J_{PtP} = 2916$ Hz. As the pincer core is the same for complexes **3** and **4** the difference in the $^1J_{PtP}$ values is due to the difference in *cis* influence of the methyl and chloride ligands. As



Scheme 1. Synthesis of ligand **1** and phosphine selenide **2**. *Reagents and conditions:* (i) Li, THF, −78 °C → rt, 40 min; (ii) NH_4Cl, −78 °C → rt, 30 min; (iii) dibromo-*m*-xylene, THF, −78 °C → rt, 30 min; (iv) excess Se, $CHCl_3$, reflux, overnight.