

Chemistry of palladium(II) with *bis*(3-amidopyridine) ligands

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ARTICLE INFO

Article history:

Received 5 January 2016
 Received in revised form 10 February 2016
 Accepted 11 February 2016
 Available online 15 February 2016

Keywords:

Palladium
 Bis(amidopyridine)
 Macrocyclic
 Lantern

ABSTRACT

The coordination chemistry of palladium(II) with *bis*(3-amidopyridine) ligands [LL = 2,6-C₅H₃N(CONH-3-C₅H₄N)₂, **1**; 1,3-C₆H₄(CONH-3-C₅H₄N)₂, **2**; 1,3-C₆H₄(CONMe-3-C₅H₄N)₂, **3**; 2,5-C₄H₂S(CONMe-3-C₅H₄N)₂, **4**] has been investigated. Neutral binuclear macrocyclic complexes *trans,trans*-[Pd₂X₄(μ-LL)₂] have been characterized with X = Cl or Br and LL = **1**. Cationic complexes have been characterized as mononuclear *bis*(chelate) derivatives [Pd(LL)₂]²⁺, when LL = **3** or **4**, but a lantern complex [Pd₂(μ-LL)₄]⁴⁺, when LL = **2**. The tendency for chelation versus bridging coordination of the flexible ligands **1–4** is analyzed in terms of substituent effects on the preferred ligand conformations. In the dipalladium complexes, the macrocyclic or lantern structure can accommodate guest molecules.

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1. Introduction

The *bis*(3-amidopyridine) ligands of general formula E(CONRC₅H₄N)₂, where E may be a phenylene or other bifunctional group and R may be hydrogen or alkyl, are proving to be particularly useful for the self-assembly of macrocyclic and polymeric coordination compounds [1–50]. The ligands often have a preferred conformation, which depends on both E and R, but they are sufficiently flexible that they can form chelates, macrocycles or polymers by switching between conformers by rotation about E–C and/or C–N bonds. The versatility is illustrated in Scheme 1 by the N-methyl ligand C₄H₂S(CONMe-4-C₅H₄N)₂, **A**, and some of its complexes **B–E** [47,49,50]. It is convenient to define the ligand conformation according to whether each O=C–N–R group is *cis* (**c**) or *trans* (**t**) and then whether each O=C–C–S group is *syn* (**s**) or *anti* (**a**). For this ligand, the most stable conformation is **A-cc-aa**, in which both amide groups are in the *cis-anti* conformation, which tends to form chelate complexes or macrocycles with a short transannular distance, such as **B** in Scheme 1. However, the ligand, in its easily accessible conformations **A-cc-ss**, **A-ct-sa** and **A-tt-ss** can form macrocycles with *trans* stereochemistry and with a longer transannular distance (**C**), macrocycles with *cis* stereochemistry at each metal center (**D**) or polymers (**E**), respectively (Scheme 1) [47,49,50].

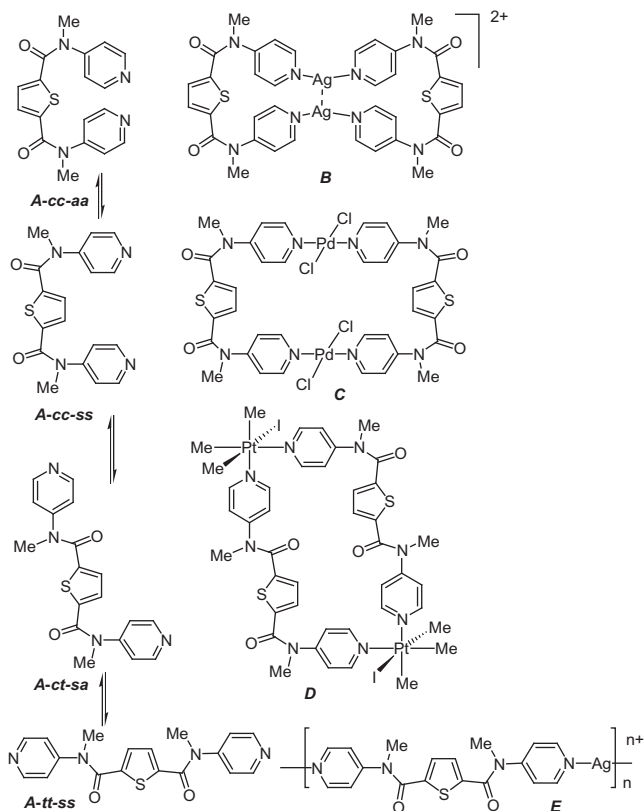
When R = H in the ligands E(CONHC₅H₄N)₂, the **tt** conformation of the amide groups is usually observed, and the primary coordination compounds can undergo further self-assembly by intermolecular NH⋯O=C hydrogen bonding, or they may act as

hosts by hydrogen bonding of the NH groups to nucleophiles or by coordination of the carbonyl groups to electrophiles [1–39]. If E = aryl, there seems to be little difference between the **s** and **a** conformers and all three forms of ligands of type **F** with **tt-aa**, **tt-sa** and **tt-ss** conformations may be found in complexes (Scheme 2) [1–16,35–38]. The ligand conformation can easily change to accommodate a variety of guests and, for this reason, the macrocyclic or lantern complexes have been termed amphitopic receptors [36]. For example, the macrocyclic complex **G** has one NH and three C=O groups directed inwards as needed to optimize binding to an N,N-dimethylformamide guest, while the lantern complex **H** has four NH and four C=O groups directed into the cavity and it can bind salts, with the anions binding to the NH groups (and also to the electrophilic Pd²⁺ centers) and with the cations binding to the carbonyl groups (Scheme 2) [35,36].

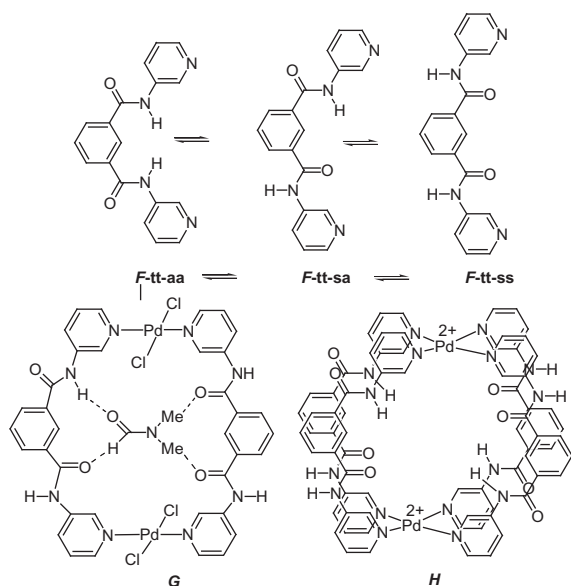
This paper reports a study of the complexes of palladium(II) with the 3-pyridyl ligands **1–4** shown in Chart 1. The ligands **1** and **2** are similar, each having NH amido substituents, but **1** [1–16] is expected to have a much stronger preference than **2** [17–34] for the **tt-aa** conformation shown in Chart 1, because of the presence of weak intramolecular NH⋯N attractions, which could be considered as weak hydrogen bonds or as dipole–dipole attractions, compared to repulsive C=O⋯N interactions in the alternative **tt-ss** conformation. Some related chemistry of these ligands with palladium(II) is known [18,35,36]. The related N-methyl ligands **3** and **4** have not been studied previously and it was of interest to compare their chemistry to both the NH analogues (Scheme 2) and the 4-pyridyl analogues (Scheme 1). The ligands **3** and **4** are expected to be most stable as the **cc-aa** conformers in Chart 1 [48,49].

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Scheme 1. Equilibria between conformers of the free ligand **A** and the structures of some of its complexes.



Scheme 2. Conformations of **F** in the free ligand and in complexes **G** and **H**.

2. Results and discussion

2.1. The synthesis and structures of the complexes

The reaction of $[\text{PdX}_2(\text{NCPH})_2]$, $\text{X} = \text{Cl}$ or Br , with the ligand **1** in a 1:1 mol ratio gave the corresponding crystalline binuclear

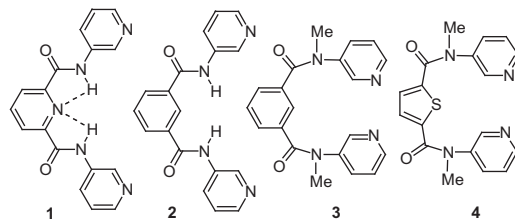
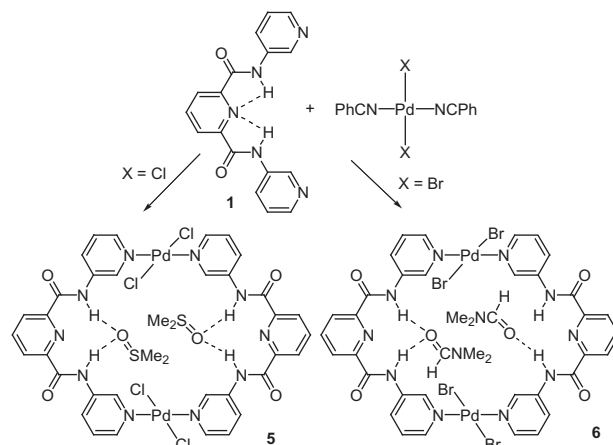


Chart 1. The bis(3-pyridyl) ligands **1–4**. The conformation shown for **1** and **2** is described as **tt-aa** while that shown for **3** and **4** is described as **cc-aa**.

complexes $[\text{Pd}_2\text{X}_4(\mu\text{-1})_2]$, **5** and **6**, with bridging bis(pyridine) ligands and not the corresponding chelate complexes (Scheme 3). The corresponding reactions with ligand **2** have been reported earlier (Scheme 2) [35] while the ligands **3** and **4** did not yield crystalline products.

The complexes **5** and **6** are sparingly soluble and could only be crystallized from solvent mixtures containing dimethylsulfoxide or *N,N*-dimethylformamide. The structures of the solvates **5** 3DMSO, MeCN and **6** 1.5DMF.2CH₂Cl₂ were determined and are shown in Fig. 2. Each has the *trans,trans* stereochemistry at the palladium (II) centers and the **tt-aa** conformation at the amide groups. As predicted, the amide units are roughly co-planar with the central C₅H₃N unit (Table 1) in order to maximize the intramolecular NH···N hydrogen bonding [16,38]. This ligand geometry leads to a large cavity in the macrocyclic structures, with the transannular distance between the two palladium atoms greater than 7 Å in each case. In complex **5** there are two DMSO molecules partly inside the cavity, hydrogen bonded weakly to the NH protons, with another DMSO molecule on the opposite side (not shown) and an acetonitrile molecule near the center of the cavity (Fig. 1a). In complex **6** there is a DMF molecule in the cavity, weakly hydrogen bonded to a pair of NH protons, and there is a disorder between a DMF molecule and a dichloromethane molecule (not shown) on the opposite side (Fig. 1b). These complexes of ligand **1** are relatively rigid receptors and the ligands do not adapt to give maximum binding to a guest molecule, in comparison to the corresponding amphitopic receptor **G** (Scheme 2) formed by the similar ligand **2** [35,36]. The ring cavities in these complexes are large enough to allow catenation, and it is possible that catenanes are present in the complexes isolated from solvents which do not hydrogen bond [39]. Solvents like DMSO are known to disfavor catenation in similar systems because the NH···O = SMe₂ hydrogen bonding present in **5** (Fig. 2a) competes with the NH···ClPd



Scheme 3. The formation of complexes **5** and **6** (the potential weak pyridyl N···H hydrogen bond or dipole-dipole attraction is shown for **1** but not for **5** and **6**).

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