Journal of Organometallic Chemistry 803 (2016) 45–50

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Dimerization of an organoplatinum complex triggered by oxidative addition: A model for dynamic ring-opening polymerization

Nancy L.S. Yue, Michael C. Jennings, Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form
5 December 2015
Accepted 11 December 2015
Available online 15 December 2015

Keywords:
Monomer-dimer ring expansion
D-ROP
Oxidative addition
Organoplatinum chemistry

ABSTRACT

The bis(pyridine) ligand thiophene-2,5-dicarboxylic acid bis(N-methyl-N-4-pyridyl-amide), **1**, reacts with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, with displacement of Me_2S, to give the chelate complex $[PtMe_2(\mathbf{1})]$, **2**, which then reacts with methyl iodide to give $[PtIMe_3(\mathbf{1})]$, **3**. Complex **3** spontaneously dimerizes to give a macrocyclic complex $[\{PtIMe_3(\mu\text{-}\mathbf{1})\}_2]$, **4**, which exists as a mixture of *anti* and *syn* isomers **4a** and **4b**, as characterized by both NMR spectroscopy and X-ray structure determination. In the complex **4***, formed by oxidative addition of CD_3I, the CH_3 and CD_3 ligands are scrambled between the axial and equatorial coordination sites at platinum(IV). The dimerization can be considered as a model for the first step in a dynamic ring-opening polymerization and occurs to give a new conformation of the flexible ligand.

1. Introduction

Dynamic ring opening polymerization (D-ROP) is often used to make macrocycles, catenanes or coordination polymers by self-assembly [1–7]. In brief, a solution containing a metal salt (MX) and a flexible bifunctional ligand (LL) may contain mixtures of complexes in the form of a chelate [MX(LL)], expanded neutral or ionic macrocycles or catenanes $[\{MX(\mu\text{-}LL)\}_n]$ or $[\{M(\mu\text{-}LL)\}_n]X_n$, and neutral or ionic linear oligomers $[XM\text{-}\{(\mu\text{-}LL)MX\}_n]$ or $[XM\text{-}\{(\mu\text{-}LL)M\}_n\text{-}X]X_n$. Any of these may crystallize from the solution, but coordination polymers may also crystallize selectively [1–11]. Sometimes, more than one form may co-crystallize, for example to give crystals contain both ring and polymer forms [8,9,12–14]. As the synthetic utility of this method has become generally recognized, the range of metal salts and ligands has been greatly expanded and it has been found that the successful crystallization of a polymer may depend on subtle features, such as the nature of the anion X^- [1]. The mechanisms of polymer formation have also been elucidated in some cases [8,9,15]. Routes to stereoregular coordination polymers and to two- and three-dimensional molecular materials have also been developed [1–6,16]. We use the acronym D-ROP to distinguish from classical ring opening polymerization (ROP), which is typically not easily reversible and usually requires a catalyst or forcing conditions [17]. In D-ROP, the crystalline material dissolves to give back the dynamic mixture of lower molecular weight complexes from which it was formed.

In previous papers, we have studied complexes of the ligand thiophene-2,5-dicarboxylic acid bis(N-methyl-N-4-pyridyl-amide), **1** (Chart 1), with silver(I) and palladium(II) [18,19]. Ligand **1** is flexible and can form conformers by rotation about the (thiophene) C–CO bond and the MeN–CO bond, and we will define the conformer according to whether the MeN–CO groups are mutually *cis* (*c*) or *trans* (*t*) and whether the SC-CO groups are *syn* (*s*) or *anti* (*a*), though it should be recognized that many conformers with different degrees of distortion from the most symmetrical planar structures are possible. The most stable conformer is expected to be **1**-*cc*-*aa* (Chart 1), in which both MeN–CO groups are mutually *cis* and both SC-CO groups are mutually *anti* [18–21]. Distorted forms of this conformer are present in the *bis*(chelate) palladium(II) complex ***A*** and the macrocyclic disilver(I) complex ***B***, which contains a metallophilic Ag..Ag bond and so can accommodate the relatively short intraligand NN distance associated with the conformer **1**-*cc*-*aa* (Chart 1). Rotation about the SC-CO bonds can give conformer **1**-*cc*-*ss*, in which the pyridyl donors are roughly parallel to each other, and this conformer is present in the protonated ligand ***C*** and in the macrocyclic palladium(II) complex ***D*** (Chart 1). Further rotation about the MeN–CO bonds can give conformer **1**-*tt*-*ss*, in which the pyridyl donors are roughly antiparallel to each other, and this conformer is present in the polymeric complex ***E***. Complexes ***B*** and ***E*** are isomers related by the D-

* Corresponding author.
E-mail address: pudd@uwo.ca (R.J. Puddephatt).

http://dx.doi.org/10.1016/j.jorganchem.2015.12.020
0022-328X/

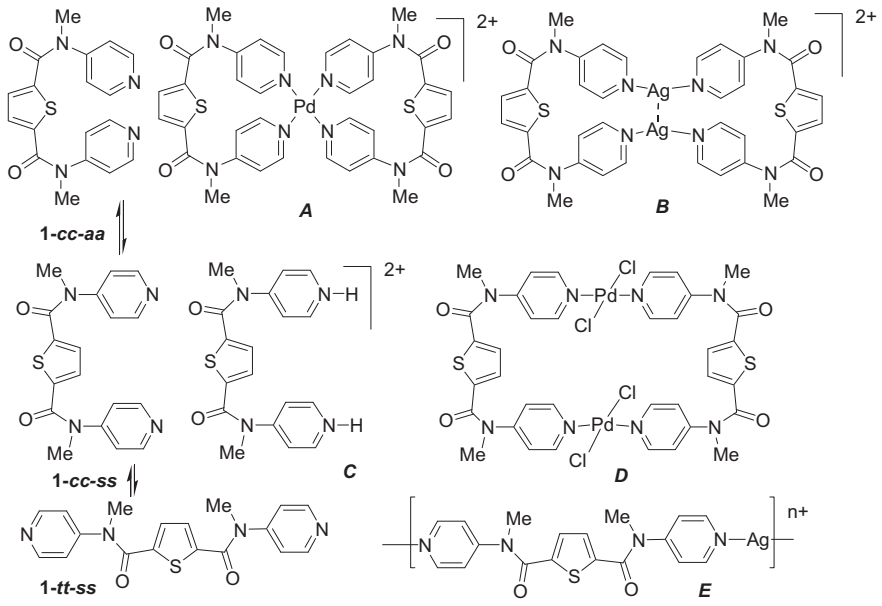


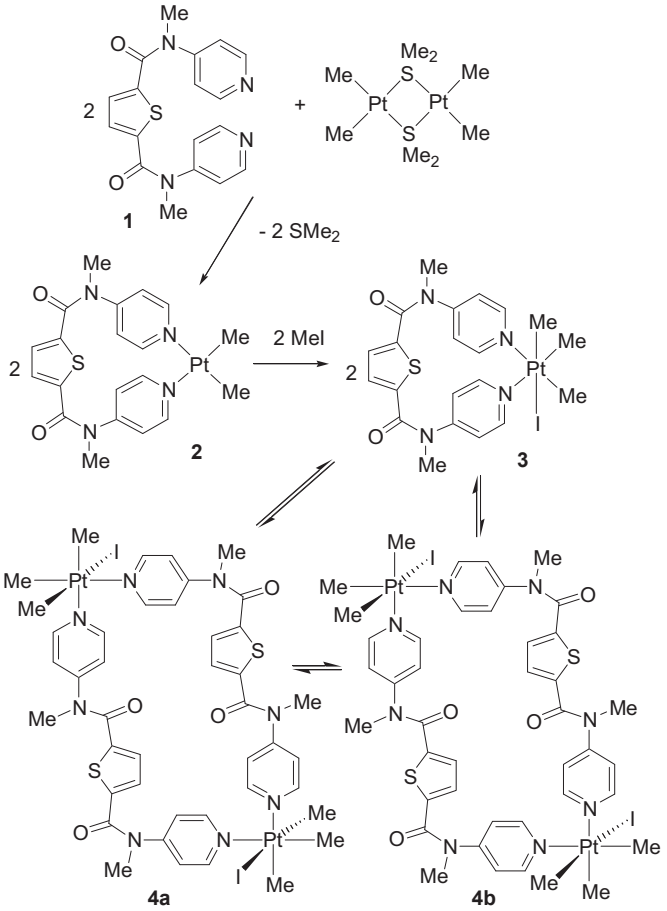
Chart 1. Conformations of ligand **1** and some known complexes of this ligand.

ROP process, and the crystalline form is anion dependent [18]. This paper will report some chemistry of ligand **1** with platinum, and illustrate how oxidative addition to platinum(II) can trigger a ring expansion reaction.

2. Results and discussion

The new chemistry is summarized in Scheme 1. The reaction of ligand **1** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in acetone solution occurred, with displacement of Me_2S, to give the chelate complex $[PtMe_2(\mathbf{1})]$, **2**, which formed as a yellow precipitate. Complex **2** was sparingly soluble in acetone. It was more soluble in dichloromethane or chloroform, but it reacted slowly with these solvents to give complex mixtures, probably by initial oxidative addition of a C—Cl bond [22,23]. Complex **2** was characterized in the ^{1}H NMR spectrum by a single methylplatinum resonance at δ 0.72, with coupling constant ^2J(PtH) = 88 Hz, typical of a dimethylplatinum(II) complex with *cis*-$PtMe_2N_2$ coordination [24]. The effective two-fold symmetry was also indicated by the presence of single resonances for the thiophen protons [δ(CH) = 7.65], for the *ortho* [δ(CH) = 8.74] and *meta* [δ(CH) = 6.94] protons of the pyridyl groups, and for the MeN groups [δ(Me) = 3.34]. The NMR data show the presence of only one isomer, but the evidence does not exclude the possibility of formation of an oligomeric structure, such as a dimer, trimer or tetramer with bridging ligands **1**. However, the MALDI-MS showed the major ion at m/z = 577, as expected for the monomeric dimethylplatinum(II) complex **2**.

Oxidative addition of methyl iodide to dimethylplatinum(II) complexes usually occurs easily and with *trans* stereochemistry by the S_N2 mechanism, so reaction with **2** was expected to give complex **3** [24–26]. However, the ^{1}H NMR spectrum of the product indicated that a more complex mixture was formed. Finally, single crystals were obtained and a structure determination (Fig. 1) showed the presence of the dimer **4**. The structure contains two platinum(IV) centers, each with the common *fac*-$PtMe_3IN_2$ coordination, which are related by a crystallographic inversion center. There was disorder of the mutually *trans* methyl and iodide groups with the major occupancy C(1) and I(1), shown in Fig. 1, refining to 82% and the reverse minor occupancy [C(2) and I(2), not shown in



Scheme 1. Formation of the organoplatinum complexes **2**–**4**.

Fig. 1] at 18%. In the dimer, the major component certainly has the *anti* stereochemistry of the two $PtIMe_3$ groups shown in Fig. 1. For the minor component, there are several possible interpretations,