



# One-pot synthesis of self-assembled heteroleptic palladium(II) complexes with tmeda: An application of ligand exchange reactions



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## ABSTRACT

One-pot synthesis of self-assembled heteroleptic complexes of general formula  $[Pd_x(tmeda)_x(L)_y](NO_3)_{2x}$  is achieved by combining required amount of tmeda, a chosen ligand L and  $Pd(NO_3)_2$  under suitable reaction conditions. The strategy is devised using our understanding of a special variety of ligand exchange reactions (LER) around palladium(II) centers as modeled in this work. The one-pot synthesis technique is thus considered as an application of the unique LER.

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Deployment of small building blocks to manufacture larger molecules by self-assembly method is regarded as an interesting alternative to the covalent synthesis. A variety of metal-assisted multinuclear discrete architectures are prepared by utilizing this self-assembly route [1]. Rigid square planar coordination geometry and moderately labile metal–ligand interactions in the complexes of palladium(II) make it unique from other metals in designing multinuclear discrete architectures [2]. This  $d^8$  metal ion has been used as such [3] or in its *cis*-protected form [4] where four and two coordination sites are available around the metal center, respectively. In order to produce a suitable *cis*-protected palladium(II) component, e.g. *cis*- $Pd(X-X)(monoanion)_2$ , the metal ion is combined with a bidentate chelating ligand X–X and then manipulated through a few steps. The partially blocked Pd(II) components are further complexed with chosen ligands in a classical manner to get a variety of multinuclear assemblies with the general formula  $[Pd_x(X-X)_x(L)_y](monoanion)_{2x}$ . A new method for the synthesis of  $[Pd_x(bpy)_x(L)_y](NO_3)_{2x}$  was reported by us where the self-assemblies could be prepared in a single step in one-pot [5,6] by simply combining bpy,  $Pd(NO_3)_2$  and a ligand L. This finding is in contrast with the multistep classical synthesis where we need to prepare the partially blocked palladium(II) unit *i.e.* *cis*- $[Pd(bpy)(NO_3)_2]$  and then combine it with the chosen ligand. The success of our one-pot synthesis can be attributed to the thermodynamic and kinetic stability of  $[Pd_x(bpy)_x(L)_y](NO_3)_{2x}$  as compared to the other possible compounds generated in the one-pot. The incorrectly formed assemblies are self-healed due to the dynamic nature of Pd(II)–N bonds. The above mentioned one-pot synthesis strategy is inspired from a special kind of ligand exchange reactions (LER) where the combination of  $[Pd(bpy)_2](NO_3)_2$  and  $[Pd_m(L)_n](NO_3)_{2m}$  resulted in

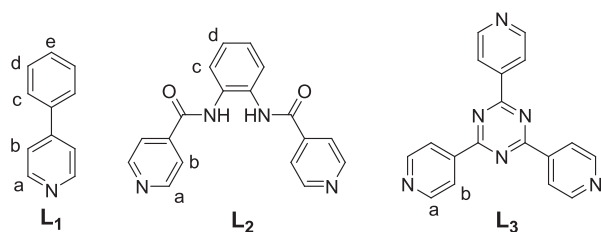
complete reorganization of the components present in a system to form  $[Pd_x(bpy)_x(L)_y](NO_3)_{2x}$  as the exclusive product [7]. Incidentally, the combination of  $[Pd(en)_2](NO_3)_2$  and  $[Pd_m(L)_n](NO_3)_{2m}$ , depending on ligand, resulted in no change or formation of a portion of  $[Pd_x(en)_x(L)_y](NO_3)_{2x}$  [8]. The synthesis of  $[Pd_x(en)_x(L)_y](NO_3)_{2x}$  by one-pot method is thus unmanageable [6].

Due to the good solubility, stability and crystalline nature of  $[Pd_x(tmeda)_x(L)_y](NO_3)_{2x}$ , the compounds of this class are in focus in recent literatures [9]. We considered to check the feasibility of the one-pot synthesis of such molecules by combining tmeda,  $Pd(NO_3)_2$  and a ligand L in one-pot. The related LER are also modeled in this work as a prerequisite before attempting the one pot synthesis. The pyridine appended ligands **L1–L3** and the corresponding tmeda based complexes **1–3** studied in this work are shown in Figs. 1 and 2. The other complexes *i.e.* **4** and **5–6** shown in Fig. 3 are used to study the LER. The combination of  $[Pd(tmeda)_2](NO_3)_2$ , **4** and  $[Pd(L1)_4](NO_3)_2$ , **5** resulted in complete sort-out of the components *via* ligand exchange reactions to give  $[Pd(tmeda)(L1)_2](NO_3)_{2x}$ , **1** as the exclusive product. Combination of tmeda,  $Pd(NO_3)_2$  and the ligand **L1** in one-pot resulted in the compound **1** in a quantitative manner. Subsequently the other tmeda based complexes *i.e.* the binuclear **2** and the hexanuclear **3** were also prepared by the one-pot strategy.

The new complex  $[Pd(tmeda)(L1)_2](NO_3)_2$ , **1** has been prepared by the combination of *cis*- $[Pd(tmeda)(NO_3)_2]$  and the monodentate ligand **L1** at 1:2 ratio under suitable reaction conditions (see in supporting information). The reported [6] complex **5** was prepared by the complexation of the ligand **L1** with Pd(II). Ligand exchange reactions around the Pd(II) centers in the complexes **1**, **4** and **5** were studied by recording their  $^1H$  NMR spectra under various conditions following a protocol [8] established by us. The compound **1** was heated at 90 °C in DMSO- $d_6$  where upon it remained intact (Eq. (1)) as concluded from the

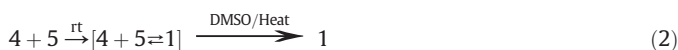
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Fig. 1. The ligands **L1** to **L3**.

observation that the  $^1\text{H}$  NMR spectra recorded at different interval of times are all same. This indicates that no ligand exchange reactions occurred in **1**. However, combination of equimolar amount of  $[\text{Pd}(\text{tmeda})_2](\text{NO}_3)_2$ , **4** and  $[\text{Pd}(\text{L1})_4](\text{NO}_3)_2$ , **5** in  $\text{DMSO-d}_6$  generated a small amount of **1** even at room temperature. The mixture was completely converted to **1** within one hour when heated at  $90^\circ\text{C}$  (Eq. (2), Table 1, Fig. 4).

The new complex  $[\text{Pd}_2(\text{tmeda})_2(\text{L2})_2](\text{NO}_3)_4$ , **2** could be prepared by the combination of *cis*- $[\text{Pd}(\text{tmeda})(\text{NO}_3)_2]$  and the bidentate ligand **L2** at 1:1 ratio. The new complex **6** having a novel and rare architecture could be prepared from the complexation of the ligand **L2** with  $\text{Pd}(\text{II})$ . Detail of the synthesis and characterization of **2** and **6** is given in supporting information. While the compound **2** remained intact when heated in  $\text{DMSO-d}_6$ , combination of **4** and **6** at 4:1 molar ratio led to the formation of **2** (Table 1, Fig. 5). The reorganization of **4** and **6** to afford the complex **2** was attained within one hour when heated at  $90^\circ\text{C}$ . In fact a small proportion of **2** could be observed at room temperature after the mixing was carried out.



The complex **3** was prepared following a reported method [10]. The complex **3** remained intact when heated in  $\text{DMSO-d}_6$ . However, no further ligand exchange reaction could be studied in this case since no single discrete structure is expected from the complexation of **L3** with  $\text{Pd}(\text{II})$ .

In view of the ligand exchange reactions described in the previous section, it was rationalized that the one-pot combination of *tmeda*,  $\text{Pd}(\text{NO}_3)_2$  and the ligand **L1** at 1:1:2 ratio in  $\text{DMSO-d}_6$  should exclusively result in the compound **1**. This proposition was found to be valid when an experiment was actually carried out in  $\text{DMSO-d}_6$ . However,  $\text{DMSO}$  is not a preferred solvent due to its high boiling nature as the isolation of the product from the reaction mixture, if required, could be cumbersome. We found a mixed solvent system of  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$  at 1:1 ratio as convenient alternative for the isolation purpose. The synthesis

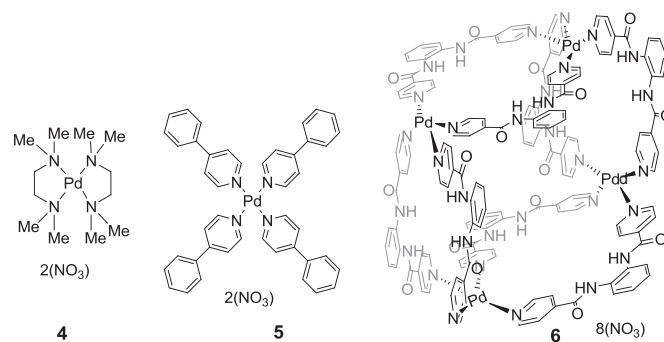
Fig. 3. The complexes **4–6**.

Table 1

Ligand exchange reactions for various complexes in  $\text{DMSO-d}_6$ .

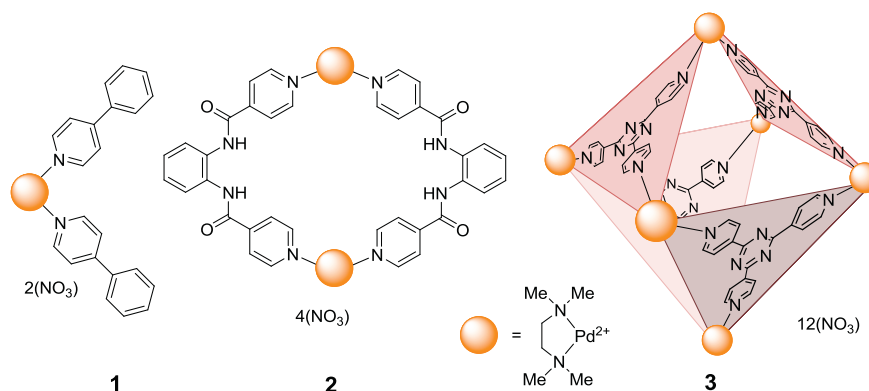
Ligand exchange reactions	Temperature ( $^\circ\text{C}$ )	Time (h)
$4 + 5 \rightarrow 1$	90	1
$4 + 6 \rightarrow 2$	90	1

of **1** was carried out under similar reaction conditions for both the classical and one-pot methods where  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  (1:1) was employed as the solvent system. This ensured appropriate comparison of the methods.

A 1:1:2 mixture of *tmeda*,  $\text{Pd}(\text{NO}_3)_2$ , and the ligand **L1** was taken in  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  (1:1). The reaction mixture was stirred at  $70^\circ\text{C}$  for 1 h and the clear solution was evaporated at room temperature. The solid so obtained from the one-pot synthesis was washed with  $\text{DCM}$ , diethyl ether and finally dried under vacuum to obtain the product as a pale yellow solid.  $^1\text{H}$  NMR spectrum of the sample recorded in  $\text{DMSO-d}_6$  suggests the formation of **1**. The  $^1\text{H}$  NMR spectrum of **1** was also recorded in  $\text{CD}_3\text{CN}:\text{D}_2\text{O}$  (1:1). ESI-MS of the complex showed peak at  $m/z = 266.00$  corresponding to  $[\text{1}-2(\text{NO}_3)]^{2+}$  further supporting the formation of complex **1**. Crystal structure of the complex **1** confirms its formation as discussed in a later section.

The one-pot reaction was also carried out in  $\text{CD}_3\text{CN}:\text{D}_2\text{O}$  (1:1) to monitor the evolution of **1**. The reaction mixture was thus followed by  $^1\text{H}$  NMR technique at regular time interval (see in supporting information). Some amount of the complex **1** was formed, upon mixing the three components, even at room temperature. Maximum conversion of the mixture to form the complex **1** was achieved within one hour when heated at  $70^\circ\text{C}$ .

The classical method of the synthesis for the targeted compound is actually a multistep process. In the first step *cis*- $[\text{Pd}(\text{tmeda})(\text{Cl})_2]$  was prepared by the reported method from  $\text{PdCl}_2$  [11]. In the next step the compound *cis*- $[\text{Pd}(\text{tmeda})(\text{NO}_3)_2]$  was prepared from *cis*- $[\text{Pd}(\text{tmeda})(\text{Cl})_2]$  by following the method used for the preparation of

Fig. 2. The complexes **1–3**.

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