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Intramolecular C−H Activation Directed Self-Assembly of an Organoplatinum(II) Molecular Square

Shu-Bin Zhao, Rui-Yao Wang, and Suning Wang*

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Received January 14, 2007; E-mail: wangs@chem.queensu.ca

Pd^{II} or Pt^{II} nanoscopic macrocycles and cages are of current interest because of their great potential in guest−host chemistry and catalysis.[1−4] The commonly used strategy for assembling Pd^{II} or Pt^{II} macrocycles or cages is the use of "linker" ligands such as polypyridines or polyphosphines via ligand substitution reactions. For example, Stang and co-workers have explored extensively the syntheses of many molecular polygons and polyhedra by using preassembled Pd^{II}/Pt^{II} acceptor units and appropriate linkers.[3] Fujita and co-workers have demonstrated the use of highly effective guest-templated self-assembly methods to achieve elegant Pd^{II}/Pt^{II} nanocages.[4] The majority of previously reported Pd^{II} or Pt^{II} molecular assemblies are ionic, but several examples of neutral Pt^{II} molecular macrocycles are known.[5]

One attractive but hardly explored approach is the use of a chelate ligand capable of undergoing chelate ring opening and the subsequent intramolecular C−H activation, hence creating a new binding site, as an internal linker for the formation of Pt^{II} macrocycles and cages. Ring opening process without C−H activation for polymerization of ferrocene derivatives has been successfully and extensively explored by Manners and co-workers.[6] The feasibility of using ring opening and C−H activation processes for assembling polymeric organoplatinum compounds was demonstrated by Young and co-workers.[7] They observed that, upon heating, the 2,2′-bipy ligand in Pt(2,2′-bipy)Ph_2 undergoes a "roll-over" C3 C−H cyclometalation, resulting in the elimination of benzene, and the successive self-assembly of insoluble Pt polymers via the freed N donor site and the Pt acceptor site.[7] However, due to the geometry of 2,2′-bipy, it is not possible to use it and the derivatives to achieve cyclic Pt(II) structures without using external linkers. Although intramolecular cyclometalation involving C−H bond activation is a fairly common phenomenon among Pd or Pt compounds,[8] using this process in a controlled manner to construct molecular macrocycles and cages has hardly been explored. We report herein a rare example of spontaneous self-assembly by a mononuclear complex Pt(NPA)$(CH_3)_2$ (**1**), NPA = *N*-(2′-pyridyl)-7-azaindole,[9] into an organoplatinum Pt_4 macrocycle Pt_4(*N,C,N*-NPA)$_4$$(CH_3)_4$ (**2**) via a roll-over cyclometalation driven self-assembly process at ambient temperature.

Complex **1** was prepared by the reaction of $[PtMe_2(\mu\text{-}SMe_2)]_2$[10] with NPA in THF at −10 °C. **1** is stable in the solid state at ambient temperature or in solution below 5 °C. It is characterized by NMR spectroscopy in CD_2Cl_2 at −20 °C. In either THF, CH_2Cl_2, or benzene solution, **1** undergoes clean transformation to produce **2** at ambient temperature, which has been fully characterized by NMR, elemental analysis, and X-ray diffraction.

As shown by the diagrams in Figure 1, **2** has a highly rigid cyclic Pt_4 structure. Through an anionic "*N,C,N*" tridentate mode, the NPA ligand exhibits a dual role both as a chelating ligand and as a bridging ligand. The four Pt subunits in **2** are related by an approximate S_4 axis. The four Pt atoms are not coplanar with a butterfly shape. The two diagonal Pt···Pt distances are 8.34 and 8.85 Å, while the four edge Pt···Pt distances are 6.14, 6.26, 6.15, and 6.25 Å. To minimize the steric interactions between neighboring py groups, the 7-azaindolyl (azain) N atom shows large distortion from linear coordination to the Pt center. The average deviation from linearity as defined by the angle between the Pt−N (azain) vector and the corresponding N···C (*para*) vector is ~30°. Accordingly, the Pt−N (azain) distances, 2.135 Å on average, are much longer than those of Pt−N (py), 2.108 Å on average. The py ring and the azain ring in each NPA ligand are out of coplanarity by a dihedral angle of ~13.5° on average. Interestingly, as shown in Figure 1, the internal cavity in **2** has a distinct tetrahedral shape, defined by the four py groups.

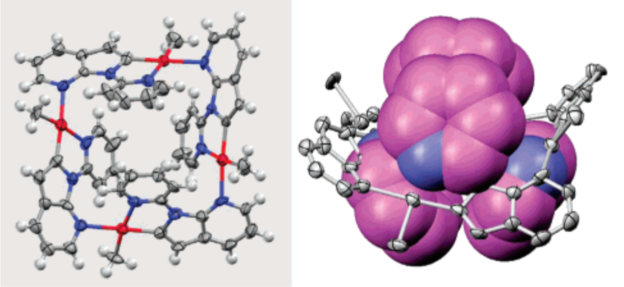

Figure 1. Left: the molecular structure of **2** with 50% ellipsoids. Right: space-filling drawing showing the internal cage formed by the four pyridyl groups.

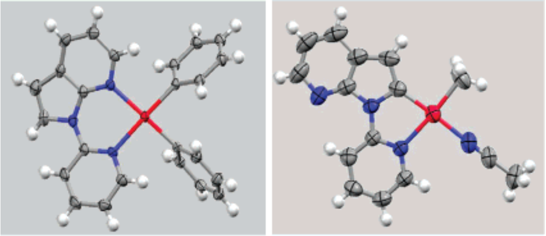

Figure 2. Left: the molecular structure of **3**. Right: the molecular structure of Pt(*N,C,N*-NPA)$(CH_3)(CH_3CN)$, **E-MeCN**. Both structures are shown with 50% thermal ellipsoids.

Our earlier investigation on Zn(NPA)$(O_2CR)_2$ complexes[9] established that the NPA ligand is a poor *N,N*-chelating ligand and has a strong tendency to dissociate from the metal center in solution due to the chelate ring strain and the interactions between the *ortho*-hydrogen atoms on the py ring and the azain ring in the complex. We believe that the same poor stability of the *N,N*-chelate mode of NPA in **1** drives the facile roll-over cyclometalation process. Indeed, the crystal structure of the analogue compound Pt(NPA)-Ph_2 (**3**) (Figure 2) shows that the py and the azain ring have a dihedral angle of 22.4° and a short separation distance of 2.02 Å between the two *ortho*-hydrogen atoms, much less than the sum of van der Waals radii (2.40 Å).[11] In addition, the formation of a non-strained five-membered *N,C*-chelate ring in the product may also facilitate the **1** to **2** transformation.

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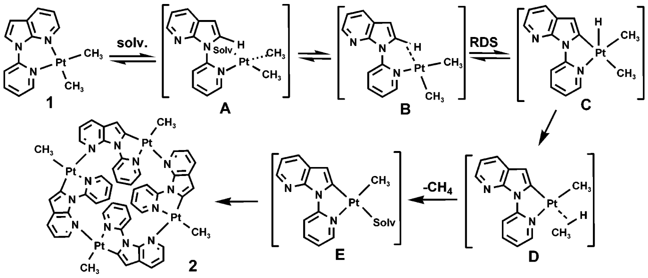
Scheme 1



To gain insight into the reaction, the conversion process of **1** to **2** was monitored by ^{1}H NMR spectra in CD_2Cl_2 (see Figure S3), which revealed that, at room temperature, **1** undergoes a rapid intramolecular roll-over metalation via clean elimination of 1 equiv of CH_4 and the quantitative generation of the cyclic Pt_4 complex **2** (Scheme 1). The metalation occurs selectively at the C2 position of the azain ring, as evident by the evolution of diagnostic ^{195}Pt$-$^{1}H ($^3J = 27.0$ Hz) coupling of the C3 proton. Significant downfield shift for several of the aromatic proton signals was observed from **1** to **2**, consistent with the congested cyclic structure of **2**. The fact that no insoluble polymeric or other oligomeric species were observed other than compound **2** indicates that the roll-over cyclometalation driven self-assembly process is highly selective and specific. The geometry of the NPA ligand clearly plays a key role in this unusual process, and $\pi-\pi$ interactions between adjacent ligands in **2** may also play a role.

On the basis of established mechanistic features of cyclometalation processes,[8a,b] a rational pathway consistent with our preliminary results is proposed and shown in Scheme 1. The discriminatory Pt$-$N bond breaking step was found to be fast and reversible. The facile generation of a three-coordinate Pt^{II} center and its high electron richness enable the subsequent oxidative addition of the *ortho*-C$-$H bond on the azain ring via **B**, leading to a five-coordinate *N,C*-chelating Pt^{IV} hydride intermediate **C**. Due to the stronger *trans*-effect of the C2 atom over the pyridyl N atom in **C**, the subsequent reductive elimination of CH_4 from **C** proceeds preferentially via the intermediate **D**, resulting in the clean formation of the *cis*-aryl, methyl isomer **E**, which, upon generation, spontaneously self-assembles to the cyclic Pt_4 compound **2**. The selective and clean formation of isomer **E** confirms that the metalation occurs through an oxidative addition pathway. The proposed mechanism is also supported by the fact that σ-C$-$H-bound Pt^{II} complexes and dimethyl hydride Pt^{IV} complexes have been well demonstrated as intermediates in the hydrocarbon C$-$H activation process.[12]

Kinetic analyses established a first-order decay of **1** with time. Using the reaction rate constants obtained at several different temperatures, activation parameters $\Delta H^\ddagger = 19.6 \pm 0.7$ kcal·mol^{-1} and $\Delta S^\ddagger = -4.6 \pm 1.0$ cal·mol^{-1}·K^{-1} were obtained after fitting a linear first-order Eyring plot (see Figure S3). The first-order kinetic behavior and the small entropy are in good agreement with an intramolecular cyclometalation process. To establish the rate-determining step (RDS), the analogue Pt(2-D-NPA)$(CH_3)_2$, **1A** (where the proton on C2 is replaced by a deuterium), was synthesized. Kinetic isotope effect (KIE) study using **1** and **1A** revealed a primary KIE ($K_H/K_D = 2.8(2)$) at 24 °C, confirming that the C$-$H cleavage step is the RDS. Furthermore, we observed that the cyclometalation process of **1** or **1A** results in the exclusive formation of CH_4 or CDH_3, respectively, and there is no H/D scrambling of the CH_3 groups on the Pt center with either the deuterated solvent (CD_2Cl_2, C_6D_6, CD_3CN, CD_3OD, or D_2O) or the D atom on C2 in the transformation of **1A**, an indication that the loss of CH_4 from **C** is much faster compared to H/D scrambling process and irreversible.[13]

^{1}H NMR experiments also established that the observed rate constant of the reaction is not affected by the concentration of H_2O in CD_2Cl_2. However, the presence of a stronger coordinating solvent such as CH_3CN does retard the formation of **2**, and the reaction terminates as **E** is trapped by CH_3CN, as confirmed by ^{1}H NMR data and the isolation of the complex, Pt(*N,C*-NPA)$(CH_3)(CH_3CN)$, **E-CH$_3$CN** (its structure is shown in Figure 2). Furthermore, with $[CD_3CN]$ at ~0.5 M and [**1**] at 0.04 M in CD_2Cl_2, a secondary KIE ($K_H/K_D = 1.08(3)$) for the cyclometalation process was observed (see Figure S4), supporting that the conversion of the solvent adduct **A** to the σ-C$-$H-bound **B** becomes the RDS in the presence of a strong coordinating solvent. We also studied Pt(2-Me-NPA)$(CH_3)_2$, **1B**, which does not undergo roll-over cyclometalation at room temperature, and no evidence of metalation involving the py ring was observed, based on NMR data.

In summary, we have demonstrated that the NPA ligand is very effective in directing intramolecular C$-$H activation on a Pt(II) center via a facile and regiospecific roll-over cyclometalation process and in achieving the self-assembly of a rare cyclic organoplatinum Pt_4 structure. We have established that the key step in this self-assembly process is the C$-$H bond cleavage.

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Supporting Information Available: Experimental details for all compounds; NMR and kinetics data; complete crystal data and diagrams with labeling schemes for **2**, **3**, and **E-CH$_3$CN**. This material is available free of charge via the Internet at http://pubs.acs.org.

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