

Origin for Fluxional Structure of Tetracoordinate Pd<sup>II</sup> Complexes<sup>†</sup>Ock Keum Kwak, Jeong-Seon Choi, Kyungok Park,<sup>‡</sup> and Jong Keun Park\*

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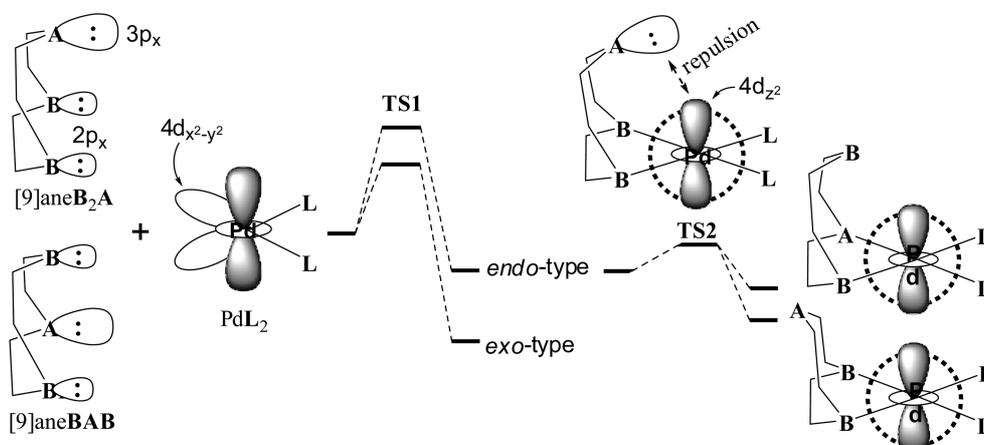
**Key Words :** Orbital interaction, Geometric configuration, Relative energy, d<sub>z</sub><sup>2</sup>-orbital, Tridentate macrocycles

In the Pd-catalyzed cross-coupling reactions, the PdL<sub>2</sub> complexes with the bulky and electron-rich L ligands (phosphines, NHCs, etc) are important compounds as a Pd<sup>(0)</sup>(L)<sub>n</sub>-precursor.<sup>1-8</sup> The catalytic activity of Pd<sup>(0)</sup>(L)<sub>n</sub>-precursors was influenced by the electronic property of the strong σ-donor and the steric effect of the bulky L ligands.<sup>4-8</sup> Due to the electron-transfer from the strong σ-donor L ligand to Pd, the oxidation state of Pd in the neutral [Pd<sup>(0)</sup>L<sub>n</sub>X] catalysts is zerovalent.<sup>1-3</sup> In some X-ray crystallography results,<sup>9,10</sup> the Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> complexes with mixed hard/soft tridentate ligand have been observed as a five-coordinate geometry with an apical (soft A ⋯ Pd<sup>II</sup>) interaction. In Pd<sup>(0)</sup>(η<sup>2</sup>, η<sup>2</sup>, η<sup>2</sup>-C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>Me<sub>2</sub>) complexes with an aza-macrocyclic ligand,<sup>7,8</sup> the six coordination bonds of the three olefin units with Pd were symmetrically formed *via* three (olefin ⋯ Pd<sup>II</sup>) interactions. Meanwhile, in hydration reactions on square planar [PdCl<sub>4</sub>]<sup>2-</sup> complexes, two vertical (H<sub>2</sub>O ⋯ Pd<sup>II</sup>) and (HOH ⋯ Pd<sup>II</sup>) interactions for the ligand exchange processes were investigated theoretically<sup>11-13</sup> and experimentally.<sup>14</sup> With increasing the strength of the fifth (solvent ⋯ Pd<sup>II</sup>) interaction, the replacement of the equatorial (Pd-Cl) bond with (solvent ⋯ Pd<sup>II</sup>) takes place *via* a five-coordinate transition states.

Is there any relationship between the relative stability and fluxional configuration of the Pd isomers (*exo*- and *endo*-

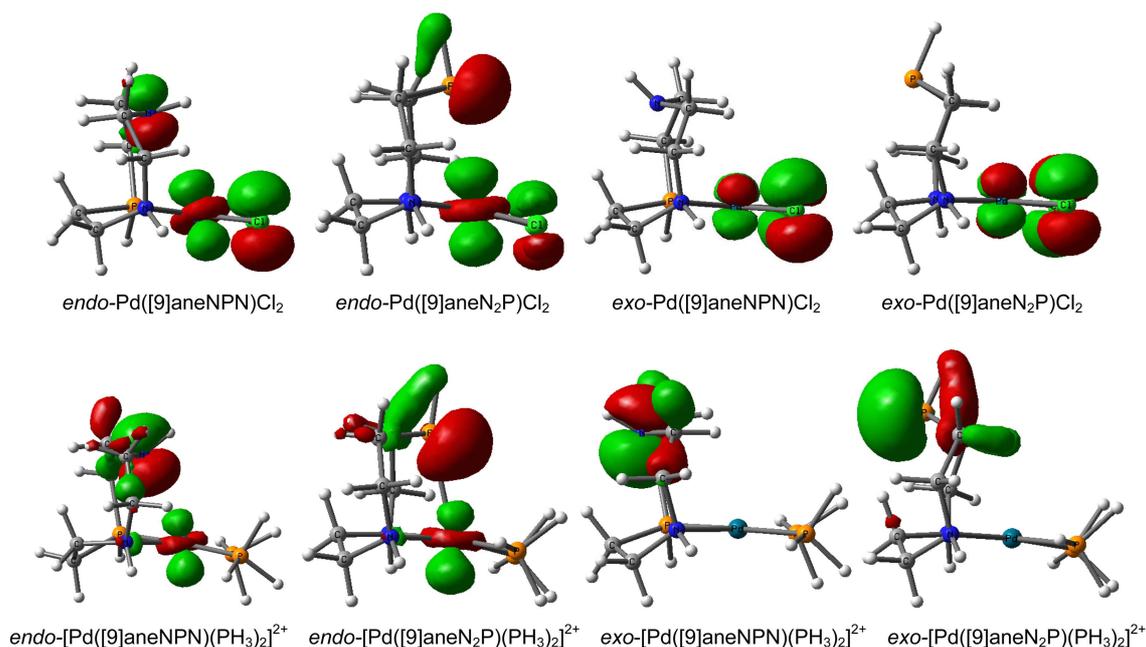
types) and the apical (soft P ⋯ Pd<sup>II</sup>) interaction in the Pd complexes? The unusual stereochemistry of square planar Pd<sup>II</sup> complexes might be influenced by the fifth special (soft P ⋯ Pd<sup>II</sup>) interaction,<sup>1-10</sup> and the conformational rearrangement for the relative stability.<sup>11-14</sup> The vacant bond on the z-axis allows the occupied d<sub>z</sub><sup>2</sup>-orbital of Pd<sup>II</sup> to interact with the Lewis acid ligand (σ-acceptor), but it is difficult for electron-rich substrates and Pd<sup>II</sup> to interact apically (σ-donor ⋯ filled d<sub>z</sub><sup>2</sup>-orbital). Therefore, for Pd([9]aneB<sub>2</sub>A)L<sub>2</sub>, the apical (σ-donor ⋯ filled 4d<sub>z</sub><sup>2</sup>-orbital) repulsion shown in Scheme 1 is suggested. In the present work, we have investigated the relative stabilities and extraordinary structures of the macrocyclic Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> complexes within the frameworks of the orbital interactions. The equilibrium geometric structures of tetracoordinate palladium [Pd([9]aneB<sub>2</sub>A)L<sub>2</sub>, Pd([9]aneBAB)L<sub>2</sub> (A: P; B=N; L=Cl<sup>-</sup>, PH<sub>3</sub>)] complexes were fully optimized with the B3P86/6-311+G\*\* (LanL2DZ for Pd) level using Gaussian 03.<sup>15</sup>

Optimized geometric structures of tetracoordinate Pd([9]aneN<sub>2</sub>P)L<sub>2</sub> {Pd([9]aneN<sub>2</sub>P)L<sub>2</sub>} isomers including HOMO were represented in Figure 1 and their parameters were listed in Table 1. In the Pd complexes, Pd<sup>II</sup> locates at the center of the tetracoordinate Pd complexes with a ([9]aneN<sub>2</sub>P) ligand and two L monodentates. In *endo*-Pd([9]aneN<sub>2</sub>P)Cl<sub>2</sub>



**Scheme 1.** The apical (soft A ⋯ Pd<sup>II</sup>) repulsion between the soft A and the d<sub>z</sub><sup>2</sup>-orbital in *endo*-Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> (B=N; A=P; L=Cl<sup>-</sup>, PH<sub>3</sub>).

<sup>†</sup>This paper is to commemorate Professor Kook Joe Shin's honourable retirement.



**Figure 1.** Geometric structures of tetracoordinate  $[\text{Pd}(\text{[9]aneN}_2\text{P})\text{L}_2$ ,  $[\text{Pd}(\text{[9]aneNPN})\text{L}_2$  ( $\text{L}=\text{Cl}^-$ ,  $\text{PH}_3$ )] complexes including HOMO optimized at the B3P86//6-311+G\*\*/(lan12DZ for Pd) levels.

$\{\text{endo-Pd}(\text{[9]aneNPN})\text{Cl}_2\}$ , the electron densities of HOMO ( $2a_{1g}$ ) are represented on the  $4d_{z^2}$ -orbital, the Cl ligand, and the third binding A site. By the electronegativity of Cl, the electron density of the tridentate transfers toward the *trans*-Cl ligand through the  $\text{Pd}^{\text{II}}$  center. The large lobe of the soft A site repulsively interacts with the increased lobe of  $4d_{z^2}$ -orbital. Therefore, the repulsion between two orbitals took place, and the  $\text{Pd}^{\text{II}}$  center lies slightly below the mean plane ( $\text{B}_2\text{PdCl}_2$ ). As shown in Table 1, the distance between the  $\text{Pd}^{\text{II}}$  center and the third A site increases slightly. The relative energy of  $\text{endo-Pd}(\text{[9]aneNPN})\text{Cl}_2$  is lower than that of  $\text{endo-Pd}(\text{[9]aneN}_2\text{P})\text{Cl}_2$ , and the Pd complexes of the *exo*-

type are more stable than that of the *endo*-type.

In  $[\text{Pd}(\text{[9]aneB}_2\text{A})(\text{PH}_3)_2]^{2+}$ , the electron density of HOMO of the A site and the  $4d_{z^2}$ -orbital are enlarged by the electronegativity of the A site and the donicity of  $\text{PH}_3$ . Because of the electronic repulsion between the increased  $\sigma$ -orbital and the filled  $d_{z^2}$ -orbital, the lobe size of the  $d_{z^2}$ -orbital is not symmetric. Therefore, the potential energy of the A site increases, and the large  $\sigma$ -lobe of the A site is energetically close to the highly unoccupied  $3a_{1g}$ -orbital of  $\text{PdL}_2$ . As a result, the strong apical (soft  $\text{A} \cdots \text{Pd}^{\text{II}}$ ) interaction between the axially soft A site and the Pd center occurred potentially. The  $\text{Pd}^{\text{II}}$  center lies slightly above the mean plane. The

**Table 1.** Optimized average bond distances ( $\text{\AA}$ ) and relative energies (eV) of the equilibrium structures  $\text{Pd}(\text{[9]aneB}_2\text{A})\text{L}_2$  and  $\text{Pd}(\text{[9]aneBAB})\text{L}_2$  at the B3P86 level

Compound	Average distance				Relative energy	
	$R_{\text{Pd-N}}^a$	$R_{\text{Pd-P}}^a$	$R_{\text{Pd} \cdots \text{N}}^b$	$R_{\text{Pd} \cdots \text{P}}^b$	$\Delta E_{\text{NPN-N}_2\text{P}}^c$	$\Delta E_{\text{exo-endo}}^d$
<i>endo</i> -Pd([9]aneNPN)Cl <sub>2</sub>	2.113	2.225	3.040		-0.28	0.00
<i>endo</i> -Pd([9]aneN <sub>2</sub> P)Cl <sub>2</sub>	2.088			3.033	0.00	0.00
	2.041 <sup>e</sup>	2.334 <sup>e</sup>	2.298 <sup>e</sup>			
<i>exo</i> -Pd([9]aneNPN)Cl <sub>2</sub>	2.106	2.346	3.471		-0.35	-0.13
	2.124 <sup>f</sup>	2.342 <sup>e</sup>		3.087 <sup>f</sup>		
<i>exo</i> -Pd([9]aneN <sub>2</sub> P)Cl <sub>2</sub>	2.095			3.868	0.00	-0.06
<i>endo</i> -[Pd([9]aneNPN)(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	2.195	2.289	2.848		0.13	0.00
<i>endo</i> -[Pd([9]aneN <sub>2</sub> P)(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	2.142	2.340 <sup>g</sup>		2.782	0.00	0.00
<i>exo</i> -[Pd([9]aneNPN)(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	2.154	2.363	3.504		-0.40	0.00
<i>exo</i> -[Pd([9]aneN <sub>2</sub> P)(PH <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup>	2.129			3.963	0.00	0.05

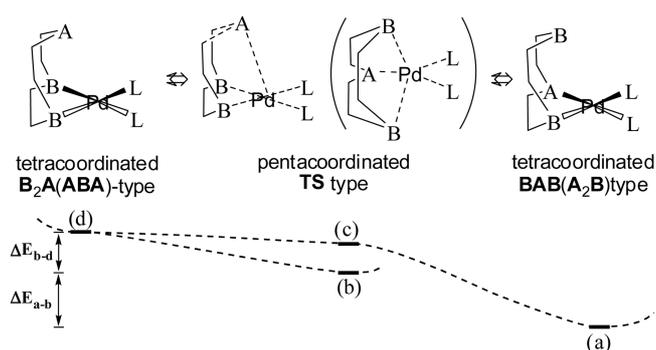
<sup>a</sup>Bond lengths between Pd and the equatorial site. <sup>b</sup>Bond lengths between Pd and the axial site. <sup>c</sup>Relative energy gap between  $\text{Pd}(\text{[9]aneB}_2\text{A})\text{L}_2$  and  $\text{Pd}(\text{[9]aneBAB})\text{L}_2$ . <sup>d</sup>Energy gap between *endo*- and *exo*-types. <sup>e</sup>Ref. 10. <sup>f</sup>Ref. 9. <sup>g</sup>Ref. 6.

distance between the Pd<sup>II</sup> center and the third A site decreases. In particular, in [Pd([9]aneN<sub>2</sub>P)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, pentacoordinate Pd complexes were formed by an axial (Pd-A) bond of  $R_{(A\cdots Pd)} = 2.782 \text{ \AA}$ . The vertical (soft A $\cdots$ Pd<sup>II</sup>) interaction shows in an irregular fashion such as a pentacoordinate Pd complex. And the relative energy of *endo*-[Pd([9]aneN<sub>2</sub>P)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> is lower than that of *endo*-[Pd([9]aneNPN)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, and the potential energy of the *exo*-type is similar to that of the *endo*-type. Meanwhile, in *exo*-Pd([9]aneN<sub>2</sub>P)Cl<sub>2</sub> and Pd([9]aneNPN)Cl<sub>2</sub>, no lobes of the HOMO were found at the axial A (or B) site, while in *exo*-[Pd([9]aneN<sub>2</sub>P)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and *exo*-[Pd([9]aneNPN)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, no lobes of the HOMO were found at the Pd center. Therefore, the repulsive interaction between two orbitals does not take place, and mean planes of the Pd complexes are flat.

By the experimental results,<sup>3-10</sup> unexpected pentacoordinate structures of Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> complexes with the fifth apical (A-Pd) bond have been synthesized. The (soft A $\cdots$ Pd<sup>II</sup>) interaction has been conditionally dependent on the geometric constraints (multidentate coordinations, polymeric side interactions) and the special counter-ions for [Pd([9]aneN<sub>2</sub>S)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> and [Pd([9]aneN<sub>2</sub>S)<sub>2</sub>]Cl<sub>2</sub>·H<sub>2</sub>O. According to the relative stability of geometric configuration, the selective coordination bonds of A and B on ([9]aneA<sub>2</sub>B) can occur at the apical or basal position. The unusual stereochemistry of tetracoordinate Pd complexes has been described with the electronic property of the soft  $\sigma$ -donor<sup>3-8</sup> and steric effect<sup>3-10</sup> of the multidentate ([9]aneA<sub>2</sub>B) ligand. In the ligand exchange processes of Pd complexes,<sup>11-14</sup> the mechanisms for the reactions were described by two models such as (H<sub>2</sub>O $\cdots$ d<sub>z<sup>2</sup></sub>-orbital) and (OH<sub>2</sub> $\cdots$ d<sub>z<sup>2</sup></sub>-orbital). However, the former (H<sub>2</sub>O $\cdots$ d<sub>z<sup>2</sup></sub>-orbital) interaction is rarely formed because of electrostatic repulsions. Meanwhile, the [Pd([9]aneN<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and [Pd([9]aneN<sub>3</sub>)<sub>2</sub>(H[9]aneN<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> complexes with tridentate ligands does not have an apical (soft A $\cdots$ Pd<sup>II</sup>) interaction and the third apical N-site directed to the outer of coordination plane in range of 2.982-3.499 Å.

Why does the change of the geometric configuration from the vertical ligand to equatorial direction occur? The equatorial (soft P $\cdots$ Pd<sup>II</sup>) bond is stronger than that of the axial (hard N $\cdots$ Pd<sup>II</sup>) interaction. The soft P sites of [9]aneN<sub>2</sub>P coordinates preferentially to the Pd center at the equatorial direction than the hard atoms (N). As shown in Table 1, the relative energy level between *endo*-[Pd([9]aneN<sub>2</sub>P)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> and *endo*-[Pd([9]aneNPN)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> is low. Pd([9]aneB<sub>2</sub>A)Cl<sub>2</sub> without the axial (soft A-Pd) bond is more unstable than Pd([9]aneBAB)Cl<sub>2</sub>, which had an equatorially soft A site.

The structural variations and the relative energies of the unstable Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> {or Pd([9]aneABA)L<sub>2</sub>} complex compared with the stable Pd([9]aneBAB)L<sub>2</sub> {or Pd([9]aneA<sub>2</sub>B)L<sub>2</sub>} complex are represented in Figure 2. In [Pd([9]aneB<sub>2</sub>A)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, the 3a<sub>1g</sub>-orbital plays an important role as a bridge for pentacoordinate PdL<sub>5</sub> intermediates. *Via* the bridged 3a<sub>1g</sub>-orbital, a pentacoordinate [Pd([9]aneB<sub>2</sub>A)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> structure with an axially strong (soft A-Pd) bond was formed as a local minimum for the path: (d)→(b). To create a more energetically stable structure, the axial (soft A



**Figure 2.** The variation of the structural configuration from the unstable *endo*-Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> complex to the stable *endo*-Pd([9]aneBAB)L<sub>2</sub> including the relative energy level (A: P; B: N; L: Cl<sup>-</sup>, PH<sub>3</sub>). (a), (b), (c), and (d) are a relative energy level of *endo*-Pd([9]aneB<sub>2</sub>A)L<sub>2</sub>, *endo*-Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> with axial (A-Pd), estimated TS point between two structures, and *endo*-Pd([9]aneBAB)L<sub>2</sub>, respectively.

$\cdots$ Pd<sup>II</sup>) interaction was converted to an equatorial (soft A $\cdots$ Pd<sup>II</sup>) interaction *via* the transition trigonal bipyramidal or square pyramidal structure {path: (d)→(c)→(a) for Pd([9]aneB<sub>2</sub>A)Cl<sub>2</sub> and [Pd([9]aneABA)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>}. The interconversion of the two geometries occurred in a simple way via the lower potential energy barrier. As a result, the unusual stereochemistry of square planar Pd complexes may be influenced greatly by the relatively stable geometric rearrangement using strongly apical (soft A $\cdots$ Pd<sup>II</sup>) interaction.

In conclusion, we investigated the uncommon structures and relative stabilities of the Pd([9]aneB<sub>2</sub>A)L<sub>2</sub> complexes. The coordination bond of the soft A site to the 4d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital in the equatorial direction was more preferential than that of the hard B site. In [Pd([9]aneB<sub>2</sub>A)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>, the repulsion between the large  $\sigma$ -lobe of the axial A site and the filled 4d<sub>z<sup>2</sup></sub>-orbital was strong, and simultaneously, the potential energy of the A site increased. The increased a<sub>1g</sub>-orbital (enrich electron density) of the axial A site could be shared with the unoccupied 3a<sub>1g</sub>-orbital of PdL<sub>2</sub>. Therefore, the pentacoordinate [Pd([9]aneB<sub>2</sub>A)(PH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> intermediate species can be easily formed through an axial (soft A $\cdots$ Pd<sup>II</sup>) interaction that had a low energy barrier. Meanwhile, because the relative potential energy of Pd([9]aneBAB)L<sub>2</sub> was lower than that of Pd([9]aneB<sub>2</sub>A)L<sub>2</sub>, the axial (soft A $\cdots$ Pd<sup>II</sup>) interaction turned in the equatorial (soft A $\cdots$ Pd<sup>II</sup>) direction *via* the pentacoordinate transition state. In Pd-mediated cross-coupling reactions, the unoccupied 3a<sub>1g</sub> (or occupied 2a<sub>1g</sub>)-orbital of the PdL<sub>2</sub> complexes forms a bridge orbital that interacts with the  $\sigma$ -donor (or  $\sigma$ -acceptor) of the substrates.

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