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Theoretical study of β-Hydrogen elimination of ethyl palladium complexes

○Rado Raharintsalama[a], Hiroaki Munakata[a], Michihisa Koyama[a], Momoji Kubo[a,b], Akira Miyamoto[a,c]
[a]*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University,*
Aoba-yama 07, Sendai 980-8579,Japan
[b]*PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi,Saitama 332-0012, Japan*
[c]*New Industry Creation Hatchery Center, Tohoku University Aoba-yama 10, Sendai 980-8579, Japan*

[Introduction]

Progresses in computational and theoretical methods have led to give significant impact in both understanding and simulating reactions catalyzed by various Pd complexes. To perform that purpose, fundamental understanding of reaction mechanisms catalyzed by organometallic complexes is quite essential. Thermal decomposition of mono-alkyl-palladium halide complexes to produce olefins involves β-hydrogen-elimination via agostic intermediates. Kinetic and chemical studies of this decomposition revealed there are two pathways; one major route involving dissociation of the halide, X, ligand to generate an unstable cationic ethyl-palladium species, this subsequently being rapidly thermolysed, evolving olefin and a minor pathway proceeding from the neutral complex without dissociation of the anionic X ligand [1].

[Method]

The Material Studio DMol^3 program was used. All molecular geometries were obtained by LDA optimization with DNP basis sets and energies were calculated at GGA/PW91 functional level. We also employed accelerated quantum chemical molecular dynamics software "Colors". All the parameters used for "Colors" were determined by first-principles calculations.

[Results]

The decomposition of the monoethyl-palladium complexes were carried out by taking the neutral model, $EtPd(Cl)(PMe_3)_2$, and the solvated cationic model, $[EtPd(PMe_3)_2(EtOH)]^{+1}$.

Reaction pathway via neutral species: Starting from $EtPd(Cl)(PMe_3)_2$, the relative energy difference was shown to be 16.66 kcal/mol to get the state of ethylene and the hydrido-palladium halide complex, where an agostic intermediate was not stabilized as the intermediate equilibrium state. (see Fig.1-(A)). Reaction pathway via cationic species: Starting from the solvated cationic palladium complex, $[EtPd(PMe_3)_2(EtOH)]^{+1}$, the agostic intermediate was found as the stable equilibrium state, and the relative energy level being 6.95 kcal/mol higher. (see Fig. 1-(B)). The geometry of this intermediate is shown in Fig. 2. The agostic intermediate was converted to the state of the ethylene and cationic hydrido-palladium complex, $[HPd(PMe_3)_2(EtOH)]^{+1}$, in addition the energy increase from the initial state to the last state was shown to be 20.01 kcal/mol. (see Fig. 1-(B)) For the cationic species route, the existence of the stable agostic intermediate decreases the energy height from 20.01 kcal/mol to 13.06 kcal/mol to get the last state. (see Fig. 1-(B)) Solvent effects and transition states are under investigation.

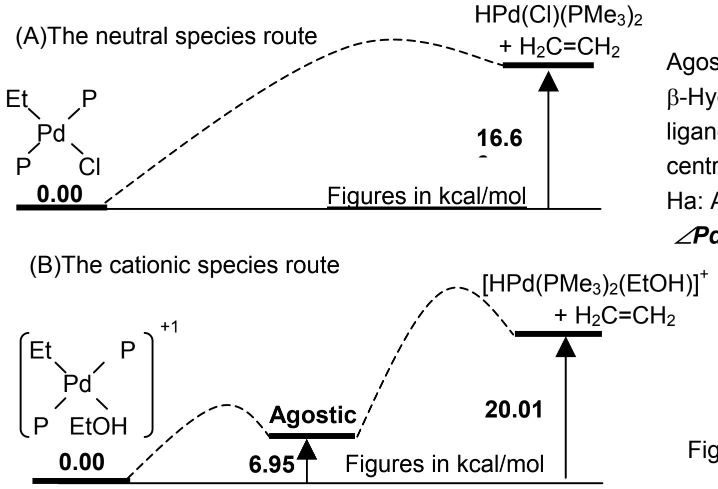

Fig. 1. Comparison of relative energies between (A) the neutral species route and (B) the cationic species route

Agostic interaction:
β-Hydrogen of ethyl-ligand interacts with central palladium atom.
Ha: Agostic hydrogen
∠Pd-C1-C2 = 83.27°

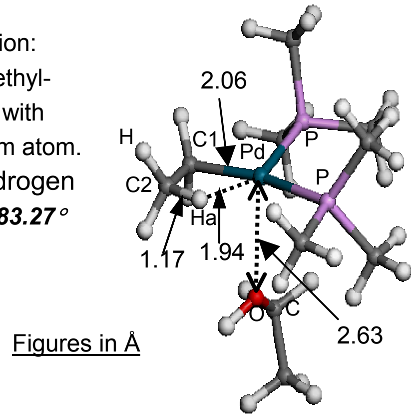

Fig. 2 The geometry of the cationic agostic complex, $[EtPd(PMe_3)_2(EtOH)]^{+1}$

[Reference]

[1] F. Kawataka et al., *Organometallics*, **38** (1994) 112.