

## Computational Chemistry Study on Palladium Hydrido-complexes and on Their Roles in Reactions Catalyzed by Palladium Complexes

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Density functional theory calculations were applied to investigate geometrical and electronic properties of palladium hydrido-complexes,  $\text{trans}-(\text{Me}_3\text{P})_2\text{PdHX}$ , and ethyl palladium complexes,  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdHX}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ . Effects of substituents, halogen ligands, on geometric parameters, atomic charges and relative stabilities for  $\text{trans}-(\text{Me}_3\text{P})_2\text{PdHX}$  and  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdHX}$  were investigated. Preliminary studies on  $\beta$ -hydrogen elimination of  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdHX}$  to form ethene and hydrido-palladium complexes were explored.

Key words: Density functional theory, Hydrido-palladium complex, Alkyl-palladium complex,  $\beta$ -hydrogen elimination, catalysis

### 1. INTRODUCTION

Transition metal hydrido-complexes are extremely important compounds, which show specific importance in various fields of chemistry. They play significant roles in theoretical and reaction chemistry. Among them, hydrido-palladium complexes take special places where organic synthesis, catalysis, and organometallic chemistry are related to this unique class of compounds hydrido-complexes. Many books [1-3] and excellent reviews [4-9] have been published on various aspects of hydrido-transition metal chemistry. Among the group VIII transition metals, nickel, palladium and platinum, it was shown that only the platinum had been explored as a well-defined series of hydrido-complexes, mostly uninuclear complexes of the type  $\text{trans-L}_2\text{Pt}(\text{H})\text{X}$ .

These compounds were prepared by the reduction of a bis(tertiary phosphine)platinum dihalide, using reagents resulting a strongly basic environment. The stabilities of similar hydrido-complexes of nickel and palladium decrease dramatically when going from platinum to nickel and palladium, strong reducing agents being not applicable for nickel and palladium congeners. The hydrido-palladium complexes decompose rapidly in acidic or basic media. The first hydrido-palladium complex being isolated and structurally characterized was  $[(\text{Et}_3\text{P})_2\text{Pd}(\text{H})\text{Cl}]$  [10-13]. Since then a number of neutral and cationic hydrido-palladium complexes have been synthesized and characterized. The stable hydrido-palladium complexes stabilized by bulky tertiary phosphine ligands were prepared in both neutral and cationic forms [14-16]. Pd-catalyzed reactions have been described in many experimental papers, including catalytic reactions such as oxidation reactions, allylic alkylation reactions, telomerization reactions, water gas shift reaction, reduction of various substrates and others. Many reactions involving hydrogen transfer steps seem to proceed via hydrido-palladium complexes as intermediates. Usually Pd hydrido-complexes are unstable in catalytic reaction media and the reactivity of Pd hydrido-complexes still remains insufficiently explored. Recent progresses in both computational tools and theoretical methods have led to

a new decade where calculations give significant impact in both understanding and simulating reactions catalyzed by various Pd complexes.  $\beta$ -Hydrogen elimination of transition metal alkyls is one of the most important elementary processes in organometallic chemistry and catalytic reactions. A series of monoethylpalladium complexes coordinated various electronegative ligands,  $\text{trans}[\text{PdEt}(\text{X})-(\text{PMe}_3)_2]$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{O}_2\text{CCH}_3, \text{OPh}$ , etc., have been prepared [17-19]. In decomposition of alkyl-palladium complexes to form olefins, the reaction pathway via  $\beta$ -hydrogen-elimination is generally considered and an involvement of hydrido-palladium complexes as reaction intermediates is quite plausible.

In this study, we investigated geometrical parameters, electronic properties, stabilities and reactivities of hydrido-palladium complexes and ethyl palladium complexes and their roles in catalytic reactions using Density Functional Theory method.

### 2. METHODS

Density functional method calculations were performed on current studies by using the Material Studio DMol<sup>3</sup> program, ver.2.2. Atomic orbital basis sets used throughout were standard DMol<sup>3</sup> double numerical atomic basis sets augmented with polarization functions. The local density approximation (LDA) with the Vosko-Wilk-Nusair (VWN) local functional was applied to optimize geometries. Energies were calculated on the LDA optimized geometries at the level of a generalized gradient approximation (GGA) with Perdew and Wang functionals PW91. All geometrical parameters are obtained from LDA optimization and all energetic properties are evaluated using GGA/PW91 energy calculation. Reaction energies were calculated using following equation:  $\Delta E_{\text{react}} = E_{\text{product}} - E_{\text{reactant}}$ , where  $\Delta E_{\text{react}}$ ,  $E_{\text{product}}$ , and  $E_{\text{reactant}}$  represents the binding energy difference of products and reactants for the corresponding reaction, a product binding energy and a reactant binding energy respectively. The negative  $\Delta E_{\text{react}}$  values mean that the product states are energetically favorable. The visualizer module of Cerius software by Accelrys Corporation was used to display and

analyze the models.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Geometrical parameters of trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, X= Cl, Br, I and atomic charges

The sketches of geometries of trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, are shown in Fig.1-(a), -(b). For the trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, the calculations were performed with Cs symmetry constraint to keep the ethyl group in eclipsed conformation. Similarly, the calculations for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X were performed with Cs symmetry constraint. Both trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X complexes show to take slightly distorted square planar conformations. The Pd-X bond distances of trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X increased by changing substituents from Cl, to I, (Pd-Cl < Pd-Br < Pd-I), as shown in Table I.

The Pd-X bond distances of trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X showed similar trend by changing substituents, (Pd-Cl < Pd-Br < Pd-I), as shown in Table II. The Pd-I bond distances for both trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)I and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)I were shown to be increased, distances being 2.70 and 2.71 Å, respectively.

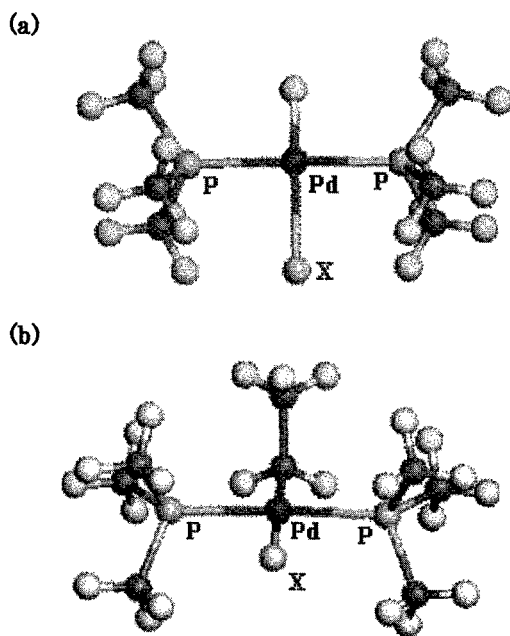


Fig. 1. The geometries of trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X (a) and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X (b). Unmarked white and gray balls represent hydrogen and carbon, respectively. (X= Cl, Br, I)

Table I The selected bond lengths (Å) and bond angles (°) in trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X.

Bonds	Distance [Å] – Angle [°]		
	X=Cl	X=Br	X=I
Pd-H	1.57	1.57	1.57
Pd-X	2.39	2.52	2.70
Pd-P	2.28	2.28	2.29
P-C	1.81	1.81	1.81
C-H	1.10	1.10	1.10
P-Pd-P	178.66	179.25	175.55
H-Pd-X	179.68	179.95	179.98

Mulliken population analyses were performed to characterize atomic charges for those complexes, and results are presented in Table III and Table IV. Charges on central metal Pd atoms for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X were shown to be negative and charges on hydrido H atoms for the complex to be slightly negative. For the complex having the substituent, I, the charge on the Pd atom showed increased negative value.

The charge on the central metal Pd atom for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, where X=Cl, Br, was shown to be slightly negative and the charge on the Pd atom for the complex having the substituent, I, showed increased negative value.

#### 3.2 Formation Energies for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X and trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X

The formation energies,  $\Delta E_{\text{form}}$ , for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X, where X = Cl, Br, and I, were calculated in terms of the following reaction equation.



$$E_{[(\text{Me}_3\text{P})_2\text{Pd}(0)]} + E_{[\text{HX}]} = E_{[(\text{Me}_3\text{P})_2(\text{H})\text{Pd}(\text{II})\text{X}]} - \Delta E_{\text{form}} \quad (2)$$

Table II The selected bond lengths (Å) and bond angles (°) for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X.

Bonds	Distance [Å] – Angle [°]		
	X=Cl	X=Br	X=I
Pd-X	2.41	2.52	2.71
Pd-C	2.07	2.07	2.08
Pd-P	2.29	2.30	2.31
P-C	1.81	1.81	1.81
C-H	1.10	1.10	1.10
C-C	1.51	1.52	1.52
P-Pd-P	174.81	176.37	177.60
C-Pd-X	178.27	177.16	177.28

Table III Atomic charges in trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X.

Atoms	Charges		
	X=Cl	X=Br	X=I
Pd	-0.17	-0.19	-0.24
P	0.49	0.48	0.47
H*	-0.05	-0.04	-0.04
X	-0.51	-0.50	-0.44
C	-0.55	-0.54	-0.54
H	0.15 ~ 0.21	0.15 ~ 0.20	0.14 ~ 0.19

H\*: Hydrogen atom bonded with Pd

H: Hydrogen atom bonded with C (methyl)

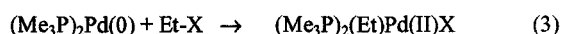
Table IV Atomic charges in trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X.

Atoms	Charges		
	X=Cl	X=Br	X=I
Pd	-0.04	-0.05	-0.10
P	0.49	0.49	0.47
C*	-0.42	-0.42	-0.42
C(ethyl)	-0.35	-0.35	-0.36
X	-0.51	-0.51	-0.45
C	-0.54 ~ -0.59	-0.54 ~ -0.59	-0.53 ~ 0.59
H	0.12 ~ 0.20	0.12 ~ 0.20	0.13 ~ 0.19

The formation energies,  $\Delta E_{\text{form}}$ , for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X, where X=Cl, Br, and I, were shown in Table V, together with HOMO-LUMO energy gaps. The formation energies  $\Delta E_{\text{form}}$  increased negative values by changing substituents, from Cl to Br, I. The complex having substituent, I, was shown to be most stable in this series and thermo-chemical stability trend for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X follows Cl < Br < I.

The HOMO-LUMO energy gap order for the complex, trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(H)X, was observed to be Cl>Br>I, as shown in Table V. The complex having substituent, I, had the lowest energy gap.

The formation energies,  $\Delta E_{\text{form}}$ , for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, where X = Cl, Br, and I, were calculated similarly in terms of the following reaction equation.



$$E_{[(\text{Me}_3\text{P})_2\text{Pd}(0)]} + E_{[\text{Et-X}]} = E_{[(\text{Me}_3\text{P})_2(\text{Et})\text{Pd}(\text{II})\text{X}]} - \Delta E_{\text{form}} \quad (4)$$

The formation energies,  $\Delta E_{\text{form}}$ , for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, where X=Cl, Br, and I, were shown in Table VI, together with HOMO-LUMO energy gaps. The formation energies  $\Delta E_{\text{form}}$  increased negative values by changing substituent, from Cl to Br, I. The complex having substituent, I, was shown to be most stable in this series and thermo-chemical stability trend for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X follows Cl < Br < I.

The HOMO-LUMO energy gap order for the complex, trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, was observed to be Cl>Br>I, as shown in Table VI. The complex having substituent, I, had the lowest energy gap.

### 3.3 Decomposition of alkyl-palladium complexes

In the process of decomposition of alkyl-palladium complexes to form olefins, the reaction pathway via  $\beta$ -hydrogen elimination reaction is generally considered and an involvement of hydrido-palladium complexes as reaction intermediates is quite plausible. Tentative reaction pathway of  $\beta$ -H-elimination of the alkyl-palladium complex, trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X, is shown in Fig. 2. Comparison of ground state energies for reactants and the sum of products energies was examined. The reactions proceed to produce the hydrido-palladium complex and olefin and another reaction

Table V Formation energies  $\Delta E_{\text{form}}$  for trans-(Me<sub>3</sub>P)<sub>2</sub>-Pd(H)X, where X = Cl, Br and I, with HOMO-LUMO energy gaps

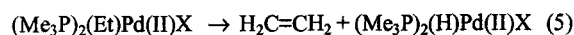
X	$\Delta E_{\text{form}}$ (kcal/mol)	HOMO-LUMO (eV)
Cl	-24.56	3.99
Br	-26.23	3.94
I	-35.89	3.46

Table VI Formation energy  $\Delta E_{\text{form}}$  for trans-(Me<sub>3</sub>P)<sub>2</sub>Pd-(Et)X, where X = Cl, Br and I, with HOMO-LUMO energy gaps.

X	$\Delta E_{\text{form}}$ (kcal/mol)	HOMO-LUMO (eV)
Cl	-18.94	3.68
Br	-23.38	3.60
I	-25.64	3.41

pathway to produce the zero-valent Pd(0) complex, olefin and HX acid.

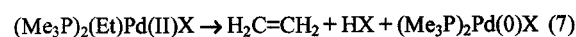
The reaction energies for  $\beta$ -H-elimination of trans-(Me<sub>3</sub>P)<sub>2</sub>-Pd(Et)X to produce olefin were calculated in terms of the following scheme and equation.



$$E_{[(\text{Me}_3\text{P})_2(\text{Et})\text{Pd}(\text{II})\text{X}]} = E_{[\text{H}_2\text{C}=\text{CH}_2]} + E_{[(\text{Me}_3\text{P})_2(\text{H})\text{Pd}(\text{II})\text{X}]} - \Delta E_{\text{react}} \quad (6)$$

The values for reaction energies are shown in Table VII. Positive values correspond to endothermic reactions. Lower value means thermo-chemically preferred state. The reaction starting from the complex trans-(Me<sub>3</sub>P)<sub>2</sub>-Pd(Et)I showed the lowest value in this series.

The reaction energies for  $\beta$ -H-elimination of trans-(Me<sub>3</sub>P)<sub>2</sub>-Pd(Et)X to produce the zero-valent Pd(0) complex, olefin and HX acid were calculated in terms of the following scheme and equation.



$$E_{[(\text{Me}_3\text{P})_2(\text{Et})\text{Pd}(\text{II})\text{X}]} = E_{[\text{H}_2\text{C}=\text{CH}_2]} + E_{[\text{HX}]} + E_{[(\text{Me}_3\text{P})_2\text{Pd}(0)\text{X}]} - \Delta E_{\text{react}} \quad (8)$$

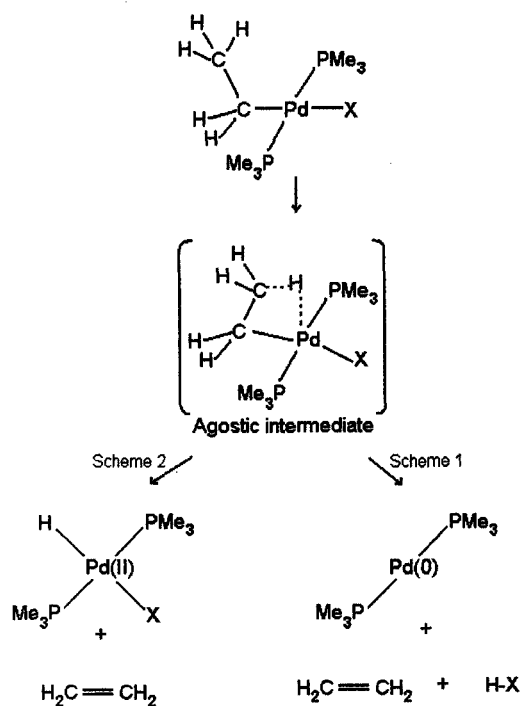


Fig. 2 Tentative reaction pathway of  $\beta$ -H-elimination of the trans-(Me<sub>3</sub>P)<sub>2</sub>Pd(Et)X.

Table VII Reaction energies  $\Delta E_{\text{react}}$  for  $\beta$ -H-elimination to produce ethene and trans-(Me<sub>3</sub>P)<sub>2</sub>(H)Pd(II)X, where X = Cl, Br, and I.

X	$\Delta E_{\text{react}}$ (kcal/mol)
Cl	16.69
Br	16.32
I	15.53

Table VIII Reaction energies  $\Delta E_{\text{react}}$  for  $\beta$ -H-elimination to produce  $(\text{Me}_3\text{P})_2\text{Pd}(0)$ , ethene and HX, where X = Cl, Br, and I.

X	$\Delta E_{\text{react}}$ (kcal/mol)
Cl	41.26
Br	47.68
I	51.50

The values for reaction energies are shown in Table VIII. Positive values correspond to endothermic reactions and all of these values showed larger positive values compared with those values of reactions to form  $\text{trans}-(\text{Me}_3\text{P})_2(\text{H})\text{Pd}(\text{II})\text{X}$ .

The reaction pathway starting from the complex,  $\text{trans}-(\text{Me}_3\text{P})_2\text{Pd}(\text{Et})\text{X}$  to produce  $\text{trans}-(\text{Me}_3\text{P})_2(\text{H})\text{Pd}(\text{II})\text{X}$  and ethene is energetically preferred compared with the reaction pathway to produce  $(\text{Me}_3\text{P})_2\text{Pd}(0)$ , ethene and HX.

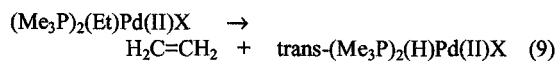
To investigate further detailed reaction mechanisms, determination of transition-state intermediates for reaction pathways are required and transition-state search is under investigation.

#### 4. CONCLUSION

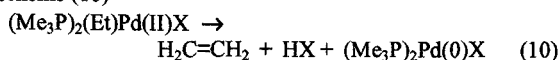
Using density functional theory method, Dmol<sup>3</sup> molecular properties for  $\text{trans}-(\text{Me}_3\text{P})_2\text{PdHX}$  and  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdX}$ , where X = Cl, Br and I, and preliminary reactions of  $(\text{Me}_3\text{P})_2(\text{Et})\text{PdX}$  to produce ethene were studied. Both  $\text{trans}-(\text{Me}_3\text{P})_2\text{PdHX}$  and  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdX}$  showed to have slightly distorted square planar conformations. Bond distances of Pd-X were elongated by changing substituents X, from Cl to Br and I for both the hydrido-palladium complex and ethyl-Pd complex. Trend for stabilities of  $\text{trans}-(\text{Me}_3\text{P})_2\text{PdHX}$  was shown to be  $\text{Cl} < \text{Br} < \text{I}$  and similar trend was observed for  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdX}$ .

Decomposition of  $\text{trans}-(\text{Me}_3\text{P})_2(\text{Et})\text{PdX}$  was studied, where tentative reaction pathways via  $\beta$ -hydrogen elimination was considered. The reaction scheme involving hydrido-palladium complex formation led to form ethene, and another reaction scheme involving Pd(0) complex formation led to produce ethene and HX.

Reaction energies for both schemes were evaluated and it was shown that the reaction scheme (9)



was energetically favorable compared with the reaction scheme (10)



To investigate further detailed reaction mechanisms, determination of transition-state intermediates for reaction pathways are required and transition-state search is under investigation.

#### REFERENCES

- [1] E. L. Muetteries, "Transition metal hydrides", Ed. by Marcel Dekker, New York, (1971)
- [2] R. Bau, "Transition metal hydrides", Ed. By Adv. Chem. Ser. (1978), pp.167
- [3] A. Dedieu, "Transition metal hydrides", Ed. By VCH Publishers, New York (1991)
- [4] Green, M. L. H.; Jones, D. J. Adv. Inorg. Chem. Radiochem., 7, 115 (1965)
- [5] R. A. Henderson, Transition Met. Chem., 13, 474 (1988)
- [6] R. H. Crabtree, Acc. Chem. Res., 23, 95 (1990)
- [7] P. G. Jessop and R. H. Morris, Coord. Chem. Rev., 121, 155 (1992)
- [8] D. M. Heinkekey and W. Oldham, J. Chem. Rev., 93, 913 (1993)
- [9] R. H. Crabtree, Angew. Chem., Int. Ed. Engl., 32, 789 (1993)
- [10] E. H. Brooks and F. Glocking, J. Chem. Soc. A, 1241 (1966)
- [11] E. H. Brooks and F. Glocking, J. Chem. Soc. A, 1030 (1967)
- [12] M. L. Schneider and H. M. M. Shearer, J. Chem. Soc. Dalton Trans., 354 (1973)
- [13] H. Munakata and M. L. H. Green, Chem. Comm., 881 (1970)
- [14] H. Munakata and M. L. H. Green, J. Chem. Soc. A, 469 (1971)
- [15] H. Munakata; D.Phil. Thesis, Oxford University, Oxford, England (1971).
- [16] F. Kawatake, Y. Kayaki, I. Shimizu, and A. Yamamoto, Organometallics, 13, 3517 (1994)
- [17] K. Nagayama, I. Shimizu and A. Yamamoto, Bull. Chem. Soc. Jpn., 74, 1803 (2002)
- [18] T. Saito, H. Munakata and H. Imoto, Inorg. Synth., 17, 83 (1977)
- [19] H. Munakata, T. Saito, Inorg. Synth., 17, 88. (1977)

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