Organometallics **2006,** *25,* 812−819

Articles

β-Heteroatom versus *β*-Hydrogen Elimination: A Theoretical Study

Haitao Zhao, Alireza Ariafard, and Zhenyang Lin*

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received August 15, 2005

β-Heteroatom and β-hydrogen eliminations of the model complexes $[L_2PdCH_2CH_2X]^+$ ($L_2 = H_2PCH_2CH_2PH_2$; X = halides, OMe, OH, OAc) were studied using density function theory calculations at the B3LYP level. Our calculations indicate that for the complexes where X = Cl, Br, and I β-heteroatom eliminations are thermodynamically and kinetically more favorable. For the complexes where X = F, OH, OMe, and OAc, β-hydrogen elimination is kinetically more favorable than β-heteroatom elimination. However, the products (hydride-olefin complexes) formed from the kinetically favorable β-hydrogen elimination are thermodynamically unstable relative to the pre-eliminated species (Pd-alkyl containing a β-X to metal dative bond). Implications of these results on the palladium-catalyzed reactions have been discussed.

Introduction

β-Elimination[1] serves as an important step in many transition-metal-catalyzed reactions. For example, β-hydrogen eliminations, which have been extensively studied experimentally[2] and theoretically,[3] play important roles in transition-metal-catalyzed reactions. In addition to β-hydrogen elimination, β-heteroatom eliminations are also often involved in transition-metal-catalyzed reactions.[4]

An interesting phenomenon is that when both the heteroatom and hydrogen are on the β-carbon atom to a metal center, β-hydrogen eliminations can be observed for some complexes, while for the other complexes, β-heteroatom eliminations can be observed. For example, the palladium-catalyzed Heck reaction of vinyl acetate with iodobenzene affords stilbene; in this reaction, the primary product is β-phenylvinyl acetate, which reacts again with iodobenzene, and the last step is elimination of β-OAc to give stilbene.[1d,5] Jordan and co-workers investigated the reaction of vinyl chloride with cationic palladium(II) olefin polymerization catalysts. They found that polymerization is terminated by a facile β-Cl elimination.[4e,f] Elimination of a β-heteroatom is not always faster and more favorable than that of a β-hydrogen. For example, the palladium-catalyzed Heck carbopalladation/cyclization domino reaction proceeds by β-hydrogen elimination from the cyclizing insertion product to afford aldehyde, and no β-OH elimination occurs from the same carbon to give alkene.[6] A question can be raised from these experimental results. Which elimination is more preferred for a given

---

* Corresponding author. E-mail: chzlin@ust.hk.

[1] (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley & Sons, Ltd: New Jersey, 2005. (b) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*, 1st ed.; Prentice Hall: New Jersey, 1996. (c) Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: New York, 1988. (d) Suji, J. *Palladium Reagents and Catalysts: New Perspectives for the 21st Centry*, 2nd ed.; John Wiley & Sons, Ltd: Chichester, 2004.

[2] For reviews and recent studies relative to β-hydrogen elimination, see: (a) Gellman, A. J. *Acc. Chem. Res.* **2000**, *33*, 19. (b) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (c) Gais, H. J.; Bruns, P. R.; Raabe, G.; Hainz, R.; Schleusner, M.; Runsink, J.; Babu, G. S. *J. Am. Chem. Soc.* **2005**, *127*, 6617. (d) Mueller, J. A.; Goller, C. P.; Sigman, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9724. (e) Lazzaroni, R.; Settambolo, R.; Prota, G.; Botteghi, C.; Paganelli, S.; Marchetti, M. *Inorg. Chim. Acta* **2004**, *357*, 3079. (f) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226. (g) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022. (h) Lautens, M.; Fang, Y. Q. *Org. Lett.* **2003**, *5*, 3679. (i) Qadir, M.; Priestley, R. E.; Rising, T.; Gelbrich, T.; Coles, S. J.; Hursthouse, M. B.; Sheldrake, P. W.; Whittall, N.; Hii, K. K. *Tetrahedron Lett.* **2003**, *44*, 3675. (j) Casey, C. P.; Carpenetti, D. W. *J. Organomet. Chem.* **2002**, *642*, 120. (k) Shultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975. (l) Kawabe, M.; Murata, M. *Macromol. Chem. Phys.* **2001**, *202*, 2440. (m) Blum, O.; Milstein, D. *J. Organomet. Chem.* **2000**, *594*, 479. (n) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 7220. (o) Komiya, S.; Yasuda, T.; Fukuoka, A.; Hirano, M. *J. Mol. Catal. A, Chem.* **2000**, *159*, 63.

[3] (a) Ng, S. M.; Zhao, C.; Lin, Z. Y. *J. Organomet. Chem.* **2002**, *662*, 120−129. (b) Huang, X.; Zhu, J.; Lin, Z. Y. *Organometallics* **2004**, *23*, 4154. (c) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984. (d) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109. (e) Stromberg, S.; Zetterberg, K.; Siegbahn, P. E. M. *J. Chem. Soc., Dalton Trans.* **1997**, 4147. (f) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746.

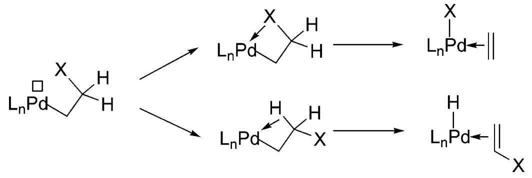
[4] For reviews and recent studies relative to β-heteroatom elimination, see: (a) Muzart, J. *Tetrahedron* **2005**, *61*, 4179. (b) Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132. (c) Hiwatari, K.; Kayaki, Y.; Okita, K.; Ukai, T.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2237. (d) Lei, A. W.; Lu, X. Y.; Liu, G. S. *Tetrahedron Lett.* **2004**, *45*, 1785. (e) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600. (f) Foley, S. R.; Stockland, R. A.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350. (g) Zhu, G. G.; Zhang, Z. G. *J. Org. Chem.* **2005,** *70*, 3339. (h) Liu, G. S.; Lu, X. Y. *Tetrahedron Lett.* **2003**, *44*, 467. (i) Xie, X.; Lu, X. Y.; Liu, Y. Y.; Xu, W. *J. Org. Chem.* **2001**, *66*, 6545. (j) Liu, G. S.; Lu, X. Y. *Tetrahedron Lett.* **2002**, *43*, 6791. (k) Lei, A. W.; Liu, G. S.; Lu, X. Y. *J. Org. Chem.* **2002**, *67*, 974. (l) Zhang, Q. H.; Lu, X. Y.; Han, X. L. *J. Org. Chem.* **2001**, *66*, 7676. (m) Lei, A. W.; Lu, X. Y. *Org. Lett.* **2000**, *2*, 2357. (n) Murakami, M.; Igawa, H. *Helv. Chim. Acta* **2002**, *85*, 4182. (o) Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F.; Parisi, L. M. *J. Organomet. Chem.* **2003**, *687*, 562.

[5] Kasahara, A.; Izumi, T.; Fukuda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 551.

[6] Kressierer, C. J.; Müller, T. J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5997.

10.1021/om050703v CCC: $33.50

Scheme 1



complex having a heteroatom and hydrogen on the same β-carbon to the metal center, heteroatom or hydrogen? Scheme 1 summarizes the two possible eliminations for a given complex.

Previous studies for early transition metal complexes showed that β-heteroatom (halide and OR) eliminations are kinetically and thermodynamically feasible.[7] The feasibility of the β-heteroatom elimination for early transition metal complexes is not surprising. In principle, β-heteroatom elimination breaks an M−C bond and forms an M−X bond. For early transition metals, M−X bonds are much stronger than M−C bonds. For example, the calculated bonding energy difference between Ta−OH and Ta−C is about 53.1 kcal/mol, and the difference between Ta−Cl and Ta−C is about 35.6 kcal/mol. The driving force for β-heteroatom eliminations is the formation of strong M−X bonds.[7] In contrast, β-heteroatom eliminations from late transition metal complexes are anticipated to be less favorable because M−X bonds are much weaker. For example, the bond dissociation energy of a Pt−Cl bond is estimated to be only ca. 10 kcal/mol greater than that of a Pt−Me bond.[4f,8] Goddard and co-workers investigated the chain propagation steps for palladium-catalyzed polymerization of polar olefins (methyl acylate, vinyl acetate, acrylonitrile, and vinyl chloride) theoretically.[9] They found that β-Cl elimination is an easy process.

It is necessary to study the two competing elimination processes in more detail for late transition metal complexes. Through the studies, we hope to gain more insight into the factors influencing β-heteroatom elimination. A fundamental understanding of these factors will help to find a better synthetic strategy. Palladium complexes have been widely used as catalysts in organic reactions. Experiments show that both neutral and cationic Pd complexes undergo β-elimination reactions.[4] Therefore, we have chosen several cationic palladium(II) model complexes, $[L_2PdCH_2CH_2X]^+$ ($L_2 = H_2PCH_2CH_2PH_2$; X = halide, OMe, OH, OAc), for our study. In this paper, theoretical calculations based on the B3LYP density functional theory[10] have been carried out to examine the relative easiness of β-heteroatom versus β-hydrogen eliminations.

Computational Details

Molecular geometries of the model complexes were optimized without constraints at the Becke3LYP (B3LYP)[10] level of density functional theory. Frequency calculations at the same level of theory have also been performed to identify all the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The effective core potentials (ECPs) of Hay and Wadt with a double-ζ basis set (LanL2DZ)[11] were used to describe Pd, Cl, Br, I, and P. The 6-31G** basis set was used for H, C, F, and O. Polarization functions were also added for Cl ($\zeta_d = 0.514$), Br ($\zeta_d = 0.389$), I ($\zeta_d = 0.266$), and P ($\zeta_d = 0.340$).[12] All calculations were performed with the Gaussian 03[13] software package.

To test the effect of basis sets on the calculated energies, we also performed single-point calculations for those species involved in the β-X and β-H eliminations of $[L_2PdCH_2CH_2X]^+$ ($L_2 = H_2PCH_2CH_2PH_2$; X = Br) by replacing the LanL2DZ and 6-31G** basis sets mentioned above with the SDDAll[14] and 6-311G** basis sets, respectively. Using the smaller basis set, the relative energies of **PRDX**, **TSX**, **PCX**, **TSPC**, **PCH**, **TSH**, and **PRDH** are −25.0, −12.8, −14.7, 0.7, 0.0, 9.2, and 5.9 kcal/mol, respectively. Using the larger basis set, the relative energies of **PRDX**, **TSX**, **PCX**, **TSPC**, **PCH**, **TSH**, and **PRDH** are −26.3, −12.9, −14.4, 2.1, 0.0, 7.2, and 4.4 kcal/mol, respectively. These additional calculations suggest that the basis set dependence is small.

Results and Discussion

As mentioned in the Introduction, the most important aim of this study is to compare β-heteroatom versus β-hydrogen elimination in the cationic palladium(II) complexes $L_2Pd(CH_2CH_2X)$ (Scheme 1) where the heteroatoms X are halides (F, Cl, Br, and I), OH, OMe, and OAc.

The potential energy profiles corresponding to the β-hydrogen and β-heteroatom elimination processes of the complexes $[L_2Pd(CH_2CH_2X)]^+$ are shown in Figure 1. Selected bond distances of the optimized structures are given Figure 2. Different abbreviations are used in Figures 1 and 2 for different transition states and complexes. **PCX** and **PCH** stand for the starting complexes that are involved in the β-X and β-H elimination processes, respectively. **PRDX** and **PRDH** represent products that are obtained from the elimination reactions of **PCX** and **PCH**, respectively. **TSPC** represents the transition states that connect **PCX** and **PCH**. **TSX** and **TSH** represent the transition states of β-X and β-H eliminations, respectively. **TSPCX** used in Figure 1c represents the transition states between two **PCX** minima.

We classified our results into three cases according to the results of our calculations. In the first case (case A), having X = Cl, Br, and I, the β-X eliminations are thermodynamically and kinetically preferred. In this case, β-X elimination has lower reaction barrier and **PRDX** is thermodynamically very stable (see Figure 1a). The second case (case B), having X = OMe, OH, and F, is related to the one where the β-H elimination has a smaller barrier than the β-X elimination (see Figure 1b). The third case (case C) is for X = OAc (see Figure 1c).

---

[7] Cundari, T. R.; Taylor, C. D. *Organometallics* **2003**, *22*, 4047.

[8] Altakhin, G.; Skinner, H. A.; Zaki, A. A. *J. Chem. Soc., Dalton Trans.* **1984**, 371.

[9] Philipp, D. M.; Muller, R. P.; Goddard, W. A.; Storer, J.; McAdon, M.; Mullins, M. *J. Am. Chem. Soc.* **2002**, *124*, 10198.

[10] (a) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

[11] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

[12] Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Huzinaga, S., Ed.; Elsevier Science: Amsterdam, 1984.

[13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B05; Gaussian, Inc.: Pittsburgh, PA, 2003.

[14] Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

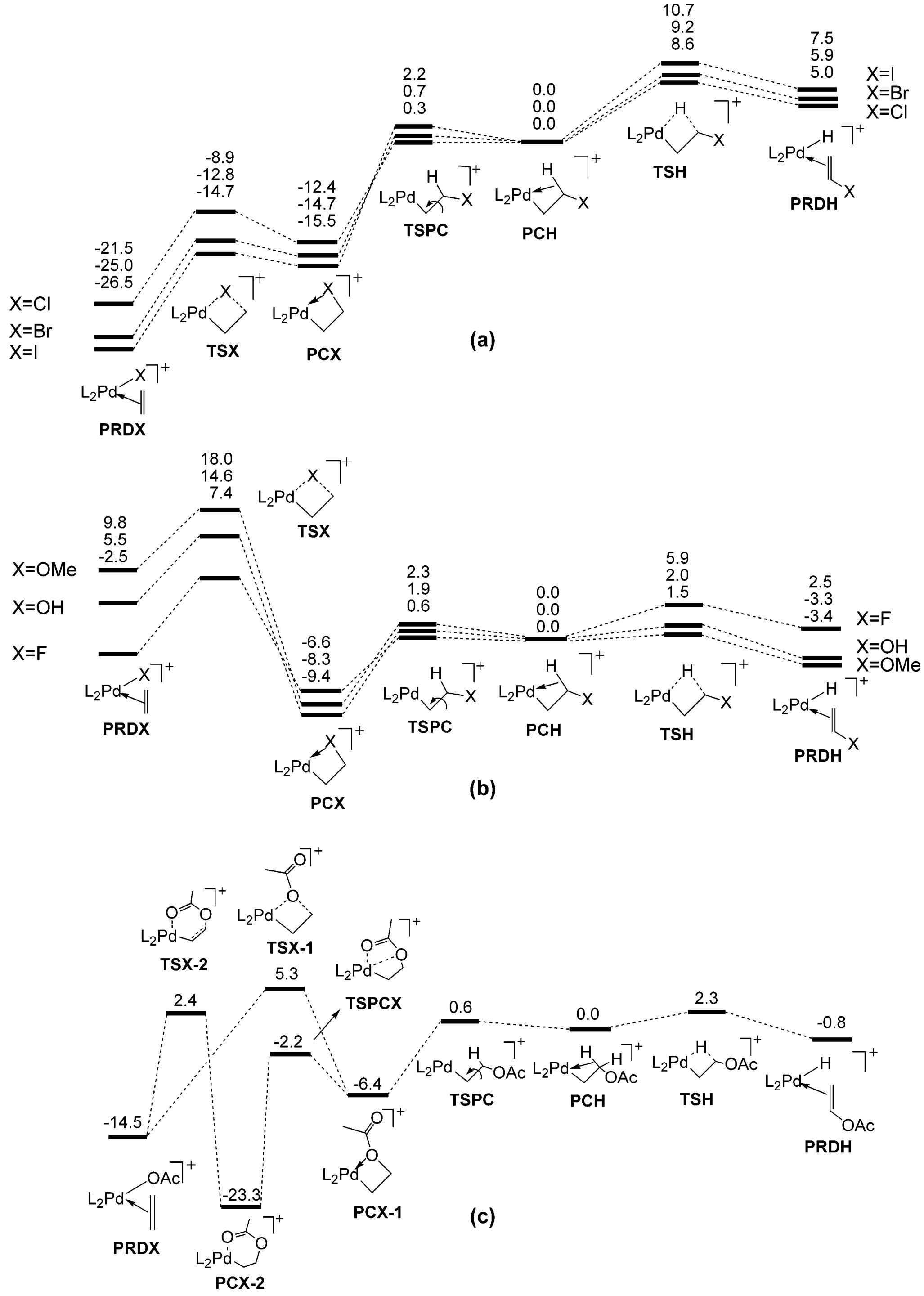


Figure 1. Energy profiles relevant to β-hydrogen and β-heteroatom eliminations. The relative energies (ΔE) are given in kcal/mol. (a) Case A, $[L_2PdCH_2CH_2X]^+$ where X = Cl, Br, and I. (b) Case B, $[L_2PdCH_2CH_2X]^+$ where X = F, OH, and OMe. (c) Case C, $[L_2PdCH_2CH_2X]^+$ where X = OAc.

Interconversion between PCX and PCH. PCH can be converted to **PCX** by rotation of CH_2X about the C−C bond. In cases A and B, the rotation barriers are in the range 0.3−2.3 kcal/mol. **PCX** are more stable than **PCH**. The higher stability of **PCX** relative to **PCH** can be related to the stronger interaction between the heteroatoms and the metal center. X having lone pairs of electrons that occupy energetically high lying orbitals is more capable of donating its electrons to the metal center than C−H, having a σ-bonding pair of electrons that occupy an energetically low lying σ orbital. The relatively less stable **PCX** when X = F in comparison with **PCX** when X = OMe and OH (Figure 1b) is indeed related to the case where the lone pair orbital of F used to coordinate with the metal center is lying lower in energy than those of OH and OMe. We performed calculations on CH_3CH_2X (X = F, OH, OMe) and found that the HOMO orbital energies are −8.74, −7.11, and −6.79 eV, respectively. **PCX** where X = OMe is relatively less stable in comparison with **PCX** where X = OH, probably due to steric effects. The poorer tendency of C−H to donate its σ-bonding electrons gives weak agostic bonds[15] for all the **PCH** species. The agostic interactions are expected to be comparable for all

---

[15] (a) Clot, E.; Eisenstein, O. *Struct. Bond.* **2004**, *113*, 1. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (c) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

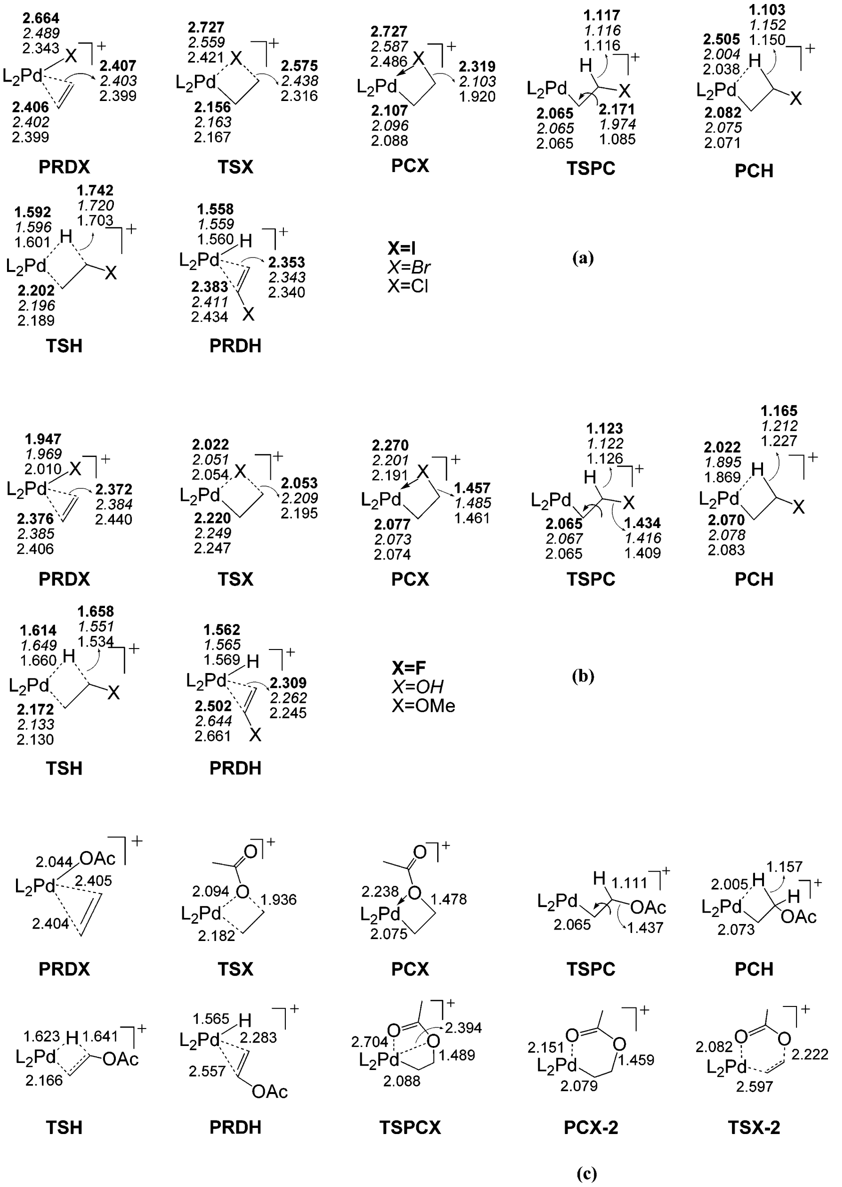


Figure 2. Selected bond distances of the optimized structures. The bond distances are given in angstroms. (a) Case A, $[L_2PdCH_2CH_2X]^+$ where X = Cl, Br, and I. (b) Case B, $[L_2PdCH_2CH_2X]^+$ where X = F, OH, and OMe. (c) Case C, $[L_2PdCH_2CH_2X]^+$ where X = OAc.

PCH complexes. Therefore, they were used as the references for comparing the stability of different complexes in the energy profiles.

The reaction energies of **PCH** → **PCX** range from −6.4 to −15.5 kcal/mol. From Figure 1, it is clear that the **PCX** complexes in case A have stronger Pd−X interactions than those in case B. Understanding the results requires an analysis of the calculated structural parameters. The results show that the C−X bond distances in **PCX** are significantly longer than those in the X-substituted ethane, which were optimized at the B3LYP level. The change in the C−X bond distances from CH_3CH_2X to **PCX** is most significant for C−I (0.13 Å, 5.9%) and least significant for C−OMe (0.045 Å, 3.2%) and was found to decrease in the trend for the complexes where X = I > X = Br > X = Cl > X = F > X = OH > X = OAc > X = OMe. Table 1 shows the calculated Wiberg bond indices[16] (from NBO[17] calculations) for various Pd−X bonds in **PCX**, **TSX**, and **PRDX**. The bond indices clearly indicate that stronger Pd−X interactions were calculated for **PCX** when X = I, Br, and Cl. Smaller Pd−X bond indices were calculated for **PCX** when X = OAc, OMe, OH, and F.

Table 1. Calculated Wiberg Bond Indices of the Pd−X Bonds in PCX, TSX, and PRDX

X	**PCX**	**TSX**	**PRDX**	ratio 1[a]	ratio 2[b]
I	0.341	0.386	0.463	0.884	0.737
Br	0.291	0.360	0.430	0.808	0.677
Cl	0.239	0.338	0.409	0.708	0.584
OAc	0.157	0.235	0.293	0.667	0.535
OMe	0.166	0.376	0.427	0.441	0.388
OH	0.179	0.399	0.477	0.450	0.376
F	0.126	0.321	0.388	0.392	0.324

[a] The ratio between the Pd−X bond indices of **PCX** and **TSX**. [b] The ratio between the Pd−X bond indices of **PCX** and **PRDX**.

In case C, two stable **PCX** structures (named **PCX-1** and **PCX-2**) with different carboxylate oxygens (O=C and O−C) forming dative bonds to the metal center were found from our calculations (Figure 1c). **PCX-1** can be converted to **PCX-2** with a small barrier of 4.2 kcal/mol. The reaction energy of **PCX-1** → **PCX-2** is −16.9 kcal/mol. Several X-ray crystal

---

(16) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(17) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1.

Table 2. Calculated Bond Dissociation Energies (kcal/mol) of the C−X Bonds in CH_3CH_2X and the Pd−X Bonds in PRDX Complexes

X	E_{C-X}	D_{C-X}[a]	E_{Pd-X}[b]	$E_{Pd-X} - E_{C-X}$
I	58.4	56.4	42.9	−15.5
Br	68.7	70.5	50.0	−18.8
Cl	81.0	84.6	58.2	−22.8
F	114.7	110.7	73.8	−40.9
OMe	82.7	84.8	37.6	−45.1
OH	93.9	93.9	52.6	−41.3
OAc	86.4	86.5[c]	56.3	−30.1

[a] Values from ref 18. [b] Model complexes used are $[Pd(H_2PCH_2CH_2PH_2)(CH_2{=}CH_2)X]^+$. [c] Bond dissociation energy of the $CH_3COO{-}CH_2CH_2CH_3$ bond from ref 19.

structures of chelate species similar to **PCX-2** have been reported, suggesting that **PCX-2** is very stable.[4b] **PCH** can be converted to **PCX-1** with a very small barrier (0.6 kcal/mol).

***β*-X Elimination.** The most noticeable difference between the first two cases is the reaction energies of the *β*-X eliminations (**PCX → PRDX)**. The **PCX → PRDX** reactions in case A are exothermic, while the reactions in case B are endothermic. A simple estimation is used to explain the observed reaction energy differences. The reaction energy for a given **PCX → PRDX** *β*-X elimination can be written as follows.

$$\Delta E = -[E(\mathrm{Pd-X}) + E(\mathrm{Pd-||}) - E(\mathrm{Pd-C}) - E(\mathrm{C-X}) - E(\mathrm{Pd-(X-C)})] \quad (1)$$

where E(A−B) is the bond dissociation energy of the A−B bond and E(Pd−(X−C)) represents the bond energy derived from the C−X to metal dative interaction in **PCX**. If we assume that the bond dissociation energies of the Pd−|| and Pd−C bonds do not change significantly from one complex to another and that the C−X agostic interaction energies, E(Pd−(X−C)), do not play a major role in the significant difference in the reaction energies of the *β*-X eliminations (**PCX → PRDX)** between the two cases, ΔE can be further expressed as in eq 2.

$$\Delta E = -[E(\mathrm{Pd-X}) - E(\mathrm{C-X}) + \mathrm{constant}] \quad (2)$$

E(C−X) and E(Pd−X) were computed by the following equations:

$$CH_3CH_2X \rightarrow CH_3CH_2 + X \quad (3)$$

$$L_nPdX \rightarrow L_nPd + X \quad (4)$$

In eq 4, L_nPdX represents **PRDX**, $[Pd(H_2PCH_2CH_2PH_2)(CH_2{=}CH_2)X]^+$. Table 2 lists the calculated bond dissociation energies of the C−X bonds in CH_3CH_2X and the Pd−X bonds in **PRDX**. For comparison, Table 2 also includes the bond dissociation energies of the C−X bonds available from the literature.[18,19] The calculated C−X bond dissociation energies are in good agreement with those reported in the literature. From Table 2, we can see that the E(Pd−X) − E(C−X) values for X in case A are less negative than those for X in case B. The more negative E(Pd−X) − E(C−X) values indicate that the C−X bonds are much stronger than Pd−X bonds, and the driving force for **PCX → PRDX** is smaller.

The data presented in Table 2 show that for **PRDX** when X = halides the Pd−X homolytic bond dissociation energies (E_{Pd-X}) decrease down the group and span a range from 73.8 kcal/mol (X = F) to 42.9 kcal/mol (X = I). The results reflect the increasing size and decreasing eletronegativity of X down the group. The Pd−X bond dissociation energies for the **PRDX** complexes when X = OMe, OH, and OAc are in the range from 37.6 to 56.3 kcal/mol. Interestingly, the Pd−OMe bond is the weakest bond among the three Pd−OR bonds. Both electronic and steric effects are operative here. The electron-releasing property of Me increases the electron repulsion between the metal d electrons and the lone pairs of electrons on the oxygen atom. The steric effect of Me also weakens the Pd−OMe bonding interactions. The Pd−OAc bond is the strongest bond among the three Pd−OR bonds. The *π*-conjugation in the CO_2 moiety of the OAc ligand reduces the electron repusion mentioned above and, therefore, enhances the Pd−OAc bonding interactions.

A similar trend is also seen for the C−X bond energies in CH_3CH_2X when X = halide in Table 2. The C−X bond energies decrease down the group and in the range of 58.4 (X = I) to 114.7 (X = F) kcal/mol. As we discussed above, increasing size and decreasing eletronegativity decrease the C−X orbital overlaps and subsequently decrease the C−X homolytic bond dissociation energy.[20] Oxygen is approximately the same size as fluorine but has a different electronegativity. Higher electronegative fluorine has a shorter C−F bond length and has better interaction with carbon, making C−F a stronger bond when compared to the C−OR bond.

Complexes in case A undergo **PCX → PRDX** *β*-X elimination reactions with small barriers. The exothermic reactions facilitate the reactions. The elimination barriers increase in the trend for the complexes where X = I (0.8 kcal/mol) < X = Br (1.9 kcal/mol) < X = Cl (3.5 kcal/mol). Comparing the structures of **PCX** with **TSX**, we found that the **TSX** structures for the complexes in case A belong to early transition states, which are reactant-like. Especially for X = I, the Pd−X bond distances in **PCX** and **TSX** are almost the same and the C−X and Pd−C bond lengths do not change much from **PCX** to **TSX**. In Table 1, the calculated bond indices for the Pd−X bonds in **PCX** are very close to those of **TSX** for complexes in case A. The ratios between the Pd−X bond indices of **PCX** and **TSX** (ratio 1) are greater than 0.7.

The *β*-X eliminations (**PCX → PRDX)** for complexes in case B have much higher reaction barriers. The barriers increase in the trend for the complexes where X = F (14.0 kcal/mol) < X = OH (24.0 kcal/mol) < X = OMe (26.3 kcal/mol). The high barriers are closely related to the endothermic **PCX → PRDX** elimination due to the relatively weak Pd−X bonds in **PRDX** and the strong C−X bonds in **PCX**.

As mentioned above, two **PCX** structures (**PCX-1** and **PCX-2**) were found for X = OAc. **PCX-1** can be converted to **PCX-2** with a small barrier of 4.2 kcal/mol or undergo *β*-X elimination to give **PRDX** directly with a moderate reaction barrier (11.7 kcal/mol). The thermodynamically and kinetically stable **PCX-2** undergoes **PCX-2 → PRDX** *β*-X elimination with a high barrier of 25.7 kcal/mol. Cationic nickel(II) and palladium(II) complexes containing a six-membered ring similar to that of **PCX-2** (X = OAc) can be found in the literature,[4b] supporting the finding that **PCX-2** (X = OAc) is highly stable.

***β*-H Elimination.** From Figure 1, we can see that the *β*-H eliminations (**PCH → PRDH**) for the complexes having X = OR are exothermic, while the *β*-H eliminations for the complexes having X = halides are endothermic. We could follow the energetic discussion employed above to understand the

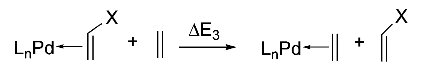
---

[18] Lide, D. R. *CRC Handbook of Chemistry and Physics*, 84th ed.; CRC Press: Boca Raton, 2004.

[19] Holman, R. W.; Sumpter, T. L.; Farrar, J.; Weigel, K.; Bartmess, J. E. *J. Phys. Org. Chem.* **1997**, *10*, 585.

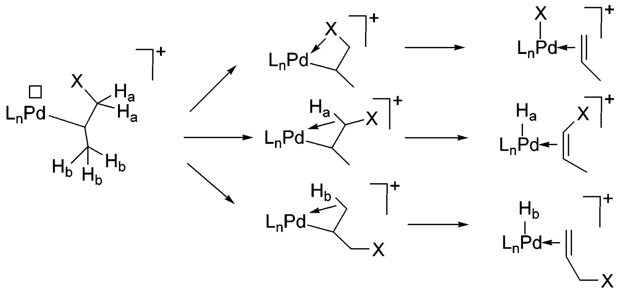
[20] Sakaki, S.; Biswas, B.; Musashi, Y.; Sugimoto, M. *J. Organomet. Chem.* **2000**, *611*, 288.

Scheme 2



X	F	Cl	Br	I	OAc	OH	OMe
ΔE_3	-1.25	-3.77	-3.60	-3.23	1.92	8.43	10.56

Scheme 3



different thermochemistry here. However, the situation here is much more complicated. The carbon−carbon π bonds formed in **PRDH** are expected to have very different bond energies, which are hard to evaluate computationally, in the presence of different substituents X. Instead, we found that binding energies of the substituted olefins determine the stability of **PRDH** and affect the reaction energies of the β-H eliminations (**PCH** → **PRDH**). We designed an isodesmic reaction[21] (Scheme 2) to estimate the binding energies of different substituted olefins relative to that of ethylene. The model complexes used in Scheme 2 are $[PdCl(\eta^2\text{-}CH_2CHX)(H_2PCH_2CH_2PH_2)]^+$. The relative binding energies give information regarding the energetics of the **PCH** → **PRDH** β-H elimination reactions.

The results given in Scheme 2 show that the strongest binding has the olefin having a methoxy substituent (OMe), and the weakest binding has the olefin having a chlorine substituent. The halide-substituted olefins have smaller binding energies than ethylene, while the OR-substituted olefins give greater binding energies. The results suggest that the electron-donating properties of the olefin ligands determine the binding energies. The OR substituents are stronger π donors than the halide substituents. Therefore, the olefins having OR substituents have greater binding energies. Indeed, the C═C π orbitals of the OR-substituted olefins lie higher in energy than those of the halide-substituted olefins. For example, the C═C π orbital energies are −5.9 eV for X = OMe, −6.1 eV for X = OH, and −7.1 eV for X = Cl.

The reaction barriers of the β-H eliminations (**PCH** → **PRDH**) are closely related to the stability of **PRDH**. Therefore, β-H eliminations for those having the OR substituents have smaller barriers (1.5−2.3 kcal/mol). The barriers increase down the group for those having X = halides and span a range from 5.9 kcal/mol (X = F) to 10.7 kcal/mol (X = I).

Competitive *β*-Elimination Reactions from Two Different *β*-Carbons. A question can be raised after the discussion above. When there are two different β-carbon atoms in which one of the β-carbon atoms has two hydrogen atoms concomitant with an X substituent and the other has only hydrogen atoms, which elimination is preferred, β-H$_a$, β-H$_b$, or β-X elimination (Scheme 3)? To answer this question, the cationic palladium(II) complexes $[L_2Pd(CH_3CHCH_2X)]^+$ ($L_2 = H_2PCH_2CH_2PH_2$; X = Cl, OMe, OAc) (Scheme 3) were chosen to study these competing reactions.

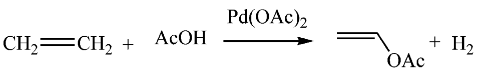
Figure 3 shows the potential energy profiles corresponding to the β-H and β-X elimination processes for the three model cationic complexes $[L_2Pd(CH_3CHCH_2X)]^+$. Figure 3 shows that the profiles related to the β-H$_a$ and β-X eliminations are almost the same as those shown in Figure 1, indicating that introducing the CH_{b3} subtituent at the α-carbon of the model complexes does not change the relative easiness of the β-H$_a$ and β-X eliminations.

From Figure 3, we can see that, for all the cases, **PCH-2** are more stable than **PCH-1**. Examining the structures of **PCH-2**, we find that the X group and the metal fragment are in a synclinal arrangement rather than in an anti-periplanar arrangement. The synclinal conformation adopted by **PCH-2** suggests that van der Waals attractive interactions exist between the X group and the metal fragments. **PCH-2** are more stable than **PCH-1**, implying that the van der Waals attractive interactions in **PCH-2** are more favorable.

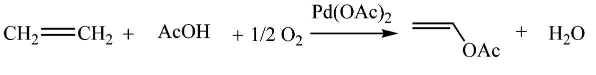
Figure 3 shows that **PRDH-2** where X = Cl and OAc have stability comparable to **PRDH-1**. **PRDH-2** where X = OMe is less stable than **PRDH-1**. The higher stability of **PRDH-1** versus **PRDH-2** when X = OMe is related to the fact that the OMe-substituted olefin ligand in **PRDH-1** has greater Pd(II)-binding energy discussed above.

Comments on Experimental Observations. On the basis of our calculations, it is evident that the types of the X substituent govern the competing reactions between the β-H and β-X eliminations. Many experiments show that the β-X eliminations when X = Cl, Br, and I are generally preferred,[4e−k] consistent with our calculations.

For the complexes having X = OR, the β-H eliminations are kinetically more favorable than the β-X eliminations. However, the products obtained from the β-H eliminations (**PRDH**) are less stable than the intermediates **PCX**. To get the β-H elimination products, the olefins produced need to dissociate quickly from the metal center. Additional driving force is normally required to make the reactions more exothermic. For example, vinyl acetate is produced commercially from ethylene, AcOH, and O_2 using Pd catalyst. Studies show that the mechanism of this reaction is first acetoxypalladation of the ethylene followed by β-H elimination.[22] From our calculations, the β-H elimination is endothermic. Therefore, addition of O_2 is necessary because formation of H_2O via oxidation of H_2 with O_2 provides the thermodynamic driving force, which shifts reaction 6 toward the vinyl acetate. In a recent study, it has also been shown that oxidation of hydrogen to H_2O can transform the energetically neutral or slightly endothermic reactions to highly exothermic reactions.[23]



(5)



(6)

Reactions of propylene with AcOH and O_2 using Pd(II) catalyst were reported to give **2** and **3** by β-H eliminations from

---

[21] Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

[22] For reviews and recent theoretical studies of acetoxylation of olefins, see: (a) Moiseev, I. I.; Vargaftik, M. N. *Coord. Chem. Rev.* **2004**, *248*, 2381. (b) Kozitsyna, N. Y.; Vargaftik, M. N.; Moiseev, I. I. *J. Organomet. Chem.* **2000**, *594*, 274. (c) Tsuji, J. *New J. Chem.* **2000**, *24*, 127. (d) Kragten, D. D.; van Santen, R. A.; Lerou, J. J. *J. Phys. Chem. A* **1999**, *103*, 80. (e) Kragten, D. D.; van Santen, R. A.; Neurock, M.; Lerou, J. J. *J. Phys. Chem. A* **1999**, *103*, 2756.

[23] Batsanov, A. S.; Collings, J. C.; Fairlamb, I. J. S.; Holland, J. P.; Howard, J. A. K.; Lin, Z. Y.; Marder, T. B.; Parsons, A. C.; Ward, R. M.; Zhu, J. *J. Org. Chem.* **2005**, *70*, 703

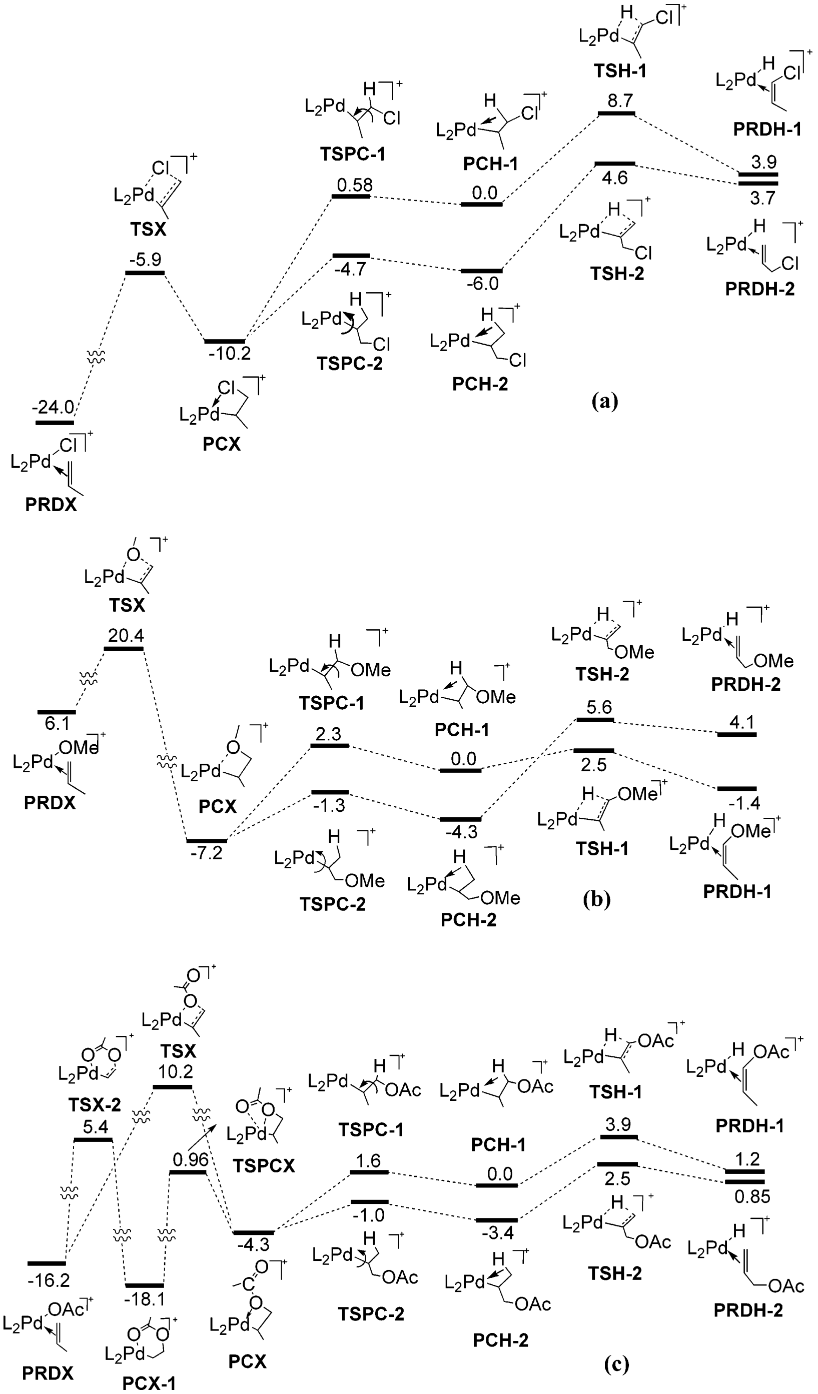
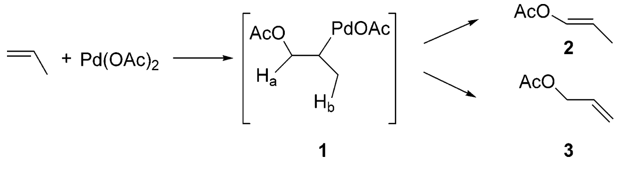


Figure 3. Energy profiles relevant to β-hydrogen and β-heteroatom eliminations. The relative energies (ΔE) are given in kcal/mol. (a) Case A, $[L_2Pd(CH_3CHCH_2X)]^+$ where X = Cl, Br, and I. (b) Case B, $[L_2Pd(CH_3CHCH_2X)]^+$ where X = F, OH, and OMe. (c) Case C, $[L_2Pd(CH_3CHCH_2X)]^+$ where X = OAc.

Scheme 4

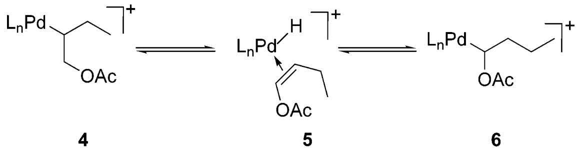


the intermediate **1** (Scheme 4); the allyl acetate **3** is the major product.[1d] Again, O_2 is necessary for the products obtained via β-H elimination. Our calculations (Figure 3) show that β-H_b elimination is more feasible than β-H_a elimination, consistent with the experimental observation that **3** is the major product.

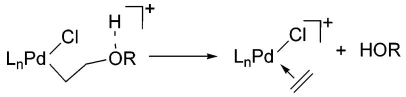
It should be addressed here that a β-H elimination yields a hydride that can easily reinsert into the olefin.[4b,9] This phenomenon has been commonly observed in experiments for complexes having X = OR. This is because the β-H eliminations from the complexes having X = OR have small barriers and the products are less stable than **PCX**. For example, complex **4** can undergo "chain running" via β-H elimination and readdition processes, to migrate to the carbon α to acetate (Scheme 5).[4b]

Lu and co-workers found that halide ions can inhibit β-H elimination and promote β-OR elimination in acidic media for Pd(II)-catalyzed reactions.[24] Explanations in the literature for

Scheme 5



Scheme 6



the results are that the presence of excess halide ions makes the palladium coordinatively saturated and the β-H eliminations not as feasible.[24] In addition, Lu and co-workers felt that coordination of halide ions to palladium increases the electron density of the metal center, resulting in the weakening of the Pd−C bond and promoting the β-OR elimination.[24]

Our calculations show that the OR group can easily dissociate with the help of H^+ in acidic media (Scheme 6). For example, OR elimination for the process shown in Scheme 6 is highly exothermic (−11.4 kcal/mol) with a barrier of only 8.2 kcal/mol when R = H.[25] These results suggest that acidic reaction conditions are also important in addition to blocking the empty coordination site by the excess halide ions.

Conclusions

In this paper, the competing processes of β-heteroatom versus β-H elimination for the model complexes $[L_2PdCH_2CH_2X]^+$ ($L_2 = H_2PCH_2CH_2PH_2$; X = halides, OMe, OH, OAc) have been theoretically investigated.

Our calculations indicate that for the complexes where X = Cl, Br, and I, the β-X eliminations are thermodynamically and kinetically more favorable. For the complexes where X = F, OH, OMe, and OAc, the β-H eliminations are kinetically more favorable than the β-X elimination. However, the products (hydride-olefin complexes) formed from the kinetically favorable β-H elimination (**PRDH**) are thermodynamically unstable relative to the pre-eliminated species (Pd-alkyl containing a β-X to metal dative bond). Therefore, to get the β-H elimination products, additional driving force is required to make the reactions exothermic. For example, conversion of $H_2C{=}CH_2 \rightarrow H_2C{=}CH(OAc)$ catalyzed by palladium complexes often requires addition of oxidants to make the reactions, $H_2C{=}CH_2 + HOAc \rightarrow H_2C{=}CH(OAc) + H_2O$, exothermic.

In comparison with β-H elimination, β-OR elimination is kinetically less favorable. To obtain the kinetically unfavorable β-OR elimination products, excess halide additions and an acidic condition are necessary. The excess halide ions block the empty coordination site, preventing the β-H elimination, and the acidic condition helps elimination of the OR group via formation of the stable HOR molecule.

The complexes having two different β-carbon atoms in which one of the β-carbon atoms has two hydrogen atoms concomitant with an X substituent and the other β-carbon atom has only hydrogen atoms were also studied. Calculations indicate that introducing an alkyl substituent at the α-carbon of the model complexes does not change the relative easiness of the β-H and β-X eliminations.

Acknowledgment. The authors acknowledge financial support from the Hong Kong Research Grants Council (HKUST 6023/04P and DAG05/06.SC19), the University Grants Committee of Hong Kong through the Area of Excellence Scheme (Aoe/P-10/01).

Supporting Information Available: Cartesian coordinates for all the calculated structures are available free of charge via the Internet at http://pubs.acs.org.

OM050703V

---

(24) (a) Lu, X. Y. *Chin. J. Org. Chem.* **2001**, *21*, 769. (b) Zhang, Z. G.; Lu, X. Y.; Xu, Z. R.; Zhang, Q. H.; Han, X. L. *Organometallics* **2001**, *20*, 3724. (c) Zhu, G. X.; Lu, X. Y. *Organometallics* **1995**, *14*, 4899.

(25) Solvent effects were considered for the reaction shown in Scheme 6 as suggested by one of the referees. Single-point energy calculations with the PCM method were done using methanol ($\epsilon = 32.63$) as the solvent. The PCM calculations give a similar reaction barrier (9.4 kcal/mol).