ELSEVIER

Journal of Organometallic Chemistry 662 (2002) 120–129

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Theoretical studies on the β-hydrogen elimination reactions of palladium and platinum alkoxide complexes containing bidentate ligands

Sze Ming Ng, Cunyuan Zhao, Zhenyang Lin *

Department of Chemistry and Open Laboratory of Chirotechnology of Institute of Molecular Technology for Drug Discovery and Synthesis, The University Grant Committee Area of Excellence Scheme (Hong Kong), The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received 6 June 2002; accepted 11 August 2002

Abstract

The selection of reaction pathways between the β-hydrogen elimination and σ-bond metathesis followed by reductive elimination of palladium and platinum alkoxide complexes containing bidentate ligands, $L_2MX(OCY_2H)$ ($L_2 = CH_2NCHCHNCH_2$ and $PH_2CH_2CH_2PH_2$; M = Pd and Pt; X = CH_3, OCH_3, NH_2, OH, HCOO, Cl and Br; Y = H and F), have been investigated by density functional theory calculations at the level of B3LYP. The effects of *cis*-ligand X, bidentate ligand L_2, transition metal M and substituents Y have been examined. The results show that Pd complexes with ligands X = OCH_3, NH_2, OH and HCOO favor the σ-bond metathesis followed by a reductive elimination reaction pathway leading to the metal-hydride products while complexes with ligand X = CH_3 favor the β-hydrogen elimination pathway. Both reaction pathways are found possible for complexes with ligands X = Cl and Br when M = Pd and Y = H. It is also found that Pt complexes have higher reaction barriers and complexes with phosphine bidentate ligands have lower reaction barriers when compared to their analogous Pd complexes containing amine bidentate ligands. F substituted alkoxy ligands decrease the β-hydrogen elimination pathways barriers. It is also found that the β-hydrogen elimination pathway is always preferred when the ligand dissociation from the four-coordinate complexes is the initial event for the reactions.

Keywords: β-Hydrogen elimination; Palladium and platinum alkoxide complexes; Bidentate ligands

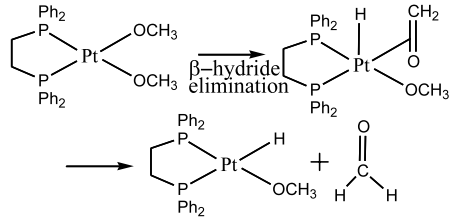
1. Introduction

The oxidation of alcohols to aldehydes and ketones is one of most important reactions in organic chemistry because it can convert one functional group to another [1]. From oxidative reagents to organometallic catalysis, there are various methods to perform this process. In 1949, Westheimer published the first organometallic catalysis in the alcohol oxidation by dioxochromium(VI) complexes [2]. Since then, chemists have been putting their eyes in using transition metals to catalyze the oxidation of alcohols to aldehydes and ketones with both economic and environmental advantages. Palladium [3,4], platinum [5], cobalt [6], copper [7,8], ruthenium [9,10], and iridium [11] have been reported as effective catalysts of the above mentioned oxidation reactions.

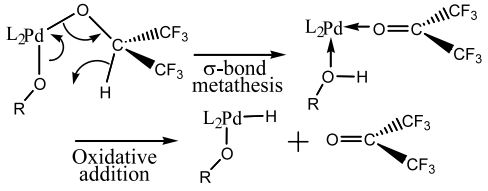
In the catalytic processes, β-hydrogen elimination always plays a key role for forming products, such as aldehydes or ketones. In Scheme 1, the hydrogen atoms bonded to the β-carbon atom of an alkoxy group can be directly transferred to the metal center and a carbonyl functional group is generated. This mechanism is called 'one-step β-hydrogen elimination' and has been used to explain the pathway of the conversion of (dppe)Pt$(OCH_3)_2$ to (dppe)Pt(H)(OCH_3) [5]. However, there is another possible mechanism involving two-step reactions. The conversion is completed through a σ-bond metathesis followed by an oxidative addition (Scheme 2). One of the hydrogen atoms bonded to the β-carbon

* Corresponding author. Fax: +852-2358-1594
E-mail address: chzlin@ust.hk (Z. Lin).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01898-3



Scheme 1. The β-hydrogen elimination reaction pathway in the conversion of $(dppe)Pt(OCH_3)_2$ to $(dppe)Pt(H)(OCH_3)$.



Scheme 2. The σ-bond metathesis reaction pathway in the conversion of $L_2Pd(OC(CF_3)_2H)(OR)$ to $L_2Pd(H)(OR)$.

of the alkoxy group is first transferred to the *cis*-ligand (X). HX and aldehydes or ketones are formed and weakly coordinated to the metal center. Then HX undergoes an oxidative addition. The two-step conversion has been suggested for the conversion of fluorinated alkoxide to metal-hydride complexes based on the fact that a close C–H···O contact is found in the crystal structure of $[Pd(OCH(CF_3)_2)(OPh)(bpy)]$ [4].

Apparently, the reaction steps involved in the two different mechanisms are all fundamental reactions which are well-recognized in organometallic chemistry. It is stimulating to investigate the factors affecting the reaction pathways leading to the same β-hydrogen elimination products by computational approaches. Comparing these two reaction pathways allow us to know the favorable process when different ligand environments are present. Our purposes here are to systematically study the factors influencing the reaction pathways. The fundamental understanding of these factors will assist the experimental efforts in finding better catalysts.

2. Computational method

Full geometry optimizations of model complexes $L_2MX(OCY_2H)$ were done at the Becke3LYP (B3LYP) level of density functional theory [12]. Here, $L_2 = CH_2NCHCHNCH_2$ (denoted by (N ∼ N)) and $PH_2CH_2CH_2PH_2$ (denoted by (P ∼ P)) which are the simplified form of bipyrimidine (bpym) and 1,2-bis(diphenylphosphino)ethane (dppe); M = Pd and Pt; X = CH_3, OCH_3, NH_2, OH, HCOO, Cl and Br; Y = H and F. The effective core potentials (ECPs) of Hay and Wadt with double-ξ valence basis set (LanL2DZ) [13] were used to describe Cl and Br in the complexes. The modified LanL2DZ basis set was chosen for Pd and Pt [14]. Polarization functions were also added for Cl ($\xi_d = 0.514$) and Br ($\xi_d = 0.389$) [15] Except for those atoms in the bidentate ligand where 6-31G [16] was used, the 6-31G** basis set was for all other atoms.

Frequency calculations based on the same calculation method and basis sets were carried out to confirm the characteristics of all optimized structures as minima or transition states. As a testing case, calculations of intrinsic reaction coordinates (IRC) [17] were also performed for the (N ∼ N)Pd(OH)(OCH_3) system to confirm that the transition state is connecting the two corresponding minima. The effect of triple-ξ d functions of the transition metals has been examined for the (N ∼ N)Pd(OH)(OCH_3) system by further splitting the LanL2DZ basis set. The relative energies using the triple-ξ d functions differ only slightly from the results obtained with the medium-size basis sets described above. The changes are within 2.0 kcal mol^{-1}. To examine the effect of electron correlation, we performed the CCSD(T) calculations for the (N ∼ N)PdCl(OCH_3) system. The choice of the chloride system is because the two studied reaction pathways are competing. The CCSD(T) calculations of such a case allow us to test the reliability of the B3LYP results. In the CCSD(T) calculations, 6-31G** is used only for the transferring hydrogen instead of the whole OCH_3 group. The zero-point energy corrections and entropy contributions in the evaluation of the free energies at the level of CCSD(T) were obtained on the basis of the B3LYP results. The relative free energies at the level of CCSD(T) are calculated to be 53.80 kcal mol^{-1} for **TS1** and 60.66 kcal mol^{-1} for **TS2a**, while the relative free energies at the level of B3LYP are 46.22 and 48.02 kcal mol^{-1} for **TS1** and **TS2a**, respectively. These results suggest that the energy difference between **TS1** and **TS2a** for the chloride case increases from ca. 2.0 to 7.0 kcal mol^{-1}. Based on these calculations, we estimate that there is an error of 5 kcal mol^{-1} in terms of comparing the relative easiness of reactions when we use the B3LYP results. Fortunately, the energy difference between **TS1** and **TS2a** for each of other studied systems is greater than 7 kcal mol^{-1}. With the suggestion of one reviewer, we performed an additional CCSD(T) test on the (N ∼ N)Pd(OH)(OCH_3) system. The CCSD(T) calculations give 49.21 and 31.65 kcal mol^{-1} for **TS1** and **TS2a**, respectively, in comparison to 48.85 and 27.61 kcal mol^{-1} at the B3LYP level. Again, the error is within 5 kcal mol^{-1}. Due to the extremely expensive calculations at the CCSD(T) level, more CCSD(T) test calculations are out of our computing capacity. In view of the calculations for the two systems mentioned above, we expected that the conclusions made based on the B3LYP results should be qualitatively correct. It is our

main objective in this paper to determine the trend and effect of various ligands on the reaction preference.

Natural bond order (NBO) analyses were also performed using the NBO program [18] as implemented in the GAUSSIAN-98 package. All the calculations are performed with the GAUSSIAN-98 software package [19] on Pentium III personal computer with the Linux Red-Hat 6.1 and 7.1 environments.

3. Results and discussion

As mentioned in Section 1, there are two main reaction pathways leading to the same β-hydrogen elimination products (see Fig. 1). For the convenience of our discussion in the following sections, the one-step β-hydrogen elimination processes is denoted as pathway 1 while the two-step σ-bond metathesis is denoted as pathway 2.

Different abbreviations are used for different transition states and intermediates of different pathways (Fig. 1). Fig. 2 shows a typical example of the calculated structures of (N ∼ N)Pd(OH)(OCH_3). **PC** stands for starting complexes, which are metal-alkoxide complexes. **TS1**, **TS2a** and **TS2b** stand for the transition states of the one-step β-hydrogen elimination process in pathway 1, σ-bond metathesis process and oxidative addition in pathway 2, respectively. The optimized **TS1** for pathway 1 is a five-coordinated structure in which the active hydrogen atom is transferred to the metal center from the direction perpendicular to the square plane, whereas the optimized **TS2a** structures for pathway 2 possess a five-membered ring geometry formed by the active hydrogen atom and the *cis*-ligand. The atoms in the five-membered ring are approximately coplannar, except for **TS2a** of $L_2Pd(CH_3)(OCH_3)$ which will be discussed below. **INT** stands for the intermediates between the σ-bond metathesis and oxidative addition in pathway 2. In the intermediates (**INT**), the aldehyde and HX are weakly coordinated to a Pd(0)/Pt(0) metal center. **PRD** represents products formed from the two reaction pathways, a metal-hydride and an aldehyde.

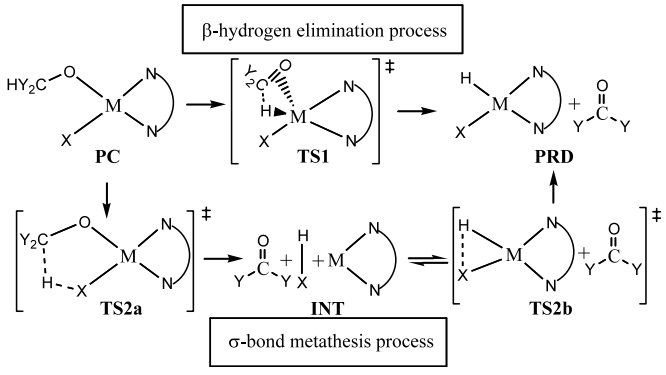


Fig. 1. The β-hydrogen elimination and σ-bond metathesis reaction pathways in the conversion of (N ∼ N)M(X)(OCY_2H) to (N ∼ N)M(H)(X) + CH_2O.

In the following discussions, free energies are used instead of the reaction energies with zero point energy correction because inter-molecular reactions are considered and the entropy contribution is important. Table 1 lists the relative free energies and the reaction energies with zero point energy correction (in parentheses) of species involved in the two reaction pathways for various $L_2PdX(OCH_3)$ model complexes. From Table 1, we can see that the entropy contribution is very important for **TS2b** and **PRD** because they include more molecules in comparison to **PC**.

3.1. Reaction pathway preference

The energetics of all calculated structures (**PC**, **TS**, **INT**, **PRD**) are given in Table 1. In all the cases, **TS2b** are always lower in energy than **TS2a**. This suggests that once **INT** is formed, the oxidation addition becomes an easy step. From the results of our calculations (see Table 1), we can classify three situations in terms of preference in different reaction pathways (Fig. 3). The first case (case A) is that pathway 1 is clearly preferred. In this case, the one-step transfer has lower reaction barriers. Interestingly, there is only one example, $L_2Pd(CH_3)(OCH_3)$ (Fig. 3a), which belongs to this case. The second case (case B) is that pathway 2 is clearly preferred because of lower reaction barriers of the σ-bond metathesis. Complexes preferring pathway 2 include those with X = OH, OCH_3, NH_2 and HCOO (Fig. 3b). And the third case (case C) is that pathways 1 and 2 are competitive, having no much energy difference between **TS1** and **TS2a**. Instead of having an oxidative addition transition state, **TS2b** corresponds to the dissociation of **INT** into three species, L_2Pd, HCHO and HX. In other words, no oxidative addition transition states have been found for X = Cl and Br. The sum of the energies from the three stable species is considered as the barrier (**TS2b**) of the reaction pathway. Complexes $L_2PdCl(OCH_3)$ and $L_2PdBr(OCH_3)$ belong to this case (Fig. 3c).

In case B, the relative free energies of **TS2a** are always lower than those of **TS1**. Examining the four ligands (OCH_3, OH, NH_2 and HCOO) for complexes belonging to this case, we find that these ligands have electron lone pair(s) available for the active transferring hydrogen. Therefore, the lone pairs of the *cis*-ligands X play a very important role to lower down the **TS2a** energies. The importance of lone pairs in facilitating σ-bond metathesis reactions has also been found in other related systems [20].

When the active hydrogen atom is transferred to the *cis*-ligand X, the ligand X acts as a conjugated base attracting a proton. One can consider the transferring hydrogen atom as having the protonic character. There-

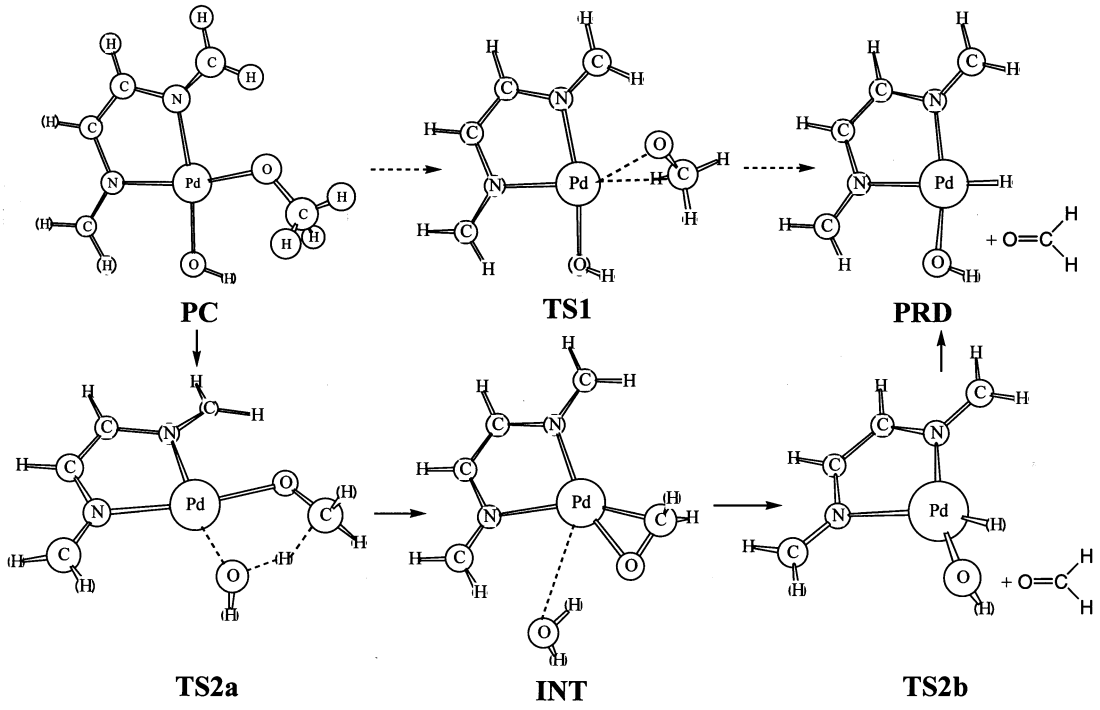


Fig. 2. The B3LYP calculated structures of species involved in the one-step β-hydrogen elimination and the two-step σ-bond metathesis reaction pathways for (N ~ N)Pd(OH)(OCH_3) in each step of the reaction pathway.

fore, it is expected that certain correlation exists between the energies of **TS2a** and the pK_a values of HX. Table 2 lists the related pK_a values of HX [21]. If the pK_a value is more negative, the equilibrium of $HX+H_2O \leftrightarrow H_3O^+ + X^-$ will shift to the X^- side. In other words, a more positive pK_a value favors HX and the lone pair electron of X^- is more basic. In the σ-bond metathesis step, the *cis*-ligand X takes away the transferring hydrogen atom, similar to a situation that a conjugated base takes a proton to form an acid. Using the acid–base concept,

Table 1
The relative free and reaction energies with zero point energy correction (in parentheses) of reactants, transition states, intermediates and products in the one-step β-hydrogen elimination and two-step σ-bond metathesis reactions of complexes $L_2PdX(OCY_2H)$

X	PC	TS1	TS2a	INT	TS2b	PRD
(N ~ N)PdX(OCH_3)						
CH_3	0.00 (0.00)	39.32 (37.98)	64.94 (64.41)	−16.06 (−11.85)	12.18 (24.61)	2.76 (14.24)
OCH_3	0.00 (0.00)	40.53 (39.11)	25.70 (25.10)	−13.29 (−12.13)	24.35 (36.16)	3.35 (13.98)
NH_2	0.00 (0.00)	46.21 (45.50)	26.28 (25.70)	−13.70 (−12.17)	19.42 (31.73)	3.93 (15.02)
OH	0.00 (0.00)	42.85 (42.02)	27.61 (27.16)	−11.37 (−10.46)	24.17 (36.29)	3.98 (14.93)
HCOO	0.00 (0.00)	43.56 (44.06)	35.42 (36.81)	−2.63 (−0.18)	10.22 (23.69)	4.60 (15.75)
Cl	0.00 (0.00)	46.22 (45.47)	48.02 (49.15)	9.08 (10.22)	30.87 (52.17)	2.27 (13.47)
Br	0.00 (0.00)	46.24 (45.46)	50.60 (51.74)	17.23 (18.95)	34.18 (55.56)	0.63 (11.76)
(N ~ N)PtX(OCH_3)						
CH_3	0.00 (0.00)	46.36 (46.07)	76.15 (77.07)	−0.92 (2.72)	27.62 (41.52)	−0.85 (10.73)
OH	0.00 (0.00)	50.32 (49.44)	41.54 (40.93)	0.70 (1.30)	34.16 (46.75)	1.04 (12.07)
Cl	0.00 (0.00)	52.50 (51.64)	69.00 (70.64)	22.66 (24.39)	57.89 (79.13)	−1.36 (9.94)
(P ~ P)PdX(OCH_3)						
CH_3	0.00 (0.00)	35.75 (35.61)	56.25 (56.92)	−27.16 (−24.74)	1.76 (13.32)	−2.84 (8.87)
OH	0.00 (0.00)	39.87 (39.92)	16.48 (16.14)	−27.71 (−26.00)	8.76 (20.17)	−3.31 (7.59)
Cl	0.00 (0.00)	43.06 (42.69)	34.76 (36.13)	−5.12 (−4.29)	7.94 (28.06)	−5.13 (5.98)
(N ~ N)PdX(OCF_2H)						
CH_3	0.00 (0.00)	31.53 (30.90)	66.68 (66.86)	−6.24 (−4.19)	14.11 (27.92)	4.70 (17.54)
OH	0.00 (0.00)	34.17 (33.37)	38.71 (38.89)	−4.38 (−3.95)	24.78 (38.16)	4.58 (16.80)
Cl	0.00 (0.00)	35.97 (36.78)	53.94 (57.24)	13.66 (17.30)	23.97 (47.65)	−4.63 (8.94)

The energy unit is in kcal mol^{-1}.

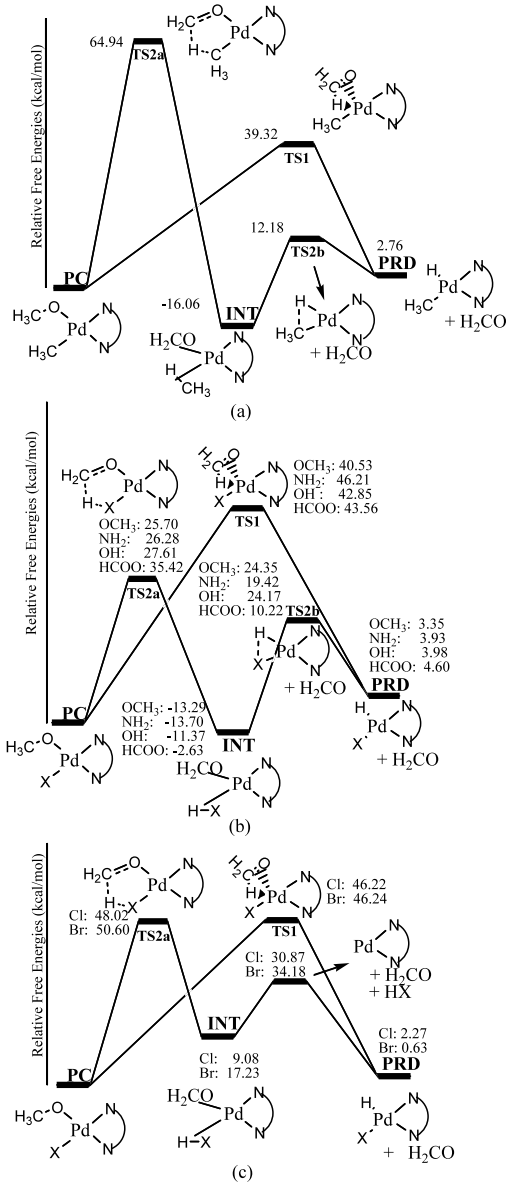


Fig. 3. The energy profiles of the reaction pathways with relative free energies (kcal mol^{-1}): (a) case A, (N ~ N)PdX(OCH_3) when X = CH_3; (b) case B, (N ~ N)PdX(OCH_3) when X = OCH_3, NH_2, OH and HCOO; (c) case C, (N ~ N)PdX(OCH_3) when X = Cl and Br.

we can understand that the more positive pK_a, the higher the basicity of the lone pair electrons of X^-, leading to the easier formation of HX. Therefore, the **TS2a** transition states have lower energies for complexes having ligands X with a stronger basicity in addition to the available lone pair(s) for abstraction of the transferring hydrogen. For example, the higher basicities of OCH_3^-, OH^- and NH_2^- give the lower **TS2a** accordingly.

The reaction pathways of $L_2Pd(CH_3)(OCH_3)$ (X = CH_3) belong to case A. An extremely high energy of **TS2a** is found. The relative free energy of **TS1** is comparatively lower. Although the pK_a value of H–CH_3 is >40, CH_3 does not have additional lone pair electrons to abstract the transferring hydrogen. In the transition state (**TS2a**), the transferring hydrogen atom is approaching one of the three C–H bonds in the CH_3 group. Such a three-center-two-electron bonding situation is very unfavorable. Therefore, the relative free energy of **TS2a** in the X = CH_3 case is significantly higher than other cases in which the transferring hydrogen atom and the lone pair electrons of the *cis*-ligand can interact.

As mentioned before, a negative pK_a value of HX implies less basicity of the *cis*-ligand X in (N ~ N)PdX(OCH_3). For complexes $L_2PdX(OCH_3)$ when X = Cl and Br, the σ-bond metathesis barriers are expected not to be low (see Fig. 3c). Although both chloride and bromide have lone pairs to receive the transferring hydrogen, the calculation results suggest that the basicities of the chloride and bromide are not stronger enough to lower the **TS2a** relative energies significantly. Therefore, the two reaction pathways are competitive for complexes when X = Cl and Br. The **TS2a** barrier of the Cl case is slightly lower than that of the Br case, indicating that Br^- is less basic than Cl^-. Because of their weak H–X (X = Cl, Br) bonds, no oxidative addition transition states corresponding to the addition of H–X (X = Cl, Br) to the L_2Pd fragment have been found. Instead, the dissociation products can be considered as **TS2b** (see Fig. 3c).

3.2. Metal effect

Palladium and platinum are in the same group and have similar chemical properties. However, Pd is a second row transition metal while Pt is a third row one. Replacing Pd by Pt in our calculations, we can examine how the change of the metal center affects the relative reaction barriers.

Table 3 compares the reaction barriers, i.e. the relative free energies of **TS1** and **TS2a** with respect to their referencing **PC**s (reactants), for complexes (N ~ N)PdX(OCH_3) and (N ~ N)PtX(OCH_3). In all three

Table 2
The relationship between the pK_a values and the **TS2a** free energies of complexes (N ~ N)PdX(OCH_3) with different *cis*-ligands X

HX	HBr	HCl	HCOOH	CH_3OH	H_2O	NH_3	CH_4
pK_a	<-5	−2.2	3.76	15.5	15.7	33	>40
TS2a (kcal mol^{-1})	50.60	48.01	35.42	25.70	27.61	26.28	64.94

Table 3
Comparison of relative free energies and the reaction energies with zero point energy correction (in parentheses) (kcal mol^{-1}) between (N ~ N)PdX(OCH_3) and (N ~ N)PtX(OCH_3)

Case	TS	(N ~ N)Pd-N)PdX(OCH_3)	(N ~ N)Pt-N)PtX(OCH_3)	$\Delta\Delta E$ [a]
Case A (CH_3)	**TS1**	39.32 (37.98)	46.36 (46.07)	7.04 (6.75)
	TS2a	64.94 (64.41)	76.15 (77.07)	11.21 (12.66)
Case B (OH)	**TS1**	42.85 (42.02)	50.32 (49.44)	7.47 (7.42)
	TS2a	27.61 (27.16)	41.54 (40.93)	13.94 (13.77)
Case C (Cl)	**TS1**	46.22 (45.47)	52.50 (51.64)	6.28 (6.17)
	TS2a	48.02 (49.15)	69.00 (70.04)	20.98 (20.89)

[a] $\Delta\Delta E$ = (N ~ N)PtX(OCH_3) − (N ~ N)PdX(OCH_3).

cases, the (N ~ N)PtX(OCH_3) complexes have higher **TS1** and **TS2a** energies than the Pd analogs. These results suggest that the third-row transition metal (Pt) has stronger bonding interactions with ligands, stabilizing the stable species, such as reactants, more than the transition state species. In all case, the metal effect is more significant for **TS2a** (see $\Delta\Delta E$ in Table 6). In other words, the barriers of **TS2a** increase more when compared to the increase of **TS1**. The implication of this metal effect is as follows. For complexes belonging to case A in which pathway 1 is preferred, the reaction pathway preference does not change with the substitution of Pd by Pt as the metal center. For complexes belonging to case B in which pathway 2 is preferred, the preference may be switched as a results of replacing Pd by Pt. Based on the trend shown in Table 1, we predict that the Pd and Pt complexes with X = HCOO likely prefer different reaction pathways because the energy barrier difference between **TS1** and **TS2a** for (N ~ N)PdX(OCH_3) (X = HCOO) is not large. For complexes belonging to case C in which the two reaction pathways are competitive, the one-step β-hydrogen elimination becomes preferred as a result of the metal center replacement.

In transition metal chemistry, the metal–ligand interaction becomes stronger down the group. This effect is due to that the d orbitals of third row Pt are more diffuse than those of second row Pd. Fig. 4 shows the Wiberg bond indices (from NBO calculations) for some selected structures. More positive value means stronger bonding interactions. The bonding interactions between Pt and ligands are consistently stronger than those between Pd and ligands.

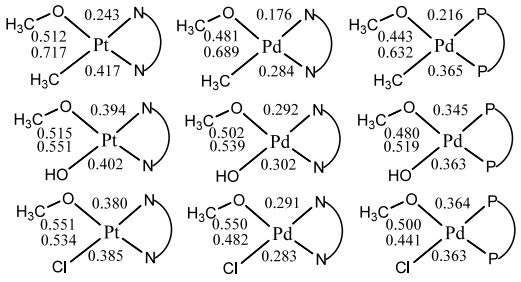


Fig. 4. Calculated Wiberg bond indice of the (N ~ N)PdX(OCH_3), (N ~ N)PtX(OCH_3) and (P ~ P)PdX(OCH_3) complexes when X = CH_3, OH and Cl.

In pathway 1, the *cis*-ligand is not directly involved in the reaction pathway and the transferring hydrogen atom is approaching the metal center directly. Therefore, only one bond breaking and one bond formation are involved in pathway 1. However, in pathway 2, both alkoxy group and *cis*-ligand leave away from the metal center. It is expected that the replacement of Pd by Pt increase the difficulty of the path. Therefore, the σ-bond metathesis increases more its barrier (**TS2a**) than the β-hydrogen elimination does when Pd is replaced by Pt.

3.3. Bidentate ligand effect

Besides the (N ~ N) ligands, (P ~ P) diphosphine-ligands are also commonly used in metal catalysts, such as DPPE. Results of our calculations using a model chelating ligand $H_2PCH_2CH_2PH_2$ are discussed below.

Table 4 shows the energy barriers for the reactions of (N ~ N)PdX(OCH_3) and (P ~ P)PdX(OCH_3). Interestingly, the discussion above shows that changing the metal center from Pd to Pt increases the reaction barriers. However, changing the bidentate ligand from diamine to diphosphine ligand decreases the reaction barriers. In other words, complexes having diphosphine ligands have small reaction barriers than the corresponding N ~ N complexes.

Phosphine ligands are expected to have greater *trans* influence when compared to amine ligands [22]. Therefore, the metal–X and metal–OCH_3 bonding will be weakened in the presence of the diphosphine as the

Table 4
Comparison of relative free energies and the reaction energies with zero point energy correction (in parentheses) (kcal mol^{-1}) between (N ~ N)PdX(OCH_3) and (P ~ P)PdX(OCH_3)

Case	TS	(N ~ N)PdX(OCH_3)	(P ~ P)PdX(OCH_3)	$\Delta\Delta E$ [a]
Case A (CH_3)	**TS1**	39.32 (37.98)	35.75 (35.61)	−3.57 (−2.37)
	TS2a	64.94 (64.41)	56.25 (56.92)	−8.69 (−7.49)
Case B (OH)	**TS1**	42.85 (42.02)	39.87 (39.92)	−2.98 (−2.10)
	TS2a	27.61 (27.16)	16.48 (16.14)	−11.13 (−11.02)
Case C (Cl)	**TS1**	46.22 (45.47)	43.06 (42.69)	−3.16 (−2.78)
	TS2a	48.02 (49.15)	34.76 (36.13)	−13.26 (−13.02)

[a] $\Delta\Delta E$ = (P ~ P)PdX(OCH_3) − (N ~ N)PdX(OCH_3).

bidentate ligand. Fig. 4 shows the Wiberg bond indices (from NBO calculations) for various (N ~ N)PdX(OCH_3) and (P ~ P)PdX(OCH_3) model complexes. The bond indices clearly indicate that the greater *trans* influence of phosphine ligands leads to smaller metal–X and metal–OCH_3 bond indices which are calculated for the P ~ P complexes.

The strong *trans* influencing properties of the phosphine ligands give weaker metal–alkoxy bonds and allow stronger C–O bonding in the alkoxyl group, favoring the one-step β-hydrogen elimination process and leading to smaller reaction barrier of **TS1**. Similarly, the stronger metal–phosphine bonding also weakens the metal–X interaction. The lone pair on X becomes more active in abstracting the transferring hydrogen which acts as a proton as discussed above. Therefore, the barriers of the σ-bond metathesis process are also decreased from the N ~ N complexes to the P ~ P complexes. Table 4 shows that the decreasing effect due to the substitution of N ~ N by P ~ P in the metal complexes is again more significant for **TS2a** than for **TS1**. The consequence of the decreasing effect can be summarized as follows. For complexes belonging to case A, the pathway preference may change because of the change in the chelating ligand. In view of the significant energy difference between **TS2a** and **TS1** for (N ~ N)PdX(OCH_3) (X = CH_3) (see Fig. 3a), we do not however expect a switch in the preference of reaction pathways. For complexes belonging to case B, we do not expect a change in the preference because **TS2a** is already lower than **TS1**. For complexes belonging to case C, the competitive situation will be changed. The two-step reaction pathway becomes favored.

The substitution of Pd by Pt increase the **TS2a** barriers more in compare to **TS1** while the substitution of N ~ N by P ~ P decrease the **TS2a** barriers more. Therefore, it is expected that the preferences of reaction pathways for the (P ~ P)PtX(OCH_3) complexes should resemble those for (N ~ N)PdX(OCH_3) complexes. As a result, the thermolysis of (dppe)Pt(OCH_3)$_2$ is predicted to follow the two-step σ-bond metathesis process instead of the one step β-hydride elimination which was proposed [5]. The experimentally proposed reaction pathway was mainly based on the fact that the thermolysis shows no kinetic deuterium isotopic effect and on an assumption that the β-hydride elimination step is fast and the dissociation of formaldehyde is the rate-determining step. Base on our calculations, the **INT** species formed from the σ-bond metathesis is stable. The dissociation of formaldehyde may also be very important in this case. In addition, the calculated **TS2a** and **TS2b** structures are close to each other in energy. Therefore, the complicated reaction mechanism in which there is no apparent rate-determining step may give no obvious deuterium isotopic effect.

3.4. Alkoxide ligand effect

Besides the effects mentioned above, the alkoxy group is also an important factor influencing the selection of reaction pathways.

Table 5 shows the computational results for (N ~ N)PdX(OCH_3) and (N ~ N)PdX(OCF_2H). From the table, we can see that the **TS1** energies for (N ~ N)PdX(OCF_2H) are lower while the **TS2a** energies are higher when compared to those of (N ~ N)PdX(OCH_3). In other words, the more electronegative substituents on the methyl group of OCH_3 increase the reaction barrier of **TS2a** but decrease the barrier of **TS1**. These results are quite surprising and opposed to what we thought before the calculations. As discussed above, the transferring hydrogen in the two-step σ-bond metathesis acts as a proton in the reaction process. The fluorine substituents would be expected to increase the protonic character of the transferring hydrogen, leading to smaller **TS2a** barriers. The results are actually opposite. Carefully examining the structural parameters of (N ~ N)PdX(OCH_3) and (N ~ N)PdX(OCF_2H) in their ground states (see Table 6), we found that the carbon–oxygen distances are significantly shorten in (N ~ N)PdX(OCF_2H). Apparently, the electronegative substituents withdraw the electron density away from the bonded carbon. The depletion of the electron density on the β-carbon center is made up by the lone pair of the metal-bonded oxygen, giving some character of C=O double and therefore increase the hydridic, instead of protonic character of the transferring hydrogen. Table 7 also lists the calculated NBO natural charges for the metal center and X moiety in (N ~ N)PdX(OCH_3) and

Table 5
Comparison of relative free energies and the reaction energies with zero point energy correction (in parentheses) (kcal mol^{-1}) between (N ~ N)PdX(OCH_3) and (N ~ N)PdX(OCF_2H)

X	Y	TS1	TS2a
CH_3	H	39.32 (37.98)	64.94 (64.41)
	F	31.53 (30.90)	66.68 (66.86)
OH	H	42.85 (42.02)	27.61 (27.16)
	F	34.17 (33.37)	38.71 (38.89)
NH_2	H	46.21 (45.50)	26.28 (25.70)
	F	32.67 (31.88)	35.57 (35.42)
OCH_3	H	40.53 (39.11)	25.70 (25.10)
	F	31.93 (31.37)	35.96 (36.73)
HCOO	H	43.56 (44.06)	35.42 (36.81)
	F	38.13 (38.52)	41.78 (42.53)
Cl	H	46.22 (45.47)	48.02 (49.15)
	F	35.97 (36.78)	53.94 (57.24)
Br	H	46.24 (45.46)	50.60 (51.74)
	F	40.49 (39.81)	56.39 (58.43)

Table 6
Selected structural parameters of (N ~ N)PdX(OCH_3) and (N ~ N)PdX(OCF_2H)

X	(N ~ N)PdX(OCH_3) **PC**			(N ~ N)PdX(OCF_2H) **PC**		
	O–C	Pd–O	Pd–X	O–C	Pd–O	Pd–X
CH_3	1.391	1.989	2.040	1.307	2.031	2.030
OH	1.393	1.984	1.973	1.318	2.016	1.961
NH_2	1.392	1.985	2.027	1.316	2.021	2.019
HCOO	1.401	1.979	2.043	1.333	2.006	2.036
OCH_3	1.394	1.994	1.994	1.313	2.053	1.972
Cl	1.403	1.969	2.343	1.329	2.006	2.329
Br	1.403	1.968	2.487	1.330	1.999	2.474

All the distances are in Å.

Table 7
Natural atomic charges for Pd and X moiety in the (N ~ N)PdX(OCH_3) and (N ~ N)PdX(OCF_2H) **PC** complexes

X	Natural charge			
	(N ~ N)PdX(OCH_3) **PC**		(N ~ N)PdX(OCF_2H) **PC**	
	Pd	X	Pd	X
CH_3	0.66263	−0.91123	0.67442	−0.88597
OH	0.82294	−0.99525	0.83187	−0.97884
NH_2	0.73496	−1.15018	0.75368	−1.12687
OCH_3	0.82392	−0.79649	0.84826	−0.76229
HCOO	0.82915	−0.74022	0.85671	−0.73097
Cl	0.75997	−0.57616	0.76750	−0.52253
Br	0.72110	−0.54588	0.74257	−0.50683

(N ~ N)PdX(OCF_2H). The fluorine substituents increase the positive charge at the metal center.

In the one-step classical β-hydrogen eliminations, the transferring hydrogen atom acts as a hydride. A hydride-like hydrogen atom favors a direct attack on the positive metal center. A more positive charge of the metal center further enhances the preference. Therefore, it is understandable that the fluorine substituents lower down the barriers for the one-step β-hydrogen elimination. The calculations show a decrease of 5–13 kcal mol^{-1} in the barriers for the substituents effect.

In the two-step σ-bond metathesis, the transferring hydrogen acts as a proton. A proton-like hydrogen atom is attracted by the negatively charged *cis*-ligand forming a five-members ring transition state. Since the metal center losses the electron donation from the alkoxy group, metal center will seek compensation from the *cis*-ligand. When the *cis*-ligand bears less negative charge, the σ-bond metathesis become more difficult. The charges of the *cis*-ligand X in (N ~ N)PdX(OCF_2H) are always less negative than those of (N ~ N)PdX(OCH_3) (see Table 7). Therefore, the substitution increases the barrier for the σ-bond metathesis.

Concluding the alkoxide ligand effect, we predict that for complexes belonging to case B, the pathway preference may be switched, i.e. pathways 1 and 2 become competitive or pathway 1 is even preferred. For complexes belonging to case C, the competitive situation will be changed. The one-step reaction pathway becomes significantly favored.

3.5. Comments on the ligand dissociative reaction pathway

Besides the aforementioned pathways, dissociation of one arm of the bidentate ligand producing a 14-electrons intermediate followed by β-hydrogen elimination or σ-bond metathesis is also a possible reaction pathway. The low coordination intermediate can promote the β-hydrogen elimination rapidly. We examine how a three-coordinate complex undergoes the relevant reactions. We calculated the energy profiles for dissociating one arm of the (N ~ N) bidentate ligand followed by β-hydrogen elimination and σ-bond metathesis pathways for (N ~ N)Pd(OH)(OCH_3) (Fig. 5). Starting from the three-coordinate complex, the β-hydrogen elimination requires a barrier of only 1.79 kcal mol^{-1} (see Fig. 5). For the σ-bond metathesis process via the three-coordinate complex, the barrier is calculated to be 16.58 kcal mol^{-1}. These calculations suggest that three-coordinate complexes indeed favor a β-hydrogen elimination in general in view of the significant change in the preference of reaction pathways. In other words, if reactions start with the ligand dissociation, the β-hydrogen elimination should be the main reaction pathway for most cases.

Reactions passing through the ligand dissociation or not largely depend on the experimental systems. High coordination number together with bulky ligands such as PPh_3 will favor the dissociation pathway. Many experimental evidences show that for four-coordinate Pd(II)/Pt(II) complexes bidentate ligands are normally attached to the metal center during the reaction [23–25]. The dissociation of the bipyrimidine in our studied systems during the reactions seems unlikely. For complexes containing labile monodentate ligands, the phosphine dissociation is possible [25,26].

The dissociation of X^- ligand is another possible reaction pathway. Under environment of polar solvents, this is likely the event [25,27]. Many theoretical calculations [28,29] have been done based on such a three-coordinate cationic analogous species $[L_2(M)(CH_2R)]^+$. Once the cationic species is formed, β-hydrogen elimination occurs rapidly with very small reaction barriers [28,29]. The charge separation due to the dissociation of X^- in non-polar solvents is expected to be difficult. For example, the Cl^- binding energy with Pt complex in gas phase is about 150 kcal mol^{-1} from the calculation done by Hush and coworkers [30]. Therefore, the results presented here represent the situation when less polar solvents and bidentate ligands are used.

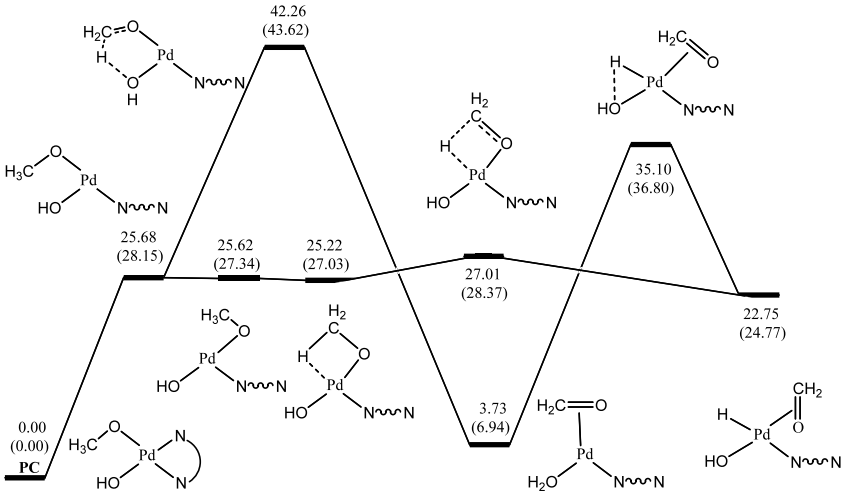


Fig. 5. The energy profiles of the reaction pathways with relative free energies (kcal mol^{-1}) and reaction energies with zero point energy correction (in parentheses) (kcal mol^{-1}) via a dissociation of one arm of the bidentate ligand in the $(N \sim N)Pd(OH)(OCH_3)$ complex.

4. Conclusion

The β-hydrogen elimination (pathway 1) and σ-bond metathesis (pathway 2) processes of $L_2MX(OCH_2Y)$ ($L_2 = CH_2NCHCHNCH_2$ and $PH_2CH_2CH_2PH_2$; M = Pd and Pt; $X = CH_3$, OCH_3, NH_2, OH, HCOO, Cl and Br; Y = H and F) have been investigated by density functional theory calculations. In the selection of reaction pathways, three cases for $(N \sim N)PdX(OCH_3)$ have been classified. Case A is that pathway 1 is clearly preferred, including the complex when $X = CH_3$. Case B is that pathway 2 is clearly preferred, including model complexes when $X = OH$, OCH_3, NH_2 and HCOO. Case C is that pathways 1 and 2 are competitive, including model complexes X = Cl and Br. A Pt metal center increases the reaction barriers when compared to a Pd metal center while a diphosphine ligand decreases the reaction barriers in comparison to a diamine ligand for both pathways 1 and 2. The effects of the metal center and the bidentate ligand are found to be more significant for pathway 2 than for 1. The substituents on the oxygen-bonded carbon of the alkoxy group also have significant effect on the reaction pathway preference. The more electronegative substituents (F) on the methyl group of OCH_3 increase the reaction barriers of pathway 2 but decrease the barriers of pathway 1. It should be noted that the β-hydrogen elimination pathway is always preferred when the ligand dissociation from the four-coordinate complexes is the initial event for the reactions.

Acknowledgements

This work was supported by the Research Grants Council of Hong Kong and the University Grants Committee of Hong Kong through the Area of Excellence Scheme (Aoe).

References

[1] R.A. Sheldon, J.K. Kochi, Metal Catalyzed Oxidations of Organic Compound (Chapter 6), Academic Press, New York, 1981.
[2] F. Westheimer, Chem. Rev. 45 (1949) 419.
[3] G.J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636.
[4] G.M. Kapteijn, D.M. Grove, H. Kooijman, W.J.J. Smeets, A.L. Spek, G. van Koten, Inorg. Chem. 35 (1996) 526.
[5] H.E. Bryndza, J.C. Calabrese, M. Marsi, D.C. Roe, W. Tam, J.E. Bercaw, J. Am. Chem. Soc. 108 (1986) 4805.
[6] T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, Tetrahedron Lett. 36 (1995) 6923.
[7] I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Science 274 (1996) 2044.
[8] I.E. Markó, A. Gautier, I. Chellé-Rugnaut, P.R. Giles, M. Tsukazaki, C.J. Urch, S.M. Brown, J. Org. Chem. 63 (1998) 7576.
[9] I.E. Markó, P.R. Giles, M. Tsukazaki, I. Chellé-Rugnaut, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. 119 (1997) 12661.
[10] A. Dijksman, I.W.C.E. Arends, R.A. Sheldon, Chem. Commun. 1591 (1999).
[11] O. Blum, D. Milstein, J. Am. Chem. Soc. 117 (1995) 4582.
[12] (a) A.D. Becke, Phys. Rev. A 38 (1988) 3098;
(b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200;
(c) C. Lee, W. Yang, G. Parr, Phys. Rev. B 37 (1988) 785.
[13] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1995) 299.
[14] M. Couty, M.B. Hall, J. Comput. Chem. 17 (1996) 1359.
[15] J. Andzelm, S. Huzinaga, Gaussian Basis Sets for Molecular Calculations, Elsevier, New York, 1984.
[16] (a) M.S. Gordon, Chem. Phys. Lett. 76 (1980) 163;
(b) P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213;
(c) R.C. Binning, Jr., L.A. Curtiss, J. Comput. Chem. 11 (1990) 1206.
[17] (a) K. Fukui, J. Phys. Chem. 74 (1970) 4161;
(b) K. Fukui, Acc. Chem. Res. 14 (1981) 363.
[18] E.D. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, NBO version 3.1.

[19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN-98 (Revision A.5), Gaussian, Inc, Pittsburgh, PA, 1998.

[20] A. Milet, A. Dedieu, G. Kapteijn, G. van Koten, Inorg. Chem. 36 (1997) 3223.

[21] L.G. Wade, Jr., Organic Chemistry, 3rd ed., Prenctice Hall International, London, 1995, p. 26.

[22] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., John Wiley & Sons, 1988, p. 1300.

[23] R.A. Periana, J.D. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, Science 280 (1998) 560.

[24] T.M. Gilbert, I. Hristov, T. Ziegler, Organometallics 20 (2001) 1183.

[25] J. Zhao, H. Hesslink, J.F. Hartwig, J. Am. Chem. Soc. 123 (2001) 7220.

[26] I.S. Liamas, J.A. Gladysz, J. Am. Chem. Soc. 114 (1992) 2136.

[27] F. Kawataka, Y. Kayaki, I. Shimizu, A. Yamamoto, Organometallics 13 (1994) 3517.

[28] S. Strömberg, K. Zetterberg, P.E.M. Siegbahn, J. Chem. Soc. Dalton Trans. (1997) 4147.

[29] D.G. Musaev, M. Svensson, K. Morokuma, Organometallics 16 (1997) 1933.

[30] K. Mylvaganam, G.B. Bacskay, N.S. Hush, J. Am. Chem. Soc. 122 (2000) 2041.