

# Why Do Pt(PR<sub>3</sub>)<sub>2</sub> Complexes Catalyze the Alkyne Diboration Reaction, but Their Palladium Analogues Do Not? A Density Functional Study

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The B3LYP hybrid density functional method has been applied to study theoretically the mechanism of the Pd(0)-catalyzed alkyne diboration reaction. It has been found that this reaction proceeds via the same mechanism as the Pt(0)-catalyzed diboration reaction and involves the following steps: (i) coordination of diborane R<sub>2</sub>B–BR<sub>2</sub> to the Pd(0) complex, (ii) oxidative addition of the B–B bond to Pd, (iii) dissociation of one phosphine ligand, (iv) coordination of acetylene, (v) insertion of acetylene into one of the Pd–B bonds, (vi) isomerization of the resultant complex accompanied by recoordination of a phosphine ligand, and (vii) reductive elimination of the alkenyl–diboron products. However, the Pd(0) complex cannot catalyze the alkyne diboration reaction, while its Pt(0) analogue can. The main reason for this difference is found to be in the oxidative addition process of the B–B bond to M(PH<sub>3</sub>)<sub>2</sub>. This step takes place for M = Pt with a 14.0 kcal/mol activation barrier and is exothermic, but it does not take place for M = Pd, where the addition product is not stable due to a very small reverse barrier. The origin of this inactivity of Pd(0) is the d<sup>10</sup> → sd<sup>9</sup> promotion energy, which is not required for Pt(0) with the sd<sup>9</sup> ground state.

## I. Introduction

Transition-metal-catalyzed alkene and alkyne boration reactions are attractive methods to produce the alkyl- or alkenylboron derivatives with defined regio- and stereochemistry and have increased the potential applications of boron derivatives in synthetic organic chemistry.<sup>1</sup> The transition-metal-catalyzed hydroboration of alkenes and alkynes with catecholborane or polyhedral boranes has been studied extensively by both experimental<sup>1</sup> and theoretical<sup>2</sup> methods. Recently, much interest has moved to Pd(0)- and Pt(0)-catalyzed alkyne and alkene diboration reactions with pinacol ester derivatives.<sup>3</sup> In general, it has been shown that (i) Pt(0) complexes catalyze cis addition of the B–B bond in pinacol ester derivatives, (OCH<sub>2</sub>)<sub>2</sub>B–B(OCH<sub>2</sub>)<sub>2</sub>, to alkynes but not to alkenes, and (ii) Pd(0) complexes, the best catalysts for the silyl- and stannylation, do not catalyze alkyne and alkene diboration reactions. The origins of the observed differences in the catalytic activity of Pt(0) and Pd(0) complexes for alkyne diboration reactions still remain unclear.

In our previous paper,<sup>4</sup> we reported studies of Pt(0)-catalyzed alkyne and alkene diboration reactions with (OH)<sub>2</sub>B–B(OH)<sub>2</sub> as a model of (OCH<sub>2</sub>)<sub>2</sub>B–B(OCH<sub>2</sub>)<sub>2</sub> used in the experiments.<sup>3</sup> In general, our findings can be summarized as follows:

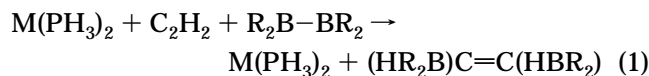
(1) The Pt(0)-catalyzed alkyne/alkene diboration reaction may proceed via two different paths, A and B (see Scheme 1). Path A involves the following steps: (i) coordination of the diborane, (ii) oxidative addition of the B–B bond to the Pt(0) complex, (iii) endothermic dissociation of one of the phosphine ligands, (iv) coordination of alkyne/alkene to Pt, (v) insertion of alkyne/

alkene to the Pt–B bond, (vi) isomerization of the resultant complex accompanied by recoordination of a phosphine ligand, and (vii) reductive elimination of the alkenyl/alkane–diboron products. In path B,<sup>5</sup> the initial step is coordination of alkyne/alkene to the Pt complex, followed by dissociation of one of the phosphine ligands and oxidative addition of the B–B bond to Pt(PR<sub>3</sub>)(C<sub>2</sub>H<sub>x</sub>) in either a planar (where atoms B, B, C, C, and P are on the same plane) or perpendicular (where BPtB and PPtC planes are perpendicular to each other) manner, leading to a square-planar or tetrahedral intermediate, (BR<sub>2</sub>)<sub>2</sub>Pt(PR<sub>3</sub>)(C<sub>2</sub>H<sub>x</sub>), respectively. The tetrahedral intermediate lies 4.4 kcal/mol lower than the planar cis intermediate, which is also involved in path A and is separated from the latter with a small barrier. However, the barrier from the tetrahedral to the planar trans intermediate is high (21 kcal/mol). Therefore, we conclude that the tetrahedral intermediate (BR<sub>2</sub>)<sub>2</sub>Pt(PR<sub>3</sub>)(C<sub>2</sub>H<sub>x</sub>) will rearrange to the square-planar cis intermediate and paths A and B will merge. By comparing these two paths and calculating the binding energies of Pt(PR<sub>3</sub>)<sub>2</sub> with bulkier diboranes B<sub>2</sub>R<sub>2</sub> and substituted alkynes/alkenes used in the experiments, we conclude that path A is energetically more favorable than path B in the real Pt(0)-catalyzed alkyne/alkene diboration reaction.

(2) The observed different catalytic behavior of Pt(PH<sub>3</sub>)<sub>2</sub> on the two substrates, C<sub>2</sub>H<sub>2</sub> (reactive) and C<sub>2</sub>H<sub>4</sub> (nonreactive), is the result of the differences in the barrier heights for insertion of hydrocarbons into the Pt–B bond, which is calculated to be 9.0 and 22.9 kcal/mol for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, respectively. This difference is essentially dictated by the thermochemistry of the

insertion process,  $\text{Pt}(\text{PH}_3)[\text{BR}_2]_2(\text{C}_2\text{H}_x) \rightarrow \text{Pt}(\text{PH}_3)(\text{BR}_2-\text{C}_2\text{H}_x\text{BR}_2)$ , which is found to be 28.1 kcal/mol exothermic for  $\text{C}_2\text{H}_2$ , but 4.1 kcal/mol endothermic for  $\text{C}_2\text{H}_4$ , and has been explained in terms of a smaller substrate deformation energy and a larger B–C “bond” energy in  $\text{Pt}(\text{PH}_3)(\text{BR}_2-\text{C}_2\text{H}_x\text{BR}_2)$  for  $\text{C}_2\text{H}_2$  than for  $\text{C}_2\text{H}_4$ .

The present work is a continuation of our previous studies,<sup>4,5</sup> and the goal is to investigate the mechanism of the alkyne diboration reaction with the Pd(0) complex at the same level of theory. We believe that, by comparing the mechanism of the reaction



for Pd(0) and Pt(0), we can gain much insight into the

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experimentally observed differences between their catalytic behaviors. While the results for M = Pt have been published,<sup>4</sup> we have included some of them in the current paper to make easier comparison with M = Pd. In our previous studies,<sup>2a,4</sup> was shown that  $(\text{HO})_2\text{B}-\text{B}(\text{OH})_2$  and  $\text{HB}(\text{OH})_2$  are good models for the pinacol ester and catechol borane, respectively. Therefore, we will continue using  $(\text{HO})_2\text{B}-\text{B}(\text{OH})_2$  to model the pinacol ester derivatives used in the experiments. The  $\text{Pd}(\text{PR}_3)_2$  complex is modeled by  $\text{Pd}(\text{PH}_3)_2$ .

## II. Calculation Procedure and Evaluation of the Models

The geometries of the reactants, intermediates, transition states, and products of reaction 1 for M = Pd and R = OH are optimized using the B3LYP hybrid density functional theory<sup>6</sup> with a standard double- $\zeta$  quality basis set, lanl2dz, associated with the relativistic effective core potential (ECP) for the metals<sup>7a</sup> and the nonrelativistic ECP for phosphorus<sup>7b</sup> atoms (below denoted as BSI). Normal-mode analysis has been performed only for a few transition states, which will be described in more detail in the discussions. The energetics of the optimized structures were recalculated using a larger basis set (below denoted as BSII), which includes the double- $\zeta$  + polarization basis set of Dunning for the main group elements<sup>8</sup> and lanl2dz + polarization f function<sup>9</sup> for the transition-metal atoms. No zero-point correction was added to the energies presented in the tables. All calculations were performed by our modified Gaussian-92/DFT package.<sup>10,11</sup>

In our previous studies<sup>4</sup> we demonstrated that the current method is adequate to describe the geometries and relative energies of critical structures in reaction 1 for M = Pt. In the present studies we further tested the reliability of the B3LYP method for M = Pd. The calculated energy differences between the low-lying  $^3\text{D}(s^1d^9)$  and  $^1\text{S}(s^0d^{10})$  electronic states of the Pd and Pt atoms, as well as the M–BR<sub>2</sub>, M–PH<sub>3</sub>, and PH<sub>3</sub>–MPH<sub>3</sub> binding energies of the MBR<sub>2</sub>, MPH<sub>3</sub>, and M(PH<sub>3</sub>)<sub>2</sub> complexes (where M = Pd and Pt, and R = H and OH), at the B3LYP and CCSD(T) levels with the BSII are shown in Table 1. As seen in Table 1, the ground state of the Pd atom is calculated to be the  $^1\text{S}(s^0d^{10})$  state. The high-spin state  $^3\text{D}(s^1d^9)$  lies 14.5 and 19.2 kcal/mol higher at the CCSD(T) and B3LYP levels, respectively, versus 21.9 kcal/mol from the experiment.<sup>12</sup> However,

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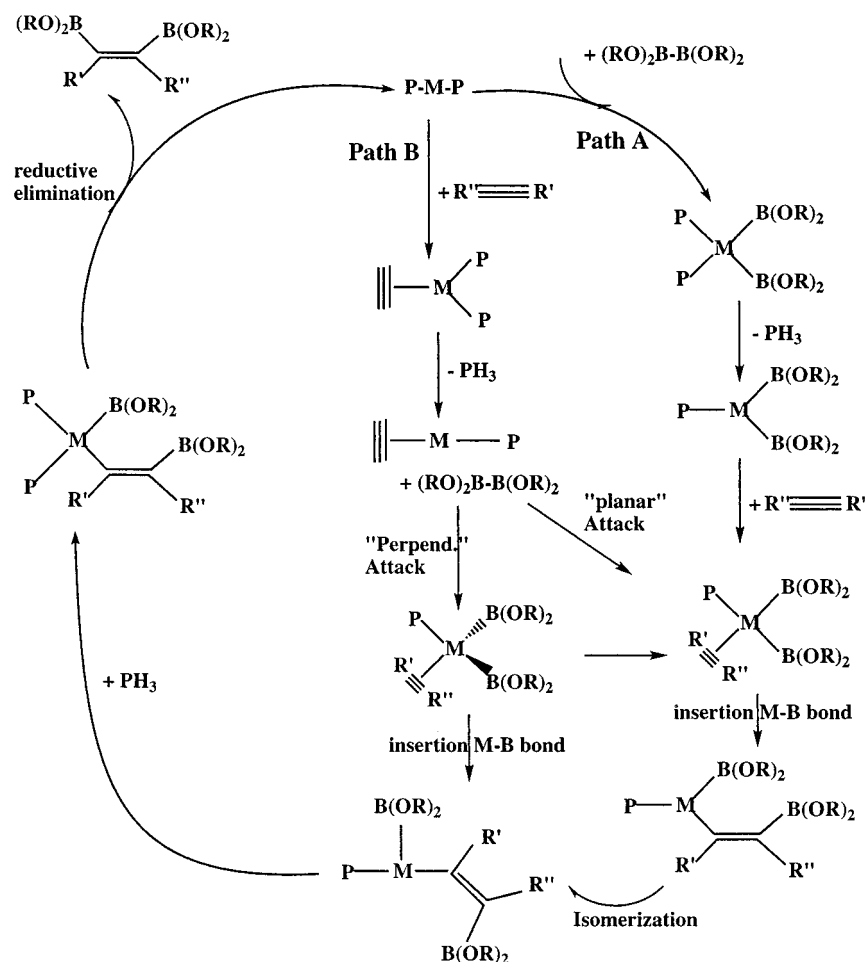
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**Scheme 1. Proposed Mechanism of the  $M(PR_3)_2$ -Catalyzed ( $M = Pd$  and  $Pt$ ) Alkyne Diboration**

**Table 1. Relative Energies (kcal/mol) of Two States of Atom  $M$  and the  $M-BR_2$ ,  $M-PH_3$ , and  $PH_3-MPH_3$  ( $M = Pd$  and  $Pt$ ) Binding Energies (kcal/mol) at the B3LYP/II and CCSD(T)/II Levels Using the B3LYP/I Optimized Geometries<sup>a</sup>**

	state	CCSD(T)/II	B3LYP/II	expt
Pd	<sup>3</sup> D, s <sup>1</sup> d <sup>9</sup>	0.0	0.0	0.0
	<sup>1</sup> S, s <sup>0</sup> d <sup>10</sup>	-14.6	-19.2	-21.9
Pt	<sup>3</sup> D, s <sup>1</sup> d <sup>9</sup>	0.0	0.0	0.0
	<sup>1</sup> S, s <sup>0</sup> d <sup>10</sup>	15.1	13.9	11.1
PdBH <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	62.0	66.8	
Pd(OH) <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	60.2	62.8	
PtBH <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	93.3	96.8	
Pt(OH) <sub>2</sub>	<sup>2</sup> A <sub>1</sub>	91.0	89.1	
PdPH <sub>3</sub>	<sup>1</sup> A'	29.1	33.3	
Pd(PH <sub>3</sub> ) <sub>2</sub>	<sup>1</sup> A <sub>1</sub>	28.7	27.3	
PtPH <sub>3</sub>	<sup>1</sup> A'	51.7	54.6 (56.6) <sup>b</sup>	
Pt(PH <sub>3</sub> ) <sub>2</sub>	<sup>1</sup> A <sub>1</sub>	41.4	38.9 (38.3) <sup>b</sup>	

<sup>a</sup> The total energy of BR<sub>2</sub> is -25.817 789 and -25.935 421 au for R = H, and -176.066 975 and -176.547 552 au for R = OH at the CCSD(T)/II and B3LYP/II levels, respectively. The total energy of PH<sub>3</sub> is -8.210 04 and -8.30162 au at the CCSD(T)/II and B3LYP/II levels, respectively. No zero-point energy is included.

<sup>b</sup> The numbers in parentheses are calculated using the B3LYP/II optimized geometries.

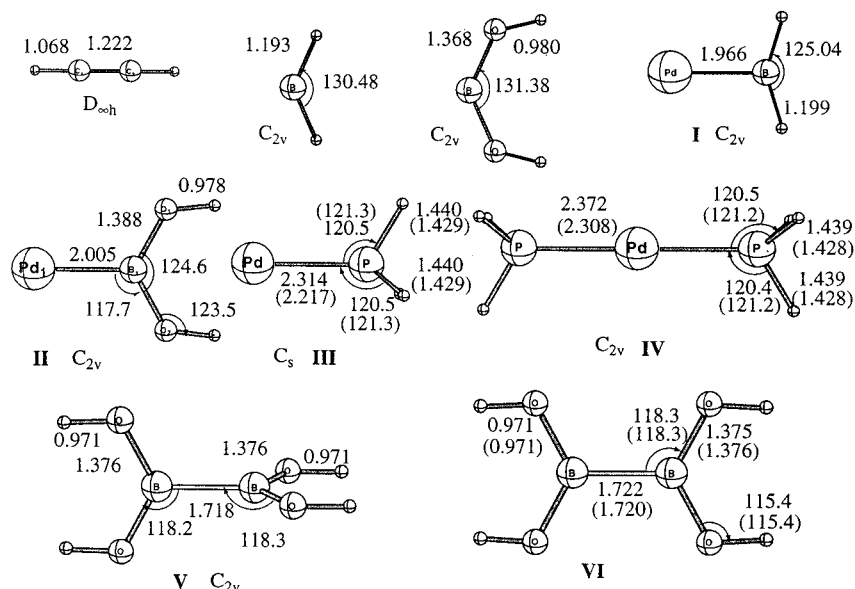
for the Pt atom the <sup>3</sup>D(s<sup>1</sup>d<sup>9</sup>) state is calculated<sup>4</sup> to be the ground state, and the <sup>1</sup>S(s<sup>0</sup>d<sup>10</sup>) state is 15.1 and 13.9 kcal/mol higher at the CCSD(T) and B3LYP levels, respectively, versus 11.1 kcal/mol from the experiment.<sup>12</sup> Thus, the B3LYP/II approach gives better agreement with experiment than the CCSD(T)/II by a few kilocalories/mole, with only 2–3 kcal/mol off from

the experimental values. As seen in Table 1, the M-BR<sub>2</sub>, M-PH<sub>3</sub>, and PH<sub>3</sub>-MPH<sub>3</sub> binding energies of the MBR<sub>2</sub>, MPH<sub>3</sub>, and M(PH<sub>3</sub>)<sub>2</sub> complexes, respectively, calculated at the CCSD(T) and B3LYP levels are different up to 4.0 kcal/mol regardless of the metal and substituents in the boryl group. Therefore, we conclude that the B3LYP/II//B3LYP/I approach used throughout the current paper is nearly as reliable as the CCSD(T)/II//B3LYP/I method.

Finally, we note that in the experiment P(Ph)<sub>3</sub> is used as a ligand, while we have used PH<sub>3</sub> in our calculations. We do not expect any qualitative change in the reaction mechanism because the Ph groups are planar and therefore do not cause as much steric repulsion as branched alkyl groups such as *tert*-butyl. However, the basicity of P(Ph)<sub>3</sub> and PH<sub>3</sub> might differ, and it might be interesting in the future to investigate the effect of this difference using our recently developed IMOMM, IMOMO, or ONIOM method.<sup>13</sup>

In section III, we briefly discuss the structures and bonding pictures of the reactants. In section IV we discuss the potential energy surface (PES) of reaction 1 for M = Pd. In section V we compare the PESs of reactions 1 between M = Pt and Pd. In the final section VI we make a few conclusions.

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**Figure 1.** B3LYP/I optimized geometries (in Å and deg) of the PdBR<sub>2</sub> complex, BR<sub>2</sub> (where R = OH and H), and the reactants PdPH<sub>3</sub>, Pd(PH<sub>3</sub>)<sub>2</sub>, and [B(OH)<sub>2</sub>]<sub>2</sub>. Numbers in parentheses are at the B3LYP/II level.

**Table 2.** Calculated MO Energies (au; B3LYP/I Level) and Mulliken Orbital Populations (B3LYP/II Level) for M(PH<sub>3</sub>)<sub>2</sub> (Linear and Bent) and (BR<sub>2</sub>)<sub>2</sub>M(PH<sub>3</sub>)<sub>2</sub> Where (M = Pd and Pt)

complex	M = Pd				M = Pt			
	irrep	eigenvalue	character	population	irrep	eigenvalue	character	population
linear M(PH <sub>3</sub> ) <sub>2</sub>	a <sub>1</sub>	-0.177 88	s/d <sub>z</sub> <sup>2</sup>	s <sup>2.66</sup> p <sup>6.05</sup> d <sup>9.47</sup>	b <sub>1</sub>	-0.193 41	d <sub>xz</sub>	s <sup>2.91</sup> p <sup>5.98</sup> d <sup>9.21</sup>
	a <sub>1</sub>	-0.188 51	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>		a <sub>1</sub>	-0.193 45	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>	
	b <sub>1</sub>	-0.188 53	d <sub>xz</sub>		a <sub>1</sub>	-0.200 01	s/d <sub>z</sub> <sup>2</sup>	
	b <sub>2</sub>	-0.214 37	d <sub>yz</sub>		b <sub>2</sub>	-0.235 30	d <sub>yz</sub>	
	a <sub>2</sub>	-0.214 37	d <sub>xy</sub>		a <sub>2</sub>	-0.235 32	d <sub>xy</sub>	
	b <sub>2</sub>	-0.294 96	M-PH <sub>3</sub>		b <sub>2</sub>	-0.306 82	M-PH <sub>3</sub>	
bent <sup>a</sup> M(PH <sub>3</sub> ) <sub>2</sub>	a <sub>1</sub>	-0.364 13	M-PH <sub>3</sub>		a <sub>1</sub>	-0.412 65	M-PH <sub>3</sub>	
	b <sub>2</sub>	-0.158 66	d <sub>yz</sub>	s <sup>2.21</sup> p <sup>6.22</sup> d <sup>9.53</sup>	b <sub>2</sub>	-0.161 33	d <sub>yz</sub>	s <sup>2.56</sup> p <sup>6.19</sup> d <sup>9.35</sup>
	a <sub>1</sub>	-0.189 61	s/d <sub>z</sub> <sup>2</sup>		a <sub>1</sub>	-0.196 94	s/d <sub>z</sub> <sup>2</sup>	
	b <sub>1</sub>	-0.203 22	d <sub>xz</sub>		b <sub>1</sub>	-0.211 16	d <sub>xz</sub>	
	a <sub>2</sub>	-0.204 85	d <sub>xy</sub>		a <sub>2</sub>	-0.214 10	d <sub>xy</sub>	
	a <sub>1</sub>	-0.213 35	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>		a <sub>1</sub>	-0.228 03	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>	
oxidative addition product	b <sub>2</sub>	-0.316 34	M-PH <sub>3</sub>		b <sub>2</sub>	-0.340 06	M-PH <sub>3</sub>	
	a <sub>1</sub>	-0.330 12	M-PH <sub>3</sub>		a <sub>1</sub>	-0.362 08	M-PH <sub>3</sub>	
	a <sub>1</sub>	-0.195 06	M-B ant-b	s <sup>2.66</sup> p <sup>6.53</sup> d <sup>9.09</sup>	a <sub>1</sub>	-0.204 11	s/d <sub>z</sub> <sup>2</sup>	s <sup>2.90</sup> p <sup>6.49</sup> d <sup>8.88</sup>
	a <sub>1</sub>	-0.247 14	M-B bond		a <sub>2</sub>	-0.243 95	d <sub>xy</sub>	
	b <sub>2</sub>	-0.249 77	M-B/PH <sub>3</sub>		b <sub>1</sub>	-0.245 18	d <sub>xz</sub>	
	a <sub>2</sub>	-0.251 11	d <sub>xy</sub>		a <sub>1</sub>	-0.248 35	M-B bond	
	b <sub>1</sub>	-0.251 17	d <sub>xz</sub>		b <sub>2</sub>	-0.254 34	M-B/PH <sub>3</sub>	
	a <sub>1</sub>	-0.277 94	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>		a <sub>1</sub>	-0.279 23	d <sub>x<sup>2</sup>-z<sup>2</sup></sub>	

<sup>a</sup> At the M(PH<sub>3</sub>)<sub>2</sub> geometry of the oxidative addition product M(PH<sub>3</sub>)<sub>2</sub>[B(OH)<sub>2</sub>].

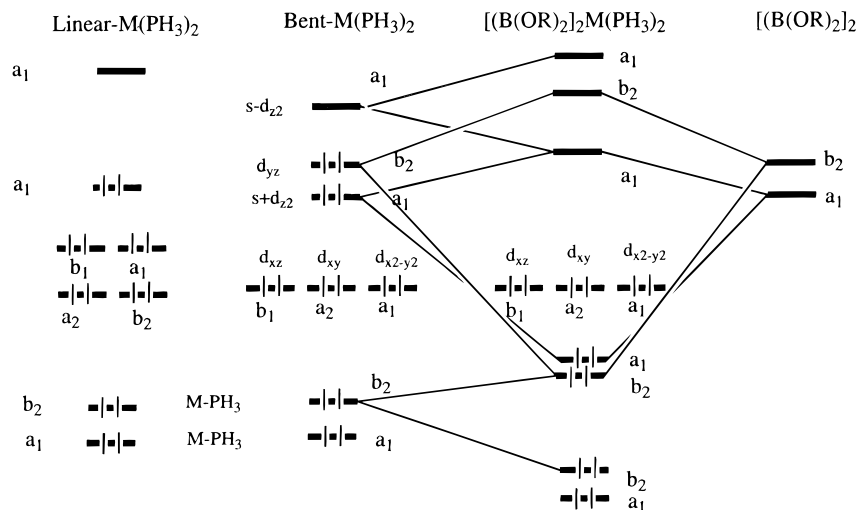
### III. Properties and Bonding Picture of the Reactants

The structures of the reactants of reaction 1, Pd(PH<sub>3</sub>)<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and B<sub>2</sub>[(OH)<sub>2</sub>]<sub>2</sub>, are shown in Figure 1. The Pd-P distance in Pd(PH<sub>3</sub>)<sub>2</sub> is a little longer than the Pt-P distance in Pt(PH<sub>3</sub>)<sub>2</sub>. The bonding picture and stability of the complexes Pd(PH<sub>3</sub>)<sub>2</sub> and Pt(PH<sub>3</sub>)<sub>2</sub> were the subjects of extensive studies.<sup>14</sup> We will only briefly recall the main conclusions from previous studies<sup>14</sup> and compare them with our results. Of the two B<sub>2</sub>[(OH)<sub>2</sub>]<sub>2</sub> structures, we will use structure VI, as discussed previously.<sup>4</sup>

First of all it is well-documented<sup>14</sup> that the metal atom in the complex M(PH<sub>3</sub>)<sub>2</sub> is Pd(0) or Pt(0) with the d<sup>10</sup> configuration. Addition of two phosphines to M stabilizes d<sup>10</sup> with respect to s<sup>1</sup>d,<sup>9</sup> so that the ground state of M(PH<sub>3</sub>)<sub>2</sub> becomes a linear d<sup>10</sup> singlet for both M = Pd and M = Pt. This stabilization of d<sup>10</sup> arises from the donation of the phosphine lone pair to the empty metal s orbital (Lewis base/Lewis acid interaction), leading to strong bonding. The Mulliken populations of the metal atoms in the linear M(PH<sub>3</sub>)<sub>2</sub> complexes in Table 2 are consistent with this conclusion.

Second, Goddard and co-workers<sup>14b,c</sup> concluded that the oxidative addition reaction A-B + M(PH<sub>3</sub>)<sub>2</sub> → (A)(B)M(PH<sub>3</sub>)<sub>2</sub> involves a change in the effective electronic configuration of M from a d<sup>10</sup> configuration for M(PH<sub>3</sub>)<sub>2</sub> to an s<sup>1</sup>d<sup>9</sup> configuration for (A)(B)M(PH<sub>3</sub>)<sub>2</sub>. The reason is simple: the d<sup>10</sup> configuration cannot make covalent bonds since all d<sup>10</sup> orbitals are doubly occupied,

(14) (a) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482. (b) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115. (c) Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609. (d) Hay, P. J. *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, 1992; pp 127-147 and references therein.



**Figure 2.** Orbital correlation diagram for  $M(PH_3)_2[B(OR)_2]_2$ , where  $M = Pd$  and  $Pt$ .

while the  $s^1d^9$  configuration with two singly occupied orbitals can form two  $sd$  hybrids and is capable of forming covalent bonds. As has been pointed out, the oxidation state of  $Pd$  and  $Pt$  complexes should be interpreted in terms of maximum covalency rather than the degree of oxidation. In other words, the metal atom is not oxidized during the addition of the  $A-B$   $\sigma$  bond, but rather the metal is promoted from the  $d^{10}$  state to the  $s^1d^9$  state. The Mulliken population data presented in Table 2 for the  $(BR_2)_2M(PH_3)_2$  complexes are consistent with this argument. On the other hand, during the reductive elimination reaction  $(A)(B)M(PH_3)_2 \rightarrow A-B + M(PH_3)_2$  the electronic configuration of the  $M$  atom changes from  $s^1d^9$  in  $(A)(B)M(PH_3)_2$  to  $d^{10}$  in  $M(PH_3)_2$ .

According to the orbital correlation diagram in Figure 2 (see also Table 2), in the linear  $M(PH_3)_2$  complex,  $d$  orbitals are split into three groups, two of which are degenerate. The highest occupied orbital (HOMO) is mainly the  $s + d_{z^2}$  orbital of the metal atom. The low-lying unoccupied molecular orbitals (LUMOs) are  $M s - d_{z^2}$  and  $p$  orbitals. Two  $M-PH_3$  bonding orbitals lie below the  $d$  orbitals. Upon  $P-M-P$  bending, the arrangement of  $d$  orbitals changes from those in the linear structure; most significantly, the  $d_{yz}$  ( $b_2$ ) orbital becomes the HOMO. The HOMO along with the LUMO ( $a_1$ , roughly  $s - d_{z^2}$ ) will interact with the vacant  $\sigma(b_2)$  and  $\sigma(a_1)$  orbitals of the  $B-B$  group, leading to the oxidative addition of the  $B-B$  to the metal.

Finally, the calculated  $M-PH_3$  and  $H_3PM-PH_3$  binding energies of  $M(PH_3)$  and  $M(PH_3)_2$  are 33.3 and 27.3 kcal/mol for  $M = Pd$  and 54.6 and 38.9 kcal/mol for  $M = Pt$ , respectively, at the B3LYP/II level. The  $M-PH_3$  and  $H_3PM-PH_3$  bonds are 21.3 and 11.6 kcal/mol stronger for  $M = Pt$  than for  $M = Pd$ , respectively. Bearing the above discussion in mind, we can start our discussion on the mechanism of reaction 1 for  $M = Pd$  and  $Pt$ .

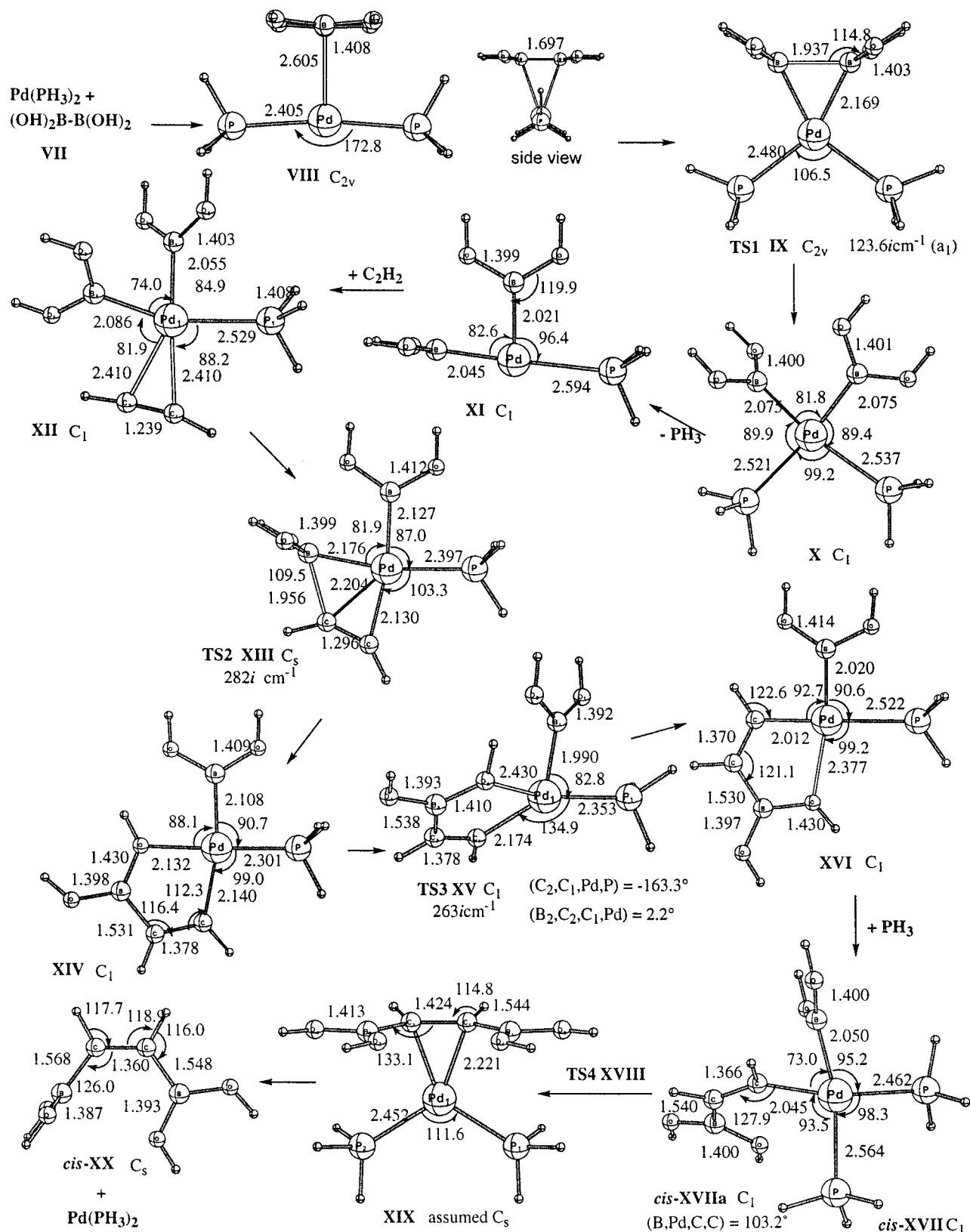
#### IV. The Mechanism of the Reaction $Pd(PH_3)_2 + C_2H_2 + R_2B-BR_2 \rightarrow Pd(PH_3)_2 + (HR_2B)C=C(HBR_2)$

As shown in Scheme 1, reaction 1 may proceed via two distinct paths, A and B. In path A the first step is coordination of  $R_2B-BR_2$  to the  $Pd$  complex, while the

first step of path B is coordination of acetylene to  $Pd(PH_3)_2$ . As mentioned in the Introduction, our previous papers on the  $Pt$  system<sup>4,5</sup> show that path A is the more favorable one when large substituted diborane and alkynes are used. Furthermore, we have shown<sup>5</sup> that, even for small diborane and alkynes, path B and path A actually merge at the square-planar  $Pt(PH_3)(C_2H_2)(BR_2)_2$  complex. We expect a similar behavior in the current case for  $Pd$ . Therefore, we will investigate only path A in the present paper.

As mentioned above, the first step in path A is coordination of  $(OH)_2B-B(OH)_2$  to  $Pd(PH_3)_2$  which leads to the molecular complex  $[(OH)_2B-B(OH)_2]Pd(PH_3)_2$  **VIII** with the  $B-B$  axis perpendicular to  $P-Pd-P$ , as shown in Figure 3. The geometries of the  $(OH)_2B-B(OH)_2$  and  $Pd(PH_3)_2$  fragments of complex **VIII** are very close to those in the free molecules, with the  $B-B$  distance 0.025 Å shorter, the  $Pd-P$  bond 0.033 Å longer, and the  $P-Pd-P$  angle 7.2° smaller. The  $Pd-B$  bond length of 2.605 Å clearly shows that the nature of the  $[(OH)_2B-B(OH)_2]-Pd(PH_3)_2$  interaction is mostly a weak electron donation from the occupied metal  $d$  orbital to the empty  $p$  orbital of  $(OH)_2B-B(OH)_2$ , which is consistent with the rather small interaction energy of 3.5 kcal/mol. The molecular complex with the  $B-B$  axis parallel to  $P-Pd-P$  was found not to exist because of the unfavorable steric repulsion.

From **VIII** the reaction proceeds via activation of the  $B-B$  bond throughout transition state **IX**. As seen in Figure 3, the  $B-B$ ,  $Pd-B$ , and  $Pd-P$  bonds in **IX** are about 0.24 Å longer, 0.44 Å shorter, and 0.075 Å longer, respectively, than those in complex **VIII**. The  $P-Pd-P$  angle is reduced from 172.8° to 106.5°. These results, as well as the normal-mode analysis with one imaginary frequency of 123.6i  $cm^{-1}$ , clearly show that **IX** is a real transition state for  $B-B$  bond activation. The activation barrier is calculated to be 8.6 kcal/mol relative to complex **VIII**. The oxidative addition product **X** with the well-known square-planar structure is only about 0.1 kcal/mol lower than the activation barrier **IX**. In **X** the OBO planes are perpendicular to each other to avoid steric repulsion. A set of  $Pd-P$  bond lengths often differ by a few hundredths of angstrom, and an average value will be used in the discussions. As seen in Figure 3,



**Figure 3.** B3LYP/I optimized geometries (in Å and deg) of the intermediates and transition states of reaction 1 for  $M = \text{Pd}$ .

the Pd–P bond in **X** is significantly stretched, from 2.37 Å in free  $\text{Pd}(\text{PH}_3)_2$  to 2.53 Å. As mentioned in our previous paper,<sup>4</sup> the metal–P bond distance is rather sensitive to the quality of the basis set on P; the polarization function can shorten the Pt–P distance as much as 0.1 Å, while it does not change significantly

either other geometrical parameters or the relative energies. We may expect similar effects in the case of Pd.

From **X** the reaction may proceed in two possible ways, either (1) by coordination of the incoming acetylene and formation of the five-coordinate complex

[(OH)<sub>2</sub>B]<sub>2</sub>Pd(PH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>2</sub>) or (2) via dissociation of one of the phosphine ligands to form the three-coordinate complex [(OH)<sub>2</sub>B]<sub>2</sub>Pd(PH<sub>3</sub>) followed by coordination of acetylene. No five-coordinate complex [(OH)<sub>2</sub>B]<sub>2</sub>Pd(PH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>2</sub>) was actually found. Similar results have been found in a previous study on Pd(PH<sub>3</sub>)<sub>2</sub>-catalyzed silastannation of acetylene.<sup>15</sup> Therefore, at first, dissociation of a PH<sub>3</sub> ligand has to take place from **X**, which leads to the three-coordinate unsaturated complex **XI** with a well-defined T-shaped structure. This conclusion also is consistent with recent experimental finding; Iverson and Smith found that the stoichiometric results exclude simple, bimolecular insertion of an alkyne into Pt–B bonds of (Ph<sub>3</sub>P)<sub>2</sub>Pt(Bcat)<sub>2</sub> and that the observed dependence on phosphine and alkyne strongly favors a mechanism where phosphine dissociation generates a three-coordinate intermediate that mediates alkyne insertion.<sup>16</sup> The calculated Pd–B bond distances are shortened in **XI**, relative to those in **X**, by 0.030 and 0.054 Å for B *cis* and *trans* to the open site, respectively. The PH<sub>3</sub> dissociation energy is calculated to be 18.8 kcal/mol. Following the dissociation of PH<sub>3</sub>, acetylene coordinates to **XI** at the open site to form structure **XII**. This structure is rather floppy; the C<sub>2</sub>H<sub>2</sub> group may rotate nearly freely around the Pd–X axis, X being the center of the C–C bond of C<sub>2</sub>H<sub>2</sub>, with a barrier of less than 1 kcal/mol. Structure **XII** shown in Figure 3 is optimized with the constraint that C–C–Pd–P is coplanar. Since the Pd–C distance is rather long, 2.410 Å, and the C–C bond is very close to that in the free molecule C<sub>2</sub>H<sub>2</sub>, one may consider structure **XII** as a π complex. Forcing the C–C part to be perpendicular to the P–Pd–B plane results in a structure with nearly the same energy. The coordination energy of C<sub>2</sub>H<sub>2</sub> to **XI** is calculated to be 12.3 kcal/mol. Thus, overall **XII** lies 11.5 kcal/mol *higher* than the reactants.

The next step of the reaction is the insertion of C<sub>2</sub>H<sub>2</sub> into the Pd–B bond to form an intermediate **XIV**. During this process one of the Pd–B bonds and one of the C–C π bonds are broken, and one Pd–C σ bond is formed. The B(OH)<sub>2</sub> group rotates around the newly formed B–C bond so that the oxygen atom can interact with the open site of Pd. Consequently, the length of this interacting O–B bond is stretched to 1.430 Å, compared with the 1.398 Å of the O–B bond pointing away from the metal. The calculated Pd–P bond is shortened from 2.529 Å in **XII** to 2.301 Å in **XIV**, obviously due to the loss of a strong *trans* influence. The stage is calculated to be exothermic by 27.2 kcal/mol.

The transition state for insertion, **XIII**, has C<sub>s</sub> symmetry. Normal-mode analysis shows that the structure has one imaginary frequency of 282i cm<sup>-1</sup> in an a' irrep (irreducible representation). Note that the lowest frequency is calculated to be 19 cm<sup>-1</sup> in an a'' irrep, corresponding to rotation of a B(OH)<sub>2</sub> ligand around the B–C bond. C<sub>2</sub>H<sub>2</sub> is much closer (by 0.07 Å) to the metal in **XIII** than in **XII**. The C–C bond is stretched by 0.06 Å, and the H<sup>1</sup>–C<sup>1</sup>–C<sup>2</sup> and H<sup>2</sup>–C<sup>2</sup>–C<sup>1</sup> angles are decreased from 165.8° to 137.8° and 142.7°, respectively,

clearly showing the change of hybridization of the carbon atoms to sp<sup>2</sup>. The breaking Pd–B bond is 0.090 Å longer than in **XII**. The barrier height from **XII** is calculated to be 5.7 kcal/mol.

As discussed in the case of the Pt(0)-catalyzed diboration reaction,<sup>4</sup> the next step is the migration of the CH=CH[B(OH)<sub>2</sub>] ligand, from being *trans* to the B(OH)<sub>2</sub> ligand in complex **XIV** to being *cis* in the complex **XVI**. This process from **XIV** to **XVI** is exothermic by 16.9 kcal/mol. The reason why **XVI** is more stable than **XIV** is the arrangement of strong donating ligands; the two strong ligands B(OH)<sub>2</sub> and CH=CH[B(OH)<sub>2</sub>] are *trans* to each other in **XIV** and *cis* to each other in **XVI**. Thus the Pd–B and Pd–C bonds are weaker in **XIV** than in **XVI**, as seen from the bond distances. For example, the Pd–C bond is 0.13 Å longer in **XIV** than in **XVI**.

The optimized migration transition state **XV** has a Y shape, as shown in Figure 3. Normal-mode analysis confirms that this structure has one imaginary frequency of 263i cm<sup>-1</sup>. The CH=CH[B(OH)<sub>2</sub>] group also rotates around the Pd–C bond to avoid repulsion with the B(OH)<sub>2</sub> ligand and to retain the energy of coordination to the metal at the O end, with the B–C=C–Pd and C=C–Pd–P dihedral angles of 2.2° and –163.3° at TS3 **XV**. As the CH=CH[B(OH)<sub>2</sub>] ligand moves from the *trans* to the *cis* position (relative to the B(OH)<sub>2</sub> ligand), the B–Pd–P angle of 90.7° in **XIV** decreases to 82.8° at the TS3 **XV** and then increases back to 90.6° in the product **XVI**. The isomerization barrier height is calculated to be 15.0 kcal/mol relative to **XIV**.

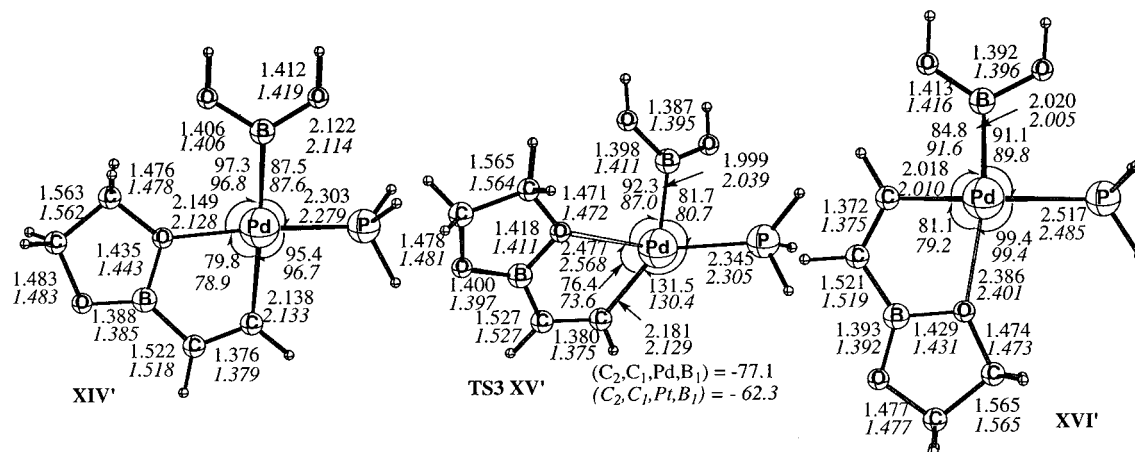
As seen in Figure 3, one of the O–H bonds of the CH=CH[B(OH)<sub>2</sub>] group in TS **XV** is twisted with the H–O<sup>4</sup>–B<sup>2</sup>–O<sup>2</sup> dihedral angle of ~40° instead of the ~0.0° angle in all other structures. However, this twist cannot take place in the real cyclic diborane and must be an artifact of the model B(OH)<sub>2</sub>. In order to examine the effect of possible twist in the real system, we have performed additional calculations for the structures **XIV'**, **XV'**, and **XVI'** with a more realistic model system (OH)<sub>2</sub>B–B(OCH<sub>2</sub>)<sub>2</sub> at the same level of the theory. The calculated geometries are presented in Figure 4, while the relative energies are given in Table 3, for both M = Pd and M = Pt. Clearly, geometrical parameters critical for the reaction in these structures hardly change. Furthermore, as seen from Table 3, the relative energies of **XV**, **XVI**, and **XVII** are very similar for the two models B<sub>2</sub>[(OH)<sub>2</sub>]<sub>2</sub> and (OH)<sub>2</sub>B–B(OCH<sub>2</sub>)<sub>2</sub>. Therefore, we conclude that the twist in B(OH)<sub>2</sub> is not of serious concern.

In the next step recoordination of PH<sub>3</sub> to **XVI** takes place without barrier and leads to the complex **XVII**. The complex **XVII** has a square-planar structure, where the Pd–P bond *trans* to B(OH)<sub>2</sub>, 2.564 Å, is longer than that *trans* to CH=CHB(OH)<sub>2</sub>, 2.462 Å, reflecting the weaker *trans* influence of the latter as was discussed for **XIV** and **XVI** above. The B–Pd–C=C dihedral angle is 103.2°, indicating that the CB(OH)<sub>2</sub> group is out of plane from the nearly square coplanar P–Pd–B–C backbone and lost the O··Pd interaction. In principle, complex **XVII** may have another isomer where the B(OH)<sub>2</sub> group is *trans* with respect to the C=C bond. As shown in the previous paper,<sup>4</sup> this structure is actually a few kilocalories/mole more stable than the *cis* structure for M = Pt. However, the isomerization from the *trans* to the *cis* is not likely to take place

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(16) Iverson, C. N.; Smith, M. R., III. *Organometallics* **1996**, *15*, 5155.

(17) Yamamoto, A. *Organotransition Metal Chemistry*; John-Wiley & Sons: New York, 1986.



**Figure 4.** B3LYP/I optimized geometries (in Å and deg) of *trans*- and *cis*-[B(OH)<sub>2</sub>]<sub>2</sub>M(PH<sub>3</sub>)(CHCH[B(OCH<sub>2</sub>)<sub>2</sub>]) (**XIV'** and **XVI'**, respectively), and the connecting transition state **XV'**, where M = Pd and Pt (in italics).

**Table 3.** Total Energy (au; Italics) of Reference Systems and Relative Energies (kcal/mol) Relative to M(PH<sub>3</sub>)<sub>2</sub> + [B(OH)<sub>2</sub>]<sub>2</sub> + C<sub>2</sub>H<sub>2</sub> (M = Pd and Pt) of Intermediates and Transition States Involved in Path A of the Diboration Reaction at the B3LYP/II Level at the B3LYP/I Optimized Geometries<sup>a</sup>

compd	Pd	Pt
M(PH <sub>3</sub> ) <sub>2</sub> , <b>IV</b>	-143.40649	-135.8314
B <sub>2</sub> (O <sub>2</sub> H <sub>2</sub> ) <sub>2</sub> , <b>VI</b>	-353.2644	-353.2644
C <sub>2</sub> H <sub>2</sub>	-77.3307	-77.3307
PH <sub>3</sub>	-8.3016	-8.3016
<b>VIII</b>	-3.5	-3.7
TS1, <b>IX</b>	5.1	10.3
<b>X</b>	5.0	-10.9
<b>XI</b>	23.8	7.9
<b>XII</b>	11.5	-5.0
TS2, <b>XIII</b>	17.2	4.0
<b>XIV</b>	-15.7 (-16.4/-16.3) <sup>b</sup>	-33.1 (-14.0/-13.9)
TS3, <b>XV</b>	0.7 (0.0/0.0)	-19.1 (0.0/0.0)
<b>XVI</b>	-32.6 (-33.3/-34.1)	-50.3 (-31.2/-34.6)
<b>XVII</b>	-38.2	-54.4
TS4, <b>XVIII</b>		-42.0
<b>XIX</b>	-73.5	-73.2
products, <b>XX</b>	-60.8	-60.8

<sup>a</sup>No zero-point energy is included. <sup>b</sup>The numbers in the parentheses are calculated relative to the isomerization transition state **XV**. The numbers before the slash stand for reaction 1 with B<sub>2</sub>((OH)<sub>2</sub>)<sub>2</sub>, while the numbers after the slash stand for reaction 1 with (OH)<sub>2</sub>B-B(OCH<sub>2</sub>)<sub>2</sub> (see the text for more detail).

because of a high barrier. The binding energy of PH<sub>3</sub> from **XVI** to **XVII** is 5.6 kcal/mol, as the interaction between Pd and O is lost in **XVII**. However, it should be noted that recoordination of this second PH<sub>3</sub> ligand is definitely needed to stabilize the following reductive elimination process, to avoid a highly unsaturated intermediate. The combined process from **XIV** to **XVII** is 22.5 kcal/mol exothermic.

From **XVII** the reductive elimination of the *cis*-B(OH)<sub>2</sub>CH=CHB(OH)<sub>2</sub> product takes place. Although a transition state has been found and characterized for M = Pt,<sup>4</sup> for M = Pd we were unable to locate a transition state **XVIII**. All our attempts led either to the product **XIX** or back to **XVII**. Since the overall process **XVII** → **XX** is highly exothermic (by 22.5 kcal/mol), one expects this transition state to be very early and the barrier to be extremely small. The product complex **XIX** is a typical π complex, with a Pd-C distance of 2.221 Å. The binding energy of **XIX** relative to the final products *cis*-B(OH)<sub>2</sub>CH=CHB(OH)<sub>2</sub> and Pt-

(PH<sub>3</sub>)<sub>2</sub> is 12.7 kcal/mol. The entire reaction 1, which is nothing but the reaction of C<sub>2</sub>H<sub>2</sub> and [B(OH)<sub>2</sub>]<sub>2</sub> to form *cis*-B(OH)<sub>2</sub>CH=CHB(OH)<sub>2</sub>, is exothermic by 60.8 kcal/mol.

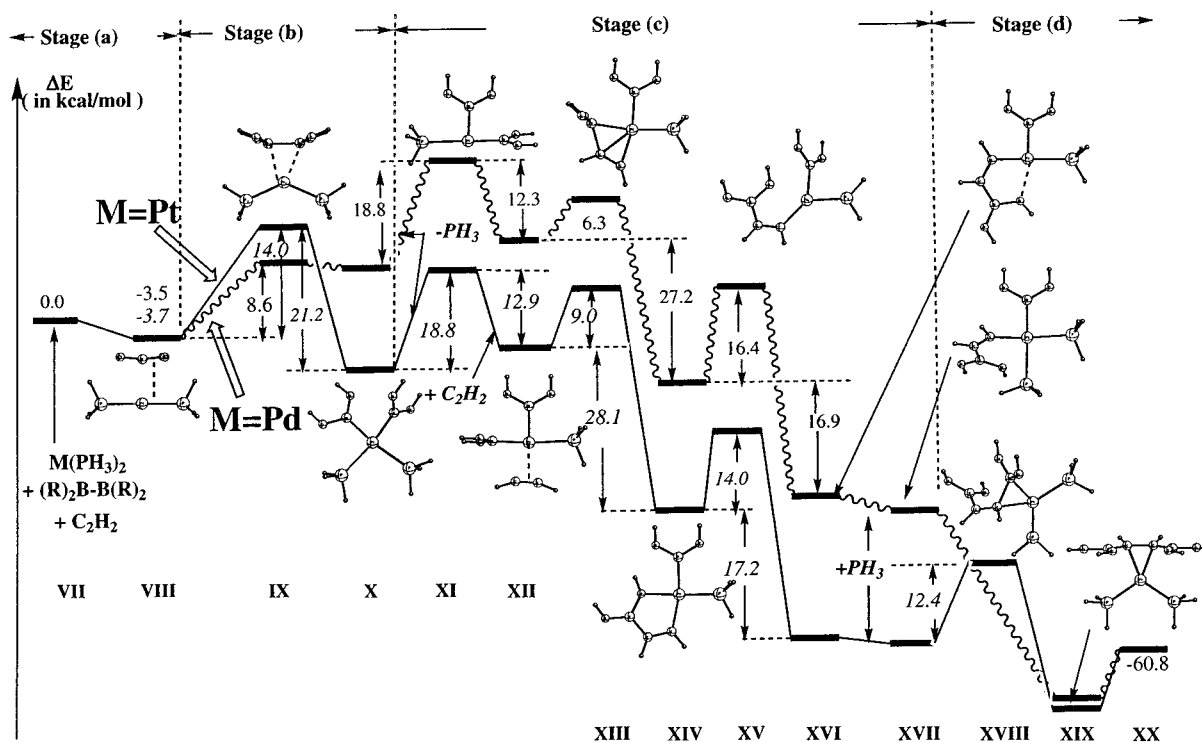
## V. Comparison of the Mechanisms of Pd(0)- and Pt(0)-Catalyzed Alkyne Diboration Reactions

In this section we will compare the PESs of alkyne diboration reaction 1 for M = Pt(0), reported in our previous paper,<sup>4</sup> and M = Pd(0) in the present paper. The energetics of the intermediates and transition states involved in reaction 1 for M = Pt is listed along with that for M = Pd in Table 3. The same labels are used for the corresponding structures for M = Pd and M = Pt. Schematic potential energy surfaces for both metals are shown in Figure 5.

For convenience of discussion, we can divide the entire PESs of reaction 1 for M = Pd and Pt into several stages, as shown in Figure 5. Stage a includes the reactants **VII** and the formation of the molecular complex [(OH)<sub>2</sub>B-B(OH)<sub>2</sub>]<sub>2</sub>M(PH<sub>3</sub>)<sub>2</sub>, **VIII**; stage b covers the processes from **VIII** to **X** that is, **VIII** → **IX** → **X**; stage c starts from the oxidative addition product **X** and covers the processes **X** → **XI** → **XII** → **XIII** → **XIV** → **XV** → **XVI** → **XVII** leading to the inserted product [CHCHB(OH)<sub>2</sub>]<sub>2</sub>M(PH<sub>3</sub>)<sub>2</sub>B(OH)<sub>2</sub>, **XVII**. The last stage (d) covers the processes **XVII** → **XVIII** → **XIX**. As seen in Table 3 and Figure 5, the PESs are quite similar for M = Pd(0) and Pt(0) on a relative scale for stages a and c. The calculated complexation energies, **VII** → **VIII**, are similar: 3.5 and 3.7 kcal/mol for M = Pd and Pt, respectively. The dissociation energy of PH<sub>3</sub> (the process **X** → **XI**), the coordination energy of C<sub>2</sub>H<sub>2</sub> (**XI** → **XII**), the insertion barrier height (**XII** to **XIII**), and the isomerization barrier height (**XIV** → **XV**) are also similar: 18.8 (18.8), 12.3 (12.9), 6.3 (9.0), and 16.4 (14.0) kcal/mol for M = Pd and Pt (in parentheses), respectively. The processes from **XII** to **XIV**, from **XIV** to **XVI**, and from **XVI** to **XVII** are exothermic by 27.2 (28.1), 16.9 (17.2), and 5.6 (4.1) kcal/mol for M = Pd and Pt (in parentheses), respectively.

However, the processes in stages b (**VIII** → **IX** → **X**) and d (**XVII** → **XVIII** → **XIX**) have several clear differences between Pd and Pt systems. First of all, the oxidative addition reaction R<sub>2</sub>B-BR<sub>2</sub> + M(PH<sub>3</sub>)<sub>2</sub> →





**Figure 5.** Comparison of the potential energy profiles for path A of the reaction:  $M(\text{PH}_3)_2 + \text{C}_2\text{H}_2 + (\text{OH})_2\text{B}-\text{B}(\text{OH})_2 \rightarrow M(\text{PH}_3)_2 + \text{C}_2\text{H}_2[\text{B}(\text{OH})_2]_2$ , where  $M = \text{Pd}$  (wavy lines and roman type) and  $\text{Pt}$  (straight lines and italicic type).

$(\text{BR}_2)_2\text{M}(\text{PH}_3)_2$  is 5.0 kcal/mol *endothermic* for  $M = \text{Pd}$ , while it is 10.9 kcal/mol *exothermic* for  $M = \text{Pt}$ , measured from the reactants. This difference in the stability of the B–B oxidative addition product of  $\text{Pd}(\text{PH}_3)_2$  and  $\text{Pt}(\text{PH}_3)_2$  can be understood by recalling the discussion on the electronic structures of  $\text{M}(\text{PH}_3)_2$  and  $(\text{BR}_2)_2\text{M}(\text{PH}_3)_2$  in section III. In the reaction the Pd and Pt atoms are promoted from the  $d^{10}$  configuration in  $\text{M}(\text{PH}_3)_2$  to the  $s^1d^9$  configuration, which is capable of forming two covalent bonds. Since the energy gap, that is, the promotion energy from the  $d^{10}$  to the  $s^1d^9$  configuration, is much larger for Pd, the oxidative addition product  $(\text{BR}_2)_2\text{M}(\text{PH}_3)_2$  is much less stable for  $M = \text{Pd}$  than for  $M = \text{Pt}$ .

The calculated oxidative addition barrier at the transition state **IX** from the molecular complex **VIII** is 8.6 and 14.0 kcal/mol for  $M = \text{Pd}$  and  $\text{Pt}$ , respectively. This seems to be contradictory to the fact that Pd–B bonds are weaker than Pt–B bonds. However, comparison of the structures of the transition state **IX** in Figure 3 shows that, although most geometrical parameters are very similar for Pd and Pt, the P–M–P angle is very different:  $106.5^\circ$  for Pd and  $139.5^\circ$  for Pt. As discussed in section III, with the smaller P–M–P angle, the  $d_{yz}$  orbital in Pd is further raised in energy and can interact more efficiently with the  $\sigma^*$  orbital of B–B. In addition, it is found that the P–M–P bending requires less energy for Pd than for Pt; bending from  $\angle\text{PMP} = 180^\circ$  to  $140^\circ$  for  $\text{Pd}(\text{PH}_3)_2$  needs only half as much energy (6.1 kcal/mol) as for  $\text{Pt}(\text{PH}_3)_2$  (12.0 kcal/mol). Overall, the activation energy is smaller for Pd than Pt. A similar conclusion has been made by Sakaki et al. on the study of the oxidative addition of the Si–X  $\sigma$  bond to the  $\text{M}(\text{PH}_3)_2$  complex (where  $M = \text{Pd}$  and  $\text{Pt}$ ).<sup>18</sup>

Because of the low TS and the high endothermicity, the oxidative addition product **X** for Pd is only 0.1 kcal/mol lower than the transition state **IX**, in contrast to Pt, where it is 21.2 kcal/mol lower. The oxidative addition product for Pd is likely to eliminate the diborane easily to go back to the reactant complex, before the next step of reaction can take place. Despite a slightly higher barrier, the next step can take place for Pt due to the thermodynamic driving force, that is, the higher reverse barrier.

To summarize,  $\text{Pd}(\text{PH}_3)_2$  does not catalyze the diboration reaction because the initial step of oxidative addition is not a favorable process, whereas its Pt analogue does activate the B–B bond and effectively catalyzes the reaction.

Finally, another difference is noticed in stage d. As seen in Figure 5, the elimination process **XVII**  $\rightarrow$  **XX** for  $M = \text{Pt}$  is exothermic by 6.4 kcal/mol and takes place with a 12.4 kcal/mol elimination barrier at the transition state **XVIII**. However, it is highly exothermic (by 22.6 kcal/mol) for Pd and takes place without a barrier. This difference can be explained by recalling that, during this process, the electronic configuration of the M atom changes from  $s^1d^9$  in  $[\text{B}(\text{OH})_2\text{CHCH}]\text{M}[\text{B}(\text{OH})_2](\text{PH}_3)_2$  to  $d^{10}$  in  $\text{M}(\text{PH}_3)_2$ . Therefore, this reductive elimination reaction is more exothermic for Pd where  $d^{10}$  is the ground state than for Pt, which has the  $s^1d^9$  ground state with  $d^{10}$  lying 13.9 kcal/mol higher.

## VI. Conclusions

From the current study we may draw the following conclusions:

(1) The  $\text{Pd}(0)$ -catalyzed acetylene diboration reaction (path A) should proceed via the same mechanism as in the  $\text{Pt}(0)$ -catalyzed reaction and involves (i) coordination

(18) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660.

of the  $R_2B-BR_2$  molecule to the Pd(0) complex, (ii) oxidative addition of the B–B bond to the Pd(0) complex, (iii) dissociation of one phosphine ligand, (iv) coordination of acetylene to the Pd atom, (v) insertion of acetylene into a Pd–B bond, (vi) isomerization of the resultant complex, accompanied by recoordination of a phosphine ligand, and (vii) reductive elimination of the alkenyl–diboron product.

(2) However, the Pd(0) complex cannot catalyze alkyne diboration reaction 1, while its Pt(0) analogue can. The main origin for this difference in the catalytic activities between Pd(0) and Pt(0) exists in the oxidative addition process of the B–B bond to  $M(PH_3)_2$ . The process occurs for  $M = Pt$  with a 14.0 kcal/mol activation barrier and is exothermic by 7.2 kcal/mol. Although the process for  $M = Pd$  has a lower (8.6 kcal/mol) barrier, it is 8.5 kcal/mol endothermic, and the reverse barrier

is only 0.1 kcal/mol! Because of this low reverse barrier, B–B oxidative addition to  $Pd(PH_3)_2$  cannot take place. The reason behind this difference has been explained in terms of the promotion energy from the  $d^{10}$  to the  $s^1d^9$  configuration of the M(0) metal atoms, which is much larger for Pd than Pt.

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