Density Functional Study on the Mechanism of Palladium(0)-Catalyzed Thioboration Reaction of Alkynes. Differences between Pd(0) and Pt(0) Catalysts and between Thioboration and Diboration

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The hybrid density functional (B3LYP) calculations have been carried out to study the mechanism of acetylene thioboration reactions catalyzed by Pd(0)/Pt(0) complexes, and the results are compared to those for the diboration reactions. The main findings can be summarized as follows. (i) No oxidative-addition product of the S−B bond to the $Pd(PH_3)_2$ was found, therefore, the oxidative-addition mechanism proposed by Suzuki et al. is not the proper one for the thioboration reaction of alkynes. (ii) We propose a new mechanism involving the following steps: (a) acetylene coordination to $Pd(PH_3)_2$, (b) dissociation of a phosphine ligand, (c) addition of the S−B bond to the metal center via a metathesis-like transition state, (d) isomerization of the resultant complex, accompanied by recoordination of the phosphine ligand, and (e) the reductive elimination of the alkenyl−thioboron product, $R'S-CH=CH-B(OR)_2$. The rate-determining stage is found to be the addition of the S−B bond to the metal center via a metathesis-like transition state. (iii) The Pd(0) complexes catalyze alkyne thioboration but not diboration, because the rate-determining barrier at the metathesis-like transition state is much higher for the latter, which has been explained in terms of the lack of hypervalency character of boron compared to sulfur. Due to the weaker C−S bond energy compared to C−B, the reductive-elimination step is highly exothermic for diboration but only slightly exothermic for thioboration. Consequently, the reductive-elimination step proceeds with a high barrier for thioboration but is barrierless for diboration. (iv) The Pt(0) complex is not expected to be a good catalyst for thioboration but is efficient for diboration. The reason behind this is the high barrier for reductive elimination, which in part comes from the promotion energy required for the metal during the process.

I. Introduction

The addition of X−B compounds (X = H, $B(OR)_2$, and heteroatoms) to an alkyne is an attractive method to produce the synthetically valuable 1-alkenylboron reagents.[1] Extensive studies show that various transition-metal compounds, in particular platinum(0) complexes, can serve as efficient catalysts for both hydroboration and diboration reactions with well-defined regio- and stereochemistry.[1] The detailed reaction mechanism of hydroboration and diboration reactions have been the subject of numerous recent experimental[2] and theoretical[3] studies. However, studies involving heteroatom-B compounds are still quite limited. Recently, Suzuki[4] and co-workers reported the Pd(0)-catalyzed addition of the 9-(alkylthio)-9-BBN (BBN = borabicyclo[3.3.1]-nonane) derivatives to terminal alkynes to produce (alkylthio)boranes, which are known as versatile reagents to introduce thio groups into organic molecules.[5] It has been found that (i) with the presence of $Pd(PPh_3)_4$ (3 mol %), the addition of a B−S bond to terminal alkynes proceeds efficiently with high regio- and stereoselectivity; (ii) *Z*-isomers of the addition products are dominant; (iii) among the various metal compounds tested in the experiment (Pd(0), Pd(II), Cu(I), and $CoCl(PPh_3)_3$), only Pd(0) complexes exhibit high catalytic behavior; (iv) basically no difference in the reactivities of the various (alkylthio)- and (arylthio)boranes used in the experiment, except for the very sterically hindered *tert*-butylthio derivatives; and (v) the thioboration reaction is specific for terminal alkynes, thus the double

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(1) (a) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: London, 1972. (b) Brown, H. C. *Organic Synthesis via Organoboranes*; Wiley-Interscience: New York, 1975. (c) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

(2) For example, see: (a) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137 and references therein. (b) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (c) Iverson, C. N.; Smith, M. R. A., III *J. Am. Chem. Soc.* **1995**, *117*, 4403. (d) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (e) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *Organometallics* **1993**, *12*, 589. (g) Iverson, C. N.; Smith, M. R., III *Organometallics* **1996**, *15*, 5155.

(3) (a) Musaev, D. G.; Mebel, A. M.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10693. (b) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 6509. (c) Dorigo, A. E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 878. (d) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742. (e) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355.

(4) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219.

(5) (a) Mikhailov, B. M.; Bubnov, Y. N. In *Organoboron Compounds in Organic Synthesis;* OPA: Amsterdam, 1984; pp 693. (b) Mukaiyama, T.; Inomata, K.; Muraki, M. *J. Am. Chem. Soc.* **1973**, *95*, 967.

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bonds in the conjugated alkynes remained intact during the reaction.

The proposed mechanism of the present reaction by Suzuki and co-workers[4] involves an oxidative addition of the B−S bond to the Pd(0) complex, the insertion of an alkyne into the Pd−B or Pd−S bond, and the reductive elimination of the alkenyl−thio−boron products. However, the first step of this proposed mechanism is not supported by their experiment; the oxidative-addition product of B−S to the Pd(0) complex is not observed, and attempts to detect an intermediate by ^{11}B and ^{31}P NMR were unsuccessful.[4] Furthermore, this mechanism left several important questions unclear. (a) Insertion of the alkyne into which bond, Pd−B or Pd−S, is more favorable? (b) Why does Pd(0) catalyze the thioboration reaction but not the diboration reaction of alkynes? Is it due to the different thermodynamic stability of certain intermediates involved in the two reactions or do the two reactions simply follow different pathways? (c) Since Pt(0) compounds are found to be efficient catalysts of alkyne diboration reactions, do they catalyze alkyne thioboration reactions as well?

To answer those questions and to clarify the detailed reaction mechanism of the Pd(0)-catalyzed alkyne thioboration process, we have carried out density functional calculations for the model reaction:

$$\mathrm{Pd(PH_3)_2} + \mathrm{C_2H_2} + \mathrm{(OR)_2B{-}SR'} \rightarrow \mathrm{Pd(PH_3)_2} + \mathrm{(OR)_2B{-}CH{=}CH{-}SR'} \quad (1)$$

We have also carried out calculations for a few important intermediates by replacing Pd by Pt, to investigate the possibility of using Pt(0) compounds as the catalyst for the thioboration reactions of alkynes.

The paper is organized as follows. In section II, we shall discuss computational methods used throughout this paper along with some calibration calculations for the models employed in this study. In section III, first we discuss the structure and energetics of the intermediates and transition states involved in the catalytic cycle. Next, we will compare the reaction mechanism with that of the diboration reaction of alkynes. Then, we look at the reactivity of Pt(0) compounds in the thioboration reactions and compare with that of Pd(0). Finally, in section IV, we make a few conclusions.

II. Computational Methods and Calibration Calculations

In the current work, we have used SH and $B(OCH_2)_2$ to model the SR′ and $B(OR)_2$ in reaction 1, and PH_3 is used to model PPh_3. The geometries of the reactants, intermediates, transition states, and products have been optimized with the hybrid density functional theory (B3LYP)[6] with the standard double-ζ quality basis set, Lanl2dz, associated with the relativistic effective core potential (ECP)[7] for the metals and nonrelativistic ECP for the P and S atoms[8] (denoted below as BSI). This BSI includes polarization d functions on P and S, since in our previous studies polarization functions have been found to be essential for the metal−P bond length. Normal-mode analyses have been performed for all of the transition states to verify their character. The energetics of the optimized structures have also been calculated using a larger basis set, BSII, by adding a polarization f function[9] to the metal and (d,p) polarization functions to the main-group elements.[10] All of the calculations have been carried out with our own modified Gaussian-94 package.[11]

Table 1. Bond Energies (kcal/mol) of R′S−B(OCH$_2$)$_2$, Pd−SR′ (R′ = H, CH$_3$), Pd−B(OCH$_2$)$_2$, and B(OCH$_2$)$_2$−B(OCH$_2$)$_2$ and Exothermicity of Reaction 1 at Various Levels Using B3LYP/BSI-Optimized Geometries[a]

compound	B3LYP/BSII// B3LYP/BSI	CCSD(T)/BSII// B3LYP/BSI
	Bond Energy	
HS−B(OCH$_2$)$_2$, **II**	−104.1	−105.3
CH$_3$S−B(OCH$_2$)$_2$, **III**	−100.2	
HS−B(OH)$_2$	−103.6	−104.6
B(OCH$_2$)$_2$−B(OCH$_2$)$_2$	−109.6	
Pd−SH, **IV**	−48.4	−41.4/−45.0[b]
Pd−SCH$_3$, **V**	−44.5	−37.2/−41.6[b]
Pd−B(OCH$_2$)$_2$, **VI**	−64.0	−60.5/−66.9[b]
	Exothermicity of Reaction	
(HS)CH=CH(B(OCH$_2$)$_2$), **VII**	−35.3	
(HS)CH=CH(B(OCH$_2$)$_2$), **VIII**	−32.9	
(CH$_3$S)CH=CH(B(OCH$_2$)$_2$), **IX**	−32.6	
(CH$_3$S)CH=CH(B(OCH$_2$)$_2$), **X**	−35.0	

[a] No zero-point energy included. [b] Extrapolated value with CCSD(T). See text for detail.

In our previous studies of the Pt(0)/Pd(0)-catalyzed acetylene diboration reactions,[3d,e] we have shown that the B3LYP/BSII//B3LYP/BSI methods gave reliable geometries and energetics. To calibrate the method for the current sulfur-containing system, we have calculated the bond energy of HS−B(OCH$_2$)$_2$, Pd−SH, and Pd−B(OCH$_2$)$_2$ at different levels of theories as shown in Table 1. The optimized structures are shown in Figure 1. As seen in Table 1, the B3LYP and CCSD(T) results agree reasonably well for most bond energies, except for the Pd−S bond in which case the two methods differ by ∼7 kcal/mol. However, it is well-known that the CCSD(T) method is more sensitive to the quality of the basis set, while the dependence for B3LYP is somewhat less significant. Within the spirit of PCI-80,[12] we extrapolated the correlation effect from the CCSD(T) value by 20%, and the derived Pd−X (X = B, S) bond energies are also given after the slash in Table 1. It is seen that the agreement between B3LYP/II and the extrapolated CCSD(T) results are quite reasonable, within 3−4 kcal/mol.

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(6) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(7) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(8) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(9) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; and Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(10) (a) Dunning, T. M., Jr. *J. Chem. Phys.* **1971**, *55*, 716. (b) Dunning, T. M., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(11) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J. B.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Cui, Q.; Musaev, D. G.; Svensson, M.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 10936.

(12) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. *J. Chem. Phys.* **1996**, *104*, 9546.

Table 2. Total Energy (Hartrees, Italic) of Reactants and Relative Energies (kcal/mol) of Intermediates and Transition States at the B3LYP/BSII Level at B3LYP/BSI-Optimized Geometries for Pd(0)- and Pt(0)-Catalyzed Thioboration and Pd(0)-Catalyzed Diboration of C_2H_2[a]

compound	Pd	Pt[b]	Pd−diboration[c]
$M(PH_3)_2$, **I**	*−143.42604*	*−135.85217*	*−143.42604*
$HS-B(OR)_2$, **II**	*−264.80864*	*−187.40084*	
C_2H_2	*−77.335247*	*−77.335247*	*−77.335247*
$B(OCH_2)_2-B(OCH_2)_2$			*−508.098353*
PH_3	*−9.3097014*	*−9.3097014*	*−9.3097014*
$M(PH_3)_2 + C_2H_2 + (HS)BR_2$	0.0	0.0	0.0
$M(PH_3)_2(C_2H_2)$, **XI**	−12.4/−11.6[a]//−17.1[d]		−12.4
$M(PH_3)(C_2H_2)$, **XII**	−0.0/0.4//0.9		−0.0
XIII, **TS**	18.6/19.9		34.1[e]
XIV, **TS**	20.1		
XV	−18.1/−17.2		(−15.7)
XVI	16.1		
XVII, **TS**	−8.9		
XVIII	−16.0		
XIX, **TS**	∼20.0		(0.7)
XX	−16.7		(−32.6)
XXI	−30.6	−42.4	(−38.2)
XXII, **TS**	−18.1	−14.5	
XXIII	−43.6		(−73.5)
I + **VII/VIII**	−35.3/−32.9		(−60.8)
XXV		0.1	(5.0)

[a] The data given in this table, in general, do not include the zero-point corrections (ZPC), except the values given after the slash which include unscaled ZPC. [b] For Pt, the model used for borane is $B(OH)_2$. [c] For the diboration reaction, numbers in parentheses are from our previous studies with $B(OH)_2-B(OH)_2$ as the diborane.[3d,e] [d] Numbers given after the double slash (//) were obtained at the CCSD(T)/BSII level. [e] For structure **XXIV**.

The calculated HSB angle, 94.4°, in our model reactant $HS-B(OCH_2)_2$, **II**, is very close to that, 92.8°, in the H_2S molecule calculated at the same level of theory. Furthermore, one also sees that one of the O atoms and the H(S) atom are located close to each other in the reaction product, **VII**, which might come from the weak electrostatic interaction between them. Indeed, the isomer **VIII**, in which the H−S bond is positioned away from the borane ring, is 2.4 kcal/mol higher than **VII**. However, in the experimentally used 9-(alkylthio)-9-BBN, this angle should be larger due to the steric interaction between alkyl and boryl ligands. To examine our model with the HS group, we have carried out calculations for the reactants and products by replacing HS with the CH_3S group. The optimized structures are **III** and **IX** and **X** for the reactant and the two isomers of the product, respectively. In **III**, the CSB angle is 100.0°, only 5.6° larger than the corresponding HSB angle in **II**. Larger differences are observed in the products **VII** and **IX**, clearly due to the repulsion between CH_3 and the borane ring. For instance, the BCC and CCS angles are opened up from 127.5° to 135.4° and from 129.7° to 135.4°, respectively. Energetically, however, the effect of augmenting the substituents is rather insignificant. As seen in Table 1, the bond energy of S−B in the reactant, that of the Pd−S bond, and the exothermicity of the whole reaction barely vary upon changing the model from $HS-B(OCH_2)_2$ to $(H_3C)S-B(OCH_2)_2$. Therefore, we conclude that the present models with the current method employed in this study should provide reliable information for the discussion of the reaction mechanism.

III. Reaction Mechanism of the Pd(0)-Catalyzed Thioboration Reaction of Alkynes, and Comparison with that of the Pd/Pt(0)-Catalyzed Diboration

In this section, we shall discuss the mechanism of the alkyne thioboration reaction 1 and compare it with our previous results for the Pd/Pt(0)-catalyzed diboration reaction. At first, we briefly recall the conclusions from our previous studies on the Pd(0)/Pt(0)-catalyzed diboration reaction of alkynes.[3d,e]

(i) The Pd(0)/Pt(0)-catalyzed diboration reaction of C_2H_2 may proceed via two distinct paths, **A** and **B**, as shown in Scheme 1, among which the former is energetically more favorable, and involves (a) coordination of the diborane R_2B-BR_2 to the M(0) (M = Pd, Pt) complex, (b) oxidative addition of the B−B bond to M, (c) dissociation of one phosphine ligand, (d) coordination of acetylene, (e) insertion of acetylene into one of the M−B bonds, (f) isomerization of the resultant complex accompanied by recoordination of a phosphine ligand, and (g) reductive elimination of the alkenyl−diboron products.

(ii) Experimentally, the Pt(0) complexes are found to be efficient catalyst for the diboration reaction of alkynes, while the Pd(0) complexes are found to be inactive. This difference comes from the B−B oxidative-addition step to the metal atom, which is found to be *exothermic* by 10.9 kcal/mol for Pt(0) but *endothermic* by 5.0 kcal/mol with only 0.1 kcal/mol reverse barrier for Pd(0). Therefore, the oxidative-addition process is unfavorable both thermodynamically and kinetically for Pd(0) compounds. The reason behind this has been explained in terms of the large promotion energy from the d^{10} to the s^1d^9 configuration of the Pd(0) atom.

A. Reaction Mechanism of Pd(0)-Catalyzed Thioboration Reaction of Alkynes. At first, let us consider the mechanism proposed by Suzuki and coworkers,[4] which is same as path **A** of the alkyne diboration reaction presented in Scheme 1. The first step of this reaction is proposed to be the oxidative addition of $R'S-B(OR)_2$ to the Pd(0) complex. However, the oxidative addition of S−B to Pd(0) cannot take place according to our calculations. All geometry optimizations of $(R'S)Pd(PH_3)_2[B(OR)_2]$ ended up with the dissociation of the recombined $R'S-B(OR)_2$ molecule. This

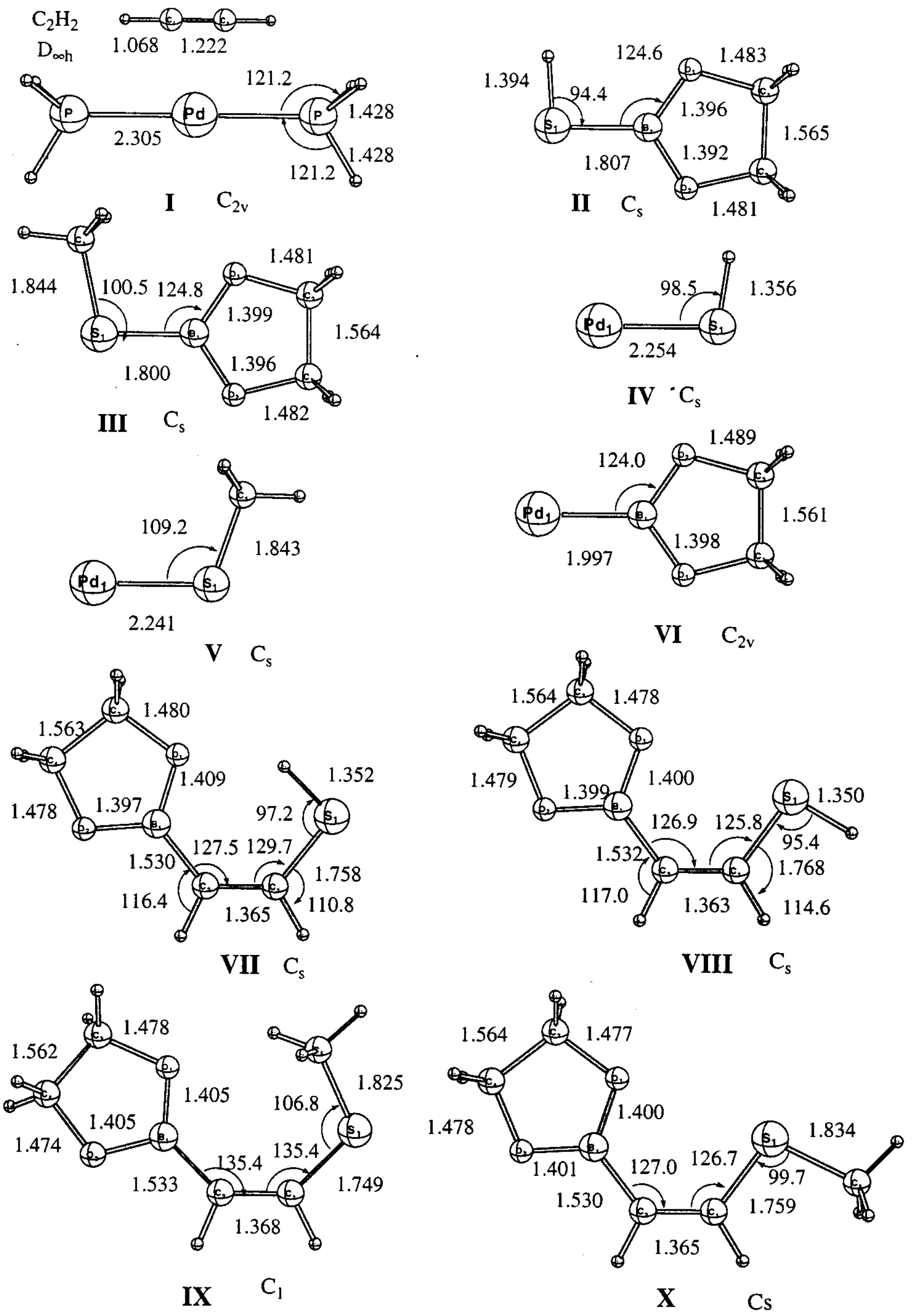

Figure 1. B3LYP/BSI-optimized geometries (Å and deg) of the reactants, products, and Pd−SH, Pd−SCH$_3$, and Pd−B(OCH$_2$)$_2$ for calibrations.

result can be understood by recalling the following facts. At first, as was discussed in our previous paper[3e] as well as by Goddard and co-workers,[13] the oxidative-addition reaction A−B + Pd(PH$_3$)$_2$ → (A)(B)Pd(PH$_3$)$_2$ involves a change in the effective electronic configuration of Pd from d^{10} to s^1d^9 because the former is not capable of forming two covalent bonds while the latter with two singly occupied orbitals clearly is. Since d^{10} is the energetically lower configuration for Pd, the $d^{10} \rightarrow s^1d^9$ promotion energy has to be paid in the bonding process. Consequently, the oxidative addition of B−B to the Pd(0) complex has been found to be *endothermic* by 5.0 kcal/mol. As shown in Table 1, the S−B bond energy, 104 kcal/mol, is nearly the same as that of the B−B bond, 109.6 kcal/mol, whereas the Pd−S bond is much weaker, by ~16 kcal/mol, than the Pd−B bond. Therefore, it is expected that the S−B oxidative-addition process will be even more endothermic than the B−B oxidative reaction, which is consistent with our finding. It should be noted that our result is also in agreement with the experimental observation that no evidence was found for the existence of the oxidative-addition product. To quote, “Attempts to detect an intermediate by ^{11}B and ^{31}P NMR were unsuccessful, presumably due to a strong thermodynamic preference for the formation of a B−S bond rather than the oxidative product in the presence of a phosphine ligand”.[4]

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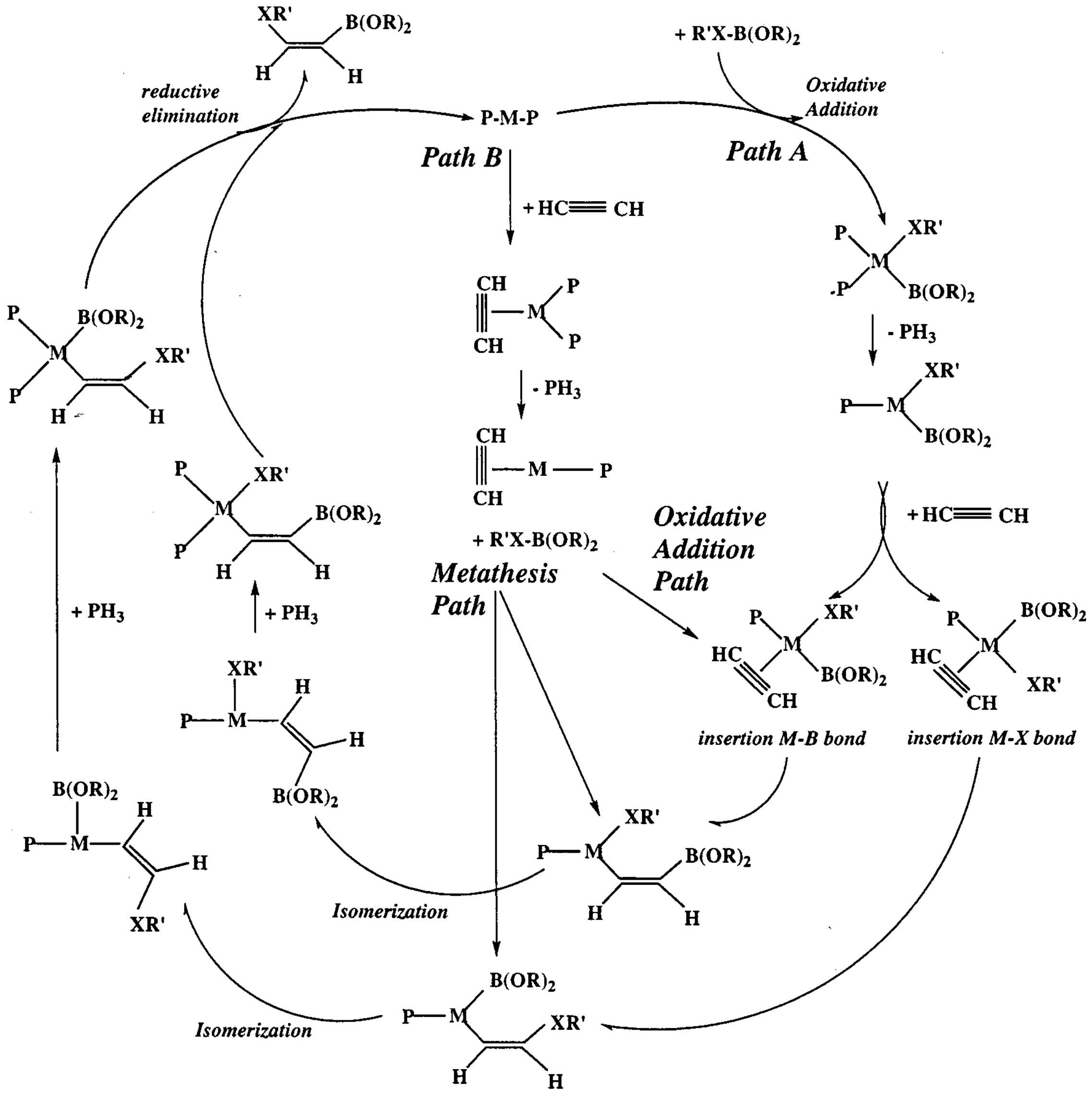
[13] (a) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115. (b) Low, J. J.; Goddard, W. A., III *Organometallics* **1986**, *5*, 609.

Scheme 1. Proposed Mechanisms of the $M(PR_3)_2$-Catalyzed Alkyne Diboration ($XR' = B(OR)_2$) and Thioboration ($XR' = SH$) Reactions



Since the oxidative addition of S−B to the Pd(0) complex cannot take place, one concludes that the mechanism (same as path **A** in Scheme 1) proposed by Suzuki and co-workers[4] is not the proper one for the alkyne thioboration reaction. Then the question is, what is the mechanism of the alkyne thioboration reaction 1? One possible choice might be the oxidative addition of S−B to $Pd(PH_3)$, after the dissociation of one PH_3 from $Pd(PH_3)_2$. However, the dissociation of PH_3 from $Pd(PH_3)_2$ has been shown to be 28.7 kcal/mol endothermic,[3e] clearly too energetically demanding. The alternative is a mechanism similar to path **B** in Scheme 1 explored in our previous study on the Pt(0)-catalyzed alkyne diboration reaction. In this path, the initial step is the coordination of alkyne to $Pd(PH_3)_2$, forming a π complex, structure **XI** in Figure 2. The coordination energy of C_2H_2 to $Pd(PH_3)_2$ is calculated to be 12.4 kcal/mol; inclusion of the zero-point corrections (ZPC) reduces this value to 11.6 kcal/mol, while the CCSD(T)/BSII method increases it to 17.1 kcal/mol. The next step is the dissociation of one PH_3 ligand, which gives the intermediate **XII**. The calculated dissociation energy of PH_3 from **XI** is only 12.4 kcal/mol, leaving complex **XII** nearly at the same in energy as the reactants. Note that ZPC reduces this value to 12.0 kcal/mol while the CCSD(T)/BSII method increases it to 16.1 kcal/mol. Clearly, the dissociation of PH_3 from **XI** is much easier than that from the reactant $Pd(PH_3)_2$, therefore, path **B** is likely to take place in reality, which will be explored in further detail. The potential-energy profile for path **B** calculated at the B3LYP/BSII level (without ZPC) is shown in Figure 3.

In general, the reaction from complex **XII** may proceed via two different paths, oxidative addition and metathesis, as shown in Scheme 1, by initially forming molecular complex $Pd(PH_3)(C_2H_2)\cdot[R'SB(OR)_2]$. However, our extensive search for this molecular complex has shown that it does not exist on the potential-energy surface of reaction 1, and the $Pd(PH_3)(C_2H_2)$ + $[R'SB(OR)_2]$ reaction proceeds without the formation a molecular complex.

Since $Pd(PH_3)(C_2H_2)$ is very similar in electronic structure to $Pd(PH_3)_2$, one would not expect the first possible path starting from **XII**, the oxidative-addition path, to be favorable for $Pd(PH_3)(C_2H_2)$. Indeed, we were not able to locate a stable oxidative-addition

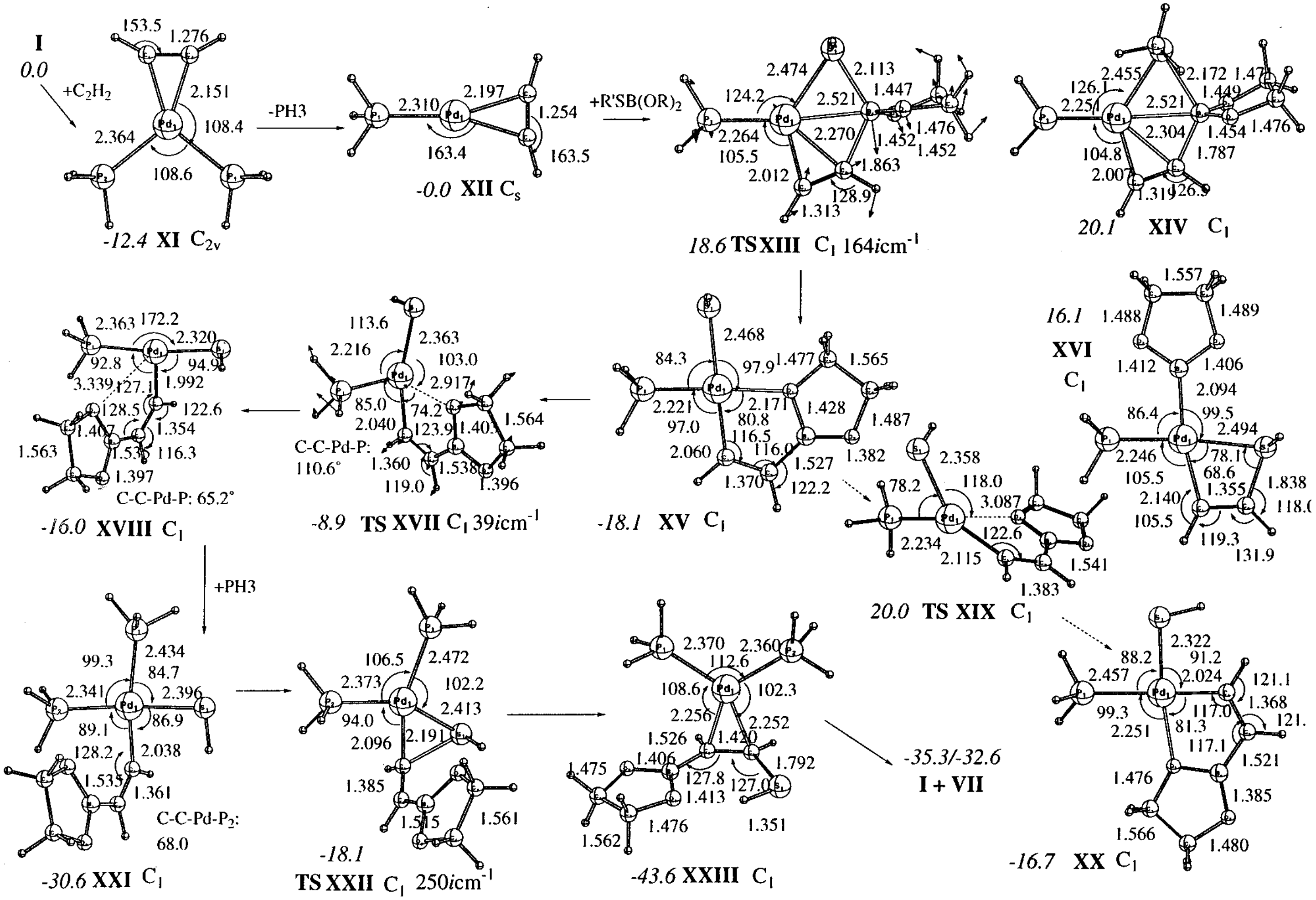


Figure 2. B3LYP/BSI-optimized geometries (Å and deg) of the intermediates and transition states in reaction 1 for Pd(0). Energetics relative to the reactants in kcal/mol are shown in italics.

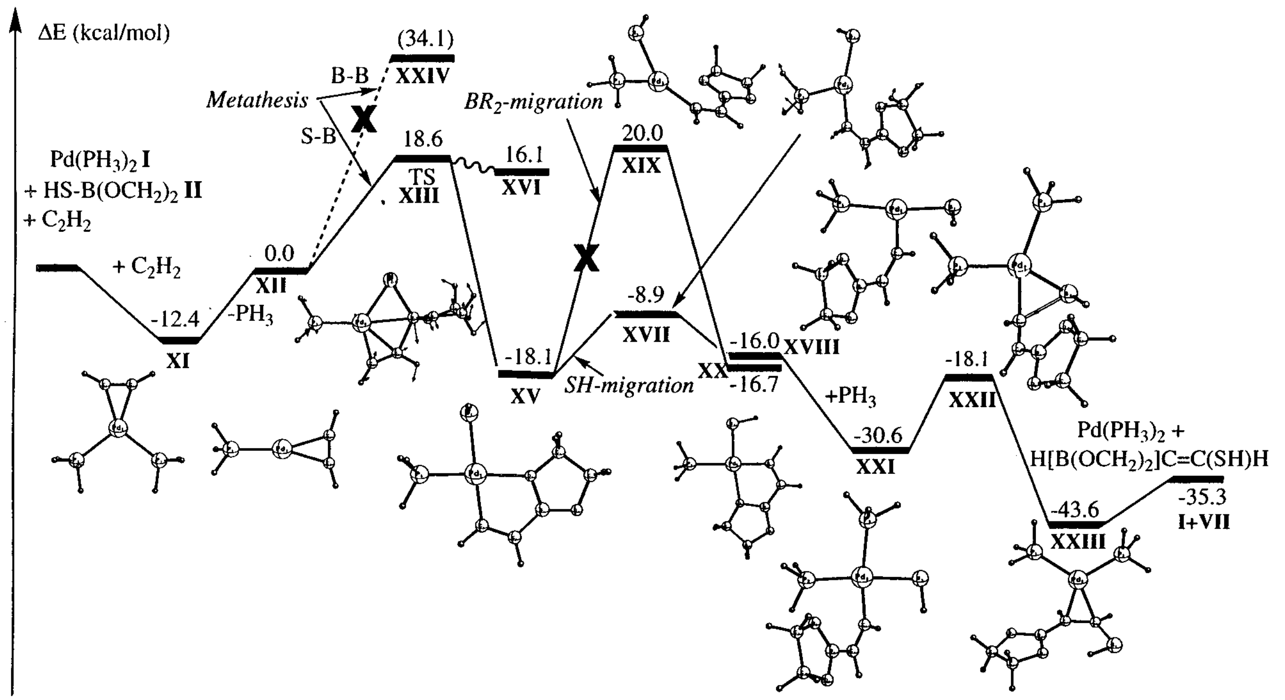


Figure 3. Potential-energy profile (without ZPC) for path B of the entire catalytic cycle of the acetylene thioboration reaction catalyzed by $Pd(PH_3)_2$ calculated at the B3LYP/BSII level. The number given in parentheses corresponds to the acetylene diboration reaction catalyzed by $Pd(PH_3)_2$.

complex $(PH_3)Pd(C_2H_2)(SH)[B(OCH_2)_2]$. Tight optimization led to the dissociation of either C_2H_2 or HS$-B(OCH_2)_2$.

The second possible path starting from **XII** might be a metathesis mechanism, proposed by us. According to this mechanism, R′S$-B(OR)_2$ may simultaneously attack Pd and one of the C atoms in $Pd(PH_3)(C_2H_2)$ and lead to two possible complexes, **XV** and **XVI** (see Figure 2). In complex **XV**, a Pd$-$S bond and a C$-$B bond are formed, while in **XVI**, a Pd$-$B bond and a C$-$S bond are formed. Similar to the situation in the diboration reaction, the oxygen atom in the $B(OCH_2)_2$ group in **XV** and the S atom in complex **XVI** interacts with the open site of the metal. There is a surprisingly large difference in the stability of these two complexes; complex **XV** lies 18.1 kcal/mol (17.2 kcal/mol with ZPC) *lower* than the reactants, while complex **XVI** is found to be 16.1 kcal/mol *higher* than the reactants. We attribute the large difference to two reasons. First of all, in **XVI**, two strong σ ligands $B(OCH_2)_2$ and CH=CH(SH) are trans to each other, thus competing in binding to the metal. Clearly, the Pd$-$C distance in **XVI**, 2.140 Å, is longer compared to that in **XV**, 2.060 Å. Second, as SH interacts with the metal in **XVI**, the four membered ring Pd$-$C$-$C$-$S is highly strained. In contrast, as the oxygen atom interacts with the open site of Pd in **XV**, a five-membered ring Pd$-$C$-$C$-$B$-$O is formed and, therefore, is less strained.

Since **XVI** is too high in energy compared to **XV**, we did not look for the transition state connecting it with **XII** + HS$-B(OCH_2)_2$. We have investigated the path leading to **XV** in more detail. The metathesis transition state, **XIII**, connecting **XII** + HS$-B(OCH_2)_2$ and **XV** is shown in Figure 2. The character of the transition state is quite obvious from its geometry. The Pd$-$S distance is calculated to be 2.474 Å, similar to that in the covalent bond length in **XV**, 2.468 Å. The C_2H_2 ligand is strongly bend toward the PH_3 ligand; the C_1-Pd-P_1 angles decreased from 163.4° in **XII** to 105.5° in **XIII.** A bond is being formed between C_2H_2 and $B(OCH_2)_2$, and the S$-$B bond is being broken. The C$-$B distance is 1.863 Å, still much longer than the normal C$-$B bond length of 1.527 Å in **XV**. The S$-$B distance is 2.113 Å, stretched from the equilibrium distance of 1.807 Å in reactant **II**. Interestingly, there is some interaction between B and the Pd atom, which is indicated by the Pd$-$B distance of 2.521 Å. Normal-mode analysis showed only one imaginary frequency of 164i cm^{-1}. The corresponding normal mode, shown in Figure 2, clearly manifests the metathesis character of the transition state. The energy of **XIII** is calculated to be 18.6 kcal/mol (19.9 kcal/mol with ZPC) above the reactants. Even though the barrier is not very low, the process is expected to be efficient due to the strong thermodynamic driving force from **XII** +**II** to **XV**, which is 18.1 kcal/mol (17.2 kcal/mol with ZPC) exothermic. In other words, the process may not be fast but the equilibrium strongly favors **XV**.

Since this metathesis transition state is an important structure on the potential energy surface of the entire reaction 1, we decided to examine our model HS$-B(OCH_2)_2$ once again by calculating the similar transition state for the larger model $(H_3C)S-B(OCH_2)_2$. The structure obtained for this new transition state, **XIV**, is presented in Figure 2. As clearly seen, the change of the model from HS$-B(OCH_2)_2$ to $(H_3C)S-B(OCH_2)_2$ has a rather small effect on both the geometry and energy. The transition state with CH_3S, **XIV**, seems to be a little earlier compared to **XIII**, as manifested by the longer S$-$B distance of 2.172 Å and the shorter C$-$B distance of 1.787 Å, which are 2.113 and 1.863 Å in **XIII**, respectively. The barrier height measured from **XII** + **III** to **XIV** is 20.1 kcal/mol, which is 1.5 kcal/mol higher than that in the case of HS. Once more, we confirmed that HS is a reasonable model for the R′S group.

Since the SH ligand and CH═CH[B(OCH$_2$)$_2$] are trans to each other in **XV**, bond formation between them is not yet possible. As discussed in our studies on the Pd/Pt(0)-catalyzed diboration reactions of alkynes,[3d,e] one of ligands, SH or CH═CH[B(OCH$_2$)$_2$], has to migrate so that they become cis to each other. If the CH═CH-[B(OCH$_2$)$_2$] ligand migrates, **XX** is formed; if the SH ligand migrates, **XVIII** is formed. In **XX**, CH═CH-[B(OCH$_2$)$_2$] becomes trans to the PH$_3$, therefore, resulting in an elongated Pd−P bond of 2.457 Å compared to 2.221 Å in **XV**. The SH is trans to the open site, which is covered by the oxygen atom in the B(OCH$_2$)$_2$ group, and consequently the Pd−S distance is shortened from 2.468 Å in **XV** to 2.322 Å in **XX**. Complex **XX** lies 16.7 kcal/mol below the reactants, i.e., 1.4 kcal/mol higher than **XV**. In **XVIII**, CH═CH[B(OCH$_2$)$_2$] is cis to the open site and, therefore, the Pd−C distance is shortened from 2.060 Å in **XV** to 1.992 Å. The B−C−C and C−C−Pd angle is opened up to ~128° from ~116° in **XV**, so that B(OCH$_2$)$_2$ avoids the repulsion from the occupied d orbitals on the Pd atom making the Pd···O distance 3.339 Å. The Pd−P and Pd−S distances are 2.363 and 2.320 Å, respectively, and they are 0.142 Å longer and 0.148 Å shorter than that in **XV**, respectively, despite the existence of an open site, **XVIII** lies only 2.1 kcal/mol above **XV**, i.e., 16.0 kcal/mol below the reactants.

During the search for the isomerization transition states from **XV** to **XVIII** and **XX**, respectively, we found that the barrier connecting **XV** and **XX** is very high, ~35 kcal/mol above **XV**. A nearly converged structure is shown in Figure 2 as **XIX.** It is interesting to note that in contrast to the corresponding structure in the diboration reaction, the oxygen atom on the migrating CH═CH[B(OCH$_2$)$_2$] stays away from the Pd metal. The Pd−O distance is 3.087 Å in **XIX** but only 2.568 Å in the corresponding TS in the diboration reaction. The loss of stabilization from the Pd−O interaction explains the higher barrier for the thioboration reaction compared to the diboration process. On the other hand, the barrier connecting **XV** and **XVIII**, which corresponds to the transition state **XVII**, has been found to be rather low, 9.3 kcal/mol relative to **XV**. The normal-mode analysis gives only one imaginary frequency which is extremely low, 39i cm^{-1}. Careful analysis of the normal mode indicates that the major component indeed corresponds to the opening up of the P−Pd−S angle, the decrease of the S−Pd−C angle, and the changes in the C−C−Pd−P and H−C−Pd−P dihedral angles, namely the desired motion from **XV** to **XVIII**. In addition, "quasi-IRC" (IRC for the first few steps and optimization thereafter) calculations confirmed that **XVII** connects **XV** with **XVIII**. The low frequency simply indicates that the potential-energy surface is very flat in the transition-state area. The character of **XVII** is also manifested from its geometrical parameters, the S−Pd−P angle is 113.6°, between the value of 84.3° in **XV** and 172.2° in **XVIII**. The dihedral angle C$_2$−C$_1$−Pd−P is 110.6° in **XVII**, halfway between ~180.0 in **XIV** and 65.2° in **XVIII**, which indicates that the CH═CH-[B(OCH$_2$)$_2$] fragment rotates around the C$_1$−Pd bond.

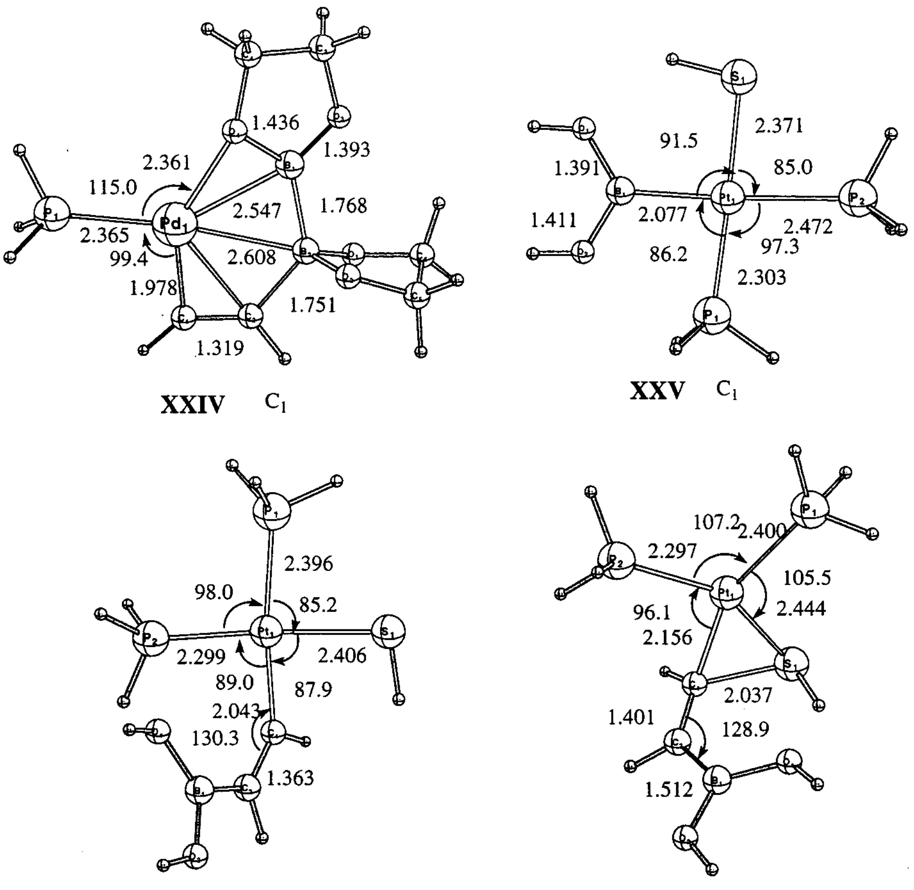
As one can see from **XVIII**, there is an open site on the Pd atom. Therefore, a PH$_3$ group is expected to come back and cover the site immediately without any barrier to form **XXI**, which adopts the geometry of a typical square-planar complex. In **XVIII**, the C−C−Pd and B−C−C angles are ~128.0°, such that B(OCH$_2$)$_2$ avoids the repulsion from the metal. The C−C−Pd−P dihedral angle is 68.0°. The different Pd−P distance reflects the difference in the binding strength of the CH═CH[B(OCH$_2$)$_2$] and SH ligands. The complex **XXI** is calculated to be 30.6 kcal/mol lower than the reactants, implying a 14.6 kcal/mol association energy for PH$_3$ to **XVIII**.

The last step of the reaction is the reductive elimination of the product (HS)CH═CH[B(OCH$_2$)$_2$] from **XXI** via the transition state **XXII**, where Pd−C and Pd−S are breaking and the C−S bond is being formed. Normal-mode analysis confirmed the identity of this elimination barrier with one imaginary frequency of 250i cm^{-1}. The barrier height measured from **XXI** is 12.5 kcal/mol. Overcoming this barrier leads to the molecular π complex **XXIII**, which has a binding energy of 8.3 kcal/mol relative to (HS)CH═CH[B(OCH$_2$)$_2$] and Pd(PH$_3$)$_2$. The exothermicity of the total reaction 1, which is nothing but C_2H_2 + HS−B(OCH$_2$)$_2$ giving (HS)CH═CH[B(OCH$_2$)$_2$], is calculated to be 35.3 kcal/mol.

In summary, we have found, as shown in Figure 3, that the thioboration reaction of C_2H_2 may proceed with the Pd(0) complex via a metathesis pathway where the S−B bond activation is found to be the rate-determining step of the entire reaction and proceeds with ~18.6 kcal/mol barrier. It is also important to note that in the whole reaction, *Z*-conformation around the double C−C bond has to be kept. Since an isomerization around the C═C bond has a significant energetic barrier, reaction 1 will exclusively lead to the *Z*-isomers of the product. These results are in agreement with experimental findings.

B. Comparison with the Pd(0)-Catalyzed Diboration Reaction. In this section, we shall compare the results for the Pd(0)-catalyzed alkyne thioboration reactions with those obtained in our previous studies on the diboration process, which was briefly presented at the beginning of section III. It should be emphasized that experimentally, Pd(0)-complexes do catalyze an alkyne thioboration reaction[4] while they do not catalyze alkyne diboration reactions.[2]

First of all, neither reactions can proceed via pathways involving the oxidative addition of B−S or B−B to the metal center since in both cases the oxidative-addition products do not exist, which is in agreement with the experimental observations.[4] As discussed above, these results can be explained in terms of the promotion energy from d^{10} to s^{1}d^9 that has to be paid in the oxidative-addition process. However, thioboration reaction 1 may proceed via a pathway involving the five-centered "metathesis" transition state **XIII**, where the Pd−S and C−B bonds are formed and the B−S and one of the π bonds of acetylene are broken simultaneously. While the d^{10} → s^{1}d^9 promotion energy of Pd(0) still has to be paid to form Pd−S and Pd−C bonds, the resultant complex **XV** is very stable due to the strong C−B bond and, therefore, provides the thermodynamic driving force for the process.



XXIV C_1 **XXV** C_1

XXVI C_1 **XXVII** C_1

268*i*cm^{-1}

Figure 4. B3LYP/BSI-optimized geometries (Å and deg) of the metathesis transition state in the diboration of C_2H_2 with the Pd(0) complex and a few structures in the thioboration reactions of C_2H_2 with Pt(0).

The barrier height corresponding to transition state **XIII**, which is found to be the rate-determining step of the entire reaction 1 is calculated to be 18.6 kcal/mol, measured from the structures **XII** + **II**. However, the same kind of "metathesis-like" transition state, structure **XXIV**, shown in Figure 4, located for the Pd(0)-catalyzed alkyne diboration reaction with $B(OCH_2)_2-B(OCH_2)_2$, lies about 34.1 kcal/mol higher than that for $B(OCH_2)_2-B(OCH_2)_2$ + $Pd(PH_3)(C_2H_2)$ (see also Figure 3). Clearly, the metathesis pathway is much more favorable for the alkyne thioboration than the diboration reaction. *This fundamental difference of the alkyne thio- and diboration reactions can be explained in terms of the hypervalent characters of the third-row atoms (sulfur in this case) compared to the second-row elements (boron in this case).* Indeed, the hypervalent character of the sulfur atom allows it to simultaneously interact with the R′ atom, $B(OR)_2$ group, and the transition-metal atom Pd, which consequently stabilizes the transition state.

Second, one should notice a clear difference in the isomerization step **XV** → **XVII** → **XVIII** and **XV** → **XIX** → **XX** between the diboration and thioboration reactions. In the diboration reaction, the migration of the $CH{=}CH[B(OCH_2)_2]$ group is found to proceed with a barrier of ~15 kcal/mol. In contrast, in the thioboration reaction the migration of the $CH{=}CH[B(OCH_2)_2]$ group is very high in energy, >30 kcal/mol, while the SH group migrates with a small barrier of 9.3 kcal/mol. In other words, the favorable isomerization process is found to be the migration of $CH{=}CH[B(OCH_2)_2]$ in the diboration reaction but the migration of SR′ for the thioboration reaction. The reason for this is clear when one considers the arrangement of strong σ ligands. In the diboration reaction, $B(OR)_2$ is stronger ligand than $CH{=}CH[B(OR)_2]$, therefore *CH*$=CH[B(OR)_2]$ *migrates* so that the $B(OR)_2$ ligands become trans to the open site. In the thioboration reaction, SR′ is a weaker ligand compared to the $CH{=}CH[B(OCH_2)_2]$ group, therefore, *SR′* migrates so that $CH{=}CH[B(OCH_2)_2]$ becomes trans to the open site.

Finally, one notices that the last step of the reductive elimination is found to be highly exothermic, 22.6 kcal/mol, and proceeds without barrier for the diboration reaction. In the current thioboration reaction, however, the final product **VII** + $Pd(PH_3)_2$ is only ~5 kcal/mol lower in energy than **XXI**; due to this smaller exothermicity, the reductive elimination occurs with a 12.5 kcal/mol barrier, which is consistent with the Hammond postulate. The difference in the exothermicities of the reductive-elimination step between the diboration and thioboration reactions can be explained in terms of a weaker bond energy compared to C−B. Indeed, the total reaction of alkyne diboration is 60.2 kcal/mol exothermic, while that of thioboration is only exothermic by 35.3 kcal/mol. Taking into account the similar bond energies of B−B and S−B, one estimates that the S−C bond is ~20 kcal/mol weaker than B−C, which is roughly the difference in the exothermicity of the reductive-elimination step.

C. Can the Pt(0) Complex Serve as an Active Catalyst for the Thioboration of Alkynes? According to experimental[2] and our previous studies,[3d] the Pt(0) complexes are excellent catalysts for diboration reactions, in contrast to the ineffective Pd(0) compounds. The reason behind of this difference has been explained in terms of the energy gap between the d^{10} and s^1d^9 configurations of the M(0) metal atoms, which is much larger for Pd than Pt. One may wonder, can Pt(0) complexes serve as active catalysts for the alkyne thioboration reaction as well?

To answer this interesting question, we have carried out limited calculations on the mechanism of the Pt(0)-catalyzed acetylene thioboration reaction with a smaller model $HS-B(OH)_2$. According to our previous studies, one only expects a large difference for the Pt(0)- and Pd(0)-catalyzed alkyne thioboration reaction in steps involving a change of the electronic configurations, namely the S−B oxidative-addition and the final reductive-elimination steps. Therefore, we have concentrated on the S−B oxidative-addition and the final elimination steps in the current work. The calculated structures for the Pt(0)-catalyzed acetylene thioboration reaction are shown in the Figure 4.

First of all, as in the case of the diboration reaction, the oxidative addition of S−B to $Pt(PH_3)_2$ is energetically more favorable than that for $Pd(PH_3)_2$: the oxidative-addition product, **XXV**, does exist as a distinct local minima, in contrast to the case involving Pd. As expected, it is not as stable as the corresponding oxidative-addition product of B−B (which has been found to be 10.9 kcal/mol lower than reactants) and lies ~0.1 kcal/mol above the reactants. Therefore, one may expect a significant activation barrier for the addition of S−B to the metal. However, since our main purpose is to investigate the possibility of Pt(0) being able to catalyze the thioboration reaction, which will be answered as we will explain, we did not pursue this barrier further. For the same reason, we did not try to study the possible metathesis addition of S−B to $Pt(C_2H_2)(PH_3)$.

Second and more importantly, the reductive-elimination barrier, measured from complex **XXVI** to the elimination TS **XXVII**, is found to be extremely high for the reaction involving Pt, 27.9 kcal/mol. The result can be easily understood as follows. Since the C−S bond is much weaker than C−B, the exothermicity of the reductive-elimination step in thioboration is found to be much smaller than that in diboration. As a consequence, according to the Hammond postulate, the reductive-elimination barrier will be significantly higher for the thioboration than the diboration reaction. Indeed, a 12.5 kcal/mol reductive-elimination barrier has been found for the Pd(0)-catalyzed acetylene thioboration reaction, while the corresponding process for the diboration reaction occurs without barrier. Furthermore, as found previously in our work, a ~12 kcal/mol barrier exists for the acetylene diboration reaction catalyzed by Pt(0). The reason for this higher barrier than in the case involving Pd(0) is that the metal atom changes its electronic configuration from s^1d^9 to d^{10} during the reductive elimination, which occurs spontaneously for Pd but requires promotion energy for Pt. Combining these facts, one expects an even higher reductive-elimination barrier for the acetylene thioboration reaction involving Pt(0) than for the diboration reaction, which is exactly what we found. In conclusion, we do not expect that a Pt(0) complex will be an efficient catalyst for the thioboration reaction due to a too high reductive-elimination barrier.

IV. Conclusions

According to the above discussion, we may draw the following conclusions:

(1) In agreement with the experimental observation,[4] no oxidative-addition product of the S−B bond to $Pd(PH_3)_2$ was found; therefore, the oxidative-addition mechanism proposed by Suzuki et al.[4] is not the proper one for the thioboration reaction of alkynes.

(2) The Pd(0)-catalyzed acetylene thioboration reaction proceeds via the path involving (a) acetylene coordination to $Pd(PH_3)_2$, (b) dissociation of one phosphine ligand, (c) addition of the S−B bond to the metal center via a metathesis-like transition state, (d) isomerization of the resultant complex, accompanied by recoordination of the phosphine ligand, and (e) the reductive elimination of the alkenyl−thioboron product $R'S-CH{=}CH-B(OR)_2$.

(3) The rate-determining stage of the entire reaction is found to be the addition of the S−B bond to the metal center via a metathesis-like transition state, which takes place with a barrier of 18.6 kcal/mol. The entire reaction 1 is exothermic by 35.3 kcal/mol.

(4) The Pd(0) complexes do catalyze alkyne thioboration but not the diboration reaction because the rate-determining barrier at the metathesis-like transition state is much lower for the former than the latter. This fundamental difference has been explained in terms of the hypervalency character of sulfur compared to boron. In the isomerization step (d) of the thioboration reaction, it is the SR′ ligand that migrates while in the diboration reaction it is the $CH{=}CH[B(OR)_2]$ ligand that migrates, which is simply a consequence of the trans influence. Finally, the reductive-elimination step is highly exothermic for the diboration reaction but only slightly exothermic for the thioboration reaction of acetylene, which has been explained in terms of a weaker C−S bond energy compared to that of C−B. As a consequence, the reductive-elimination step proceeds with a distinct barrier of 12.5 kcal/mol, which is found to be barrierless for the diboration reaction.

(5) The Pt(0) complex is not expected to be a good catalyst for the thioboration reaction of alkynes, while they are found to be efficient catalysts for the alkyne diboration reaction. The reason behind this is the high reductive-elimination barrier of ~27.9 kcal/mol, which in part comes from the promotion energy required for the metal during the process.

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