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Reaction of $BX_2{-}BX_2$ (X = H or OH) with $M(PH_3)_2$ (M = Pd or Pt). A Theoretical Study of the Characteristic Features

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The insertion of $M(PH_3)_2$ (M = Pd or Pt) into $BX_2{-}BX_2$ (X = H or OH) was theoretically investigated with the ab initio MO/MP4SDQ, SD-CI, and coupled cluster with double substitutions (CCD) methods. The MP4SDQ method provides an activation energy (E_a) and an exothermicity (E_{exo}) similar to those of the SD-CI and CCD methods (the MP4SDQ values are given here). This reaction proceeds with a moderate E_a of ∼15 kcal/mol and a considerable E_{exo} of ∼20 kcal/mol for X = OH and M = Pt and a higher E_a of 20 kcal/mol and a higher E_{exo} of 33 kcal/mol for X = H and M = Pt. It should be noted that the B−B bond, as well as the Si−Si bond, undergoes the insertion reaction of $Pt(PH_3)_2$ much more easily than does the C−C bond. However, the insertion of $Pd(PH_3)_2$ into $B(OH)_2{-}B(OH)_2$ is difficult, unlike the insertion into the Si−Si bond. The $Pt{-}BH_2$ and $Pt{-}B(OH)_2$ bond energies were estimated to be ∼60 kcal/mol, being similar to the $Pt{-}SiH_3$ bond energy and much greater than the $Pt{-}CH_3$ bond energy, while the $Pd{-}B(OH)_2$ bond energy (49 kcal/mol) was calculated to be much smaller than the $Pt{-}B(OH)_2$ bond energy. The reaction of $BX_2{-}BX_2$ exhibits interesting features; around the transition state (TS), not only the σ^* orbital of the B−B bond but also the unoccupied π and π^* orbitals can form the charge-transfer interaction with the occupied d_σ and d_π orbitals of Pt, which stabilizes the TS. This is the reason that although the B−B bond is much stronger than the Si−Si bond, the insertion of $Pt(PH_3)_2$ into $BX_2{-}BX_2$ easily occurs.

Introduction

Recently reported platinum(0)-catalyzed bisboration of alkyne[1] is one of the most attractive reactions in organometallic chemistry, since two functional groups are introduced into an organic molecule at a time. According to the catalytic cycle proposed, the insertion of platinum(0) into the B−B σ bond occurs first to yield a platinum diboryl complex. This complex plays an important role of a key intermediate, like the platinum disilyl complex which is also a key intermediate in platinum-catalyzed bis silation of alkene.[2] Actually, the reaction of diboron with $Pt(PPh_3)_2$ was recently reported to yield a platinum diboryl complex.[1b,3] Considering that the similar insertion of platinum(0) into the C−C bond is much more difficult,[4] it is necessary to carry out a detailed investigation of the insertion of platinum(0) into the B−B bond, in order to understand the catalytic bisboration reaction and to make further developments in this area.

In the present work, we theoretically investigate the reaction (eq 1) between $BX_2{-}BX_2$ and $M(PH_3)_2$ (X = H or OH; M = Pt or Pd). $B(OH)_2{-}B(OH)_2$ was examined here as a reasonable

$$BX_2{-}BX_2 + M(PH_3)_2 \rightarrow cis\text{-}M(BX_2)_2(PH_3)_2 \qquad (1)$$

model of the tetraalkoxydiboron which was used for bisboration of alkyne.[1] B_2H_4 was calculated here only for interpretational advantage, to shed some light on the characteristic features of diboron by comparing B_2H_4 with $B_2(OH)_4$.[5] Our main purposes are to estimate the activation barrier and the reaction energy, to compare this reaction with similar insertion reactions into C−C and Si−Si bonds, to clarify the characteristic features of the insertion of a transition metal element into the B−B bond, and to estimate theoretically Pt−boryl and Pd−boryl bond energies. The M−boryl bond energy has not been reported yet to our knowledge except for the $Ir{-}B(OR)_2$ bond energy estimated recently.[6]

Computations

Geometries of reactants, transition state (TS), and products were optimized with the energy gradient method at the MP2 level, using the following basis sets (BS-I): (5s 5p 3d)/[3s 3p 3d] and (5s 5p 4d)/[3s 3p 3d] were used for valence electrons of Pt and Pd with effective core potentials (ECPs) employed to replace their core electrons.[7] MIDI-4[8] and (4s)/[2s][9] sets were adopted for P, B, and H, respectively. Energy changes were evaluated with the MP4SDQ, SD-CI, and coupled cluster with double substitutions (CCD) methods, where the following better basis sets (BS-II−BS-IV) were used: In BS-II, a d-polarization function was added only to P[7] without any other modification of the BS-I. In BS-III, a d-polarization function was added to B[7] without any other modification of the BS-II. In BS-IV, (9s 5p 1d)/[3s 2p 1d],[9] (9s 5p)/[3s 2p],[9] MIDI-4*,[8] and (4s)/[2s][9] were employed for B, O, P, and H, respectively.

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(1) (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (b) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713.

(2) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

(3) Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1995**, *117,* 4403.

(4) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115; *Organometallics* **1986**, *5,* 609.

(5) We optimized the geometry of B_2H_4 in the C_{2v} symmetry like $B_2(OH)_4$, to compare $B_2(OH)_4$ with B_2H_4. This means that alternative geometry of B_2H_4 was not fully searched, and therefore, there remains some possibility that the energetics of the B−B bond is not realistic in B_2H_4.

(6) Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.

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

(8) Huzinaga, S.; Andzelm, J.; Kobukowski, M.; Radio-Andzelm, E.; Sakai, Y.; Tatewaki, M. *Gaussian basis sets for molecular calculations*; Elsevier: Amsterdam, 1984.

(9) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaeffer, H. F., Ed.; Plenum: New York, 1977; p 1.

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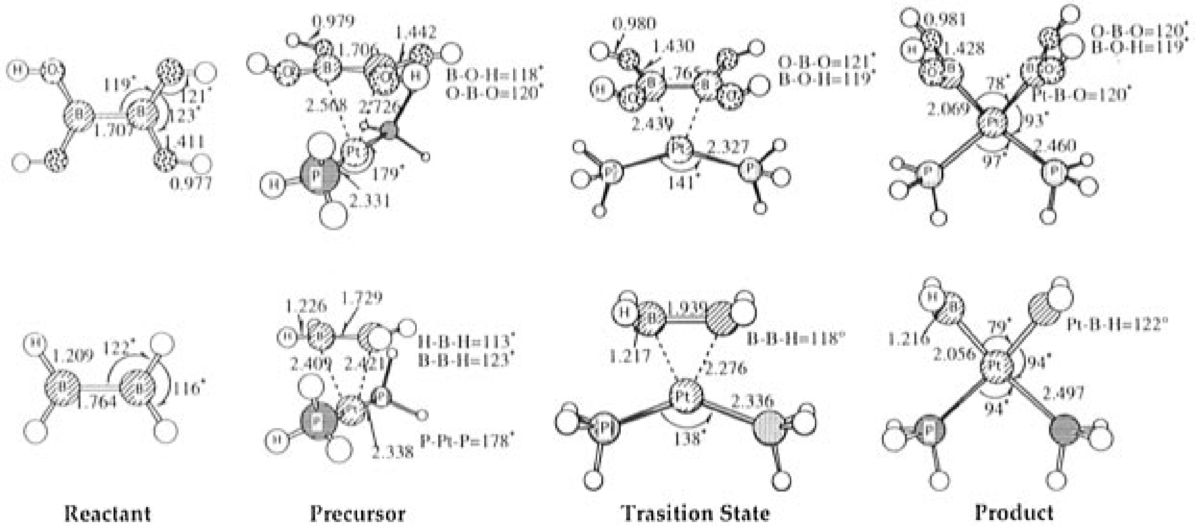

Figure 1. Geometry changes in the BX_2-BX_2 (X = H or OH) oxidative addition to $Pt(PH_3)_2$: MP2-optimized geometry; bond lengths in angstroms; bond angle in degrees.

In the SD-CI calculation, the contribution of higher order excitations was corrected with the Davidson−Silver[10] and Pople[11] methods. In the CCD calculation, the contribution of single and triple substitutions was evaluated through fourth order with CCD wave functions (this computation method is called CCD(ST4) here).[12]

The geometry of PH_3 was taken to be the same as the experimental structure of the free PH_3 molecule.[13] The Gaussian 92 program[14] was used for these calculations.

Results and Discussion

The insertion of $Pt(PH_3)_2$ into $B(OH)_2-B(OH)_2$ proceeds via a precursor complex (PC) and TS, as shown in Figure 1, where only the most stable geometry of PC is given.[15] In the PC, both diboron and $Pt(PH_3)_2$ show little distortion. In the TS, the B−B bond lengthens somewhat by 0.06 Å (~4%), while the PPtP angle (141°) is approximately intermediate between the reactant and the product. In the product, the optimized Pt−B distance and BPtB angle agree well with the experimental values.[1b,3] On the other hand, the insertion of $Pt(PH_3)_2$ into BH_2-BH_2 exhibits somewhat different features as follows: (1) in the PC, the B−B bond shortens considerably, unexpectedly, and (2) in the TS, the B−B bond lengthens considerably by 0.175 Å (~10%), and the PPtP angle is more closed. These TS geometries resemble the TS of the insertion of $Pt(PH_3)_2$ into the Si−Si bond[16] but are much more reactant-like than that of the insertion of $Pt(PH_3)_2$ into the C−C bond.[17]

Table 1. Binding Energy (BE)[a] of the Precursor Complex and Activation Energy (E_a)[b] and Reaction Energy (ΔE)[c] of the B−B Oxidative Addition (All kcal/mol) (Negative Values Represent the Energy Stabilization)

			BE	E_a	ΔE
		M = Pt			
BH_2-BH_2	BS-II	MP4SDQ	−30.2	21.0	−34.8
	BS-III	HF	−7.9	22.3	−14.7
		MP2	−38.9	20.4	−47.7
		MP3	−32.2	22.8	−40.1
		MP4DQ	−32.0	20.5	−41.2
		MP4SDQ	−35.7	21.0	−43.4
		SD-CI(DS)[d]	−32.4	21.3	−40.5
		SD-CI(P)[e]	−31.8	21.3	−39.9
		CCD(ST4)	−37.9	21.2	−43.9
	BS-IV	MP4SDQ	−32.5	21.4	−39.6
$B(OH)_2-B(OH)_2$	BS-IV	MP4SDQ	−9.2	13.3	−22.2
SiH_3-SiH_3[f]		MP4SDQ	−3.1	17.5	−34.8
CH_3-CH_3[g]		MP4SDQ	−1.1	66.0	5.2
		M = Pd			
$B(OH)_2-B(OH)_2$	BS-IV	MP4SDQ	−9.0	9.2	1.6[h]
SiH_3-SiH_3[f]		MP4SDQ	−3.0	13.3	−17.1
CH_3-CH_3[g]		MP4SDQ	−1.4	56.8	30.5

[a] BE = $E_t\{M(PH_3)_2(B_2X_4)\} - E_t\{M(PH_3)_2\} - E_t(B_2X_4)$. [b] $E_a = E_t(TS) - E_t(PC)$. [c] $\Delta E = E_t(\text{product}) - E_t\{M(PH_3)_2\} - E_t(B_2X_4)$. [d] Davidson−Silver correction for higher-order excitations.[10] [e] Pople correction for higher-order excitations.[11] [f] Reference 16. [g] Reference 17. [h] Reference 19.

The binding energy (BE) of PC, the activation energy (E_a), and the reaction energy (ΔE) were calculated by various computational methods, as shown in Table 1, where BE is the energy difference between the PC and the reactants, E_a is the energy difference between the PC and the TS, ΔE is the energy difference between the product and the reactants, and the negative value represents the energy stabilization for all these terms, and vice versa. Introduction of electron correlation significantly increases BE and E_{exo} values. Similar correlation effects on E_{exo} were also observed in the insertion of $Pt(PH_3)_2$ into C−H, Si−H, C−C, and Si−Si bonds.[16−18] The correlation effects on BE are easily interpreted in terms that the weak interaction is in general enhanced at the correlated level since

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(10) Davidson, E. R.; Silver, D. W. *Chem. Phys. Lett.* **1977**, *52*, 403.

(11) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quant. Chem. Symp.* **1977**, *11*, 149.

(12) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quant. Chem.* **1978**, *14*, 545.

(13) (a) Herzberg, G. *Molecular Spectra and Molecular Structure*; Academic Press: New York, 1974; Vol. 3, p 267. (b) PH_3 is adopted as a model of PPh_3 which was used experimentally.[1,3] Because PH_3 is a little different from PPh_3 in steric and electronic factors, the results presented here would slightly shift from the real chemistry: for instance, if the steric factor is important, the oxidative addition becomes easier in the PH_3 complex than in the PPh_3 complex, because PH_3 is smaller than PPh_3. However, if a donating ligand favors the oxidative addition, the oxidative addition becomes less easier in PH_3 than in PPh_3, since PH_3 is considered to be less donating than PPh_3.[13c] (c) Sargent, A. L.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 317.

(14) Frisch, A. M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; De Frees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(15) This geometry is 4.4 kcal/mol more stable than the C_{2v} structure in which the B−B bond is parallel to the P−Pt−P bond (MP4SDQ level).

(16) Sakaki, S.; Ogawa, M.; Kinoshita, M. *J. Phys. Chem.* **1995**, *99*, 9933.

(17) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373.

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

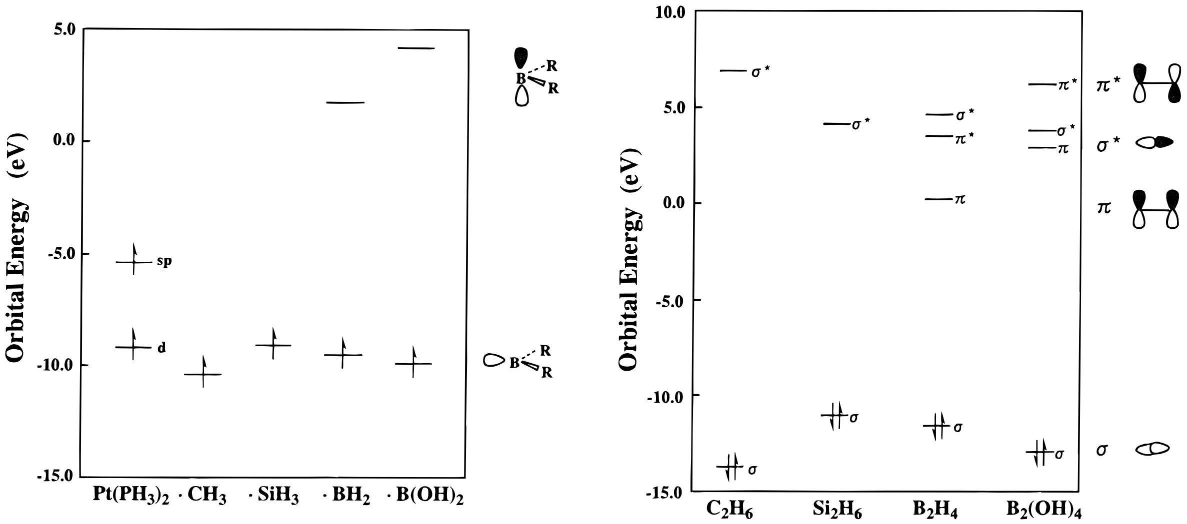

Figure 2. Orbital energies of BX_2 and B_2X_4.

the dispersion interaction is incorporated not at the HF level but at the correlated level. On the other hand, a similar E_a value is calculated at both Hartree−Fock (HF) and correlated levels, indicating that the correlation effects on E_a are not significant, unexpectedly. This result would arise from the observation that both PC and TS are similarly stabilized upon introduction of electron correlation. Although introduction of electron correlation is important for BE and ΔE values, all the methods of higher quality than the MP3 method yield similar values of BE, E_a, and ΔE (see MP2/BS-III−CCD(ST4)/BS-III given in Table 1). In particular, BE, E_a, and ΔE values at the MP4SDQ level are almost the same as those at the CCD(ST4) level.

Basis set effects on BE, E_a, and ΔE were also investigated at the MP4SDQ level. As shown in Table 1 (see MP4SDQ/BS-II, MP4SDQ/BS-III, and MP4SDQ/BS-IV), E_a little depends on the kinds of basis set used here, while BE and E_{exo} somewhat fluctuate upon going to BS-IV from BS-II. However, the difference between BS-III and BS-IV is much smaller than that between BS-II and BS-III. This means that not only is the d-polarization function added on B but also a highly flexible basis set should be used for B to calculate correctly the energy change of the insertion of transition metal element into the B−B bond. Thus, discussion based on MP4SDQ/BS-IV calculations is presented here.

There are several significant differences among $B(OH)_2-B(OH)_2$, BH_2-BH_2, CH_3-CH_3, and SiH_3-SiH_3. The PC of B_2H_4 is considerably stable, whereas the PC of $B_2(OH)_4$ is much less stable than that of B_2H_4 but still more stable than the PCs of Si_2H_6 and C_2H_6.[16,17] The remarkable stabilization of the PC of BX_2-BX_2 is not surprising, because B_2X_4 is a Lewis acid and $Pt(PH_3)_2$ is a Lewis base. Because of substantial stabilization of the PC, the insertion of $Pt(PH_3)_2$ into BH_2-BH_2 requires a considerably high E_a value of ~20 kcal/mol, which is however much lower than that of the insertion of $Pt(PH_3)_2$ into CH_3-CH_3.[4,17] On the other hand, the insertion of $Pt(PH_3)_2$ into $B(OH)_2-B(OH)_2$ proceeds with a lower E_a of ~15 kcal/mol, much more easily than the insertion into CH_3-CH_3,[4,17] and more easily than the insertion into SiH_3-SiH_3.[17] Both insertions of $Pt(PH_3)_2$ into BH_2-BH_2 and $B(OH)_2-B(OH)_2$ are much more exothermic than the insertion into CH_3-CH_3. The insertion into BH_2-BH_2 is as exothermic as the insertion into SiH_3-SiH_3, while the insertion into $B(OH)_2-B(OH)_2$ is less exothermic than the insertion into SiH_3-SiH_3. These results are easily understood in terms of bond energies, as will be discussed below.

It should be noted here that the insertion of $Pt(PH_3)_2$ into BH_2-BH_2 and $B(OH)_2-B(OH)_2$ easily proceeds like the insertion into SiH_3-SiH_3. One difference between $B(OH)_2-B(OH)_2$ and SiH_3-SiH_3 is that the insertion of $Pd(PH_3)_2$ into the B−B bond is difficult and the reverse reaction proceeds with no barrier (Table 1), unlike the insertion of $Pd(PH_3)_2$ into SiH_3-SiH_3, which easily occurs.[16,17] This would be a main reason that $Pd(PH_3)_2$ is not a good catalyst for bisboration of alkyne, as reported.[1]

The strength of the B−B and $M-BX_2$ bonds is one of the important factors determining the ease of this kind of insertion reactions. These bond energies are estimated (Table 2), considering eqs 1 and 2. Interestingly, the B−B bond of $B_2(OH)_4$ is much stronger than that of B_2H_4. Consistent with this result, the B−B bond of $B_2(OH)_4$ is much shorter than that of B_2H_4 (Figure 1). These results can be easily explained in terms of the p_π electron delocalization of OH. Although the B_2X_4 geometry is essentially the same as that of ethylene, the π orbital is unoccupied in B_2X_4 but occupied in ethylene. Since the OH group possesses an occupied p_π orbital, its p_π electrons delocalize to the unoccupied π orbital of the B−B bond. This electron delocalization results in partial occupation of the π orbital, which strengthens the B−B bond. On the other hand, such delocalization cannot occur in the case of X = H, because H has only σ electrons. Actually, the p_π orbital population of B is 0.0 in B_2H_4 but 0.274 in $B_2(OH)_4$.

$$BX_2-BX_2 \rightarrow 2BX_2 \qquad (2)$$

The stabilization of PC is significantly influenced by the above-mentioned p_π electron delocalization and the π orbital energy of B_2X_4. When X = H, the π orbital of B_2H_4 is completely unoccupied and lies at a rather low energy (Figure 2). In the PC, this π orbital can receive a lot of d electrons of Pt, which leads to stabilization of PC and the strengthening of the B−B bond. Actually, the PC of B_2H_4, $Pt(PH_3)_2(B_2H_4)$, is significantly stable and its B−B distance shortens considerably. When X = OH, the π orbital of $B_2(OH)_4$ does not need to receive a lot of electron density from Pt, since it is partially occupied and its orbital energy is rather high in the free $B_2(OH)_4$ molecule (Figure 2). Consequently, the PC of $B_2(OH)_4$,

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(19) *cis*-$Pd(B(OH)_2)_2(PH_3)_2$ is less stable than the PC by 10.6 kcal/mol (MP4SDQ). Thus, the product is slightly less stable than the TS. Nevertheless, the TS and *cis*-$Pd(B(OH)_2)_2(PH_3)_2$ were optimized, probably because the potential energy surface was flat and all the forces were smaller than the convergence thresholds.

Table 2. Bond Energies Related to the B−B Oxidative Addition (MP4SDQ; kcal/mol)

BH_2-BH_2	89.9	$Pd-B(OH)_2$	51.0
$B(OH)_2-B(OH)_2$	103.6	$Pt-SiH_3$[a,d]	57.6
SiH_3-SiH_3[a,b]	80.5	$Pd-SiH_3$[a,d]	45.3
CH_3-CH_3[b,c]	84.6	$Pt-CH_3$[c,d]	39.7
$Pt-BH_2$	64.8	$Pd-CH_3$[c,d]	27.1
$Pt-B(OH)_2$	62.9		

[a] Reference 16. [b] Evaluated from the following equation: $XH_3-XH_3 \rightarrow 2XH_3$ (X = C or Si). [c] Reference 17. [d] Evaluated from the following equation: $M(PH_3)_2 + XH_3-XH_3 \rightarrow$ *cis*-$M(XH_3)_2(PH_3)_2$ (M = Pd or Pt, X = C or Si).

$Pt(PH_3)_2\{B_2(OH)_4\}$, is less stable than $Pt(PH_3)_2(B_2H_4)$ and its B−B bond length little changes in the PC.

The $Pt-BX_2$ bond involves two interactions; one is the donating charge transfer (CT) from the sp^2 orbital of BX_2 to the unoccupied $d_\sigma sp_\sigma$ orbital of Pt, and the other is the back-donating CT from the occupied d_π orbital of Pt to the unoccupied p_π orbital of BX_2 since the BX_2 group has an unoccupied p_π orbital on the B atom (Figure 2). The latter CT is not involved in $M-CH_3$ and $M-SiH_3$ bonds because CH_3 and SiH_3 do not have an unoccupied p_π orbital. Considering these interactions, we can easily explain the difference in bond energy between $M-BX_2$ and $M-EH_3$ (E = C or Si). Since the sp^2 orbital of BX_2 (−9.9 eV for X = OH and −9.5 eV for X = H) is at a higher energy than the sp^3 orbital of CH_3 (−10.4 eV), as shown in Figure 2, the $M-BX_2$ bond receives greater stabilization from both the donating and back-donating CT interactions than the $M-CH_3$ bond. Although the sp_σ^2 orbital of $B(OH)_2$ is at a lower energy than the sp_σ^3 orbital (−9.1 eV) of SiH_3, the $M-BX_2$ bond is slightly stronger than the $M-SiH_3$ bond because of the back-donating CT interaction in the former. The $Pd-B(OH)_2$ bond is, however, similar to the $Pd-SiH_3$ bond, probably because the d_π electrons of Pd less easily delocalize to the p_π orbital of BX_2 than those of Pt, due to the lower energy of Pd d orbitals.[16] The $Pt-BH_2$ bond is slightly stronger than the $Pt-B(OH)_2$ bond, because the p_π orbital of BH_2 is at a lower energy than that of $B(OH)_2$ (Figure 2). The difference between $Pt-BH_2$ and $Pt-B(OH)_2$ bond energies is much smaller than the difference between BH_2-BH_2 and $B(OH)_2-B(OH)_2$ bond energies (Table 2). This is interpreted in terms of electron delocalization to the p_π orbital of BX_2: because the d_π electrons of Pt more easily delocalize to the p_π orbital of BX_2 than do the p_π electrons of OH, the difference between X = H and X = OH becomes smaller in $Pt(BX_2)_2(PH_3)_2$ than in BX_2-BX_2 (note that the Pt d_π orbital is at a higher energy than the OH p_π orbital).

Considering these bond energies, the difference in exothermicity of these reactions is easily understood. In the insertion of $Pt(PH_3)_2$ into BX_2-BX_2, the B−B bond is broken and the $Pt-BX_2$ bond is formed. Since the $Pt-B(OH)_2$ bond is only 2 kcal/mol weaker than the $Pt-BH_2$ bond but the B−B bond is ∼14 kcal/mol stronger in $B(OH)_2-B(OH)_2$ than in BH_2-BH_2, the insertion of $Pt(PH_3)_2$ into BH_2-BH_2 is more exothermic than that into $B(OH)_2-B(OH)_2$.[5] The difference in reactivity between BX_2-BX_2 and CH_3-CH_3 is similarly interpreted in terms of bond energies: the CH_3-CH_3 bond is as strong as the BH_2-BH_2 bond but ∼15 kcal/mol weaker than the $B(OH)_2-B(OH)_2$ bond, while both $Pt-B(OH)_2$ and $Pt-BH_2$ bonds are ∼20 kcal/mol stronger than the $Pt-CH_3$ bond. Thus, the insertion of $Pt(PH_3)_2$ into $B(OH)_2-B(OH)_2$ and BH_2-BH_2 bonds is much more exothermic than the insertion into CH_3-CH_3. On the other hand, the insertion is less exothermic than that into SiH_3-SiH_3, since the $B(OH)_2-B(OH)_2$ bond is 23 kcal/mol stronger than the SiH_3-SiH_3 bond but the $Pt-B(OH)_2$ bond is only 5 kcal/mol stronger than the $Pt-SiH_3$ bond. On the basis of these bond energies, the reason that the insertion of $Pd(PH_3)_2$ into $B(OH)_2-B(OH)_2$ is difficult, unlike the insertion into SiH_3-SiH_3, is reasonably explained as follows: Since the $Pd-B(OH)_2$ bond is as strong as the $Pd-SiH_3$ bond but the $B(OH)_2-B(OH)_2$ bond is much stronger than the SiH_3-SiH_3 bond, *cis*-$Pd\{B(OH)_2\}_2(PH_3)_2$ is much less stable than the reactant and slightly less stable than the TS,[18] unlike *cis*-$Pd(SiH_3)_2(PH_3)_2$. As a result, the B−B reductive elimination takes place with no barrier.

Although the exothermicity can be clearly explained in terms of bond energies, the unexpectedly low E_a value of the insertion reaction into BX_2-BX_2 would be related not to the bond energy but to the electronic structure of B_2X_4. B_2X_4 has the unoccupied π and π^* orbitals just above the σ^* orbital (LUMO) unlike C_2H_6 and Si_2H_6, as shown in Figure 2. Since π and π^* orbitals can form the CT interactions with the occupied d orbitals of Pt, the TS of the insertion reaction into BX_2-BX_2 would receive additional stabilization from these CT interactions, compared with the TS of the insertion reactions into C−C and Si−Si bonds in which only σ^* orbital of EH_3-EH_3 (E = C or Si) can participate in the CT interaction from the Pt d orbital.

In summary, the insertion of $Pt(PH_3)_2$ into BX_2-BX_2 exhibits characteristic features which arise from the presence of unoccupied π and π^* orbitals of diboron.

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