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Iridium-Catalyzed Borylation of Benzene with Diboron. Theoretical Elucidation of Catalytic Cycle Including Unusual Iridium(V) Intermediate

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Abstract: Iridium-catalyzed borylation of benzene with diboron was theoretically investigated with the DFT method, where an iridium(I) boryl complex, $Ir(Beg)(NN)$ **1**, and an iridium(III) tris(boryl) complex, $Ir(Beg)_3$-(NN) **14**, (eg (ethyleneglycolato) = $-OCH_2CH_2O-$, NN = $HN=CHCH=NH$ (diim) or 2,2′-bipyridine (bpy)) were adopted as models of active species and $B_2(eg)_2$ was adopted as a model of bis(pinacolato)diboron (pinacolato = $-OCMe_2CMe_2O-$). Oxidative addition of a benzene C−H σ-bond to **1** takes place with an activation barrier (E_a) of 11.2 kcal/mol, followed by reductive elimination of phenylborane, Ph−Beg, from $Ir(Beg)(H)(Ph)(diim)$ with an activation barrier of 15.6 kcal/mol. Though the oxidative addition and the reductive elimination occur with moderate activation barriers, $B_2(eg)_2$ much more easily reacts with **1** to afford **14** than does benzene, of which the activation barrier is very small (2.9 kcal/mol). Oxidative addition of the benzene C−H σ-bond to **14** occurs with a moderate activation barrier of 24.2 kcal/mol to afford an unusual seven-coordinate iridium(V) complex, $Ir(H)(Ph)(Beg)_3(bpy)$ **16**. From this complex, phenylborane Ph−Beg is produced through the reductive elimination with concomitant formation of $IrH(Beg)_2(bpy)$ **17**, where the activation barrier is 4.9 kcal/mol. Complex **17** further reacts with diboron to form $Ir(H)(Beg)_4$-(bpy) (E_a = 8.0 kcal/mol), followed by the reductive elimination of borane H−Beg (E_a = 2.6 kcal/mol) to regenerate $Ir(Beg)_3(bpy)$, when diboron exists in excess in the reaction solution. After consumption of diboron, $IrH(Beg)_2(bpy)$ reacts with borane, H−Beg, to form $Ir(H)_2(Beg)_3$ (E_a = 21.3 kcal/mol) followed by the reductive elimination of H_2, to regenerate $Ir(Beg)_3(bpy)$ with concomitant formation of H_2. Formation of the iridium(III) tris(boryl) complex **14** from $IrCl(diim)$ and diboron was also theoretically investigated; $IrCl(diim)$ undergoes two steps of oxidative addition of diboron to afford a seven-coordinate iridium(V) complex, $IrCl(Beg)_4(NN)$, from which the reductive elimination of Cl−Beg takes place easily to afford **14**. From these results, it should be clearly concluded that the iridium(III) tris(boryl) complex is an active species and an unusual iridium(V) species is involved as a key intermediate in the reaction. Detailed discussion is presented on the full catalytic cycle and the importance of a seven-coordinate iridium(V) intermediate.

Introduction

C−H σ-bond activation of hydrocarbons followed by functionalization is an attractive research subject not only from practical points of view but also from fundamental points of view in a wide area of chemistry. In particular, transition-metal catalyzed borylation of hydrocarbons through the C−H σ-bond activation is of considerable interest, since organic boryl compounds are versatile and useful materials in organic syntheses. Several C−H σ-bond activations followed by borylation with diboron and borane have been reported, recently. For instance, rhodium-catalyzed borylation of alkanes and arenes with diboron was reported by Hartwig and his collaborators.[1] In this reaction, the terminal C−H σ-bond of alkanes is activated

and the boryl group is introduced at the terminal position, interestingly. Also, the iridium-catalyzed borylation of arenes with borane was reported by Smith and his collaborators, where $CpIr(H)(Bpin)(PMe_3)$ (pin = pinacolato($-OCMe_2$-CMe_2O-)), $[IrCl(COD)]_2$/phosphine, and $Ir(Ind)(COD)$/phosphine (Ind=indenyl) were used as a catalyst.[2,3] Slightly later, similar iridium-catalyzed borylation of aromatic compounds with bis(pinacolato)diboron (eq 1) was reported by Ishiyama, Miyaura, Hartwig, and their collaborators,

$$2C_6H_6 + B_2pin_2 \rightarrow 2C_6H_5\text{-}Bpin + H_2 \qquad (1)$$
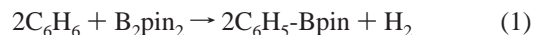
where $[IrCl(COD)]_2$/bpy (bpy = 2,2′-bipyridine or 4,4′-di-*tert*-butyl-2,2′−bipyridine) was used as a precatalyst.[4] A rhodium-

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(1) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

(2) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1999**, *121*, 7696. This work first reported the transition-metal-catalyzed borylation of aromatic compounds.
(3) (a) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E; Smith, M. R., III. *Science* **2002**, *295*, 305. (b) Cho, J. Y.; Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **2000**, *122*, 12868.

(I) complex, RhCl(N$_2$)(P^{i}Pr$_3$)$_2$, was successfully applied to the borylation of aromatic and benzylic C−H bonds with borane too.[5] The borylation of heteroaromatic compounds was successfully carried out with the same catalytic system.[6] These reactions are excellent examples of the above-mentioned functionalization through the C−H σ-bond activation.

These catalytic reactions proceed through two steps of σ-bond activation; one is C−H σ-bond activation of alkanes and arenes and the other is B−B or B−H σ−bond activation. It is of considerable interest to clarify what active species can perform these two kinds of σ-bond activation and what elementary steps are involved in the catalytic cycle. Several stoichiometric reactions of transition-metal boryl complexes with alkanes and arenes were reported,[2,7] where photoirradiation was necessary in some cases probably to produce a coordinatively unsaturated species.[2] These reactions are considered to be a model of the elementary step of the iridium-catalyzed borylation of arenes with diboron and borane. The catalytic cycles of the rhodium-catalyzed borylation of alkanes with diboron and iridium-catalyzed borylation of arenes with borane were proposed by Hartwig et al.[1] and Smith et al.,[3] respectively. In these catalytic cycles, the oxidative addition of the C−H σ-bond to rhodium-(III) and iridium(III) complexes is involved as a key elementary step.[1,3] Certainly, iridium(III) tris(boryl) complexes were isolated from the reaction of iridium(I) complexes with borane[3,8] and diboron.[4] Also, an iridium(V) tetrahydride complex, Cp*IrH$_4$ (Cp* = C$_5$Me$_5$), and iridium(V) boryl polyhydride complexes, Cp*IrH$_n$(Bpin)$_{4-n}$ (n = 2 or 3), were isolated by Bergman et al.[9] and Hartwig et al.,[10] respectively. It was experimentally reported that the stoichiometric reaction between Ir(Bpin)$_3$(bpy) (bpy = 2,2′-bipyridine) and 3 equiv of benzene leads to formation of 3 equiv of phenylborane.[4] These results suggest that the iridium(III) tris(boryl) complex is an active species in the iridium-catalyzed borylation of arenes and the oxidative addition of the C−H σ-bond to the iridium(III) center is involved in the catalytic cycle.

On the other hand, a rhodium(I) monoboryl complex was proposed as an active species in RhCl(N$_2$)(P^{i}Pr$_3$)$_2$-catalyzed borylation of arenes.[5] Though several iridium(V) and rhodium-(V) complexes were isolated, all these complexes take the structure of Cp*M(H)$_n$(L)$_{4-n}$ (L=boryl, silyl, or stanyl)[9−12] except for Ir(H)$_5$(^{i}Pr$_2$SiOSi^{i}Pr$_2$).[13] The iridium(V) complex with bpy has not been reported yet, to our knowledge.[14] Also, the

oxidative addition of several substrates to iridium(I) complexes has been reported in many works,[15] but the reductive elimination of H$_2$ from IrCl(H)$_2$(PPh$_3$)$_2$ was experimentally reported to occur easily.[16] Similarly, it was experimentally reported that thermolysis of an iridium(III) complex, Cp*Ir(H)(Cy)(PMe$_3$) (Cy = C$_6$H$_{11}$), in benzene took place through the reductive elimination of cyclohexane followed by the oxidative addition of benzene, to afford an iridium(III) complex, Cp*Ir(C$_6$H$_5$)-(PMe$_3$).[17] Thus, we must consider the possibility that an iridium-(I)boryl complex is an active species and the C−H σ-bond activation by the iridium(I)boryl complex is involved as a key elementary step in the catalytic cycle.

In this theoretical work, we investigated the [IrCl(COD)]$_2$/bpy-catalyzed borylation of benzene with diboron, since this catalytic system provides very high yields of phenylborane under mild reaction conditions (vide supra). As discussed above, the following issues should be clarified in this catalytic reaction: what is an active species, what catalytic cycle this reaction proceeds through, and what is a rate-determining step. Also, no experimental proposal has been presented about the elementary step which participates in evolution of the dihydrogen molecule, whereas the stoichiometry of the reaction requires evolution of dihydrogen molecule (see eq 1). The formation step of the iridium(III) tris(boryl) complex from the [IrCl-(COD)]$_2$/bpy system has not been experimentally proposed yet. If the iridium(III) tris(boryl) complex is an active species, this formation process should be clarified. Our purposes here are to provide clear answers to all the above-described issues and to present clear features of the whole catalytic cycle of this reaction.

Computations and Models Adopted

Geometries were optimized with the DFT method, where the B3LYP functional was used.[18,19] Transition states were ascertained by performing frequency calculations and examining what geometry changes are going to occur in the imaginary frequency. We present Supporting Information Figure S1 to show the value of the imaginary frequency and the geometry changes that are going to occur in the imaginary frequency.

Two kinds of basis set systems were used here. The smaller system (BS-I) was employed in geometry optimization. In this BS-I, usual LANL2DZ was used for Ir, where core electrons of Ir (up to 4f) were replaced with effective core potentials (ECPs) and its valence electrons were represented with a (341/321/21) set.[20] For ligand atoms, 6-31G basis sets[21] were used except for Cl for which a (21/21) set was used with the effective core potentials.[22] For B and O atoms, a d-polarization function was added.[23] For the hydride ligand and the active H atom that converts into the hydride ligand, the 6-311G set was used with a p-polarization function.[24] The better basis set system (BS-II) was employed in evaluation of energy and population changes. In BS-II, a

(4) (a) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (b) Ishiyama, T.; Takagi, J.; Hartwig, J.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *114*, 3182.
(5) Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2168.
(6) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. *Tetrahedoron Lett.* **2002**, *43*, 5649.
(7) (a) Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11357. (b) Waltz, K. M.; Hartwig, J. F. *Science* **1997**, *277*, 211. (c) Waltz, K. M.; Muhoro, C. N.; Hartwig, J. F. *Organometallics* **1999**, *18*, 3383. (d) Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358.
(8) Nguyen, P.; Blom, H. P.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329.
(9) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508.
(10) Kawamura, K.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8422.
(11) (a) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458. (b) Ricci, J. S., Jr.; Koetzle, T. F.; Fernandez, M. J.; Maitlis, P. M.; Green, J. C. *J. Organomet. Chem.* **1986**, *299*, 383.
(12) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 5458.
(13) Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *32*, 383.

(14) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; p 1059.
(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1985; pp 312 and 328.
(16) Wink, P. A.; Ford, P. C. *J. Am. Chem. Soc.* **1986**, *108*, 4838.
(17) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G.. *J. Am. Chem. Soc.* **1986**, *108*, 1537.
(18) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1983**, *98*, 5648.
(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(21) Ditchfiled, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
(22) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.
(23) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(24) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

Scheme 1

real system   model system

preliminaly calculation

R = H or t-Bu

Scheme 2
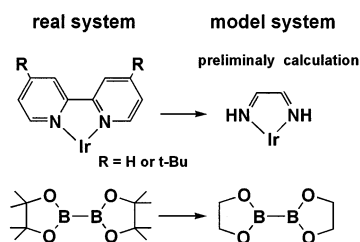
larger (541/541/111) set[20,25] was used for Ir with the same ECPs as those of BS-I. For benzene, diboron, and boryl group, 6-311G(d) sets were employed,[24] while the same basis set and ECPs as those of BS-I were used for Cl.

Since this reaction is carried out in solution, translation and rotation movements do not largely contribute to entropy. Here the entropy by vibrational frequencies is evaluated in a classical way, where vibrational frequencies are calculated by quadratic fitting of energy changes. However, the entropy effects by the vibrational frequencies do not significantly influence the energy change; see Supporting Information Table S1 for the contribution of the entropy by vibrational frequencies to the activation free energy ($\Delta G^{\circ\ddagger}$). Thus, the energy changes are given hereafter without entropy contribution.

The Gaussian 98 program package was used for all these calculations.[26] Population analysis was carried out with the method proposed by Weinhold et al.[27]

We adopted here bis(ethyleneglycolato)diboron, $B_2(eg)_2$ (eg = $-OCH_2CH_2O-$), as a model of bis(pinacolato)diboron, $B_2(pin)_2$ (pin = $-OCMe_2CMe_2O-$), as shown in Scheme 1. In the preliminary examination, we adopted the simplest diimine ($HN=CH-CH=NH$) as a model of 2,2′-bipyridine (Scheme 1). This diimine is abbreviated as diim hereafter. In the detailed examination, we adopted 2,2′-bipyridine (bpy) as a chelating ligand, since 2,2′-bipyridine and its derivative were experimentally used. We adopted here an iridium(I) monoboryl complex, Ir(Beg)(diim), and an iridium(III) tris(boryl) complex, Ir(Beg)3(diim), or Ir(Beg)3(bpy), as model of active species, since the rhodium(I) monoboryl complex was proposed as an active species in the rhodium-catalyzed borylation of arenas[4] and the iridium-(III) tris(boryl) complex was isolated in the iridium-catalyzed borylation of arenes.[3]

Results and Discussion

Reactions of Iridium(I) Monoboryl Complex with Diboron and Benzene: First, the reaction of the iridium(I) monoboryl complex, Ir(Beg)(diim) **1** (diim = $HN=CHCH=NH$), with benzene was theoretically investigated, as shown in Figure 1. In this preliminary examination, we adopted diim as a model of 2,2′-bipyridine, as described above. Since **1** is a coordinatively unsaturated complex, benzene easily coordinates with the Ir center to afford an iridium(I) benzene complex **2**. In **2**, the benzene plane is almost perpendicular to the coordinate bond, which suggests that the π orbital of benzene interacts with the
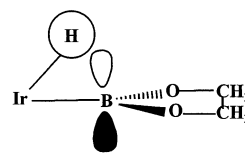
unoccupied d_σ orbital of the Ir center. This structure resembles well that of the palladium(II) benzene complex which exists as an intermediate in the C−H σ-bond activation of benzene.[28] In the transition state **TS2−3**, the C−H bond lengthens to 1.501 Å and the phenyl plane is changing its direction toward the Ir center. The Ir−H distance is much shorter than the Ir−Ph distance, as observed in usual oxidative additions of alkane and benzene to the low valent metal center.[28−32] The Ir center of the product, Ir(Beg)(Ph)(H)(diim) **3**, takes the +3 oxidation state, while the geometry is far from a square pyramidal structure that is expected to be stable when the metal center takes a d^6 electron configuration. Its geometry is similar to a trigonal bipyramid structure. This is interpreted in terms of the hydride ligand forming a bonding interaction with the boryl group, as shown in Scheme 2, because the boryl group possesses an empty p orbital on the B atom perpendicular to the Beg plane and the hydride ligand is electron-rich. Actually, the H atomic population (0.972e) of **3** is considerably smaller than that (1.138e) of an iridium(III) complex, Ir(H)(Beg)2(diim), in which the H ligand does not form any attractive interaction with the boryl ligand. The next step is the reductive elimination of phenylborane Ph−Beg from **3**, which takes place through transition state **TS3−4** to afford Ir(H)(diim)(Ph−Beg) **4**. In **TS3−4**, the Ir−B and Ir−Ph distances are slightly longer than those of **3** and the B−Ph distance (1.672 Å) is somewhat longer than that of the product (1.552 Å). These geometrical features suggest that this transition state is productlike. In **4**, phenylborane coordinates with the Ir center through the O atom, since the boryl group has a lone pair orbital on the O atom. Its coordination bond is considerably strong; the stabilization energy by the coordination is 25.0 kcal/mol.

The energy changes along these reactions are given in Figure 1 as a relative value to the reactants. The activation barrier (E_a) is 11.2 kcal/mol for the oxidative addition of benzene and 15.6 kcal/mol for the reductive elimination of phenylborane Ph−Beg. From these moderate values, it is reasonably concluded that the reaction of **1** with benzene easily takes place to afford phenylborane.

Since diboron exists in excess under the catalytic reaction conditions, we should consider the possibility that not only benzene but also diboron reacts with **1**. As shown in Figure 2, diboron approaches the Ir center of **1** to afford a precursor complex **6** in which diboron coordinates with the Ir center

(25) Couty, M.; Hall, M. B. *J. Comput. Chem.* **1996**, *17*, 1359

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

(27) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 849 and references therein.

(28) Biswas, B.; Sugimoto, M.; Sakaki, S. *Organometallics* **2000**, *19*, 3895.

(29) (a) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.*, **1991**, *113*, 5063. (b) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.*, **1993**, *115*, 2373. (c) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660. (d) Sakaki, S.; Biswas, B.; Sugimoto, M. *J. Chem. Soc., Dalton Trans.* **1997**, 803. (e) Sakaki, S.; Biswas, B.; Sugimoto, M. *Organometallics*, **1998**, *17*, 1278. (f) Sakaki, S.; Mizoe, N.; Musashi, Y.; Biswas, B.; Sugimoto, M. *J. Phys. Chem.* **1998**, *102*, 8027.

(30) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

(31) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

(32) (a) Blomherg, M. R. A.; Siegbahn, P. E. M.; Nagashima, U.; Wennerberg, J. *J. Am. Chem. Soc.* **1991**, *113*, 424. (b) Sieghahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *J. Am. Chem. Soc.* **1993**, *115*, 4191. (c) Siegbahn, P. E. M. *Organometallics* **1994**, *13*, 2833. (d) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1996**, *118*, 1487.
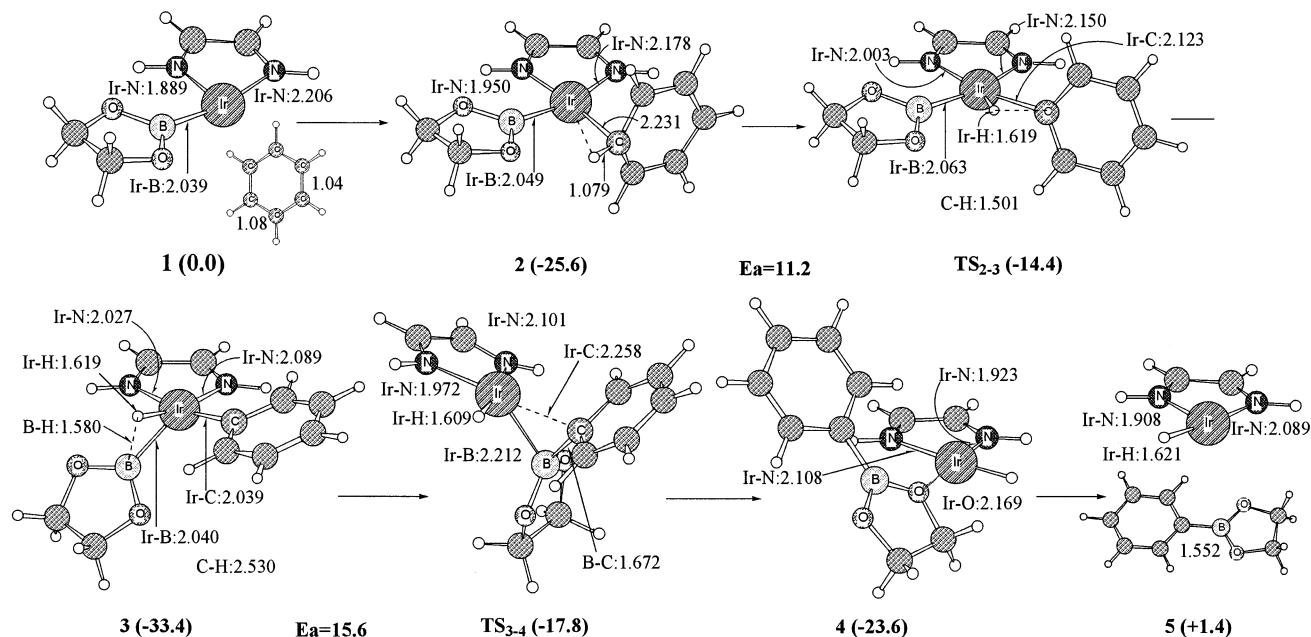
Figure 1. Geometry changes and energy changes in the reaction between Ir(Beg)(diim) and benzene (eg (ethyleneglycolato) = —OCH$_2$CH$_2$O—; diim = diimine, HN=CHCH=NH). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.
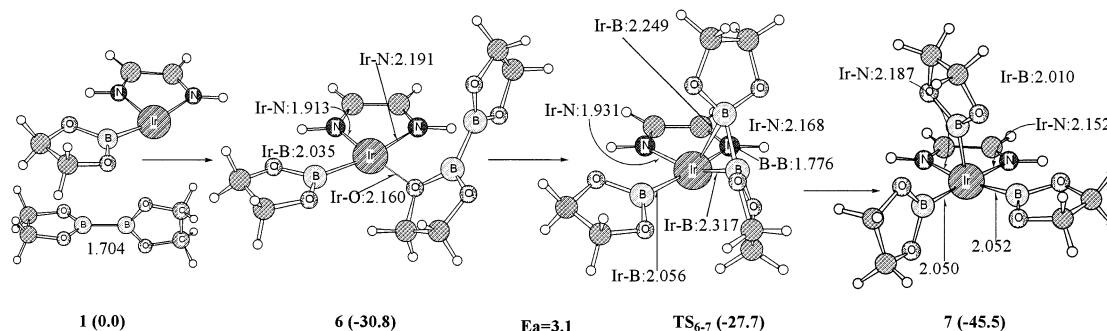
Figure 2. Geometry changes and energy changes in the reaction between Ir(Beg)(diim) and diboron, B$_2$(eg)$_2$ (eg (ethyleneglycolato) = —OCH$_2$CH$_2$O—; diim = diimine, HN=CHCH=NH). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

through the O atom like that of **4**. The binding energy (BE) is considerably large (30.8 kcal/mol). In transition state **TS$_{6-7}$**, the B—B bond somewhat lengthens to 1.776 Å, where the B—B bond is almost perpendicular to the N—Ir—N plane. This oxidative addition proceeds with a very small activation barrier of only 3.1 kcal/mol. The product, Ir(Beg)$_3$(diim) **7**, takes a typical square pyramidal structure, as expected from its d^6 electron configuration.

These energy changes clearly indicate that diboron coordinates with the Ir center of **1** with a very large stabilization energy and the oxidative addition of diboron to the Ir(I) center easily takes place with the small activation barrier. Though the borylation of benzene with **1** occurs with moderate activation barriers, the reaction between **1** and diboron more easily proceeds with a much smaller activation barrier than that between **1** and benzene. From these results, it should be concluded that **1** preferably reacts with diboron to afford the iridium(III) tris(boryl) complex **7** under the catalytic reaction conditions.

Formation of Ir(Beg)$_3$(diim) from IrCl(diim). Ir(Bpin)$_3$-(bpy) was experimentally isolated,[3] while the initial system involves [IrCl(COD)]$_2$ and bpy. Thus, it is necessary to clarify how Ir(Bpin)$_3$(bpy) is formed from [IrCl(diene)]$_2$ and diboron,

B$_2$(pin)$_2$, in the presence of bpy. If the formation of Ir(Bpin)$_3$-(bpy) needed a very large activation energy and/or if it was very endothermic, we must exclude Ir(Bpin)$_3$(bpy) from an active species and consider some other active species.

It is likely to consider that IrCl(bpy) is formed from [IrCl-(COD)]$_2$ and bpy, since bpy is a good chelating ligand. As shown in Figure 3, diboron coordinates with the Ir center of IrCl(diim) **8** to afford a precursor complex, IrCl(diim)[B$_2$(eg)$_2$] **9**, which resembles **6** well. The binding energy is 19.7 kcal/mol. The oxidative addition of diboron to the Ir center proceeds through transition state **TS$_{9-10}$** to afford IrCl(Beg)$_2$(diim) **10**. Complex **10** takes a distorted trigonal bipyramidal structure, whereas the Ir center takes a d^6 electron configuration. The distortion comes from the small B—Ir—B angle (67.6°), as shown in Figure 3. The similar small B—M—B angle has been experimentally reported in the rhodium(III) bis(boryl) complex, RhCl(Bcat)$_2$(PPh$_3$)$_2$ (cat = catecholato),[33] and platinum(II) bis-(boryl) complex, Pt(Bpin)$_2$(PR$_3$)$_2$.[34] Also, the B—Pt—B angle considerably smaller than 90° was theoretically reported in Pt-[B(OH)$_2$]$_2$(PH$_3$)$_2$.[35,36] This feature will be discussed elsewhere

(33) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367.
(34) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.: Scott, A. J.; Clegg, W.; Norman,N. C. *Organometallics* **1996**, *15*, 5137.
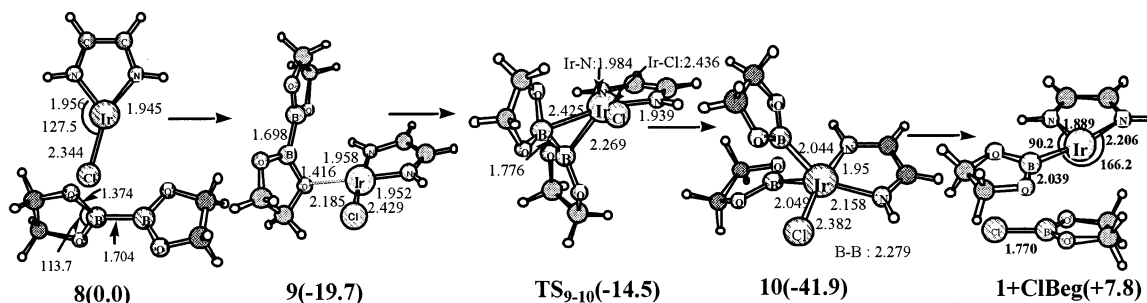
Figure 3. Geometry changes and energy changes in the reaction between IrCl(diim) and diboron, $B_2(eg)_2$ (eg (ethyleneglycolato) = $-OCH_2CH_2O-$; diim = diimine, HN=CHCH=NH). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.
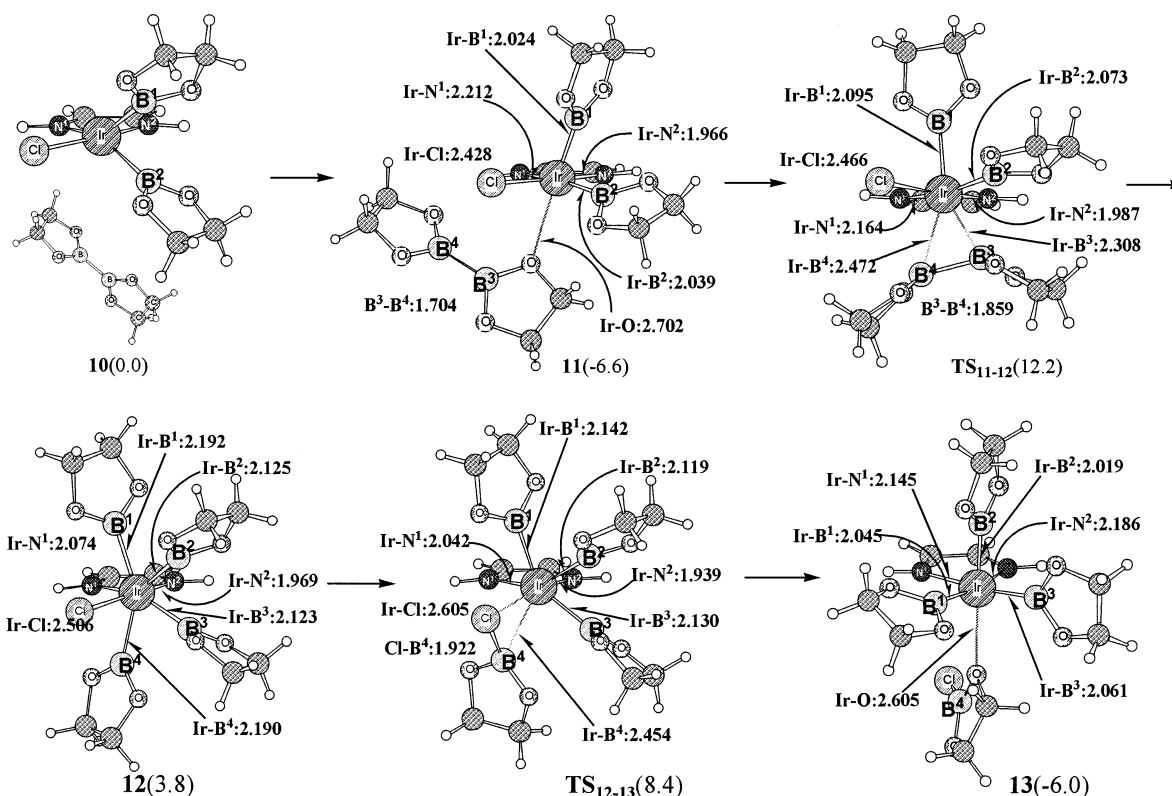
Figure 4. Geometry changes and energy changes in the reaction between IrCl(Beg)$_2$(diim) and diboron, $B_2(eg)_2$ (eg (ethyleneglycolato) = $-OCH_2CH_2O-$; diim = diimine, HN=CHCH=NH). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

in more detail,[37] since this feature would deeply relate to the stabilization of an unusual iridium(V) complex. The activation barrier and the reaction energy are calculated to be 5.2 kcal/mol and −41.9 kcal/mol, respectively, where the negative value of the reaction energy represents that the reaction is exothermic. Thus, it should be reasonably concluded that the oxidative addition of diboron to the Ir center easily takes place. If the reductive elimination of Cl-Beg occurred in the next stage, **1** would be formed. However, this reaction (eq 2) is calculated to be very endothermic (51.8 kcal/mol).
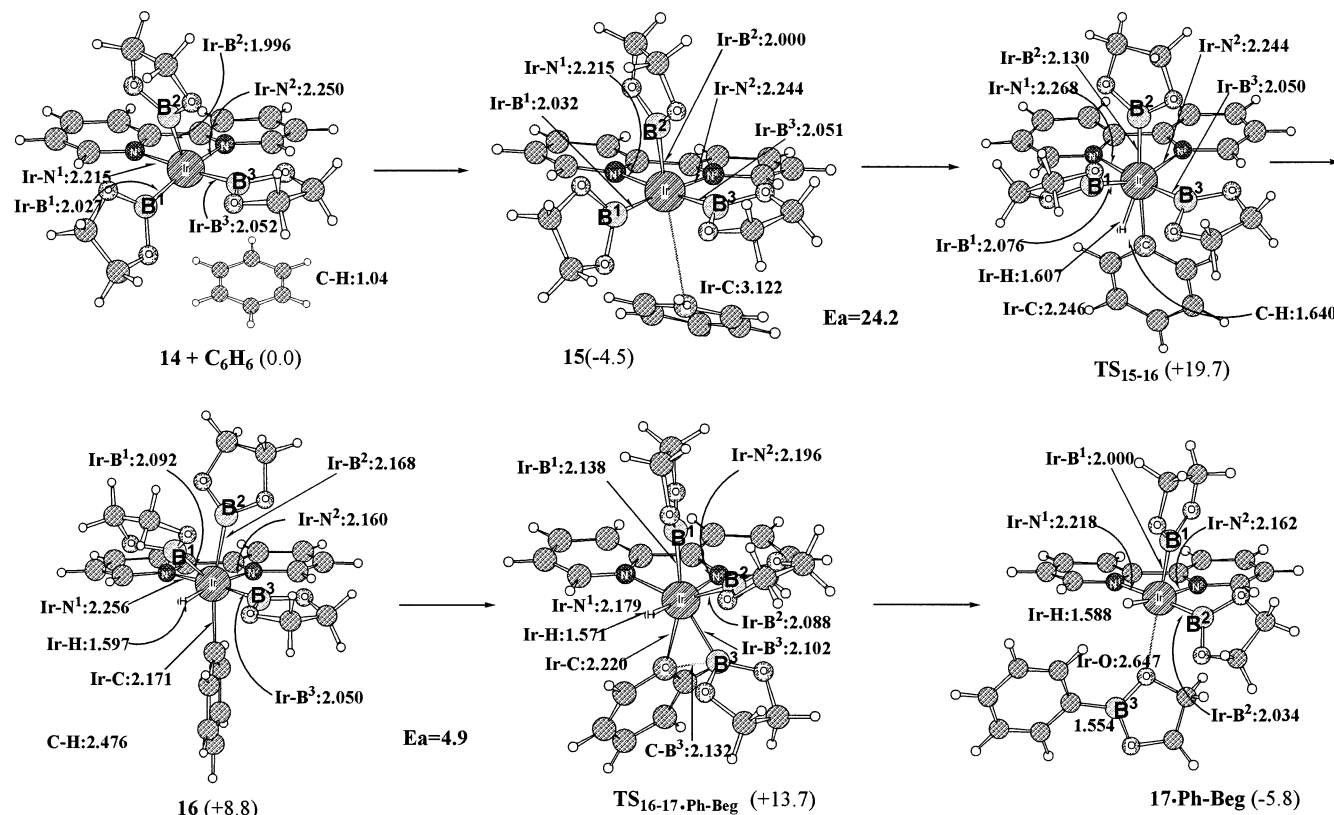
$$IrCl(Beg)_2(diim)\ \mathbf{10} \rightarrow Ir(Beg)(diim)\ \mathbf{1} + Cl\text{-}Beg$$
$$\Delta E = +51.8\ \text{kcal/mol} \quad (2)$$
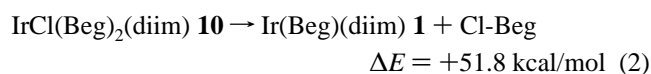
From these results, it should be concluded that the reductive elimination of Cl-Beg from **10** is very difficult.

(35) Sakaki, S.; Kikuno, T. *Inorg. Chem.* **1997**, *36*, 226.
(36) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics*, **1997**, *16*, 1355.
(37) Tamura, H.; Yamazaki, H.; Sato, H.; Sakaki, S. To be published.

We must consider the possibility that one more diboron molecule reacts with **10**, since diboron exists in excess under the catalytic reaction conditions. Actually, the oxidative addition of diboron to the Ir center takes place, as shown in Figure 4. The first step is coordination of diboron to the Ir center of **10** to afford IrCl(Beg)$_2$(diim)[$B_2(eg)_2$] **11** with a moderate stabilization energy of 6.6 kcal/mol. The B−B bond scission occurs through transition state **TS$_{11-12}$** with a moderate activation barrier (12.2 kcal/mol), to afford an iridium(V) complex, IrCl-(Beg)$_4$(diim) **12**. This iridium(V) complex is considerably interesting, as will be discussed elsewhere,[37] because it takes seven-coordinate structure with a d^4 electron configuration. The reductive elimination of Cl−Beg easily takes place through a transition state **TS$_{12-13}$**, to afford Ir(Beg)$_3$(diim)(Cl−Beg) in which Cl−Beg coordinates with the Ir center through the O atom. The activation barrier is calculated to be only 4.6 kcal/mol. These results lead to the clear conclusion that **7** is formed from **8** through oxidative additions of two molecules of diboron followed by the reductive elimination of Cl-Beg.
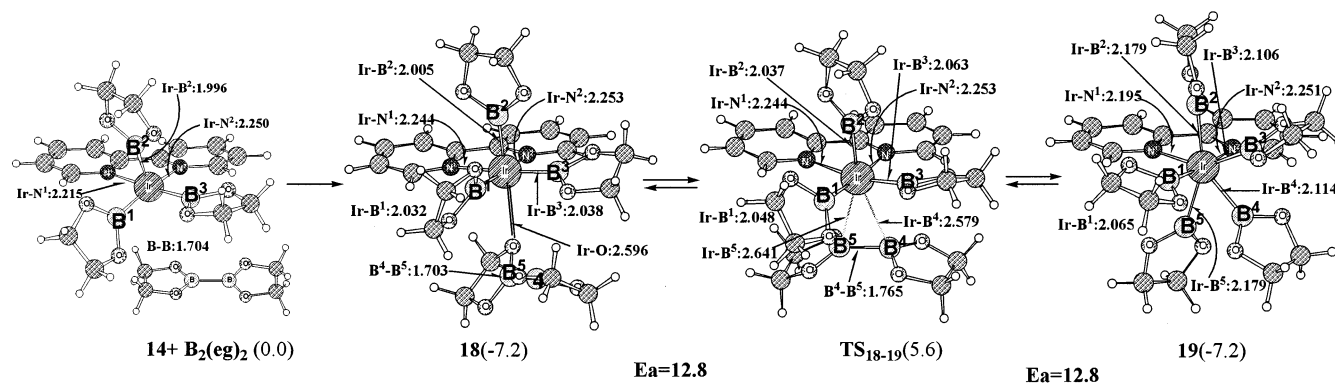
Figure 5. Geometry changes and energy changes in the reaction between Ir(Beg)$_3$(bpy) and benzene (eg (ethyleneglycolato) = −OCH$_2$CH$_2$O−; bpy = 2,2′-bipyridine). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

In conclusion, these results clearly show that Ir(Bpin)$_3$(bpy) is easily formed but Ir(Bpin)(bpy) cannot exist as a stable species under the catalytic reaction conditions. Even if Ir(Bpin)(bpy) was formed from IrCl(bpy), it easily converted to Ir(Bpin)$_3$-(bpy) through the oxidative addition of diboron to Ir(Bpin)-(bpy). Thus, we will investigate the reaction between Ir(Beg)$_3$-(bpy) and benzene in the next section, in which we will adopt 2,2′-bipyridine (bpy) instead of diim to perform a more reliable theoretical study.

Reactions of Ir(Beg)$_3$(bpy) with Benzene and Diboron. In this section, we will investigate the reactions of Ir(Beg)$_3$(bpy) **14** with benzene and diboron, because both benzene and diboron exist in excess under the catalytic reaction conditions. As shown in Figure 5, benzene approaches the Ir center of **14**, to afford Ir(Beg)$_3$(bpy)(C$_6$H$_6$) **15**, since **14** is a coordinatively unsaturated complex. In **15**, benzene takes a position so as to form a good overlap between the unoccupied d$_\sigma$ orbital of Ir and the π orbital of benzene. This coordination structure resembles well that of **2**. The bonding nature of benzene coordination will be discussed below. From **15**, the oxidative addition of benzene to the Ir center takes place through transition state **TS$_{15-16}$** to afford Ir-(Beg)$_3$(H)(Ph)(bpy) **16**. In this **TS$_{15-16}$** state, the C−H bond considerably lengthens to 1.640 Å. On the other hand, the Ir−H and Ir−Ph distances shorten to 1.607 Å and 2.246 Å, respectively. These Ir−H and Ir−Ph distances are almost the same as those of the product **16**, and the C−H distance is much longer than the usual C−H bond. These features indicate that the transition state **TS$_{15-16}$** is productlike. In **16**, five anionic ligands coordinate with the Ir center. Thus, **16** is understood in terms of a pentagonal bipyramidal seven-coordinate iridium(V) complex with a pseudo C$_5$ (H−Ir−N) axis. The iridium(V) complex,

Cp*Ir(H)$_3$(Bpin), was isolated, and its X-ray structure was reported.[10] If we consider that three occupied p orbitals of pentamethylcyclopentadienyl anion Cp*$^-$ interact with the Ir center, this complex is understood to take a seven-coordinate structure. However, it is not clear whether Cp*Ir(H)$_3$(Bpin) takes a pentagonal bipyramidal structure or not, since the positions of hydride ligands were not determined in Cp*Ir(H)$_3$(Bpin). The geometry and electronic structure of these iridium(V) complexes will be discussed elsewhere.[37] This oxidative addition needs the activation barrier of 24.2 kcal/mol. From **16**, the reductive elimination of phenylborane, Ph−Beg, takes place through transition state **TS$_{16-17·Ph−Beg}$** to afford Ir(H)(Beg)$_2$(Ph−Beg) **17·Ph−Beg**. In **TS$_{16-17·Ph−Beg}$**, the Ir−Beg and Ir−Ph distances somewhat lengthen to 2.102 Å and 2.220 Å, respectively, while the Ph−B distance is 2.132 Å. These geometrical features indicate that the Ir−Beg and Ir−Ph bonds are almost kept as those of **16** but the B−C bond has not been formed yet between boryl and phenyl groups in this transition state. In **17·Ph−Beg**, Ph−Beg coordinates with the Ir center through the O atom. The similar coordinate bond was observed in the oxidative addition of B$_2$(eg)$_2$ to the Ir center of Ir(Beg)(diim) and IrCl(diim). The reductive elimination of Ph−Beg occurs with a much small activation barrier of 4.9 kcal/mol. This is not surprising because the Ir center takes the very high +5 oxidation state.

The reaction of diboron with **14** should be investigated here, because diboron also exists in excess under the catalytic reaction conditions. As shown in Figure 6, diboron coordinates with the Ir center of **14**, to afford Ir(Beg)$_3$(bpy)[B$_2$(eg)$_2$] **18**. From **18**, the oxidative addition of the B−B σ-bond takes place through the transition state **TS$_{18-19}$** to afford Ir(Beg)$_5$(bpy) **19**. Again,

Figure 6. Geometry changes and energy changes in the reaction between Ir(Beg)₃(bpy) and diboron, B₂(eg)₂ (eg (ethyleneglycolato) = −OCH₂CH₂O−; bpy = 2,2′-bipyridine). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

the iridium(V) complex is formed with the moderate activation barrier of 12.8 kcal/mol, which is much smaller than that of the oxidative addition of benzene to **14**. Thus, the oxidative addition of diboron to the Ir center takes place more easily than that of benzene. However, the reductive elimination of diboron from **19** also easily takes place with the same activation barrier (12.8 kcal/mol). Moreover, **18** is at the same energy as that of **19**, and **15** is slightly less stable than **18** and **19** by only 2.7 kcal/mol. These results indicate that populations of **15**, **18**, and **19** are similar due to the thermal equilibrium. In other words, the oxidative addition of diboron to the Ir center more easily takes place than that of benzene, but the reverse reductive elimination also easily takes place with the same activation barrier of the oxidative addition. This equilibrium exists in the catalytic reaction but does not induce any interference to the whole catalytic cycle.

From these results, it should be reasonably concluded that Ph−Beg is easily formed through the oxidative addition of benzene to **14** followed by the reductive elimination of Ph−Beg. Our intension here is to show clearly that the unusual seven-coordinate Ir(V) complex **16** exists as a key intermediate. Though its experimental isolation is interesting, its detection and isolation are difficult because the reductive elimination of phenylborane easily takes place with a much smaller activation barrier than does the oxidative addition of benzene. However, we wish to propose a possibility that the iridium(V) complex **19** can be experimentally detected or isolated when benzene is not added in the solution and diboron is added in excess.

Reactions of Ir(H)(Beg)₂(bpy) 17 with Diboron and Benzene. We will investigate here two possibilities that **17** reacts with benzene and diboron. Diboron coordinates with the Ir center of **17** to afford an iridium(III) diboron complex, Ir(H)(Beg)₂-(bpy)[B₂(eg)₂] **20**, as shown in Figure 7. In **20**, the Ir−O distance is 2.529 Å, which is similar to those of the other iridium(III) diboron complexes. The coordination of diboron with the Ir center yields a stabilization energy of 9.4 kcal/mol. From **20**, the oxidative addition of diboron takes place through transition state **TS₂₀₋₂₁**, to yield an iridium(V) tetrakis(boryl) hydride complex, Ir(H)(Beg)₄(bpy) **21**, where the activation barrier is 8.0 kcal/mol. In **TS₂₀₋₂₁**, the B−B distance is 1.756 Å, which is longer than that of free diboron by only 0.05 Å. The Ir−B distances are 2.532 Å and 2.641 Å, being about 0.3 Å to 0.5 Å longer than those of the product. Thus, this transition state is reactant-like, in which the B−B bond is being broken and the Ir−B bonds are being formed. In **21**, the Ir center takes the +5

oxidation state in a formal sense. This complex is understood in terms of a pentagonal bipyramidal structure with a pseudo C_5 (B^2−Ir−N^1) axis. Interestingly, the Ir−Beg bonds (2.143 Å, 2.100 Å, and 2.200 Å) in the equatorial plane are somewhat longer than the axial Ir−Beg bond (2.054 Å).[37] The B−H reductive elimination takes place from **21** through **TS₂₁₋₁₄** to afford Ir(Beg)₃(bpy)(H−Beg) in which H−Beg coordinates with **14**. In this transition state, the Ir−H distance lengthens little but the H ligand is approaching the B atom of the equatorial boryl group. The Ir−Beg bond that is going to react with the H ligand slightly lengthens to 2.167 Å and the H−Ir−B angle decreases to 54.7° which is smaller than that (75.8°) of **21**. Consistent with this reactant like transition state, the activation barrier is very small (2.6 kcal/mol). Both activation barriers of the oxidative addition and the reductive elimination are much lower than that of the rate-determining step (**15→17**) of the reaction that leads to the formation of Ph−Beg. Thus, the iridium(III) tris(boryl) complex **14** is easily reproduced by the oxidative addition of diboron to **17** followed by the reductive elimination of borane when diboron exists in the reaction solution.

Benzene also reacts with **17** to afford Ir(H)₂(Beg)₂(Ph)(bpy) **22**, where two kinds of structures are possible in the product, as shown in Figure 8; in **22a**, one hydride is at a position trans to the N atom of bpy and the other hydride is at a position trans to the Ph ligand, and in **22b**, two hydride ligands are at positions trans to the N atom of bpy. This reaction is moderately endothermic by 2 to 8 kcal/mol. Though the endothermicity is not large, the reaction of **17** with diboron is much more exothermic than that with benzene, as discussed above. Moreover, the oxidative addition of benzene needs a larger activation barrier than that of diboron in general. Thus, we omitted further investigation of the oxidative addition of benzene to **17**. Of course, benzene would react with **17** when diboron and borane do not exist in the solution, as reported experimentally.[4]

Reaction of Ir(H)(Beg)₂(bpy) 17 with Borane, H−Beg. After diboron is consumed by the reaction, either benzene or borane (H−Beg) starts to react with Ir(H)(Beg)₂(bpy) **17**. As was described above, the reaction with benzene is endothermic. On the other hand, the coordination of borane with **17** leads to an iridium(III)−borane complex, Ir(H)(Beg)₂(bpy)(H−Beg) **23**, with a considerably large stabilization energy of 13.8 kcal/mol. In **23**, H−Beg is considerably distorted by the interaction with the Ir center; for instance, the B−H bond lengthens to 1.314 Å, the Ir−H distance is 1.838 Å, and the Ir−B distance is 2.215
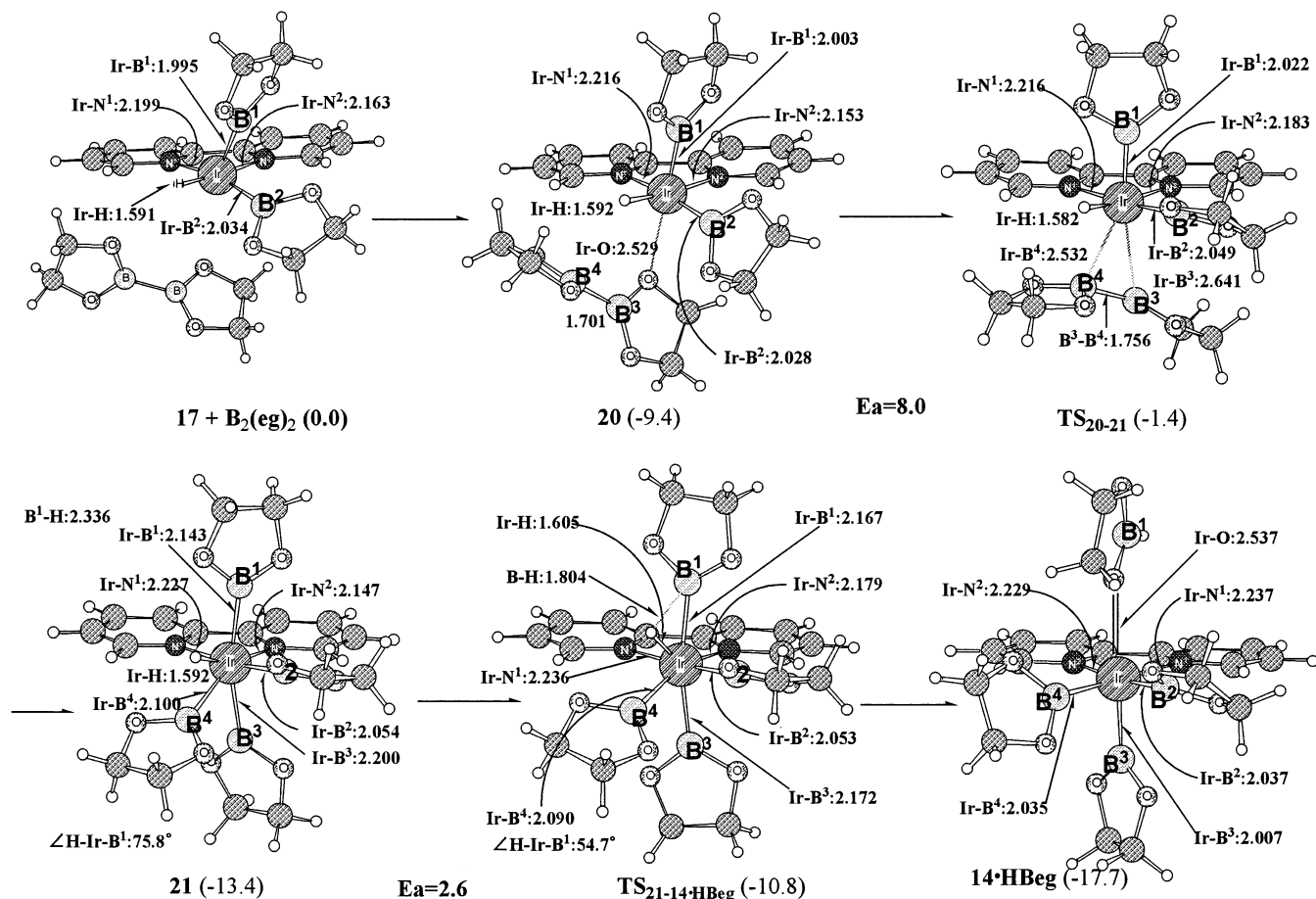
Figure 7. Geometry changes and energy changes in the reaction between IrH(Beg)$_2$(bpy) and diboron, B$_2$(eg)$_2$ (eg (ethyleneglycolato) = −OCH$_2$CH$_2$O−; bpy = 2,2′-bipyridine). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

Å. It is noted that the Ir−H^2 distance is much longer than those of such iridium(V) complexes as **16**, **19**, and **21**. Thus, there are two ways to understand **23**; in one way, **23** is understood in terms that the H−B bond of H−Beg coordinates with the Ir center through the charge-transfer interaction between the H−B bonding orbital and the empty d$_\sigma$ orbital of Ir. In the other way, **23** is understood in terms of the iridium(V) complex in which the hydride ligand forms an intramolecular charge-transfer interaction with the empty p orbital of the boryl ligand, as shown in Scheme 2. Though we do not have direct evidence to determine which understanding is correct at this moment, this complex is considered to be more or less close to the iridium-(III) complex rather than the iridium(V) complex, since **23** is formed without any barrier; in other words, the geometry optimization of **17** + H−Beg spontaneously leads to **23**. The much longer Ir−H^2 distance than the usual Ir−hydride bond provides also the other support of this understanding. The electron populations of **23** are consistent with this understanding, as will be discussed below. Similar coordination of borane with the Ti center was reported in Cp$_2$Ti(H−Bcat)$_2$,[38] where the B−H bond of H−Bcat interacts with the Ti center.

In the whole reaction, a dihydrogen molecule should be evolved, as shown in eq 1. The reductive elimination of the dihydrogen molecule can occur only when two H ligands take cis positions to each others. However, two H ligands take trans

positions to each other in **23**. Thus, **23** must isomerize to **24** in which two H ligands take positions cis to each other. The transition state of this isomerization **TS$_{23−24}$** is shown in Figure 9. In **TS$_{23−24}$**, the boryl and H ligands are going to move into the equatorial plane so that these H and boryl ligands are changing their positions to each other like Berry's pseudorotation. These geometry changes lead to **24**. In **24**, the H−Ir−H angle is very large (77.5°) and the H−H distance is 2.035 Å, which clearly shows that there is no bonding interaction between two H ligands. From **24**, the reductive elimination of the dihydrogen molecule proceeds through transition state **TS$_{24−25}$**, to afford a dihydrogen complex, Ir(Beg)$_3$(bpy)(H$_2$) **25**. In **25**, the H−H distance is 0.814 Å, and the Ir−H distances are 1.865 Å and 1.924 Å. These geometrical features are reasonable for the transition-metal dihydrogen complex. The activation barrier is 21.3 kcal/mol for the isomerization and 4.7 kcal/mol for the reductive elimination of the dihydrogen molecule, where the reaction energy is −5.2 kcal/mol. The dissociation of H$_2$ leads to regeneration of the active species, the iridium(III) tris(boryl) complex **14**. In the other possible reaction course, the H$_2$ molecule is substituted for benzene, to afford **15** directly.

Energy Changes along Whole Catalytic Cycle. Based on the above results, the catalytic cycle is schematically shown in Scheme 3, and the energy changes along the whole catalytic cycle are shown in Figure 10. Important points are summarized, as follows: The iridium(III) tris(boryl) complex, Ir(Beg)$_3$(bpy), is an active species. This species performs the C−H σ-bond

(38) Hartwig, J. F.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. *J. Am. Chem. Soc.*, **1996**, *118*, 10936.
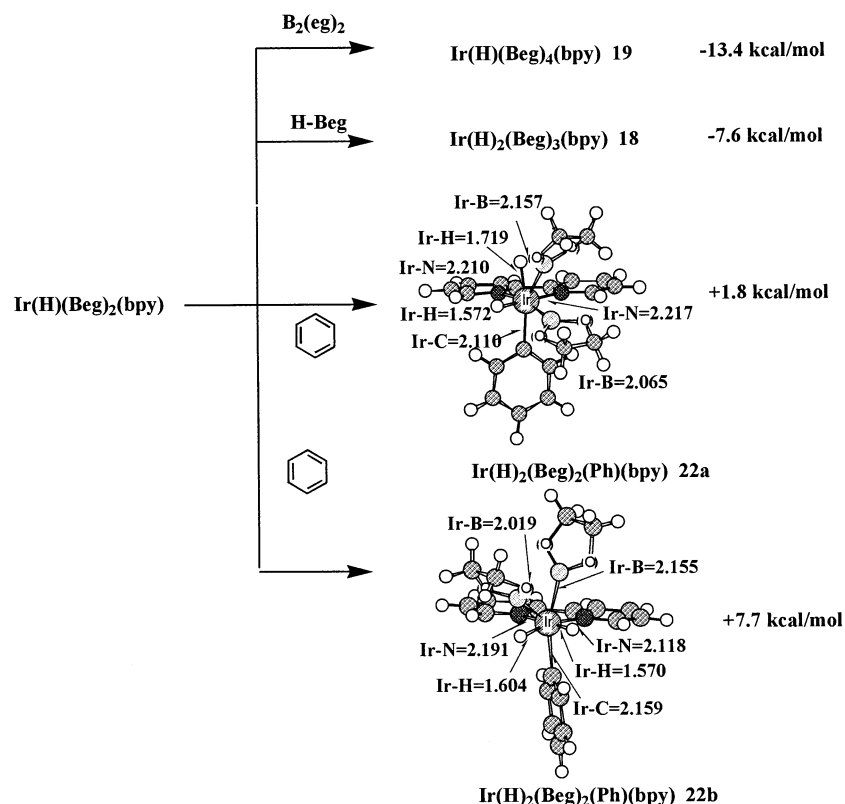
Figure 8. Energy of the reactions of Ir(H)(Beg)$_2$(bpy) with either benzene or diboron, B$_2$(eg)$_2$ (eg (ethyleneglycolato) = −OCH$_2$CH$_2$O−; bpy = 2,2′-bipyridine). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.
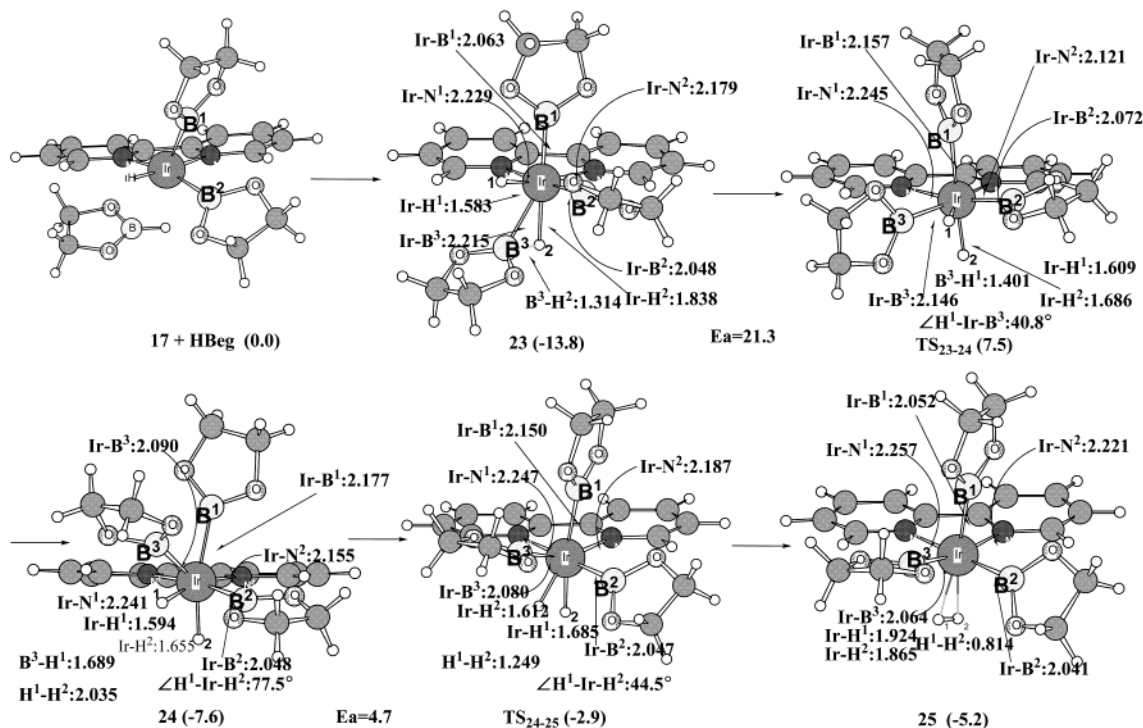
Figure 9. Geometry changes and energy changes in the reaction between IrH(Beg)$_2$(bpy) and borane, H−Beg (eg (ethyleneglycolato) = −OCH$_2$CH$_2$O−; bpy = 2,2′-bipyridine). In parentheses are the energy changes (kcal/mol) relative to the reactants. Bond lengths are in Å.

activation of benzene to afford the iridium(V) tris(boryl) hydride phenyl complex, Ir(Beg)$_3$(H)(Ph)(bpy). The reductive elimination of phenylborane takes place from this complex with concomitant formation of the iridium(III) bis(boryl) hydride complex, Ir(H)(Beg)$_2$(bpy). The activation barrier is 24.2 kcal/mol for the oxidative addition of benzene and 4.9 kcal/mol for the reductive elimination of phenylborane, as shown by the solid line in Figure 10. When diboron, B$_2$(eg)$_2$, exists in excess in the solution, the oxidative addition of diboron to Ir(H)(Beg)$_2$-(bpy) takes place with an activation barrier of 8.0 kcal/mol to

Scheme 3
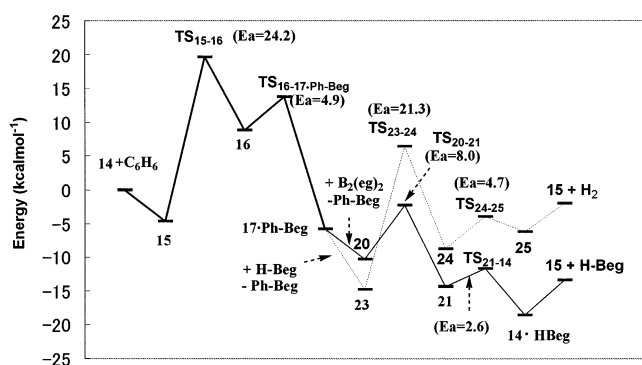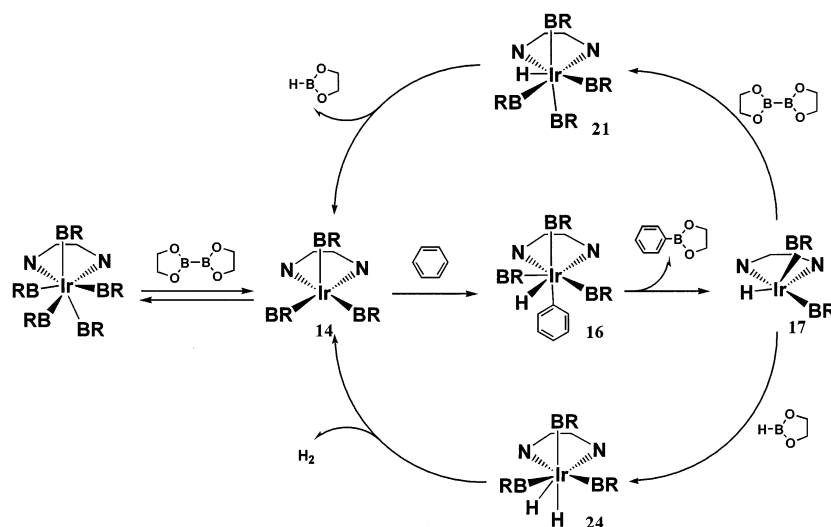
Figure 10. Energy changes along the catalytic cycles. Solid line represents the energy changes when diboron exists in excess in the solution, in other words, when Ir(H)(Beg)$_2$(bpy) **17** reacts with diboron. Dotted line represents the energy changes when diboron is consumed by the reaction, in other words, when Ir(H)(Beg)$_2$(bpy) **17** reacts with borane.

Table 1. Population Changes in the Reaction between Ir(Beg)$_3$(bpy) **14** and Benzene to Afford Ir(H)(Ph)(Beg)$_3$(bpy) **16**[a]

| | | Ir(Beg)$_3$(bpy)(C$_6$H$_6$) | | Ir(H)(Ph)(Beg)$_3$(bpy) |
	14 + C$_6$H$_6$	15	TS$_{15-16}$	16
Ir	0 (76.968)[b]	−0.005	−0.011	−0.131
bpy	0 (81.823)	−0.007	−0.075	−0.117
Beg^1	0 (37.101)	0.025	−0.064	-0.047
Beg^2	0 (36.993)	−0.006	0.101	0.065
Beg^3	0 (37.115)	0.006	−0.065	-0.096
Ph	0 (41.204)	0.035	0.154	0.240
H	0 (0.796)	−0.049	−0.040	0.086

[a] A positive value represents an increase in the population (vice versa). See Figure 5 for B^1, B^2, and B^3. [b] In parentheses are the electron populations of the reactants.

yield the iridium(V) tetraks(boryl) hydride complex, Ir(H)(Beg)$_4$-(bpy). The reductive elimination of borane, H−Beg, occurs with a very small activation barrier of 2.6 kcal/mol, to regenerate the active species, Ir(Beg)$_3$(bpy). The rate-determining step is the C−H σ-bond activation of benzene by the active species. After consumption of diboron, borane starts to react with the iridium(III) bis(boryl) hydride complex, Ir(H)(Beg)$_2$(bpy), to afford the iridium(V) tris(boryl) dihydride complex, Ir(H)$_2$-(Beg)$_3$(bpy), followed by the reductive elimination of a dihydrogen molecule, to regenerate the active species. As shown by the dotted line in Figure 10, this reaction needs a considerably larger activation barrier (21.3 kcal/mol) than the reaction between Ir(H)(Beg)$_2$(bpy) and diboron, of which the activation barrier is 8.0 kcal/mol. As a result, the regeneration of the active species becomes slower than that via the reaction between diboron and Ir(H)(Beg)$_2$(bpy). This result suggests that the reaction rate of phenylborane formation becomes slower after the consumption of diboron. More important is that the sum of **14** and H$_2$ is less stable in energy than **24** and **25**. If the dihydrogen molecule existed in the reaction solution, the back reaction took place. Thus, the dihydrogen molecule must evolve as gas from the solution to complete the catalytic cycle.

Electronic Process of Important Elementary Steps. In this section, we wish to discuss the electronic process of important elementary steps involved in the catalytic cycle. The first step
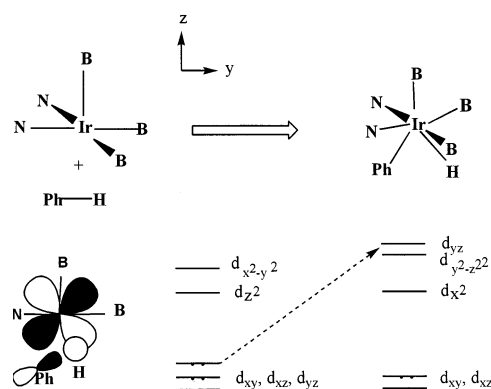
is the coordination of benzene which occurs upon going from **14** to **15**. Population changes are given in Table 1. In this step, the electron population of benzene slightly decreases by 0.014e. This decrease suggests that benzene coordinates with the Ir center by charge transfer from benzene to the Ir center. It is also noted that the population of the active H atom considerably decreases but the population of the phenyl moiety somewhat increases, where the active H atom represents the H atom that changes into the hydride ligand in the oxidative addition of benzene. Though the geometry of **15** suggests that the π orbital of benzene interacts with the empty d orbital of the Ir center, these population changes indicate that not only the charge-transfer interaction but also the polarization of the C−H bond occurs in **15**. Actually, the Ir atomic population changes little, which means that the polarization occurs to a greater extent than the charge transfer. The other change to be noted is that the population of Beg^1 considerably increases. The direct charge-transfer from benzene to Beg^1 is not responsible to the population increase, because the geometry of **15** is unfavorable for the direct charge-transfer.[39] The reason for this population change is ambiguous and detailed examination should be carried out in the future.

(39) The charge-transfer from benzene to Beg^1 is considered not to participate in this population change, because the Beg^1 plane is almost perpendicular to the benzene plane and the empty p orbital of Beg^1 cannot interact with the π orbital of benzene. One plausible reason of this population increase of Beg^1 is that Beg^1 slightly shifts from a position trans to the N atom of bpy in **14** but it is at a position just trans to the N atom in **15**. As a result, the electron donation of Beg^1 to the Ir center is suppressed by the trans-influence of bpy in **15**, which leads to the increase in the electron population of Beg^1 in **15**.

The second important process is the oxidative addition of benzene to the Ir(III) center of **15**. In the transition state **TS$_{15-16}$** of this process, electron populations of the phenyl group and the H atom increase by 0.119e and 0.009e, respectively, as expected. Consistent with these population changes, the Ir atomic population slightly decreases by 0.006e and the electron populations of bpy, Beg^1, and Beg^3 decrease by 0.068e, 0.039e, and 0.071e, respectively, to compensate the decrease in the Ir atomic population. Though the electron population of Beg^2 increases, this is not surprising because the donating Ph group is formed at a position trans to Beg^2 to suppress the charge-transfer from Beg^2 to the Ir center. The populations of the phenyl group and the H atom further increase by 0.086e and 0.125e, respectively, upon going to the product **16** from **TS$_{15-16}$**. Consistent with these population changes, the Ir atomic population decreases by 0.125e. These population changes are a common feature observed in the oxidative addition reaction. At the same time, the electron population of bpy considerably decreases. These features indicate that the charge transfer from the Ir center to benzene considerably occurs in the oxidative addition, as expected, and the decrease in Ir atomic population is compensated by the charge-transfer from bpy, Beg^1, and Beg^3 to the Ir center. Thus, these ligands play a role to accelerate the oxidative addition of benzene to the Ir center by supplying electrons to the Ir center. Though the orbital participation in the oxidative addition has been well understood in d^{10} and d^8 metal complexes,[28−32,35,40,41] we mentioned which orbital plays an important role in the oxidative addition to the Ir(III) complex, since the orbital participation has been scarcely discussed in the d^6 metal complex. Since **15** has an unoccupied coordination site, benzene approaches the Ir center from the unoccupied coordination site. Two doubly occupied d$_\pi$ orbitals expand toward benzene and one of them interacts with C−H σ^* orbital of benzene, as shown in Scheme 4. This orbital becomes unoccupied and the Ir center takes d^4 electron configuration in a formal sense after oxidative addition. In the product **16**, certainly two doubly occupied d orbitals and three unoccupied d orbitals are found, as shown in Scheme 4 and Supporting information Figure S2.

The next step is the reductive elimination of Ph−Beg, which proceeds from **16** to **17**. In this step, the electron population of the phenyl group decreases and the population of the Beg^3 group that is getting to be bound with the phenyl group also considerably decreases, as shown in Table 2. Consistent with these population changes, the Ir atomic population considerably increases. These are typical population changes observed in the reductive elimination. Also, it is noted that the electron population of bpy increases to compensate the charge transfer from Ph−Beg^3 to the Ir canter. It should be remembered that the population of bpy decreases in the oxidative addition. These population changes of bpy in the oxidative addition and the reductive elimination indicate that bpy facilitates the oxidative addition and the reductive elimination by playing a role of electron buffer.

(40) For instance, (a) Dedieu, A. *Chem. Rev.* **2000**, *100*, 543, and references therein. (b) Sakaki, S. *Bull. Korean Chem. Soc.* **2003**, *24*, 829, and references there.
(41) For instance, (a) Sargent, A. L.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 317. (b) Sargent, A. L.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 517. (c) Sakaki, S.; Ujino, Y.; Sugimoto, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3047.

Scheme 4

Table 2. Population Changes in the Reductive Elimination of Phenylborane, Ph−Beg, from Ir(H)(Ph)(Beg)$_3$(bpy) **16**^{a}

	Ir(H)(Ph)(Beg)$_3$(bpy)		Ir(H)(Beg)$_2$(bpy)(Ph−Beg^3)
	16	TS$_{16-17}$	**17·Ph—Beg**
Ir	0 (76.837)	0.044	0.065
Bpy	0 (81.707)	0.0	0.15
Beg^1	0 (37.054)	−0.007	−0.019
Beg^2	0 (37.058)	−0.008	0.096
Beg^3	0 (37.020)	−0.027	−0.319
Ph	0 (41.443)	−0.095	−0.185
H	0 (0.882)	0.092	0.209

^{a} A positive value represents an increase in the population (vice versa). See Figure 5 for B^1, B^2, and B^3, where Beg^3 undergoes the coupling with Ph to afford Ph−Beg. ^{b} In parentheses are the electron populations of the reactant.

Table 3. Population Changes by the Oxidative Addition of Diboron B$_2$(eg)$_2$ to the Iridium(III) Complex, IrH(Beg)$_2$(bpy) **17**^{a}

		IrH(Beg)$_2$(bpy)[B$_2$(eg)$_2$]		IrH(Beg)$_4$(bpy)
	17 + B$_2$(eg)$_2$	**20**	TS$_{20-21}$	**21**
Ir	0 (76.943)^b	−0.052	0.082	0.045
bpy	0 (81.846)	0.012	−0.048	−0.095
Beg^1	0 (37.021)	0.030	−0.036	0.040
Beg^2	0 (37.097)	0.054	0.003	0.043
Beg^3	0 (37.000)	−0.046	0.005	0.095
Beg^4	0 (37.000)	0.004	0.851	0.090
H	0 (1.093)	−0.002	-0.090	−0.218

^{a} A positive value represents an increase in the population (vice versa). See Figure 7 for B^1, B^2, B^3, and B,^{4} where B^{3}eg−B^{4}eg is going to react with the Ir center. ^{b} In parentheses are the electron populations of the reactant.

The oxidative addition of diboron is involved as an important elementary step of this catalytic cycle. As shown in Figures 6 and 7, the coordination of diboron to the Ir center occurs first. In this coordination, the electron population of the boryl group decreases by 0.046e, as shown in Table 3. This population decrease corresponds to the fact that the coordination of diboron to the Ir center occurs through the charge transfer from the O lone pair of Beg^3 to the Ir center. Going to **21** from **20** through **TS$_{20-21}$**, the electron populations of the boryl groups (Beg^3 and Beg^4) increase by 0.095e and 0.090e. At the same time, the electron population of bpy decreases by 0.095e like that in the oxidative addition of benzene, which indicates the important role of bpy in the oxidative addition too. The similar population changes are observed in the oxidative addition of diboron to **18**, except for the huge decrease in H atomic population in **21**. This huge decrease is interpreted in terms of two factors, as follows: The hydride ligand donates electron density to the Ir center to compensate the decrease in Ir atomic population since

Table 4. Population Changes by the Reductive Elimination of Borane, H–Beg, from IrH(Beg)$_4$(bpy) **21**[a]

	IrH(Beg)$_4$(bpy) 21	TS$_{21-14}$	Ir(Beg)$_3$(bpy)(H–Beg) 14·(H—Beg^1)
Ir	0.0 (76.989)[b]	0.042	−0.050
bpy	0.0 (81.751)	0.009	0.073
Beg^1	0.0 (37.061)	0.021	−0.213
Beg^2	0.0 (37.140)	−0.089	−0.016
Beg^3	0.0 (37.095)	0.033	−0.064
Beg^4	0.0 (37.090)	−0.037	0.045
H	0.0 (0.875)	0.021	0.224

[a] A positive value represents an increase in the population (vice versa). See Figure 7 for B^1, B^2, B^3, and B,^{4} where Beg^1 is going to react with the H ligand. [b] In parentheses are the electron populations of the reactant.

Table 5. Population Changes by the Addition of Borane, H–Beg, to the Iridium(III) Complex, Ir(H)(Beg)$_2$(bpy) **17**, and the Isomerization of **23**[a]

	Ir(H)(Beg)$_2$(bpy) 17	Ir(H)(Beg)$_2$(bpy)(H–Beg) 23	TS$_{23—24}$	Ir(H)$_2$(Beg)$_3$(bpy) 24
Ir	0 (76.943)[b]	0.058	−0.053	0014
bpy	0 (81.846)	−0.077	−0.061	−0.102
Beg^1	0 (37.021)	0.059	0.190	0.090
Beg^2	0 (37.097)	−0.012	−0.023	−0.038
Beg^3	0 (36.905)	0.159	0.048	0.187
H^1	0 (1.093)	−0.136	−0.225	−0.208
H^2	0 (1.095)	−0.050	0.125	0.058

[a] A positive value represents an increase in the population (vice versa). See Figure 8 for Beg^1, Beg^2, and Beg^3, where H^2–Beg^3 undergoes the addition to the Ir center. [b] In parentheses are electron populations in the reactant.

the Ir atomic population significantly decreases in the oxidative addition. At the same time, it forms charge-transfer interaction with one boryl group (Beg^4), as shown in Scheme 2, because the boryl group has an empty p orbital on the B atom; actually, the B–H distance is 1.702 Å in **21**. These two factors lead to the huge decrease in the electron population of the hydride.

Population changes in the reductive elimination of borane, H–Beg, from **21** are shown in Table 4. In this reaction, the H atomic population increases surprisingly, while the electron population of the boryl group (Beg^1) considerably decreases, as expected. Two plausible reasons are responsible for the increase in the H atomic population; one is that the H atomic population is too small in the reactant **21**, as discussed above. The other is that the H atom is bound with the highly electropositive B atom in the product H–Beg. In this step, the electron population of bpy somewhat increases too, like that observed in the reductive elimination of phenylborane. The Ir atomic population increases at **TS$_{21-14·H–Beg}$**, as expected, but it decreases in the product **14·H–Beg**, against our expectation. One plausible reason for the decrease is that the Ir center deviates some from the +5 oxidation state in **21** because five strongly donating ligands (one hydride and four boryl ligands) coordinate with the Ir center in **21**. Further detailed analysis is necessary regarding these changes of electron population. In this step, the electron population of bpy considerably increases, which represents that bpy facilitates this reductive elimination.

After consumption of diboron, IrH(Beg)$_2$(bpy) **17** reacts with borane to afford IrH(Beg)$_2$(bpy)(H^2–Beg^3) **23** without any barrier. As shown in Table 5, the electron population of Beg^3 considerably increases, while the H^2 atomic population of H^2–Beg^3 does not increase but decreases considerably. The population change of H^2 is reverse to that expected in the oxidative addition. Also, the direction of the Beg^3 moiety somewhat shifts

Table 6. Population Changes by the Reductive Elimination of the Dihydrogen Molecule from Ir(H)$_2$(Beg)$_3$(bpy) **24**[a]

	Ir(H)$_2$(Beg)$_3$(bpy) 24	TS$_{24-25}$	Ir (Beg)$_3$(bpy)(H$_2$) 25
Ir	0 (76.956)[b]	0.081	0.114
bpy	0 (81.744)	0.027	0.044
Beg^1	0 (37.111)	0.035	−0.055
Beg^2	0 (37.059)	0.011	0.037
Beg^3	0 (37.092)	−0.021	0.006
H^1	0 (0.885)	−0.018	0.084
H^2	0 (1.153)	−0.116	−0.231

[a] A positive value represents an increase in the population (vice versa). See Figure 9 for Beg^1, Beg^2, Beg^3, H^1, and H^2, where Beg^3 and H^2 are formed from H–Beg through the oxidative addition. [b] In parentheses are the electron populations in the reactant.

from the Ir center to the H^2 atom. From these results, it can be reasonably concluded that the coordination of H^2–Beg^3 to the Ir center occurs in **23** instead of the oxidative addition, and the polarization of H–Beg is induced by the coordination. This conclusion is consistent with the fact that **23** is formed from **17** + H–Beg without any barrier. The isomerization from **23** to **24** takes place through the transition state **TS$_{23-24}$**, which involves changes in positions of H^2 and Beg^3. The product **24** is understood in terms of the iridium(V) complex, because any H atom does not interact with each other and with any boryl group. Actually, the electron populations of the H^2 and Beg^3 groups considerably increase and the electron populations of the other H and Beg ligands decrease because they donate electrons to the electron-deficient Ir(V) center. In other words, the isomerization involves not only the position changes of H^2 and Beg^3 but also the oxidative addition of H^2–Beg^3 to the Ir center. The electron population of bpy considerably decreases upon going from **23** to **24**, which represents that bpy assists the oxidative addition of H–Beg by supplying electrons to the Ir center. The Ir atomic population decreases at **TS$_{23-24}$** but somewhat recovers in **24**. Though we cannot clearly explain that the Ir atomic population increases in **24**, one plausible explanation is found in Figure 9, as follows. The Ir center is likely considered to take a typical +5 oxidation state in **TS$_{23-24}$** since **TS$_{23-24}$** takes a pentagonal bipyramidal structure. If so, the Ir atomic population does not need to change significantly upon going from **TS$_{23-24}$** to **24**.

The reductive elimination of the dihydrogen molecule occurs from **24** to afford **25**. In this reaction, the H^2 atomic population decreases, as expected (see Table 6), while the H^1 atomic population slightly increases, which is against our expectation. This is because the H^1 atomic population is very small in **24** and the H^1 atom does not need to donate electrons to the Ir center upon the reductive elimination. The reason for the small H^1 atomic population in **24** is easily understood by inspection of the geometry of **24**. In **24**, the H^1 atom interacts with the empty p orbital of the Beg^3 group, as shown in Scheme 2, which is reflected in the rather short B^3–H^1 distance (1.689 Å). As a result, the H^1 atomic population is very small and it does not need to decrease in the reductive elimination. The Ir atomic population increases as expected, and the electron population of bpy increases too, to compensate for the electron accumulation on the Ir center. Again, bpy plays a role of electron buffer here and facilitates this reductive elimination.

Why Does the Catalytic Cycle Involve the Iridium(V) Complex? At the end of this paper, we wish to discuss the

reason that this interesting catalytic cycle involves the iridium-(V) complexes with the very high +5 oxidation state. One of the reasons is that diboron has a greater reactivity for the oxidative addition. As a result, the oxidative addition of diboron to the iridium(I) complex takes place very easily to afford the iridium(III) complex. Thus, the iridium(I) complex cannot exist as a stable species under the catalytic reaction conditions; in other words, an Ir^I/Ir^{III} catalytic cycle does not work well. The next reason is that if the iridium(I) complex is an active species, the reductive elimination of dihydrogen molecule must occur from the iridium(III) dihydride complex. However, this reductive elimination is very endothermic; The present calculation shows that the endothermicity of eq 3 is 43.6 kcal/mol.

$$Ir(Beg)(H)_2(diim) \rightarrow Ir(Beg)(diim) + H_2 \qquad (3)$$

This means that the iridium(I) complex is a strong Lewis base and favorable for the oxidative addition of H_2. In other words, the iridium(III) dihydride boryl complex is not favorable for the reductive elimination of the dihydrogen molecule. Since the dihydrogen molecule must be evolved during the reaction, the iridium center must take the +5 oxidation state to facilitate the reductive elimination of dihydrogen molecule. Finally, we must discuss the reason that the iridium(III) complex can perform the C−H σ-bond activation of benzene, since this reaction does not easily occur in general. The C−H σ-bond activation of benzene by a Pt(0) complex, Pt(PH$_3$)$_2$, was calculated to occur with an activation barrier of 24 kcal/mol.[28] The oxidative addition of benzene to the Ir(III) center can take place with a similar activation barrier. The plausible reason is that the boryl group is strongly electron releasing and the bpy ligand assists this oxidative addition by supplying electrons to the Ir center. Since the Ir(V) center needs electron-donating ligands, not bis-(catecolato)diboron but bis(pinacolato)diboron should be used in this catalytic reaction. Also, the electron-releasing substituent should be introduced to bpy; one such candidate is the OMe group.

Conclusions

Direct borylation of benzene catalyzed by the iridium complex was theoretically investigated with the DFT method. Important results are summarized, as follows: (1) The iridium(III) tris-(boryl) complex, Ir(Beg)$_3$(bpy), is an active species. (2) The C−H σ-bond activation of benzene is carried out by the oxidative addition of benzene to this iridium(III) complex to afford the iridium(V) complex, Ir(Beg)$_3$(H)(Ph)(bpy), as a key intermediate. (3) The reductive elimination of phenylborane takes place from this iridium(V) complex with concomitant formation of an iridium(III) bis(boryl) hydride complex, Ir-(Beg)$_2$(H)(bpy). (4) Diboron more easily reacts with Ir(Beg)$_2$-(H)(bpy) than does benzene to regenerate Ir(Beg)$_3$(bpy) with concomitant formation of borane, H−Beg, when diboron exists in excess in the reaction solution. (5) After consumption of diboron, Ir(Beg)$_2$(H)(bpy) starts to react with borane to regenerate Ir(Beg)$_3$(bpy) with concomitant formation of H$_2$. From these results, a reasonable catalytic cycle is presented, as shown in Scheme 3.

It is of considerable importance to clarify the reasons that not the iridium(I) boryl complex but the iridium(III) tris(boryl)

complex is an active species and the iridium(V) complex is involved as a key intermediate in the catalytic cycle. From the above results, clear conclusions are extracted, as follows: If the iridium(I) boryl complex was formed in the reaction solution, it easily underwent the oxidative addition of diboron to afford the iridium(III) tris(boryl) complex. This means that the iridium-(I) boryl complex cannot exist as a stable species under the catalytic reaction conditions. The other important point is that the reductive elimination of the dihydrogen molecule from the iridium(III) complex is considerably endothermic. On the other hand, the reductive elimination of the dihydrogen molecule easily takes place from the iridium(V) dihydride complex, because of the very high oxidation state of the iridium(V) complex. Since the dihydrogen molecule should be evolved in the catalytic cycle of this direct borylation of benzene, the catalytic cycle involves the intermediate with a high oxidation state so as to facilitate the reductive elimination of dihydrogen molecule.

There are several factors of this successful catalytic reactions; one is the use of bis(pinacolato)diboron and the other is the use of bpy. The pinacolato-boryl group is strongly electron releasing, which stabilizes the iridium(V) complex. The bpy ligand also stabilizes the high oxidation state by donating electrons to the metal center. The other reason is its planar structure which is favorable for the formation of the congested seven-coordinate Ir(V) complex.

Extension of this catalytic reaction would be possible. One key point is the stability of the iridium(V) complex. Since the iridium(V) complex takes a seven-coordinate structure, the less bulky substrate should be adopted. Benzene and aromatic compounds are favorable from this point of view, because they are planar and do not considerably induce steric repulsion. The similar substrate is a heteroaromatic compound. Certainly, the borylation of a heteroaromatic compound was successfully carried out with the same catalytic system.[6] The similar rhodium complex catalyzes this reaction less efficiently.[4] We wish to propose that introduction of electron-releasing substituents onto benzene and bpy would improve the reactivity of the rhodium system. In the [IrCl(COD)]$_2$/phosphine system,[2,3] the improvement would be achieved by usage of a less bulky donating phosphine such as PMe$_3$ and the highly reactive bis(pinacolato)-diboron.

Supporting Information Available: Figure of transition state structures with imaginary frequency and the important movements of each nuclei in the imaginary frequency (one page). Cartesian coordinates of important species including transition states (29 pages, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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