Activation of B-H Bonds in Ir(I) Complexes Supported by Phosphine with Carba-closo-dodecaborate and o-Carborane Ligand Substituents: A DFT Investigation

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ABSTRACT: The structures, stability and activation of B-H bonds of the twelve kinds of Ir(I) complexes supported by phosphine with o-carborane and carba-closo-dodecaborate ligand substituents, $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{R}=\text{Me}$, $i\text{Pr}$ and $\text{CH}(\text{CF}_3)_2$) and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{X(CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{X(C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{X}=\text{CH}_2$, NH and O) have been investigated using density functional theory (DFT) BP86 functional. Calculated results indicated that the B-H bonds in $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}(\text{CF}_3)_2)_2(\text{CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{R}=i\text{Pr}$ and $\text{CH}(\text{CF}_3)_2$), as well as $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{R(CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{R(C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{R}=\text{CH}_2$, NH and O) are both thermodynamically and dynamically favorable to be activated, in which the oxidation addition of B-H bond in $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P}(i\text{Pr})_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ is consistent with the experimental results. In contrast, the B-H bonds in $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(R)}_2(\text{CB}_{11}\text{H}_{11}^-))$ ($\text{R}=\text{Me}$ and $i\text{Pr}$) and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ cannot be activated, in

which $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P}(i\text{Pr})_2(\text{CB}_{11}\text{H}_{11}^-))$ is consistent with the experimental result. The activation of B-H bonds in carba-closo-dodecaborate phosphine and o-carborane phosphine of Ir(I) complexes depend up the distance between B-H bond and Ir(I). Moreover, two kinds of approaches to obtain B- σ -irridium (III) complexes were given by the activation of B-H bonds in Ir(I) complexes.

Introduction

Since the discovery of o-carborane in 1963 [1-8], the carboranyl- and carbollide-based transition metal complexes have been paid more attention due to their high stability [9-18]. Moreover, icosahedral carboranes are interesting alternatives to the classical alkyl and aryl ligand substituents because of their shape and 3-dimension aromaticity [19-33], such as o-carborane phosphine [29], o-bis(dimethylsilyl) carborane [30], phenyl(2-p-carboranyl)-iodonium [31], o-carboranyl phenols [32], $i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$ [33], 9,12-Bis-(4-acetylphenyl)-1,2-dicarbododecaborane [17] and so on. In addition, the cyclometalated iridium (III) complexes have been used as efficient phosphorescent emitters in organic light-emitting diodes (OLEDs) and solid-state lighting because they have excellent photophysical properties and stability [34-38]. Plenty of C- σ -carboranyl iridium complexes have been prepared by the reaction of iridium complexes and C-lithiocarboranes [39-43]. However, the B- σ -carboranyl iridium complexes are scarcely reported. Recently, interesting experimental results were found by Lavallo group, in which the B-H bond of $\text{ClIr}(\eta^2\text{-C}_8\text{H}_{12})(\text{PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$

complexes can be activated to give Ir(III) complex, while the oxidative addition of B-H bond in $\text{ClIr}(\eta^2\text{-C}_8\text{H}_{12})(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ cannot occur [44]. In order to understand the property of B-H bonds in $\text{ClIr}(\eta^2\text{-C}_8\text{H}_{12})(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ and $\text{ClIr}(\eta^2\text{-C}_8\text{H}_{12})(\text{PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ complexes, we have adopted two kind of methods to construct twelve Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents. One type is to increase the steric hindrance of the groups on phosphine, which results in the decrease of the bond angle of Ir-P-C. Another is to insert groups (CH_2 , NH and O) between P atom and C atom in carba-closo-dodecaborate and o-carborane. The structures, stability and the isomerization of the Ir(I) complexes have theoretically been investigated.

Computational Details

Twelve kinds of Ir(I) complexes of $\eta^2\text{-C}_8\text{H}_{12}\text{IrCl}(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{IrCl}(\text{PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{R}=\text{Me}$, *i*Pr and $\text{CH}(\text{CF}_3)_2$), as well as $(\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{CH}_3)_2\text{X}(\text{CB}_{11}\text{H}_{11}^-)))$ and $(\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{CH}_3)_2\text{X}(\text{C}_2\text{B}_{10}\text{H}_{11})))$ ($\text{X}=\text{CH}_2$, NH and O) and their corresponding Ir(III) complexes of $\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl}\eta^2\text{-(PR}_2(\text{CB}_{11}\text{H}_{10}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl}\eta^2\text{-(PR}_2(\text{C}_2\text{B}_{10}\text{H}_{10}))$ ($\text{R}=\text{Me}$, *i*Pr and $\text{CH}(\text{CF}_3)_2$), as well as $\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl}\eta^2\text{-(P}(\text{CH}_3)_2\text{X}(\text{CB}_{11}\text{H}_{10}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl}\eta^2\text{-(P}(\text{CH}_3)_2\text{X}(\text{C}_2\text{B}_{10}\text{H}_{10}))$ ($\text{X}=\text{CH}_2$, NH and O) obtained from the oxidative addition of B-H bond were considered. The possible isomers of these complexes were optimized using DFT BP86 functional, in combination with SDD basis set for Ir and 6-31G** basis sets for other atoms. The dispersion corrections of

the complexes were computed using DFT-D3 with BJ damping. As for the Ir(I) complexes whose energies were higher than that of the corresponding Ir(III) complexes, we have investigated the isomerization of Ir(I) complexes to Ir(III) ones. Vibrational frequencies were calculated to verify all stationary points to be the transition states or minima at the same level of theory. Intrinsic reaction coordinate (IRC) were calculated to confirm the calculated transition structures linking relevant reactants (Ir(I) complexes) and products (Ir(III) complexes). All calculations were performed with Gaussian09 program [45].

Results and Discussion

Three kinds of complexes $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ ($\text{R}=\text{Me}$, $i\text{Pr}$ and $\text{CH}(\text{CF}_3)_2$) were denoted as **A1**, **B1** and **C1**, respectively. $\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl}(\text{PR}_2(\text{CB}_{11}\text{H}_{10}^-))$ obtained from the oxidative addition of B-H bonds in **A1**, **B1** and **C1** were denoted as **A2**, **B2** and **C2**, respectively. Optimized geometries of six complexes were shown in Fig. 1S (Supporting Information). The relative energies and optimized geometries of the six complexes **A1**, **A2**, **B1**, **B2**, **C1** and **C2** were listed in Table 1 and the lowest energy structures **A1**, **B1** and **C2** were displayed in Fig. 1. As seen from Table 1, the orders of the electron energies including dispersion corrections of the six complexes are consistent with that of without them, which are **A1** < **A2**, **B1** < **B2** and **C1** > **C2**. The electron energies including dispersion correction of **A2** and **B2** are higher than that of **A1** and **B1** by 12.35 and 5.22 kcal/mol, respectively, while the electron energy with dispersion correction of **C2** is lower than

that of **C1** by 11.18 kcal/mol. Thus, the B-H bond in **C1** is thermodynamically favorable to activate to form **C2**. In addition, the relative energies including dispersion correction are at least 4.0kcal/mol lower than that of the electron energies without dispersion correction. Thus, if the electron energies of the complexes show no significant difference, the dispersion will play a key role for the order of the stability of these complexes. In addition, the large steric hindrances of R groups have contributed to the activation of B-H bond in $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$.

Fig. 1. Selected bond lengths of the lowest energy complexes

$\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ (R=Me, *i*Pr and $\text{CH}(\text{CF}_3)_2$). Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atom (in white) bonded to Ir(III) in **C2**.

Optimized bond angles of C-P-Ir of **A1**, **B1** and **C1** decrease from 116.3 to 107.1°. Thus, the steric hindrance of the groups at phosphine result in the small distance between B-H bond and Ir(I), thus leading to the activation of B-H bond. As seen from Fig. 1, optimized bond distances of Ir-P, Ir-Cl, C=C (in C_8H_{12} ligand) of **A1** are 2.369, 2.387, 1.443 and 1.419 Å, respectively, agreeing with the experiment values [44]. The bond lengths of Ir-Cl, C=C (in C_8H_{12}) of **B1** are close to those of **A1**, while Ir-P bonds are longer than that of **A1** by about 0.070 Å due to the increased steric

effect on P atom. In addition, Fig. 1 shows that the bond distances of Ir-P, Ir-Cl, Ir-B, Ir-H and C=C (in C₈H₁₂) of **C2** are 2.398, 2.557, 2.155, 1.575, 1.387 and 1.424Å, respectively, which are consistent with those of the complex **6** in Ref. 44.

Because the activation of B-H bond in **C1** is thermodynamically favorable, we have calculated the isomerization of **C1**→**C2** and displayed the transition state structure (**TS1**) and potential-energy profile in Fig. 2. The only vibrational frequency of **TS1** is 159*i*, corresponding to the transfer of the H atom from B to Ir(I), as well as B atom close to Ir(I). As seen from Fig. 2, the Gibbs free energy barrier of **C1**→**C2** is only 8.48kcal/mol, thus the isomerization of **C1**→**C2** being dynamically favorable.

Fig. 2. Optimized geometries of the transition states (**TS1**, **TS2** and **TS3**) and the potential-energy profiles (in kcal/mol) of the isomerization of **C1**→**C2**, **E1**→**E5** and **F1**→**F5**. Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atoms (in white) bonded to Ir(III) in **TS1**, **TS2** and **TS3**.

Optimized geometries of η^2 -C₈H₁₂Ir(I)Cl(PR₂(C₂B₁₀H₁₁)) (R=Me, *i*Pr and CH(CF₃)₂) were shown in Fig. 2S (Supporting Information), which are **D1**, **E1** and **F1**,

respectively. Optimized structures of the Ir(III) complexes obtained from the oxidative addition of B-H bond occurring at B3, B4, B5 and B6 positions in **D1**, **E1** and **F1** are **D2-D5**, **E2-E5** and **F2-F5** (as shown in Supporting Information Fig. 2S), respectively. The relative energies of **D1-D5**, **E1-E5** and **F1-F5** were listed in Table 1. As seen from Table 1, the energies including dispersion correlation of **D1** are lower than that of **D2-D5** by at least 3.51kcal/mol, indicating that the **D1** is more stable than **D2-D5**. In contrast, the lowest energy structure with dispersion correlation of **E1-E5** is **E5**. Thus, the activation of B-H bond in **E1** is thermodynamically favorable, which is in good agreement with the experimental results [44].

Fig. 3. Selected bond lengths of the lowest energy complexes $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}$ ($\text{PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11})$) ($\text{R}=\text{Me}$, $i\text{Pr}$ and $\text{CH}(\text{CF}_3)_2$). Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atoms (in white) bonded to Ir(III) in **D1**, **E5** and **F5**.

Moreover, according to relative energies in Table 1, the dispersion correction plays an important role for the order of the stability of **E1-E5**. Optimized bond angle of Ir-P-C in **E1** is 107.8° and close to that of in **C2**, indicating that energy order of **E1** > **E5** also arises from the steric effect. Similarly, the large steric hindrance of the

groups on P atom in **F1** results in the energy order of **F1** > **F5**. This, the oxidative addition of B-H bonds in both **E1** and **F1** are thermodynamically feasible. Optimized angle of C-P-Ir in **F1** is 105.8°, smaller than that of in **C2** and **E1**. Thus, the steric effect decreases the angle of C-P-Ir and leads to the oxidative addition of B-H bond. Therefore, 108.0° of bond angle C-P-Ir might be the critical value of the oxidative addition of B-H bond in Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents. Table 1 shows that the lowest energies structures of $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ (R=Me, *i*Pr and CH(CF₃)₂) are **D5**, **E5** and **F5**, respectively. Thus, the B-H bond situated at B6 position of the o-carboranyl is more favorable to be activated than other positions, which are consistent with the experimentally observed results [44]. Selected bond lengths of **D5**, **E5** and **F5** were illustrated in Fig. 3. The distances of Ir-P, Ir-Cl, C=C in C₈H₁₂ of **D1** (in Fig. 2S) are 2.330, 2.393, 1.442 and 1.413 Å, respectively, which are consistent with those of in **A1**. Hence, the structure of **D1** is similar to that of **A1**. The bond lengths of Ir-P, Ir-Cl, Ir-B, Ir-H, C=C(in C₈H₁₂) of **E5** are 2.392, 2.551, 2.121, 1.584, 1.389 and 1.419 Å, respectively, which are in good agreement with the experimental values [44]. The greatest difference of Ir-P, Ir-Cl, Ir-B, Ir-H, C=C in C₈H₁₂ of **F5** is only 0.007 Å compared with those of in **E5**, indicating that the groups bonded to P atom have no significant influence on the structures.

The isomerization of **E1**→**E5** and **F1**→**F5** were calculated and the corresponding transition state structures were also displayed in Fig. 2, where the two transition states are denoted to be **TS2** and **TS3**, respectively. The only vibrational

frequency of **TS2** and **TS3** is 197*i* and 127*i*, respectively, which corresponds to the transfer of the H atom from B to Ir(I) and B close to Ir(I). The Gibbs free energy barriers of **E1**→**E5** and **F1**→**F5** are 12.93 and 12.54kcal/mol, respectively. The reaction free energies of **E1**→**E5** and **F1**→**F5** are 2.49 and 13.31kcal/mol, respectively. Therefore, the activation of B-H in **E1** and **F1** are both thermodynamically and dynamically favorable.

We further adopted another method to make B-H bond approach Ir(I) in Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents, which the groups of CH₂, NH and O are inserted between P atom and carba-closo-dodecaborate (or o-carborane). $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{X(CB}_{11}\text{H}_{11}^-))}$ (X=CH₂, NH and O) are denoted as **G1**, **H1** and **I1**, respectively, and their corresponding Ir(III) complexes were denoted as **G2**, **H2** and **I2**, respectively. Optimized geometries of the six complexes were displayed in Fig. 3S (Supporting Information), and the lowest energy structures (**G2**, **H2** and **I2**) were illustrated in Fig. 4.

Fig. 4. Selected bond lengths of the lowest energy complexes

$\eta^2\text{-C}_8\text{H}_{12}\text{IrHCl(P(CH}_3)_2\text{X(CB}_{11}\text{H}_{10}^-))}$ (X=CH₂, NH and O). Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atoms (in white)

bonded to Ir(III) in **G2**, **H2** and **I2**.

The relative energies of $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl(P(CH}_3)_2\text{X(CB}_{11}\text{H}_{11}^-))$ ($\text{X}=\text{CH}_2, \text{NH}$ and O) were listed in Table 1. The orders of energies including dispersion correction of the six complexes are **G1>G2**, **H1>H2** and **I1>I2**, respectively. Thus, the inserting groups between P and o-carborane leads to the activation of B-H bond in Ir(I) complexes. Fig. 4 shows that the lengths of Ir-Cl, Ir-P, Ir-B and Ir-H bonds in **G2**, **H2** and **I2** have no significant difference, which are approximately 2.550, 2.310, 2.180 and 1.580Å, respectively. The reaction profiles of the isomerizations of **G1**→**G2**, **H1**→**H2** and **I1**→**I2** were depicted in Fig. 5. The free energy barriers are 9.13, 8.59, and 7.58kcal/mol, respectively, and the reaction free energies are 3.54, 3.57 and 5.40kcal/mol, respectively. Thus, the B-H bonds in **G1**, **H1** and **I1** are easily activated.

Fig. 5. Optimized geometries of transition states and the potential-energy profiles (in kcal/mol⁻¹) of the isomerization of **G1**→**G2**, **H1**→**H2** and **I1**→**I2**. Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atoms (in white) bonded to Ir(III) in **TS4**, **TS5** and **TS6**.

NH and O) are **J5**, **K5** and **L5**, respectively. The energies including dispersion correction of **J1**, **K1** and **L1** are higher than that of **J5**, **K5** and **L5** by 13.81, 13.65 and 14.85kcal/mol, respectively, indicating that the B-H bonds in **J1**, **K1** and **L1** are thermodynamically favorable to be activated. Moreover, the oxidation addition of B-H bonds in **J1**, **K1** and **L1** are situated at B6 position, consistent with the experiment results [44]. The distances of Ir-Cl and Ir-P bonds in **J1**, **K1** and **L1** are about 2.400 and 2.300Å, respectively, which are close to those of in **D1**. The angles of Ir-P-C(in C₂B₁₀H₁₁) of **J1**, **K1** and **L1** are 105.9, 108.3 and 100.8°, respectively, which approximate the critical value of 108.0. The distances of Ir-Cl, Ir-P, Ir-B and Ir-H bonds in **J5**, **K5** and **L5** have no significant difference, which are approximately 2.550, 2.300, 2.130 and 1.583Å, respectively.

The potential energy profiles of the reactions **J1**→**J5**, **K1**→**K5** and **L1**→**L5** were calculated and displayed in Fig. 7, the free energy barriers of the oxidation addition of B-H of **J1**, **K1** and **L1** are 7.55, 6.71, and 7.49kcal/mol, respectively, showing that the reactions are dynamically feasible. Thus, the B-H situated at B6 position in $\eta^2\text{-C}_8\text{H}_{12}\text{Ir}(\text{I})\text{Cl}(\text{P}(\text{CH}_3)_2\text{X}(\text{C}_2\text{B}_{10}\text{H}_{11}))$ (X=CH₂, NH and O) can easily be activated.

Fig. 7. Optimized geometries of transition states and the potential-energy profiles (in kcal/mol⁻¹) of the isomerization of **J1**→**J5**, **K1**→**K5** and **L1**→**L5**. Hydrogen atoms of the complexes are omitted for clarity reasons except for the hydrogen atoms (in white) bonded to Ir(III) in **TS7**, **TS8** and **TS9**.

Conclusions

In summary, we have designed twelve kinds of Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents, which are $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{PR}_2(\text{CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{PR}_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{R}=\text{iPr}$ and $\text{CH}(\text{CF}_3)_2$) and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{CH}_3)_2\text{X}(\text{CB}_{11}\text{H}_{11}^-))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{CH}_3)_2\text{X}(\text{C}_2\text{B}_{10}\text{H}_{11}))$ ($\text{X}=\text{CH}_2$, NH and O). The structures and energies of the Ir(I) and their corresponding Ir(III) complexes have been investigated using density functional theory BP86 functional in order to understand the stability and oxidation addition of B-H bond in Ir(I) complexes. The four conclusions were obtained: (i) we have theoretically explained the different experimental results of $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{iPr})_2(\text{C}_2\text{B}_{10}\text{H}_{11}))$ and $\eta^2\text{-C}_8\text{H}_{12}\text{Ir(I)Cl}(\text{P}(\text{iPr})_2(\text{CB}_{11}\text{H}_{11}^-))$; (ii) the

small distance between B-H bond and Ir(I) result in the oxidation addition of B-H bonds in Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents; (iii) dispersion correction of the energy of the iridium complexes is very important for the order of energy; (iv) we have provided two kinds of methods to obtain B- σ -iridium complexes by changing the groups at phosphine and inserting group between P atom and carba-closo-dodecaborate (or o-carborane) in Ir(I) complexes. Therefore, we anticipate that the B-H bonds in Ir(I) complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents were activated by the above strategy to obtain more B- σ -iridium complexes experimentally.

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Table 1. The relative energies (RE, in kcal/mol) of the iridium complexes supported by phosphine with carba-closo-dodecaborate and o-carborane ligand substituents

Species	RE ^{a)}	RE ^{b)}	Species	RE ^{a)}	RE ^{b)}	Species	RE ^{a)}	RE ^{b)}
A1	0.00	0.00	B1	0.00	0.00	C1	6.22	11.18
A2	17.94	12.35	B2	9.22	5.22	C2	0.00	0.00
D1	0.00	0.00	E1	0.00	0.93	F1	8.39	12.78
D2	15.05	9.70	E2	8.35	5.59	F2	5.72	5.67
D3	20.44	15.18	E3	13.90	11.46	F3	8.56	8.65
D4	19.74	14.45	E4	12.59	10.01	F4	4.91	4.71
D5	9.09	3.51	E5	2.96	0.00	F5	0.00	0.00
G1	0.00	4.96	H1	0.00	5.17	I1	0.00	6.31
G2	5.73	0.00	H2	5.00	0.00	I2	1.70	0.00
J1	4.46	13.81	K1	4.75	13.65	L1	7.00	14.85
J2	6.33	6.51	K2	5.60	5.83	L2	5.74	5.97
J3	8.91	9.08	K3	7.99	7.98	L3	8.38	8.59
J4	7.67	7.76	K4	8.63	8.61	L4	7.41	7.55
J5	0.00	0.00	K5	0.00	0.00	L5	0.00	0.00

^{a)} The relative energies without dispersion correction

^{b)} The relative energies including dispersion correction

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