Structural and Stability Studies of Titanocene Borane σ-Complexes

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The B3LYP density functional theory calculations have been performed to study the structures and stability of titanocene borane σ-complexes $Cp_2Ti(\eta^2\text{-HBcat}')L$ (L = HC≡CH, $H_2C{=}CH_2$, SiH_4, CH_4, and H_2). Due to the electron-deficient property of the boron center in the η^2-HBcat′ ligand, the borane σ-complexes having different L adopt quite different structures. In all calculated structures, the interactions between L and the boron center are important in determining the structural types as well as the stability.

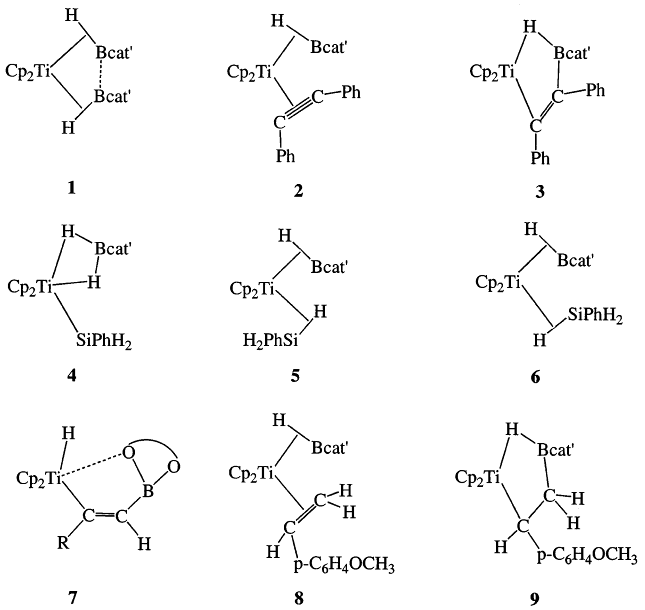
Introduction

Since the discovery of the titanocene diborane σ-complex $Cp_2Ti(\eta^2\text{-HBcat}')_2$ containing η^2-H-B in 1996,[1] a series of titanocene borane complexes $Cp_2Ti(\eta^2\text{-HBcat}')L$ (L = PMe_3, $SiPhH_3$, PhC≡CPh, and $p\text{-MeOC}_6H_4(H)C{=}CH_2$) have been synthesized through substitution reactions.[2−4] The $Cp_2Ti(\eta^2\text{-HBcat}')_2$ complex was structurally characterized and found to adopt structure **1**, in which a weak interaction between the two boron centers exists.[3,5] Molecular orbital calculations showed that the weak interaction resulted from an unusual three-center-two-electron bond in the TiB_2 triangle.[5]

Spectroscopic studies indicated that the $Cp_2Ti(\eta^2\text{-HBcat}')L$ complexes, like $Cp_2Ti(\eta^2\text{-HBcat}')_2$, are σ-complexes containing nonclassical metal−η^2-HBcat′ interactions.[3] However, these $Cp_2Ti(\eta^2\text{-HBcat}')L$ complexes were believed to have quite different structures when ligands (L) are different. For example, the $Cp_2Ti(\eta^2\text{-HBcat}')(\eta^2\text{-PhC≡CPh})$ complex was believed to adopt a structure that can be described by a resonance hybrid between two Lewis structures (**2** and **3**). The $Cp_2Ti(\eta^2\text{-HBcat}')(SiPhH_3)$ complex, which is derived from $Cp_2Ti(\eta^2\text{-HBcat}')L$ by having a silane ligand, adopts a different resonance hybrid between a hydroborato and an η^2-silane Lewis structure (**4** and **5**). It is interesting that $Cp_2Ti(\eta^2\text{-HBcat}')(\eta^2\text{-H−SiH}_2Ph)$ (**6**) is not the resulting complex although metal−η^2-silane complexes are also very common.[6−8]

Clearly, the structural features of the newly synthesized borane σ-complexes require further studies. Quantum chemical calculations are efficient and convenient approaches in determining structures of transition metal complexes.[9−11] In this paper, we reported our density functional theory calculations at the B3LYP level to give a better understanding of these transition metal complexes containing η^2-HBcat′. We hope to examine how different ligands (L) interact with the unsaturated boron center in the η^2-HBcat′ unit in the complexes and what the structural consequences are due to the interaction.

Chart 1



Computational Details

On the basis of the fact that the Becke3LYP (B3LYP) method[12] can well describe the properties of transition metal

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[‡] The University Grant Committee Area of Excellence Scheme (Hong Kong).

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compounds, all the geometries have been optimized with this method. The Stuttgart effective core potentials and basis sets[13] (sddall) are used to describe Ti and Si, whereas the 6-31G basis set[14] is used for all other atoms. Polarization functions are added for the B ($\zeta(d) = 0.388$) and Si ($\zeta(d) = 0.262$) atoms and for those H atoms ($\zeta(p) = 1.1$) directly bonded to the transition metal center. For computational simplicity, HBcat′, PhC≡CPh, p-MeOC$_6$H$_4$(H)C=CH$_2$, and SiPhH$_3$ are modeled by HB(OCH)$_2$, HC≡CH, H$_2$C=CH$_2$, and SiH$_4$, respectively. Frequency analyses have been performed for all calculated structures to confirm their characteristics as minima or transition states. All calculations are performed with the Gaussian 98 software package.[15] On the basis of the optimized structures at the B3LYP level, analyses on the Laplacian of electron density[16] were carried out with MOPLOT 2.4.[17]

To test the effect of basis sets on the calculated structures as well as on the Laplacian of electron density, we also performed a geometry optimization for the structure of [Cp$_2$Ti(η^2-HB(OCH)$_2$)(HC≡CH)] by replacing the 6-31G basis set mentioned above with 6-311G. The two optimized structures with the two different basis sets are almost identical. The changes in the bond lengths are within 0.005 Å and those in the bond angles within 0.5°. In addition, one cannot see the difference at a qualitative level between the two Laplacian plots of electron density calculated with the two different basis sets.

We are interested in the Laplacian of electron density instead of the electron density itself. This is because the Laplacian of electron density provides qualitatively clearer pictures regarding the bonding characteristics among atoms in a molecule, which can be seen from our discussion in the following sections.

Results and Discussion

The majority of complexes studied in this paper do not have X-ray crystal structures. Therefore, it is necessary to test how well the B3LYP level of theory can reproduce structures of known and related complexes. Here, we compare the calculated structure of Cp$_2$Ti(η^2-HB(OCH)$_2$)$_2$ and the X-ray crystal structure[1,3] of Cp$_2$Ti(η^2-HBcat′)$_2$. The results show that the X-ray crystal structure was remarkably reproduced at the B3LYP level of theory. Selected experimental structural parameters vs calculated ones are as follows: Ti−B, 2.335 Å vs 2.333 Å; Ti−H, 1.740 Å vs 1.746 Å; B−H, 1.250 Å vs 1.322 Å; B···B, 2.110 Å vs 2.134 Å; and B−Ti−B, 53.8° vs 54.4°. Since the detailed structure and bonding of the diborane σ-complex have been analyzed in a previous paper,[5] a deeper discussion is not necessary.

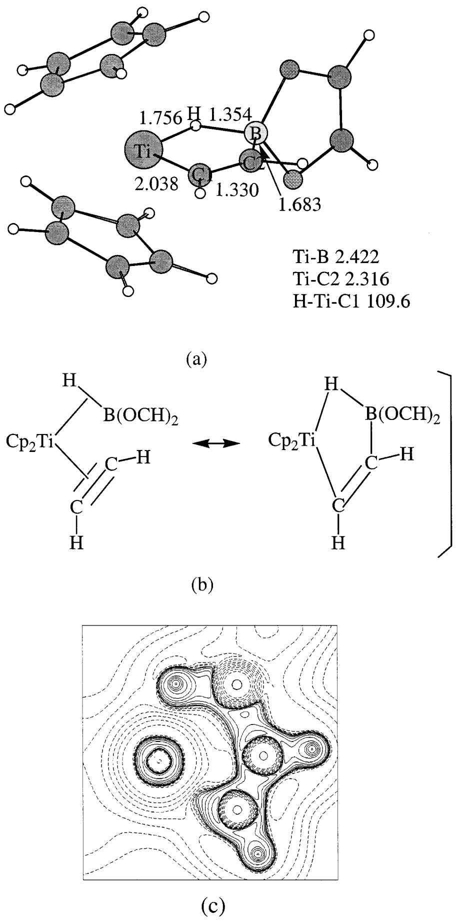

Figure 1. (a) Calculated structure for Cp$_2$Ti(η^2-HB(OCH)$_2$)(HC≡CH), (b) a resonance hybrid describing the calculated structure, and (c) a Laplacian plot of electron density on the plane containing the Ti−C1−C2−B−H five-membered ring.

Structures of Cp$_2$Ti(η^2-HB(OCH)$_2$)(HC≡CH) and Cp$_2$Ti (η^2-HB(OCH)$_2$)(H$_2$C=CH$_2$). Experimentally, the Cp$_2$Ti(η^2-HBcat′)$_2$ complex reacts with PhC≡CPh to give the alkyne adduct Cp$_2$Ti(η^2-HBcat′)(PhC≡CPh).[3] At the B3LYP level, the fully optimized Cp$_2$Ti(η^2-HB(OCH)$_2$)(HC≡CH) model complex adopts a five-membered-ring structure (see Figure 1a). Examining the calculated structural parameters, we found that the C1−C2 bond (1.330 Å) is longer than the triple bond (1.211 Å) calculated for H−C≡C−H but slightly shorter than the double bond (1.335 Å) calculated for H$_2$C=CH$_2$. The B−C2 bond (1.683 Å) is much longer than the B−C single bond (1.541 Å) calculated for H$_2$C=CH−B(OCH)$_2$. In addition, the short distance between Ti and C2 (2.316 Å) indicates their strong interaction. Apparently, the calculated structure shown in Figure 1a can only be described by a resonance hybrid between the two important Lewis structures shown in Figure 1b. The calculated structure supports Hartwig's explanation for the NMR chemical shifts observed experimentally.[3] The hydride chemical shift in the ^{1}H NMR spectrum indicates a B−H bonding interaction and also implies an electron configuration somewhere between d^0 and d^2 for the metal center while the ^{11}B NMR resonance is nearly equivalent to that of a free catecholborane.

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Although the B−C2 bond is longer than expected, the B−C2 σ-bonding interaction can be seen from the Laplacian plot of electron density obtained from the B3LYP calculations. Figure 1c shows the Laplacian plot on the plane containing the five-membered ring. In the Laplacian plot, solid contour lines denote $\nabla^2\rho < 0$, where the electron density is locally concentrated; dashed contour lines denote $\nabla^2\rho > 0$, where the electron density is locally depleted. The large concentration from the C1 atom in the direction of the Ti−C1 bond suggests the Ti−C σ-bonding character. The square-like charge concentration surrounding the Ti core implies the contribution of the Lewis structure **2** (the left one of Figure 1b), which has a formal d^2 electron configuration. The characteristics of the Laplacian could be derived from a spherical core electron density plus the contribution of electron density from electrons occupying a d orbital having four maxima in its amplitude.[18] In conclusion, the Laplacian plot also supports the structure that should be described by Figure 1b.

It should be noted here that we also obtained a structure having Ti···O coordination (see **7**) from the B3LYP calculations. In the calculated structure (**7**), the BO_2 plane is approximately coplanar with the plane containing the Ti−C−C−B centers. This structural feature is understandable because the available orbital from the metal center for bonding with the coordinated oxygen has the maximum amplitude on the plane containing the hydride and alkenyl ligands. This structural isomer has a stability similar to that of the one calculated for the alkyne adduct (Figure 1a) when the model complex is calculated, i.e., the R group in **7** is H. However, when R uses the experimental phenyl group, structure **7** is found to be 6.8 kcal/mol higher in energy than the structure having the Ti-η^2-H-B structural unit. We believe that it is the steric repulsion between Ph and the Cp ligands that prevents the formation of structure **7** in the experiment. Comparing the two calculated structures having R = H and Ph, one finds no significant change in other structural parameters except for a significant lengthening of the Ti−C1 bond distance from the structure when R = H (2.217 Å) to the structure when R = Ph (2.331 Å). The phenyl plane is found not to be coplanar with the C=C double bond moiety due to a hydrogen−hydrogen repulsion.

Calculations were further undertaken for the analogous complex $Cp_2Ti(\eta^2\text{-}HB(OCH)_2)(H_2C{=}CH_2)$ (see **8** or **9**), an alkene adduct. This complex is a model complex of $Cp_2Ti(\eta^2\text{-}HBcat')(p\text{-}MeOC_6H_4(H)C{=}CH_2)$, which is a reactive intermediate in the hydroboration reaction of olefin. The optimized structure is shown in Figure 2a. From the calculated structural parameters (H−B, 1.328 Å; C1−C2, 1.518 Å; Ti−C2, 2.381 Å; B−C2, 1.755 Å), we come to a similar conclusion that $Cp_2Ti(\eta^2\text{-}HB(OCH)_2)(H_2C{=}CH_2)$ adopts a five-membered-ring structure and can be well described by a resonance hybrid between the two Lewis structures (**8** and **9**) (see Figure 2b). The effect of the $p\text{-}C_6H_4OMe$ substituent on the five-membered-ring structural unit has also been examined (see values in parentheses in Figure 2a). Except for the lengthening of the Ti−C bond distance from the complex when R = H (2.130 Å) to the complex when R = $p\text{-}C_6H_4\text{-}OMe$ (2.197 Å), no significant change can be found for other bonds. This result suggests that the electronic effect of substituents on the B−C interaction is not significant.

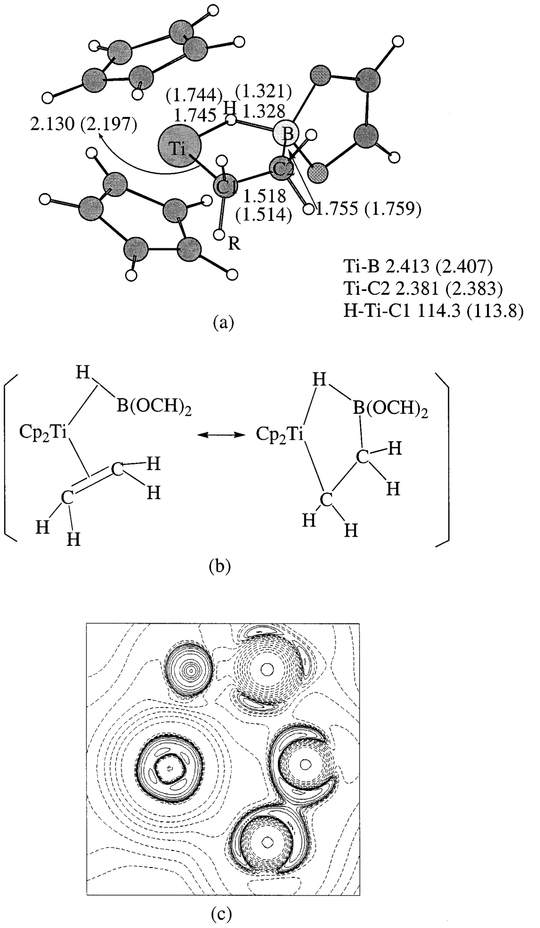

Figure 2. (a) Calculated structures for $Cp_2Ti(\eta^2\text{-}HB(OCH)_2)(H_2C{=}CHR)$ (R = H and $p\text{-}C_6H_4OMe$) (values in parentheses are for R = $p\text{-}C_6H_4OMe$), (b) a resonance hybrid describing the calculated structures, and (c) a Laplacian plot of electron density on the plane containing the Ti−C1−C2−B−H five-membered ring for the complex having R = H.

The B−C2 bond length (1.755 Å) is longer than the corresponding one in the alkyne adduct (Figure 1 a), suggesting that the Lewis structure shown in the left-hand side of Figure 2b is relatively more important. Indeed, the Laplacian plot shown in Figure 2c provides further support to the claim here. The four charge concentrations surrounding the Ti core clearly show the contribution of a formal Ti(d^2) electron configuration to the total electron density. The B−C2 σ-bonding interaction is apparently weaker as less electron density can be seen along the bond when compared to the corresponding B−C2 bond in the alkyne adduct (Figure 1).

Structure of $Cp_2Ti(\eta^2$-HBcat′)(silane). When $Cp_2Ti(\eta^2\text{-}HBcat')_2$ complex reacts with $PhSiH_3$, a silane adduct was experimentally observed.[3] Spectroscopic studies suggest that the silane adduct adopts a structure between **4** and **5**.

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(17) Interactive MOPLOT: a package for the interactive display and analysis of molecular wave functions, incorporating the programs MOPLOT (D. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koenig), and EXTREM (R. F. W. Bader and F. W. Bieger-Koenig) by P. Sherwood and P. J. MacDougall, 1989.

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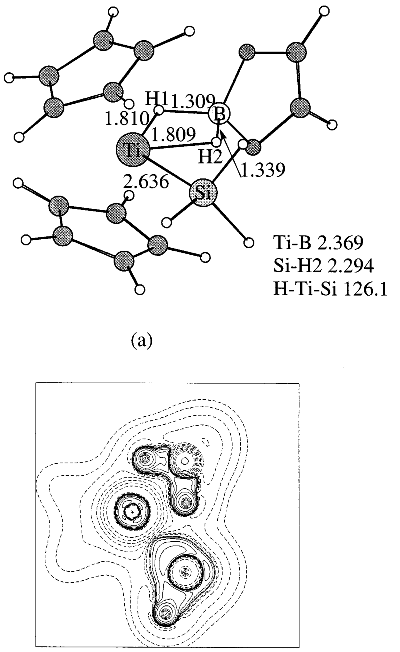

Figure 3. (a) Calculated structure for $Cp_2Ti(\eta^2\text{-HB}(OCH)_2)$(silane) and (b) a Laplacian plot of electron density on the Ti−H1−B−H2−Si plane.

The calculated structure, shown in Figure 3a, is apparently a hydroborato complex having a Lewis structure of **4**. The interaction between Si and H2 is weak with a distance of 2.294 Å. The Laplacian plot (Figure 3b) also indicates no bonding interaction between Si and H2. Charge concentrations from both Ti and Si along the Ti−Si bond can be seen, suggesting the covalent bonding nature. The results imply that the boron center of the Bcat′ unit has greater hydride affinity than the Si center.

We also obtained a structural isomer **6**, which contains both η^2-HB(OCH)$_2$ and η^2-HSiH$_3$. However, this structural isomer is 11.4 kcal/mol higher in energy than the hydroborato form. It is the high stability of the hydroborato form having strong B−H bonds that makes isomer **6** relatively unstable.

Structures of $Cp_2Ti(\eta^2$-HBcat′)(dihydrogen) and $Cp_2Ti(\eta^2$-HBcat′)(alkane). For the completeness of this work, we also performed calculations on the dihydrogen and alkane adducts to see what structures these adducts would adopt. The calculated structures are shown in Figure 4. Interestingly, these adducts do not adopt the typical nonclassical dihydrogen or η^2-H-C structures. Instead, they correspond to the hydroborato structural forms. The Laplacian plots shown in Figure 4b further confirm the classical structures.

Stabilities of the $Cp_2Ti(\eta^2$-HBcat′)L Complexes. To study the relative stabilities of the various borane σ-complexes discussed above, we calculated the reaction energies for the following chemical equation.

$$Cp_2Ti(\eta^2\text{-HB}(OCH)_2)_2 + L \rightarrow Cp_2Ti(\eta^2\text{-HB}(OCH)_2)L + HB(OCH)_2$$

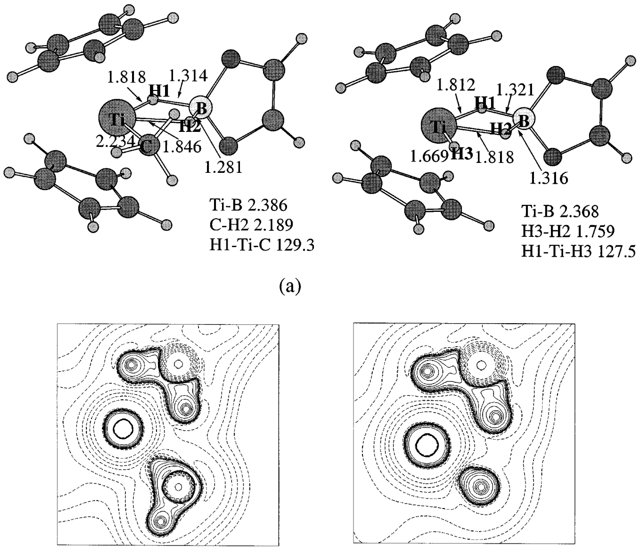

Figure 4. (a) Calculated structures for $Cp_2Ti(\eta^2\text{-H}(OCH)_2)$(dihydrogen) and $Cp_2Ti(\eta^2\text{-HB}(OCH)_2)$(alkane) and (b) the corresponding Laplacian electron density plots.

Table 1. The Reaction Energies (ΔE) Calculated for the Following Chemical Equation: $Cp_2Ti(\eta^2\text{-HB}(OCH)_2)_2 + L \rightarrow Cp_2Ti(\eta^2\text{-HB}(OCH)_2)L + HB(OCH)_2$

L	ΔE (kcal/mol)	ΔG (kcal/mol)
HC≡CH	−24.9	−27.6
$H_2C{=}CH_2$	−5.6	−5.0
SiH_4	−0.7	−1.2
CH_4	21.4	19.0
H_2	−5.2	−8.0

The results are listed in Table 1. We can see that the alkyne and alkene adducts have higher stabilities than others. The alkyne adduct has the highest stability and is also significantly more stable than the alkene adduct. Formally, the formation of the alkyne or alkene adduct corresponds to breaking a carbon−carbon π bond and forming Ti−C and B−C bonds if we consider the Lewis structures having a five-membered ring (see Figures 1b and 2b). Clearly, the significantly higher stability of the alkyne adduct is a result of stronger Ti−C (sp^2) and B−C (sp^2) bonding interactions. The alkene adduct has weaker Ti−C(sp^3) and B−C(sp^3) bonding interactions and is also expected to have greater steric interactions between the C−H bonds from the alkene unit and the two Cp rings. Comparing the silane (SiH_4) and alkane (CH_4) adducts, the silane adduct is unexpectedly more stable in reference to the substitution reaction. The formation of the alkane or silane adduct corresponds to breaking a C−H or Si−H bond and forming a Ti−C or Ti−Si bond and a B−H bond. Although the Ti−Si bond is relatively weaker than the Ti−C bond, the significant difference in the bonding energies of the C−H and Si−H bonds gives a negative ΔE for the silane adduct but a positive ΔE for the alkane adduct. It is rather surprising that the reaction energies (ΔE) for the dihydrogen and alkane adducts are very different although the H−H and C−H bonding energies are almost the same. In fact, the difference in the reaction energies is mainly raised from the different bonding energies of the Ti−C and Ti−H bonds. It is known that the L_nM−H bond is normally stronger than the L_nM−CH_3 bond by 15−25 kcal/mol.[19]

Summary

Structural aspects and stability of various titanocene borane σ-complexes $Cp_2Ti(\eta^2\text{-}HB(OCH)_2)L$ (L = HC≡CH, $H_2C{=}CH_2$, SiH_4, CH_4, and H_2) have been studied with the aid of density functional theory calculations (B3LYP). The alkyne and alkene adducts adopt five-membered-ring structures, which can be described by a resonance hybrid of two Lewis structures, supporting Hartwig's explanation for the NMR chemical shifts observed experimentally. Very different from the alkyne and alkene adducts, the silane, alkane, and dihydrogen adducts adopt hydroborato structures. The structural feature of these borane σ-complexes is governed by how the electron-deficient B center interacts with the ligand L. Without structural calculations, one cannot appreciate the structural details of these newly synthesized σ-complexes. The relative stabilities in reference to the exchange reactions among different L are related to the energies of the formation of the Ti−Si, Ti−C, and Ti−H bonds and the cleavage of the Si−H, C−H, and H−H bonds. The high stability of alkyne and alkene adducts is attributed to the fact that the adduct formation corresponds to breaking a relatively weak carbon−carbon π-bond and forming strong Ti−C and B−C σ-bonds in the resulting five-membered-ring structures.

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