Inorg. Chem. **2007**, *46*, 6091–6098

Inorganic Chemistry
Article

A Theoretical Study on the Mechanism of Boron Metathesis

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Received April 1, 2007

The mechanism of the boron metathesis reaction of the transition-metal–aminoborylene complex $Cp(CO)_2FeBN(CH_3)_2^+$ (**8**) with EX, where EX = H_3PO (**9ap**), H_3AsO (**9bp**), H_3PS (**9aq**), H_3AsS (**9bq**), CH_3CHCH_2 (**9cr**), $(NH_2)_2CCH_2$ (**9dr**), H_2CO (**9ep**), and $(NH_2)_2CO$ (**9dp**) is investigated at the B3LYP/LANL2DZ level. The analysis of bonding and charge distribution shows that the Fe–borylene complex (**8**) is a Fischer-type carbene analogue. The attack of the olefin takes place at the metal end of the M═C bond of the metal–carbene complex in olefin metathesis and proceeds via [2 + 2] cycloaddition, while in boron metathesis, the initial attack of the substrates takes place at the positively charged B atom of the Fe–borylene complex and forms the preferred acyclic intermediate. The energetics of boron metathesis is comparable to that of the olefin metathesis. Substrates that are polar and a have low-lying σ^* molecular orbital (weak σ bond) prefer the boron metathesis reaction. The relative stability of the metathesis products is controlled by the strength of the Fe–E and B–X bonds of the products **13** and **14**, respectively. We have also investigated the possibility of a β-hydride-transfer reaction in the Fe–borylene complex.

Introduction

It is fascinating to compare and contrast the chemistry of the two adjacent elements in the periodic table, boron and carbon.[1] Differences among them are plentiful. Carbon provides the basic structural framework for life, while boron is needed only in trace quantities to sustain it. Compounds of carbon provide the best examples for two-center, two-electron bonding. In contrast, boron and its compounds ushered in multicenter bonding. Despite these differences, there are several aspects common to both carbon and boron.[2−5] Advances in the chemistry of one element in a particular direction, however, can go faster than those of the other. Hydroboration, for example, was discovered in 1948 and led to a Nobel Prize for H. C. Brown.[2] It took another 30 years for hydrocarbation to be established.[3]

Olefin metathesis,[4] discovered in 1967, provides a reverse scenario. The versatility of the metathesis reaction in chemistry is recognized by the award of 2005 Nobel Prize to Robert Grubbs, Richard Schrock, and Yves Chauvin.[6] The metathesis reactions involving atoms such as Si,[7] S[8], Ga,[9] and N[10] have been slowly coming to light. There are limited examples of metathesis involving $MeB{=}C(SiMe_3)_2$,[11] and these metathesis reactions proceed through [2 + 2] cycload-

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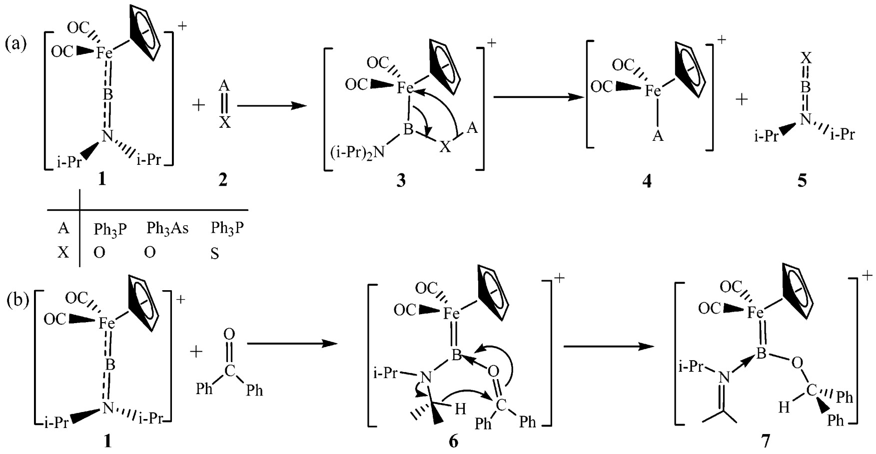
10.1021/ic700619g CCC: $37.00

Scheme 1. Schematic Representation of the Reactions of **1**: (a) Metathesis Reaction with AX and (b) β-Hydride-Transfer Reaction with Ph_2CO



dition and the regiospecificity is decided by the polarity of both B═C and the attacking double bonds. Despite the fact that there are several transition-metal−borylene complexes known,[12] no metathesis reactivity studies on those complexes have been reported to date. Even though there is a close relationship between transition-metal−borylene complexes and metal−carbene complexes, most of the earlier studies of the reactivity of borylene complexes toward unsaturated substrates containing C═C and C═O bonds have shown the borylene ligand to undergo a displacement reaction[13] rather than the cycloaddition or metathesis reactions, which are commonly observed in metal−carbenes. Recently, metathesis reactions of the transition-metal−aminoborylene complex $[Cp(CO)_2FeBN(i\text{-}Pr)_2]^+(BAr^f_4)^-$ ($Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$) (**1**) with AX (**2**), where A = Ph_3P, Ph_3As; X = O, S, were reported by Aldridge and co-workers (Scheme 1a).[14] It led to the isolation of $[Cp(CO)_2Fe(A)]^+(BAr^f_4)^-$ (**4**) and $(i\text{-}Pr)_2NBX$ (**5**). An addition-substitution pathway through intermediate **3** (Scheme 1a) was suggested for the reaction. The amino(oxo)boryl intermediate $Cp(CO)_2FeBN(i\text{-}Pr)_2OPPh_3^+$ (**3**, where A = Ph_3P, X = O) was isolated for the reaction of Ph_3PO and the Fe−borylene complex **1**.

The reaction of Ph_2CO with **1**, however, does not follow the metathesis pathway; the ligand transformation process, Meerwein−Ponndorf β-hydride transfer from an isopropyl substituent of the aminoborylene ligand to the coordinated ketone, takes place instead (Scheme 1b).[15] Obviously, not all unsaturated substrates are suitable to undergo metathesis with the borylene complex. This raises many interesting questions about the details of the reaction, the characteristics of the metal−borylene complex, and the unsaturated substrates likely to undergo boron metathesis. It will also be intriguing to probe the detailed mechanism and the energetics of the boron metathesis reaction. These questions are especially attractive in view of our interest in finding parallels in the chemistry of boron and carbon[1b−f,3b] and prompted the study of these reactions using the model borylene complex $Cp(CO)_2FeBN(CH_3)_2^+$ (**8**) with the unsaturated substrates H_3PO (**9ap**), H_3AsO (**9bp**), H_3PS (**9aq**), H_3AsS (**9bq**), CH_3HCCH_2 (**9cr**), $(NH_2)_2CCH_2$ (**9dr**), H_2CO (**9ep**), and $(NH_2)_2CO$ (**9dp**) (Scheme 2). The boron metathesis reaction of the derivative of the first three substrates with the Fe−borylene complex (**1**) is observed experimentally. The substrates **9cr**, **9dr**, **9ep**, and **9dp** were chosen so that the reactivity of the Fe−borylene complex toward alkenes and carbonyl compounds could be examined.

Computational Details

All structures were optimized using the hybrid HF-DFT method, B3LYP/LANL2DZ, based on Becke's three-parameter functional including the Hartree−Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke[16,17a,b] together with the nonlocal correction for the correlation energy suggested by Lee et al.[16,17c] The LANL2DZ basis set uses the

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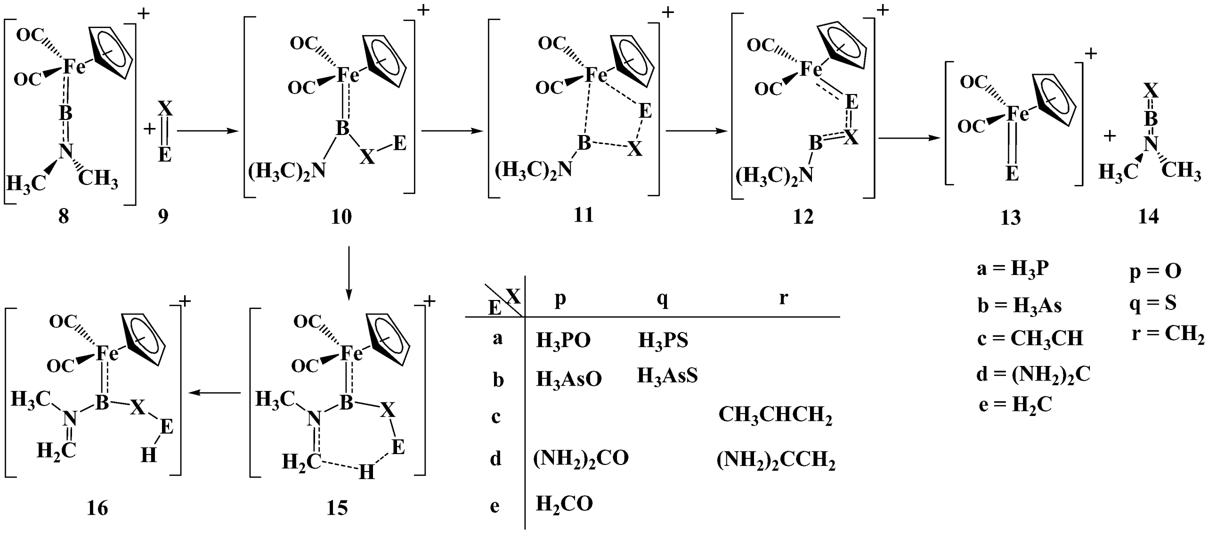
Scheme 2. Schematic Representation of the Mechanism of Boron Metathesis and β-Hydride-Transfer Reaction of the Fe−Borylene Complex **8** with EX

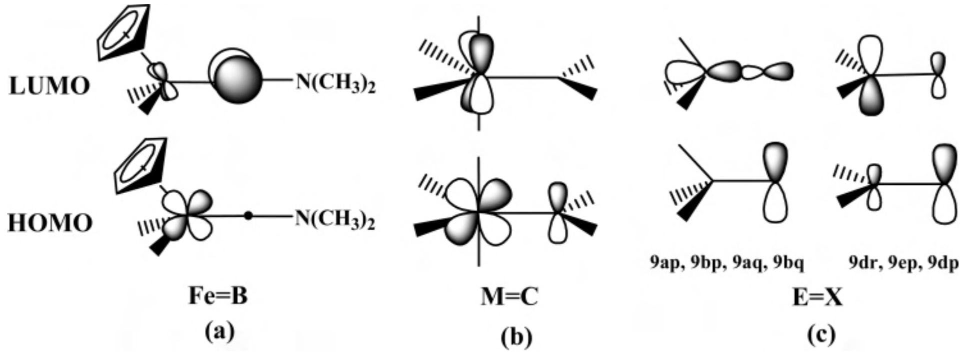


E \ X	p	q	r
a	H_3PO	H_3PS	
b	H_3AsO	H_3AsS	
c			CH_3CHCH_2
d	$(NH_2)_2CO$		$(NH_2)_2CCH_2$
e	H_2CO		

a = H_3P
b = H_3As
c = CH_3CH
d = $(NH_2)_2C$
e = H_2C

p = O
q = S
r = CH_2

Scheme 3. Schematic Representation of the HOMO and LUMO of (a) Fe−Borylene Complex, (b) the Metal−Carbene Complex, and (c) Substrates



effective-core potential of Hay and Wadt.[16,18] The nature of the stationary points was characterized by vibrational frequency calculations. The *Gaussian03* program package was used in this study.[19] The charge distributions were obtained by NBO analysis.[20]

Scheme 2 shows the numbering used. The structures are numbered using Arabic numerals. The various substrates (EX) are represented by the combination of two letters. The E is represented by five letters (**a** = H_3P, **b** = H_3As, **c** = CH_3CH, **d** = $(NH_2)_2C$, and **e** = H_2C), and the X is represented by three letters (**p** = O, **q** = S, and **r** = CH_2). For example, **10ap** describes structure number **10** in which the substrate (EX) attached to the Fe−borylene complex is H_3PO, which will correspond to the entry under row **a** and column **p** in Scheme 2. The structure numbers **13a** and **14p**, for example, represent the final metathesis products where **a** corresponds to H_3P and **p** corresponds to O.

Results and Discussion

The reactants for olefin metathesis are metal−carbene complexes and olefins, while metal−borylene complexes and polar substrates are the reactants for boron metathesis. Though the structure and bonding of borylene complexes are described in the literature,[12d,15,21] we begin with a brief recapitulation for the Fe−borylene complex $Cp(CO)_2FeBN(CH_3)_2^+$ (**8**) to understand the reaction. The details of the mechanism obtained from the theoretical calculations are discussed next, followed by the competitive β-hydride-

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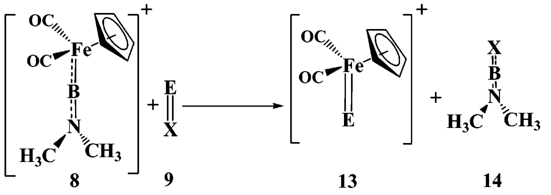
transfer reaction. Even though the aminoborylene complex is formally isolobal to the vinylidene complex,[5] the more general carbene complex for olefin metathesis was taken as the reference for comparison.

A. Electronic Structure of the Fe−Borylene Complex $Cp(CO)_2FeBN(CH_3)_2^+$ (8) and Its Metathesis Reaction. All the theoretical studies on metal−borylene complexes show that the metal−boron bond is formed by the σ donation from the boron to the metal and the π back-donation from the metal to boron.[12d,15,21] The calculated geometrical parameters of the Fe−borylene complex are close to the experimentally reported values[14] (Supporting Information). It is possible to anticipate from the difference in the electronegativity of the B and Fe atoms that the Fe−borylene complex **8** is a Fischer-type carbene analogue with a polarization of charge, making Fe the negative end. The analysis of natural charge distribution on the Fe−borylene complex **8** shows negative charge on Fe (−0.38) and positive charge on B (+0.95). The charges on the fragments, +0.34 on $Cp(CO)_2Fe$ and +0.66 on $BN(CH_3)_2$, also indicate the electropositive nature of B compared with Fe. The molecular orbital (MO) analysis shows the σ donation from B to Fe and the π back-donation from Fe to B (Supporting Information).

Generally, metal−carbenes involved in olefin metathesis are 16- or 14-electron complexes,[6,22] while the Fe−borylene **8** is an 18-electron complex with greater negative charge on the metal. The highest-occupied molecular orbital (HOMO) of the Fe−borylene complex is a nonbonding metal orbital, whereas the lowest-occupied molecular orbital (LUMO) is a π*-MO mainly localized on the B atom (Scheme 3a). This is in contrast to the carbene complexes that undergo olefin metathesis, where the HOMO is generally a π MO between the metal and the carbon and the LUMO is a d orbital on the metal (Scheme 3b). Hence, the electrophilic center is the B atom in the Fe−borylene complex and the metal atom in the metal−carbene complexes. As a result, the unsaturated substrates prefer to interact with the B atom in the Fe−borylene complex and with the metal atom in the metal−carbene complexes.

In order to understand the mechanism for boron metathesis reaction of transition-metal−borylene complexes, the model complex **8** and the substrates H_3PO (**9ap**), H_3AsO (**9bp**), H_3PS (**9aq**), H_3AsS (**9bq**), CH_3HCCH_2 (**9cr**), $(NH_2)_2CCH_2$ (**9dr**), H_2CO (**9ep**), and $(NH_2)_2CO$ (**9dp**) were used (Scheme 2). The energetics of the boron metathesis reaction, evaluated using reaction 1, gives insight into the feasibility of boron metathesis with various substrates.

The reaction energies of the Fe−borylene complex **8** with the substrates H_3PO (**9ap**), H_3AsO (**9bp**), H_3PS (**9aq**), and H_3AsS (**9bq**) are calculated to be exothermic (Table 1). The substrates **9ap** and **9bp**, which have the same X substituent (X = O), show almost similar reaction energies. Similarly, the substrates **9aq** and **9bq** (X = S) also have comparable reaction energies. The analysis of charge distribution (Table 1) shows that the more polar E−X bonds (**9ap** and **9bp**) give more exothermic reactions as compared with the less polar E−X bonds (**9aq** and **9bq**). Owing to the lower polarity of propene (**9cr**), the reaction is largely endothermic (Table 1); therefore, we did not investigate the reaction mechanism for **9cr**. The reaction of more polar H_2CO (**9ep**) is calculated to be exothermic by 1.7 kcal/mol. In order to understand the effect of electron-donating substituents, the H and CH_3 groups on carbon in **9cr** and **9ep** were substituted by NH_2 groups. The reaction of the resultant diaminoalkene (**9dr**) is exothermic by 6.2 kcal/mol. Similarly, the reaction of **9dp** is more exothermic as compared with **9ep**. It is clear from the energetics that the more polar substrates like H_3PO (**9ap**), H_3AsO (**9bp**), H_3PS (**9aq**), and H_3AsS (**9bq**) are preferred for boron metathesis reaction (Table 1). The experimental observation of the boron metathesis reaction for the derivatives of the substrates **9ap**, **9bp**, and **9bq** supports this result.



(1)

The energetics of the boron metathesis reaction can be analyzed using the relative stabilities of the Fe−E and B−X bonds of the products **13** and **14** compared to the Fe−B and E−X bonds of the reactants **8** and **9**. Reactions 2 and 3 (Table 2) are used to explain these relative stabilities. The preference for hard−hard and soft−soft interactions explains the greater stability of the B−O bond compared with the B−S bond (reactions 2a and 2b). Reaction 2c specifies that the formation of the B−C bond (**14r**) is less favorable than that of the B−O bond (**14p**). Hence, the order of stability of the B−X bond in **14** is B−O (**14p**) > B−C (**14r**) > B−S (**14q**). The formation of the Fe−P (**13a**) and Fe−As (**13b**) bonds is 41.2 and 42.8 kcal/mol more favorable when compared with the Fe−$C(NH_2)_2$ bond formation in **13d** (reactions 3a and 3c). Similarly, the reactions 3b and 3d show that the Fe−P (**13a**) and Fe−As (**13b**) bonds are 72.7 and 74.3 kcal/mol more stable than the Fe−CH_2 bond **(13e)**. The comparison of reactions 3a,b and 3c,d indicate that the Fe−C bond in Fe−$C(NH_2)_2$ is more stable than the Fe−C bond in Fe−CH_2. The π-donor NH_2 ligands raise the energy of the p orbital on the carbene, making it a better σ donor and a poor π acceptor to the metal. As a result, the Fischer carbene **13d** (Fe−$C(NH_2)_2$) is more stable compared with **13e** (Fe−CH_2). Hence, the order of stability of the Fe−E bond is as follows: Fe−As (**13b**) > Fe−P (**13a**) > Fe−$C(NH_2)_2$ (**13d**) > Fe−CH_2 (**13e**).

The greater exothermicity of the reaction 1 for the substrates H_3PO (**9ap**) and H_3AsO (**9bp**) can be attributed to the formation of the more stable B−O bond in **14p** as

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Table 1. Energies (ΔE in kcal/mol) from Reaction 1 and Distribution of Natural Charges on E and X in the Substrates **9**[a]

	substrate							
	9ap	**9bp**	**9aq**	**9bq**	**9cr**	**9dr**	**9ep**	**9dp**
ΔE	−74.4	−76.0	−43.8	−41.4	+45.5	−6.2	−1.7	−33.2
Δc	2.09	2.28	0.98	1.26	0.25	1.03	0.73	1.54
charge on E	+1.12	+1.29	+0.46	+0.69	−0.18	+0.41	+0.23	+0.84
charge on X	−0.97	−0.98	−0.52	−0.57	−0.43	−0.62	−0.51	−0.70

[a] Note that Δc is the difference between the natural charge on E and X.

Table 2. Reactions to Estimate the Relative Stabilities of Fe−E and B−X Bonds in **13** and **14**

reaction	ΔE (kcal/mol)	reaction no.
$H_3PO + (CH_3)_2NBS \rightarrow H_3PS + (CH_3)_2NBO$	−30.7	2a
$H_3AsO + (CH_3)_2NBS \rightarrow H_3AsS + (CH_3)_2NBO$	−34.5	2b
$(NH_2)_2CO + (CH_3)_2NBCH_2 \rightarrow (NH_2)_2CCH_2 + (CH_3)_2NBO$	−27.0	2c
$Cp(CO)_2FeC(NH_2)_2^+ + H_3PO \rightarrow Cp(CO)_2FePH_3^+ + (NH_2)_2CO$	−41.2	3a
$Cp(CO)_2FeCH_2^+ + H_3PO \rightarrow Cp(CO)_2FePH_3^+ + H_2CO$	−72.7	3b
$Cp(CO)_2FeC(NH_2)_2^+ + H_3AsO \rightarrow Cp(CO)_2FeAsH_3^+ + (NH_2)_2CO$	−42.8	3c
$Cp(CO)_2FeCH_2^+ + H_3AsO \rightarrow Cp(CO)_2FeAsH_3^+ + H_2CO$	−74.3	3d

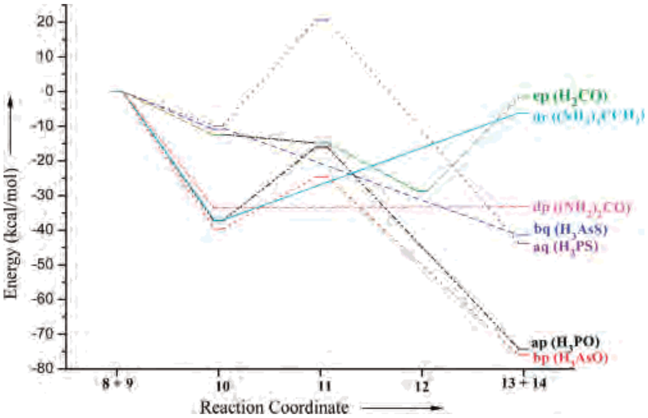

Figure 1. Reaction energy profile for metathesis reaction of the Fe−borylene complex (**8**) with the substrates (**9**) indicating the relative energies of the intermediates (**10, 11ep**, and **12**), the transition states (**11ap**, **11bp**, and **11aq**), and the products (**13** and **14**).

well as the Fe−P and Fe−As bonds in **13a** and **13b**. The reaction energies for the substrates H_3PS (**9aq**) and H_3AsS (**9bq**) are less exothermic than those for the substrates H_3PO (**9ap**) and H_3AsO (**9bp**). This is partially due to the formation of the less stable B−S bond in **14q**. The substrate **9cr** gives the least stable products due to the formation of the less stable B−C (**14r**) and Fe−CH_2 (**13e**) bonds. The relative stabilities of the Fe−$C(NH_2)_2$ (**13d**) and Fe−CH_2 (**13e**) bonds as well as the B−O (**14p**) and B−C (**14r**) bonds explain the order of energies (Table 1) for the reactions of the substrates **9dr**, **9ep**, and **9dp**. The reaction energies for the substrates are in the order **9dp** (B−O and Fe−$C(NH_2)_2$)- > **9dr** (B−C and Fe−$C(NH_2)_2$) > **9ep** (B−O and Fe−CH_2) (Table 1).

Let us now discuss the details of the individual steps involved (Figure 1). The first step of the reaction is the formation of acyclic intermediate **10**, where X of EX forms a bond with B (Scheme 2). The HOMO of the Fe−borylene complex (**8**) is a d orbital, and the LUMO is a π^* MO largely localized on B (Scheme 3a). The HOMO of the substrates **9ap**, **9bp**, **9aq**, and **9bq** is a lone pair on the more electronegative X, and the LUMO is the σ^* MO at the E−X bond (Scheme 3c). On the other hand, the HOMO of **9dr**, **9ep**, and **9dp** is a π MO, which is mainly localized on X, and the LUMO is the π^* MO mainly localized on E. Hence, the acyclic intermediate **10** is formed by the donation of electrons from the HOMO of EX to the empty p orbital on the B atom (LUMO). This is in contrast with the formation of the four-membered cyclic intermediate in olefin metathesis by the attack of the π MO of olefin to the LUMO on metal. An acyclic intermediate $Cp(CO)_2FeBN(i\text{-}Pr)_2OPPh_3^+$ (**3**, where A = Ph_3P, X = O) was isolated for the reaction of Ph_3PO and Fe−borylene complex **1**.[14] The geometrical parameters of **10ap** (Supporting Information) are comparable to this experimentally reported structure. The Fe−B−X−E dihedral angle varies within a range of 0−20° in **10ap** (18.0°), **10bp** (22.4°), and **10aq** (1.2°), but the Fe−B−S−As dihedral angle in **10bq** is 67.8°. The larger value of this dihedral angle arises from the nonbonded interaction between the large H_3As group and the ligands on Fe. The donation of π electrons from EX to the empty p orbital on B is also reflected in the elongated E−X, Fe−B, and B−N bond distances in intermediate **10** (Supporting Information). The substrates **9dr**, **9dp**, and **9ep** also form the acyclic intermediates **10dr**, **10dp**, and **10ep**.

The descending order of negative charge on X in **9** is as follows: **9bp** > **9ap** >**9dp** > **9bq** > **9dr** > **9aq** > **9ep** (Table 1), while the order of stability of the intermediate **10** is **10bp** > **10ap** > **10dr** > **10dp** > **10ep** > **10bq** > **10aq** (Figure 1). The stability of **10dr** and **10ep** is not in accordance with the order of the negative charge on X. The analysis of charge distribution shows that **10ep** should be the least stable intermediate and **10dr** should be less stable than **10dp** and **10bq**. The stability of **10dr** over **10dp** is also not in tune with the greater stability of the B−O bond compared with the B−C bond (reaction 2c). The pyramidal N atom in **9dr** becomes planar in the intermediate **10dr** and results in the delocalization of electrons in the $BCH_2C(NH_2)_2$ moiety, which causes the additional stabilization. The extent of stabilization gained by **10ep** compared with **10bq** and **10aq** is attributed to the formation of the more stable B−O bond in **10ep** rather than the weak B−S bond in **10bq** and **10aq**. Thus, in general, the intermediate **10** is more stable when the X of EX has more negative charge. After the donation of π electrons from EX to the empty p orbital on the B atom, a decrease in the positive charge on the B atom and in the negative charge on X in the intermediate **10** is observed (Supporting Information).

The transition states **11ap**, **11bp**, and **11aq** are 21.3, 15.0, and 30.4 kcal/mol higher in energy than the respective intermediates **10**. Here the major interaction is between the filled metal d orbital (HOMO) and the σ^* MO (LUMO),

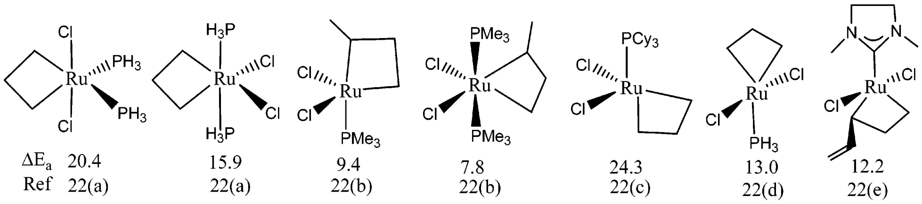

Figure 2. Four-membered transition states of different olefin metathesis reactions from the literature. The energy barriers (ΔE_a in kcal/mol) for the formation of the transition states and reference numbers are given below each structure.

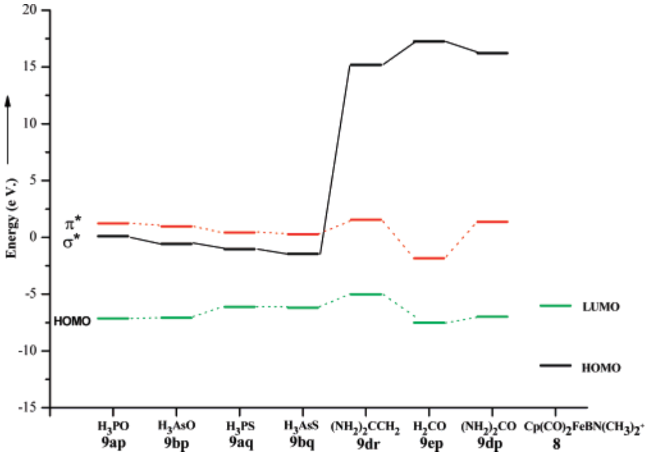

Figure 3. Correlation diagram between the HOMO, σ^*, and π^* MO levels of the substrates **9**. The HOMO and LUMO levels of **8** are also shown.

which is more localized on positively charged E (Scheme 3c). Therefore, the greater the positive charge on E in **10**, the lower the barrier for the formation of the products (Figure 1). The natural charges on E in **10ap**, **10bp**, and **10aq** are +1.15, +1.36, and +0.52, respectively. The descending order of charges on E in **10**, **10bp** > **10ap** > **10aq**, agrees with the ascending order of the energy barrier, **11bp** < **11ap** < **11aq**. It is possible that the nonbonded interaction between H_3As and the ligands on Fe, which results in the dihedral angle of 67.8° in **10bq**, prevents the approach of H_3As toward the metal center. We could not locate a transition state for this step. The cyclic intermediate **11ep** is similar to the intermediates in olefin metathesis and is formed by the donation of electrons from the d orbital of Fe (HOMO) to the empty π^* orbital (LUMO) at the O−C bond (Scheme 3, parts a and c). The C−O σ bond in **11ep** is not considerably affected in comparison to **11ap**, **11bp**, and **11aq**, and thus the four-membered cyclic intermediate can be stabilized. The structures **11dp** and **11dr** could not be located on the potential energy surface by us, probably due to the destabilizing nonbonded interaction between the ligands of the Fe−borylene complex and the substrates.

The transition states **11ap**, **11bp**, and **11aq** lead to the products **13** and **14** by breaking the Fe−B and E−X bonds. The energetics of the boron metathesis is greatly influenced by the bond energy of the Fe−E and B−X bonds in the products. The cyclic intermediate **11ep** goes to the products **13e** and **14p** via another acyclic intermediate **12ep**. The intermediates similar to **12ep** are not stationary points on the potential energy surfaces for the other substrates. The calculated energy barriers for the boron metathesis reaction are within the range of 15−30 kcal/mol. Figure 2 shows various four-membered transition states of the olefin metathesis reaction available in the literature.[22] The energy barriers for the formation of the transition states in the metathesis reaction of the Fe−borylene complex are in the range of those obtained for the olefin metathesis.

B. β-Hydride Transfer Versus Boron Metathesis. The reaction of Ph_2CO and $[Cp(CO)_2FeBN(i\text{-}Pr)_2]^+(BAr^f_4)^-$ (**1**) does not follow the metathesis pathway; the ligand transformation process, similar to the Meerwein−Ponndorf β-hydride transfer from an isopropyl substituent of the aminoborylene ligand to the coordinated ketone, takes place instead (Scheme 1b). In order to understand the energetics involved for this β-hydride transfer in comparison to the boron metathesis reaction, we have calculated the possible β-hydride-transfer products for all the substrates. The intermediate **10** can give either metathesis products (**13** and **14**) or hydride-transfer product (**16**) (Scheme 2). The metathesis products are formed by the donation of metal d electrons to the LUMO of the EX, and the hydride-transfer product is formed by the interaction of β-hydride with the LUMO of EX. Therefore, the preference of β-hydride transfer over metathesis depends upon the relative energies of these two interactions.

Figure 3 shows the correlation diagram connecting the HOMO, σ^*, and π^* MO levels of the substrates as well as the HOMO and LUMO of the Fe−borylene complex **8**. It is clear from the diagram that the substrates **9ap**, **9bp**, **9aq**, and **9bq** have a low-lying σ^* MO and the substrates **9dr**, **9ep**, and **9dp** have a low-lying π^* MO. This difference in energy levels is due to the weaker σ bond in **9ap**, **9bp**, **9aq**, and **9bq** compared with that in **9dr**, **9ep**, and **9dp**. The interaction of the hydride from the CH_3 group in $N(CH_3)_2$ with the low-lying σ^* MO of **9ap**, **9bp**, **9aq**, and **9bq** leads to the rupture of the E−X bond. As a result, β-hydride-transfer products could not be observed for these substrates. On the other hand, in the boron metathesis reaction, the metal d electrons (HOMO) are donated to the σ^* MO of the E−X bond, resulting in four-membered cyclic transition states (**11**). This transition state then undergoes Fe−B and E−X bond breaking and leads to the metathesis products **13** and **14** (Scheme 2). The β-hydride transfer is the competitive reaction to boron metathesis (Scheme 2) for the substrates with a low-lying π^* MO (**9dr**, **9ep**, and **9dp**) (Figure 3). The substrates that have a low-lying σ^* MO (**9ap**, **9bp**, **9aq**, and **9bq**) prefer boron metathesis to β-hydride transfer. Hence, substrates with a polar bond and a weak σ bond would be ideal for boron metathesis.

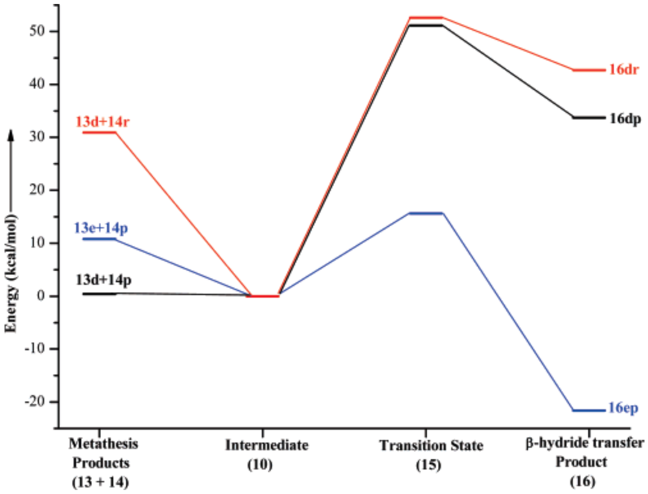

Figure 4. Relative energies of the metathesis products (**13** and **14**), the transition states (**15**), and hydride-transfer products (**16**) for the substrates **9dr**, **9ep**, and **9dp** with respect to intermediate **10**.

On the other hand, the hydride donates its electrons to the low-lying π^* MO of **9dr**, **9ep**, and **9dp** and leads to the β-hydride-transfer products **16dr**, **16dp**, and **16ep** through a six-membered cyclic transition state (**15**) (Scheme 2). The donation of metal d electrons to the π^* MO can form a four-membered cyclic intermediate as the E−X σ bond remains unbroken. However, the formation of the cyclic intermediate **11ep** is only observed for the small substrate **9ep** (H_2CO). The larger size of $(NH_2)_2C$ in **9dr** and **9dp** prevents their approach toward the metal center, and hence, intermediates **11dr** and **11dp** could not be located on the potential energy surface. This indicates that the substrates having a low-energy σ^* MO prefer the metathesis reaction over the β-hydride transfer. Both β-hydride transfer and metathesis reactions may take place when the substrates have a low-lying π^* MO. These reactions are also influenced by the steric nature of the substrates as well as the ligands on the metal−borylene complexes.

The relative energetics for the β-hydride transfer in comparison to the metathesis reaction, acquired by taking the intermediate **10** as the reference, is shown in Figure 4. The energy barriers for the formation of the transition states **15dr**, **15ep**, and **15dp** are 52.6, 15.6, and 51.1 kcal/mol, respectively (Figure 4). The order of stability of the hydride-transfer products is **16ep** > **16dp** > **16dr**. The **16ep** structure is more stable than that of **10ep**, whereas both **16dp** and **16dr** are less stable than the corresponding intermediates **10**. It is also more stable than the metathesis products **13e** and **14p** (Figure 4). On the other hand, the hydride-transfer products **16dp** and **16dr** are less stable than the corresponding metathesis products. The NH_2 group in **10dp** and **10dr** is planar and stabilized by conjugation whereas that in the transition states (**15dr** and **15dp**) as well as in the hydride-transfer products (**16dp** and **16dr)** is pyramidal. This results in the high barrier for the transition states **15dp** and **15dr** and the formation of corresponding hydride-transfer products becomes unfavorable. The greater stability of **16ep** compared with **10ep** is also attributed to the delocalization present in the CH_2NBO fragment. The nature of the β-hydride-transfer products is almost similar to the corresponding intermediates (**10**). Thus, the relative stabilities between the metathesis products and the β-hydride-transfer product in comparison to the intermediate **10** depend on the stability of the Fe−E bond formed in the metathesis product **13**. Since the Fe−C bond in $Fe-C(NH_2)_2$ is more stable than the Fe−C bond in $Fe-CH_2$, the metathesis product formation of the substrates **9dp** and **9dr** is more favorable than that of the corresponding β-hydride-transfer products. Since the $Fe-CH_2$ bond in **13e** is less stable, the metathesis product formation for **9ep** is less favorable compared with the formation of β-hydride-transfer product **16ep**. This supports the experimental observation for the formation of the β-hydride-transfer product for the reaction of Ph_2CO with **1**.

The substituents without a β-hydrogen atom on boron can be used to direct the reactivity of borylene complexes toward metathesis. In summary, β-hydride transfer from the ligand on boron may be a competitive reaction to boron metathesis. The substrates having a low-energy σ^* MO prefer boron metathesis to hydride transfer.

Conclusions

The metathesis reaction of the Fe−borylene complex takes place with the initial attack of the electronegative end (X) of the substrate EX on the B atom, leading to an acyclic intermediate **10**. The positively charged E of this acyclic intermediate accepts electrons from the metal d orbital and forms a four-membered intermediate or transition state, which depends on the σ^* and π^* levels of the substrate EX. The boron metathesis is more favorable for those substrates that have a low-lying σ^* MO (weak σ bond). The β-hydride transfer is a competitive reaction to boron metathesis for the substrates having a low-energy π^* MO. The relative stability of the products is controlled by the strength of both Fe−E and B−X bonds. The energetics of the boron metathesis reaction is comparable to that of the olefin metathesis. The metathesis reactions of the Fe−borylene complex **8** with all the substrates (Scheme 2) indicate the role of polarity in tuning the reaction in a preferred direction.

Similar transition-metal−borylene complexes with other metals are good candidates for boron metathesis reactions using polar substrates. Experimentally aryl−borylene and boryl complexes are also known to undergo different types of reactions with substrates containing double bonds, e.g., C═C and C═O. These complexes are not yet explored for the metathesis, but the present study points to a rich chemistry awaiting for the reactions of aryl−borylene and boryl complexes toward metathesis. The results on metathesis involving other metals will be published later.

Acknowledgment. We thank the Centre for Modelling, Simulation and Design (CMSD), the High Performance Computing Facility (HPCF) of the University of Hyderabad, the Maui High Performance Computing Center (MHPCC) at Hawaii, and the Supercomputer Education and Research

Centre (SERC) of the Indian Institute of Science for their computational facilities. The support of the Board of Research in Nuclear Sciences (BRNS), Mumbai, for our research in boron chemistry is gratefully acknowledged. S.D. and P.P. gratefully acknowledge research fellowships from CSIR and BRNS, respectively. We thank the referees for their valuable suggestions.

Supporting Information Available: Total energy, important geometrical parameters, natural charges, interaction diagram between $Cp(CO)_2Fe^+$ and $BN(CH_3)_2$ fragments in Fe−borylene complexes, optimized Cartesian coordinates and geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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