



# Propane CH activation by palladium complexes bearing ligands with Charge-shift bonding characteristics: A DFT study



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## ABSTRACT

Using density functional theory (DFT), we have investigated the conversion of propane to propyl trifluoroacetate catalyzed by five kinds of (bis-2BB)PdBr<sub>2</sub> complexes (bis-2BB is the derivatives of bis-2-borabicyclo[1.1.0]but-1(3)-ene). Calculated results indicate that the (bis-2BB)PdBr<sub>2</sub> catalysts are superior to the popular (bis-NHC)PdBr<sub>2</sub> complex in the desired catalytic process, consistent with the previous results of the conversion of methane to methyl trifluoroacetate catalyzed by (bis-2BB)PdBr<sub>2</sub> complexes. Moreover, calculated natural charges and Wiberg bond index (WBI) values involving Pd(II) reveal that the charge-shift (CS) bonding characteristics in the bis-2BB ligands contributes to the improved catalytic performance of the (bis-2BB)PdBr<sub>2</sub> complexes. Thus, we suggested that Pd(II)-catalysts having the ligands with CS bond might be promising organometallic catalysts for the activation and functionalization of C–H bond in alkanes.

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## 1. Introduction

Since Shilov proposed that the reactions of hydrocarbons catalyzed by transition metal complexes can be selective at low temperatures in 1997 [1], the activation and functionalization of C–H bonds in alkanes have a standing interest in experimental and theoretical fields [2–12]. In general, the catalysts for the activations of the alkane C–H bonds are platinum [13–18], palladium [19–22], rhodium [23–26] and iridium [27–29] complexes. Specially, the platinum or the palladium complexes show their capabilities of doing selective direct oxidization of lower hydrocarbons to alcohols [30–33] or carboxylic acid [19,20]. Recently, Pd(II)-(bis-NHC) (NHC is *N*-heterocyclic carbene) complexes were found to have highly catalytic activity for the activation of C–H bond in methane compared with the palladium acetate [33–36]. Also, the conversion of methane to methyl trifluoroacetate catalyzed by (bis-NHC)PdBr<sub>2</sub> complex have been investigated both experimentally [33] and theoretically [37]. Moreover, the higher activity of (bis-NHC)PdBr<sub>2</sub> complex indicates that the ligands play an important role for designing palladium complexes for the activation and functionalization of C–H bonds in methane. Afterwards, we theoretically designed five kinds of palladium complexes supported by the derivatives of bis-2-borabicyclo[1.1.0]but-1(3)-ene (bis-2BB) ligands and used these complexes to the conversion of methane

to methyl trifluoroacetate [38]. Interestingly, we found that the (bis-2BB)PdBr<sub>2</sub> complexes can improve catalytic performance compared with the (bis-NHC)PdBr<sub>2</sub> complex [38]. In addition, the calculated results reveal that the high activity of the (bis-2BB)PdBr<sub>2</sub> catalysts on the C–H bond activation in methane results from the charge-shift (CS) bond [39–43] in bis-2BB ligands. In order to further insight into the catalytic property of the (bis-2BB)PdBr<sub>2</sub> complexes toward the cleavage of C–H bond in alkane, we have theoretically investigated the conversion of propane to propyl trifluoroacetate catalyzed by (bis-2BB)PdBr<sub>2</sub> complexes in this contribution. We anticipated that the molecules with CS bonding characteristics as ligands can be used to design more efficient catalysts for C–H bond activation and functionalization, as well as the complexes bearing the ligands with CS bond were widely used in organometallic and catalytic domain.

## 2. Computational details

The structural optimization and frequency calculation of the compounds involved in the conversion of propane to propyl trifluoroacetate catalyzed by five (bis-2BB)PdBr<sub>2</sub> complexes and the analogues (bis-NHC)PdBr<sub>2</sub> complex were carried out using hybrid density functional B3LYP [44–48], in combination with the Hay-Wadt(*n*+1) effective core potential (ECP) basis set for the Pd center [49] and the standard 6-31G(d) basis set [50–52] for the other atoms. This computational methods are the same as those of employed in the literature [53]. Intrinsic reaction coordinate

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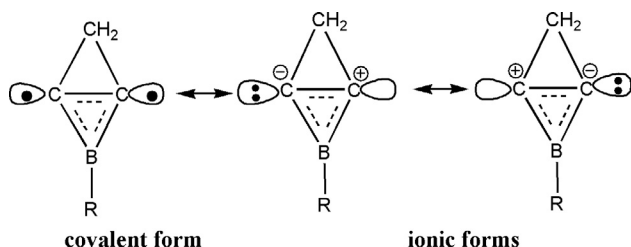
(IRC) calculations were performed in order to confirm the transition state structures connecting the reactants and products. Single point calculations were obtained by using dispersion corrected B3LYP-D3(BJ) [54–55], in combination with the Hay-Wadt(n+1) ECP basis set for the Pd atom [49] and the 6-311++G(d,p) basis set [56–58] for the other atoms.

The polarizable continuum model of conductor solvent (C-PCM) [59–60] are used to solvation effects, in which the C-PCM solvent parameters are selected as in Ref. [53]. All reported Gibbs free energies were obtained under standard conditions ( $T = 298.15$  K,  $P = 1$  atm). All the calculations involving C-PCM were performed using Gaussian 03 program [61], while the other calculations were carried out within the Gaussian 09 program [62].

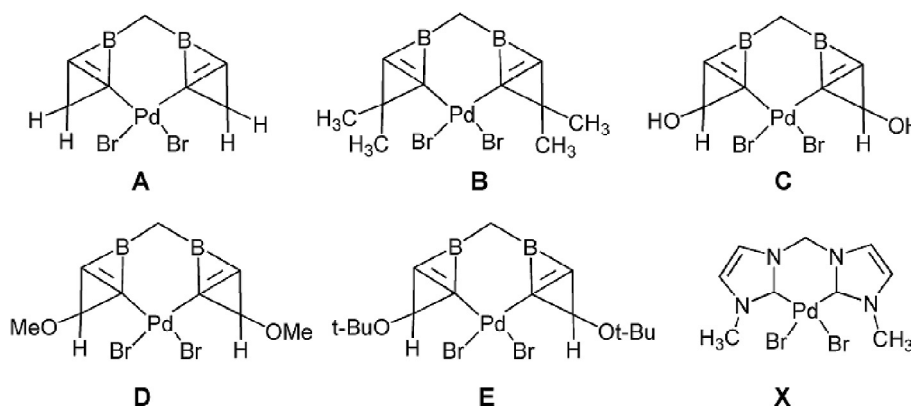
### 3. Results and discussion

The electronic structures of 2-borabicyclo [1.1.0]but-1(3)-ene (2BB) were displayed in Scheme 1. Scheme 1 shows that the  $sp^2$  hybrid orbitals of the two horizontal carbons are situated in opposite directions. According to the characteristics of CS bonding of [1.1.1]propellane [39–42], as well as chemical bond of the derivatives of 2BB, we found that the horizontal C–C bond in the derivatives of 2BB is a CS bond [43]. Moreover, we found that the ionic structures of the derivatives of 2BB can serve as ligand to coordinate with the transition metal [43].

Then the five (bis-2BB)PdBr<sub>2</sub> complexes (A–E) as catalysts for the conversion of propane to propyl trifluoroacetate were designed based on the ligand discussed above and displayed in Scheme 2. (bis-NHC)PdBr<sub>2</sub> complexes (X) used in Ref. [53] was also given in Scheme 2 for the sake of comparing with A–E. The complexes X and A–E are the catalysts for the activation of C–H bond in methane and the optimized geometries of complexes X and A–E herein can be referenced in Ref. [38].



**Scheme 1.** The charge-shift bonding of the horizontal C–C bond of the derivatives of 2-borabicyclo [1.1.0]but-1(3)-ene (2BB) arising from the mixture of covalent and ionic resonance structures.



**Scheme 2.** The structures (bis-2BB)PdBr<sub>2</sub> complexes (A–E) and (bis-NHC)PdBr<sub>2</sub> complex (X).

The reaction mechanism of (bis-2BB)PdBr<sub>2</sub> complexes (A–E) as catalysts for the conversion of propane to propyl trifluoroacetate have been investigated, following to the reaction pathway of propane to propyl trifluoroacetate conversion as identified for the complex X [53]. The reaction processes of propane to propyl trifluoroacetate conversion catalyzed by A–E was illustrated in Scheme 3. The first step (I) is that the C–H activation in propane and form (bis-2BB)Pd(*n*Pr) intermediate. In this step, the substitution of OTFA<sup>−</sup> (OTFA is CF<sub>3</sub>COO<sup>−</sup>) for Br<sup>−</sup> in (bis-2BB)PdBr<sub>2</sub> (A–E) forms (bis-2BB)Pd(OTFA)<sub>2</sub> (A1–E1), then one of OTFA<sup>−</sup> in A1–E1 is replaced by propane to give more stable structure of (bis-2BB)Pd(OTFA)(*n*-C<sub>3</sub>H<sub>8</sub>) ("A2–E2") (*n*-C<sub>3</sub>H<sub>8</sub> represents the terminal C–H bond in propane to bind Pd(II) as shown in Scheme 4, while *i*-C<sub>3</sub>H<sub>8</sub> represents the middle C–H bond in propane to bind Pd(II)). "A2–E2" forms the intermediate (bis-2BB)Pd(*n*Pr)(HOTFA) ("A3–E3", HOTFA is CF<sub>3</sub>COOH) via the proton transfer from propane to OTFA. (bis-2BB)Pd(*n*Pr) ("A4–E4") was obtained by removal of HOTFA from "A3–E3". The second step (II) is the isomerization of (bis-2BB)Pd(*n*Pr) ("A4–E4") to (bis-2BB)Pd(*i*Pr) ("A4–E4"). The last step (III) is that the oxidation and reductive elimination of "A4–E4" generates A–E and *i*Pr-OTFA. As seen from Scheme 3, the reaction processes of the conversion of propane to propyl trifluoroacetate are significantly different from that of methane to methyl trifluoroacetate because of the two kinds of different C–H bonds (terminal and middle C–H bonds) in propane and only one kind of C–H bond in methane. Thus, the C–H activation of propane is more complex than that of methane.

We first considered the first step (I) of the conversion of propane to propyl trifluoroacetate, i.e. the activation of C–H bond in propane. The reaction profiles of the activation of C–H bond in propane catalyzed by A–E were calculated and displayed in Fig. 1(1–5), respectively. Moreover, in order to compare the catalytic ability of A–E with the X used in Ref. [53], the reaction profile of the C–H activation in propane catalyzed by X was depicted in Fig. 1(6). As seen from Fig. 1(1–5), the reaction of (bis-2BB)PdBr<sub>2</sub> (A–E) + 2OTFA<sup>−</sup> → (bis-2BB)Pd(OTFA)<sub>2</sub> (A1–E1) + 2Br<sup>−</sup> is exergonic. And the reaction free energies are −51.8, −50.2, −53.2, −47.2 and −47.5 kcal/mol, respectively, which are close to that of the reaction of (bis-NHC)PdBr<sub>2</sub> (X) + 2OTFA<sup>−</sup> → (bis-NHC)Pd(OTFA)<sub>2</sub> (X1) + 2Br<sup>−</sup> as shown in Fig. 1(6). The substitution of propane for one of OTFA<sup>−</sup> in A1–E1 will form two kinds of isomers, one is Pd(II) binds to the terminal C–H bond in propane as shown in Scheme 4 ("A2–E2") and another is Pd(II) binds to the middle C–H as shown in Scheme 4 ("A2–E2"). Both substitutions of propane for one of OTFA<sup>−</sup> in A1–E1 are endothermic, consistent with that in X1. However, the energy of "A2–E2" is lower than that of "A2–E2" by 2.0, 0.6, 3.4, 2.7 and 3.1 kcal/mol, respectively. In addition, the energy barrier of "A2–E2" → "A3–E3" via "TS<sub>A2-A3</sub>"–"TS<sub>E2-E3</sub>" is also lower than

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