

# Computational study of the transmetalation process in the Suzuki–Miyaura cross-coupling of aryls

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Received 31 October 2005; received in revised form 6 February 2006; accepted 13 February 2006

Available online 6 March 2006

## Abstract

The transmetalation step of the Suzuki–Miyaura cross-coupling between aryl groups is analyzed by means of DFT calculations with the Becke3LYP functional. The halide considered is Ph–Br, and the organoboronic acid is Ph–B(OH)<sub>2</sub>. The model catalyst is Pd(PH<sub>3</sub>)<sub>2</sub>, and the base, OH<sup>−</sup>. The transmetalation is considered to start from the Pd(Ph)(PH<sub>3</sub>)<sub>2</sub>Br complex, the product of the oxidative addition. The results are compared with those of a previous study on the analogous reaction with vinyl groups, and it is shown that the reaction mechanism is very similar.

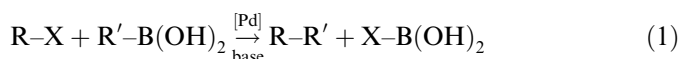
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**Keywords:** Cross-coupling; Density functional theory; Suzuki–Miyaura reaction; Transmetalation; Biaryl

## 1. Introduction

Palladium-catalyzed cross-coupling reactions provide a versatile and efficient method to C–C bond formation, permitting the synthesis of a wide variety of compounds from simple precursors [1–10]. The Suzuki–Miyaura reaction, where organoboron compounds (mainly organoboronic acids) couple with organic halides (or triflates) in presence of a Pd-catalyst and a base are among the most successful cross-coupling processes (Eq. (1)) [1–3,5,10–18]. Although boron–carbon bonds are highly covalent and inert to ionic reactions, these reagents present several advantages towards other organometallic reagents. They have been largely used in industries and laboratories because they are thermally stable, tolerate a broad range of functional

groups and reaction conditions and lead to the formation of nontoxic products [2,12,15]

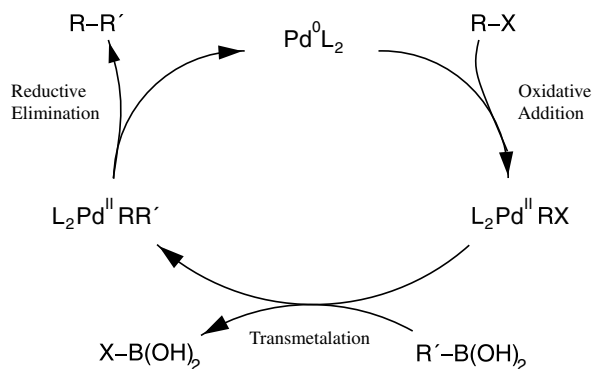


The catalytic cycle depicted in Scheme 1 is the generally accepted mechanism for the cross-coupling reactions. The catalyst is assumed to be a reactive 14-electron Pd<sup>0</sup>L<sub>2</sub> species [19–22], where L is usually phosphine. The whole mechanism could be described in three main steps [2,23]: (a) oxidative addition, (b) transmetalation, and (c) reductive elimination. Contrary to steps (a) and (c), that have been the subject of several experimental [24–30] and theoretical [31–40] studies less is known about the transmetalation process [41–50]. This is thus the most characteristic step of the cross-coupling reactions. This step seems furthermore to require the presence of a base in order to take place.

There are two main proposals for the role of the base in the transmetalation process [42]. These proposals are identified as paths A and B in Scheme 2. In path A, the base initially binds to the organoboronic acid to form the

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Scheme 1. General mechanism for cross-coupling reactions.

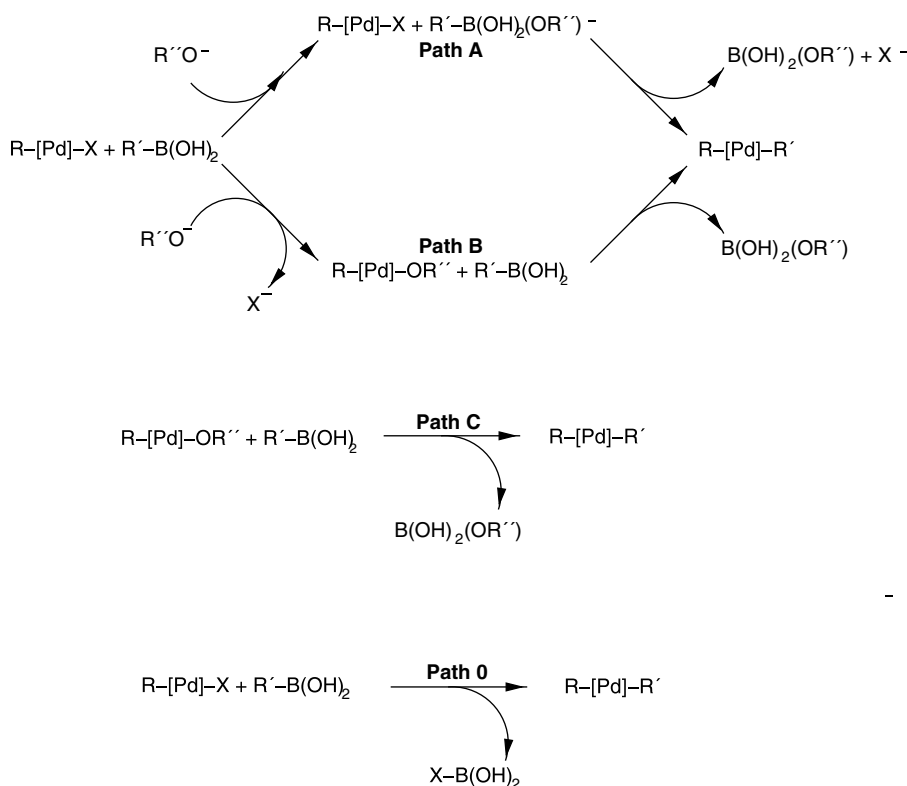
corresponding organoboronate specie  $\text{R-B(OH)}_3^-$ , which can undergo the transmetalation process with the palladium complex. In path B, the base directly replaces the halide in the coordination sphere of the palladium complex, forming an (oxo)palladium(II) complex. Experiments have shown [23,51] that once formed, this complex is able to react with the organoboronic acids without the presence of a base (path C).

Different aspects of the mechanism of cross-coupling processes have been recently studied with computational methods [40,52–66]. In particular, we have investigated proposals A, B and C for transmetalation by means of DFT calculations with Becke3LYP functional [67] for the cross-coupling reaction between vinyl groups. In that study, the starting catalyst was the complex *trans*-Pd(CH=

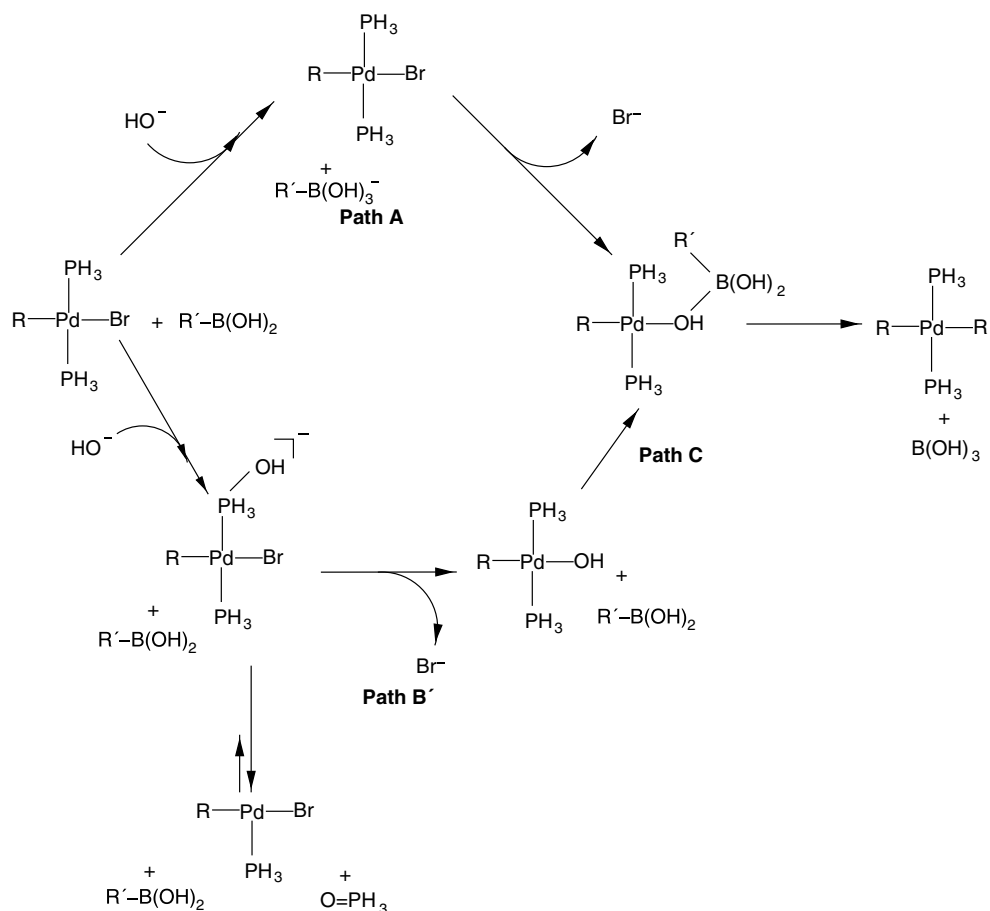
$\text{CH}_2$ )( $\text{PH}_3$ ) $_2$ Br, with  $\text{CH}_2=\text{CHBr}$  as the organoboronic acid, and  $\text{OH}^-$  as the base.

The results from our previous computational study are summarized in Scheme 3. Path A goes quite smoothly, with the highest energy transition state computed in only 4.2 kcal/mol above the separated reactants. This is not the case of path B. The base was shown unable to replace directly the bromide ligand in the Pd catalyst. An alternative path, labelled B', was found. In path B' the base initially binds to one of the phosphines and attacks the Pd center afterwards. Path B' does not seem however to be the responsible for transmetalation, because it should lead to phosphine oxidation and catalyst destruction, as is in fact observed in some experiments [44,68]. Path C, where the starting complex was the Pd(II)-oxo complex Pd(CH=CH $_2$ )( $\text{PH}_3$ ) $_2$ (OH), was also computed and found to proceed through a transition state of only 0.6 kcal/mol above the separated reactants. Path 0, where the reaction proceeds with no base, was found to have a high barrier of 44.6 kcal/mol above of the separated reactants. In addition, the steric effects of a more realistic ligand as triphenylphosphine,  $\text{PPh}_3$ , were introduced by means of ONIOM(Becke3LYP:UFF) calculations. This brought little change to the overall picture.

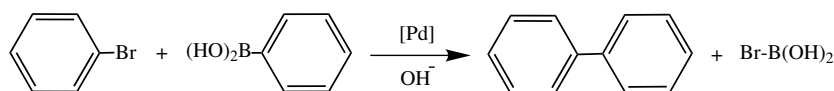
All these previous calculations were carried out on the Suzuki–Miyaura cross-coupling reactions of vinyl groups. There are some experimental results on the cross-coupling of vinyl groups, but most reactions take place between aryl groups. In the present article we intend to evaluate if the



Scheme 2. Proposals for the transmetalation process in presence (Paths A and B) and absence (paths C and 0) of a base.



Scheme 3. Summary of the pathways obtained by means of DFT calculations to clarify the role of the base in the Suzuki–Miyaura cross-coupling reaction [67].



Scheme 4. Suzuki–Miyaura biaryl reaction.

conclusions obtained for vinyl substrates are still valid for aryl substrates. In order to do it, calculations for paths 0, A and C are carried out on the aryl system presented in Scheme 4.

## 2. Computational methodology

All calculations were performed at the DFT level, by means of the hybrid Becke3LYP [69–71] functional, with a hybrid Becke3 exchange functional and a Lee–Yang–Parr correlation functional [69,70] as implemented in Gaussian98 [72]. Pd and Br atoms were described using an effective core potential (LANL2DZ) for the inner electrons [72,73], and its associated double- $\zeta$  basis set for the outer ones. In the case of Br atom d-polarization functions were added (exponent 0.4280) [74]. The 6-31G(d) basis set was used for the atoms H, B, C, O and P [75]. In the mechanisms where anionic species are involved, a set of diffuse functions were added for Br atoms [76] and B, C, O and

P atoms [77]. The structures of the reactants, intermediates, transition states and products were fully optimized in gas phase without any symmetry restriction. Transition states were identified by having one imaginary frequency in the Hessian matrix.

## 3. Results

We present in this section our theoretical studies on the transmetalation step of the coupling reaction between PhBr, **1**, and PhB(OH)<sub>2</sub>, **2**. The reaction is mediated by Pd(PH<sub>3</sub>)<sub>2</sub>, **3** as catalyst in the presence of OH<sup>-</sup>, **4**, as the base. The starting complex for the transmetalation process is *trans*-Pd(Ph)(PH<sub>3</sub>)<sub>2</sub>Br, **5**, which is generally accepted as the product for the oxidative addition of **1** to **3**. All the energies presented in the computed profiles will be referred to the corresponding separate reactants.

*Path 0*: The first path studied was the transmetalation process between *trans*-Pd(Ph)(PH<sub>3</sub>)<sub>2</sub>Br, **5** and PhB(OH)<sub>2</sub>,

2, producing *trans*-Pd(Ph)<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub>, **6**, and BrB(OH)<sub>2</sub>, **7**, in the absence of a base.

Fig. 1 presents the optimized geometries and Fig. 2 the energy profile of this transmetalation process. Before the transmetalation itself, the complex **I01** is formed. It corresponds to the hydrogen-bonded complex between **5** and **2**, with a H···Br distance of 2.538 Å. The transmetalation takes place in one step, represented by the transition state, **TS01** (317i cm<sup>-1</sup>). A concerted mechanism is observed, with the bromide migrating from the Pd center to the organoboronic acid and the phenyl ligand leaving to the metal. The B–C and Pd–Br breaking bonds were computed as 2.175 and 3.273 Å, respectively. The distance of the forming bond between Pd and C was 2.251 Å. In the products **6** and **7** the distances of the formed bonds Pd–C and Br–B become 2.118 and 1.962 Å, respectively.

As shown in the energy profile (Fig. 2) the initial hydrogen-bond complex **I01** is 9.4 kcal/mol below the separated reactants (**5** and **2**). The overall reaction is endothermic by 32.3 kcal/mol, with the energy barrier of the transition state (**TS01**) 48.7 kcal/mol above the separated reactants. This profile is a clear evidence of the impossibility of the transmetalation process in the absence of the base.

*Path A:* This path starts from the Pd complex, **5**, and Ph–B(OH)<sub>3</sub><sup>-</sup>, **8**. The latter species is formed from the reaction between OH<sup>-</sup> and the organoboronic acid, in a process that was shown to be practically barrierless for the vinyl analogous [67].

Fig. 3 presents the geometries of selected structures for path A and Fig. 4 presents the energy profile for this process. The initial approach between **5** and **8** produces the intermediate **IA1**. After that the process evolves in two

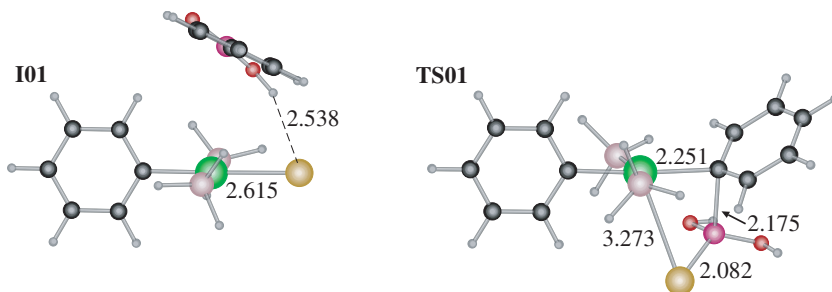


Fig. 1. Geometries of selected structures for reaction path 0. Distances are in angstroms.

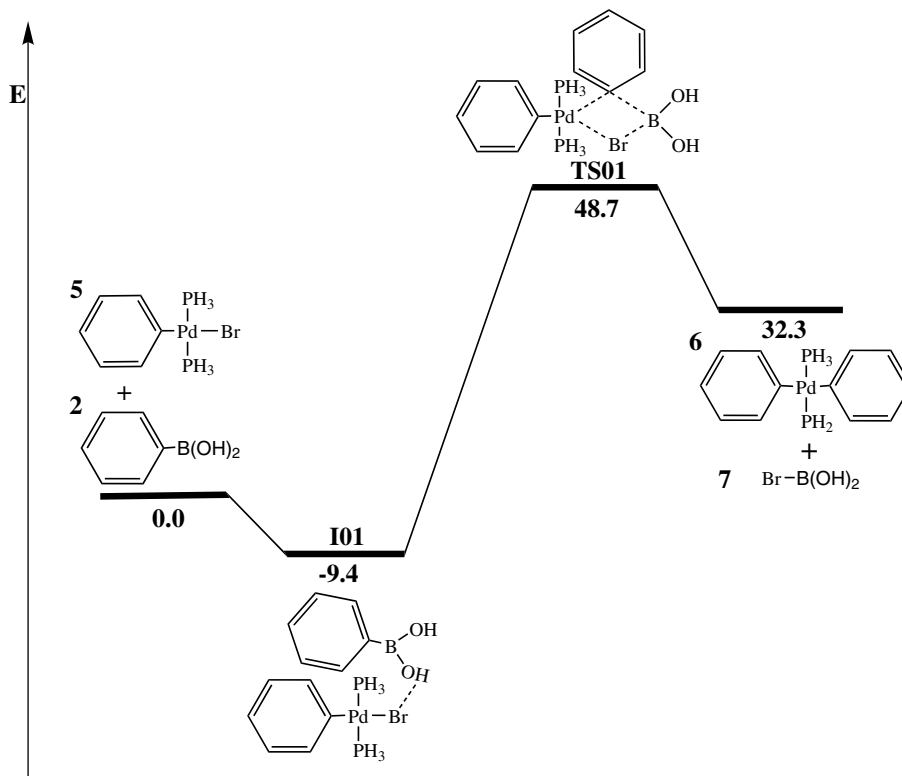


Fig. 2. Energy profile for transmetalation path 0.

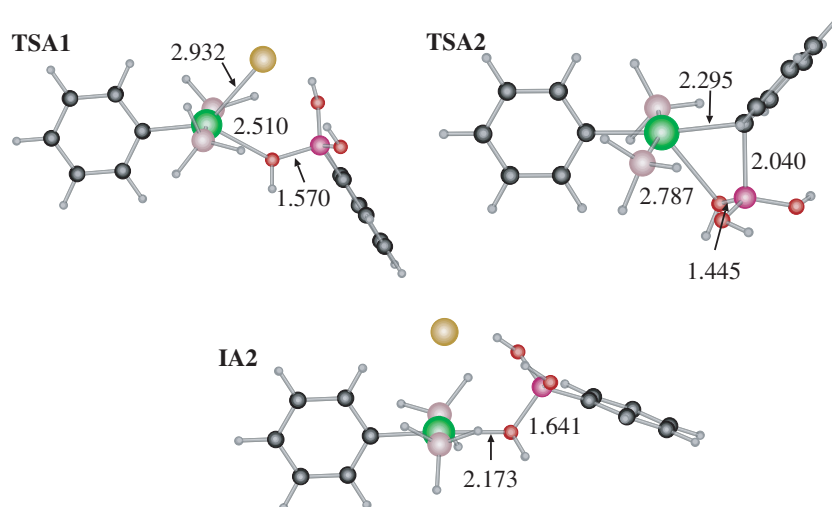


Fig. 3. Geometries of selected structures for reaction path A. Distances are in angstroms.

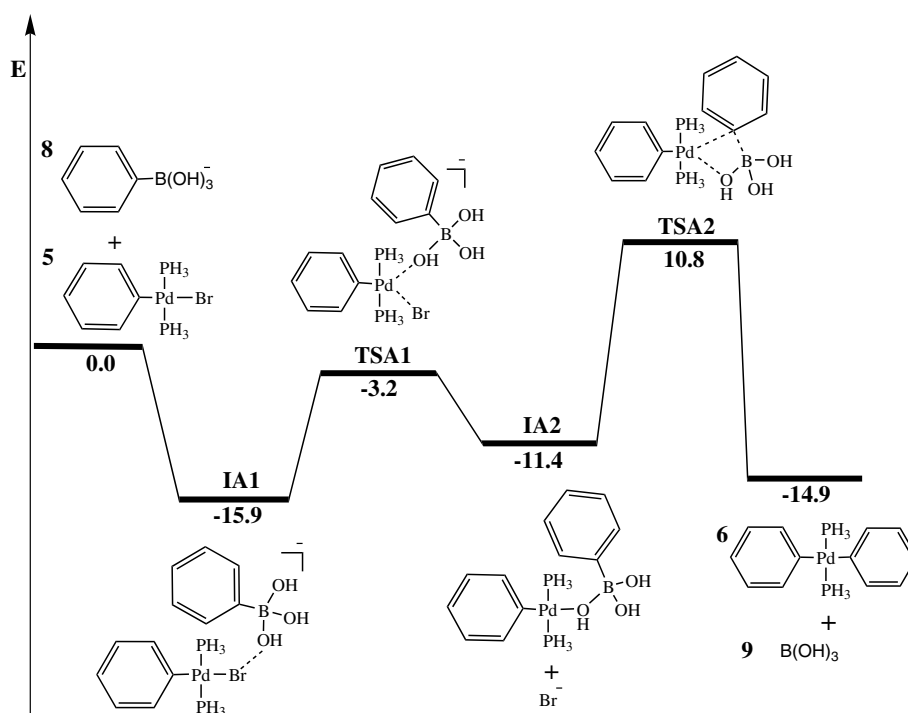


Fig. 4. Energy profile for transmetalation path A.

stages. In the first one the boronic acid replaces the bromide in the Pd complex. This process produces the intermediate **IA1** by going through the **TSA1** ( $69i\text{ cm}^{-1}$ ) transition state. At **TSA1** the distance of the breaking bond Pd–Br and the forming Pd–O are computed as 2.932 Å and 2.510 Å, respectively. These distances became 2.173 and 3.637 Å in the intermediate **IA2**, respectively. Once the  $\text{Br}^-$  is released it does not participate in the remaining process and it does not need to be further considered.

In the next step the transmetalation itself takes place, leading to the formation of products **6** and **9**. The transition state **TSA2** ( $287i\text{ cm}^{-1}$ ) represents a concerted process

where the phenyl migration from the boronic species to the metal is carried out, while the  $\text{B}(\text{OH})_3$  group is released. The distances of the forming Pd–C and breaking Pd–O are 2.787 and 2.040 Å, respectively.

As shown by the energy profile (Fig. 4) the initial intermediate **IA1** is  $-15.9\text{ kcal/mol}$  lower in energy than the reactants (**8** and **5**). The energy of the next intermediate **IA2** is  $-11.4\text{ kcal/mol}$ , whereas the transition state **TSA1** presents a computed energy of  $-3.2\text{ kcal/mol}$ . Finally, the energy of the last transition step (**TSA2**), where the phenyl definitely occupies a coordination site in the Pd center, was calculated in  $10.8\text{ kcal/mol}$  above the separated reactants.

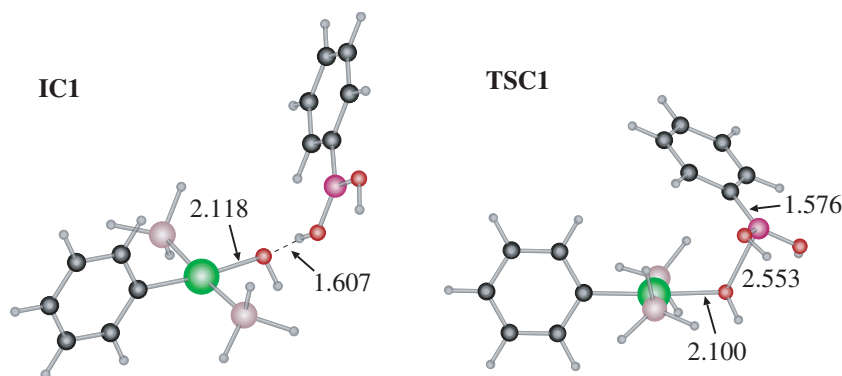


Fig. 5. Geometries of selected structures for reaction path C. Distances are in angstroms.

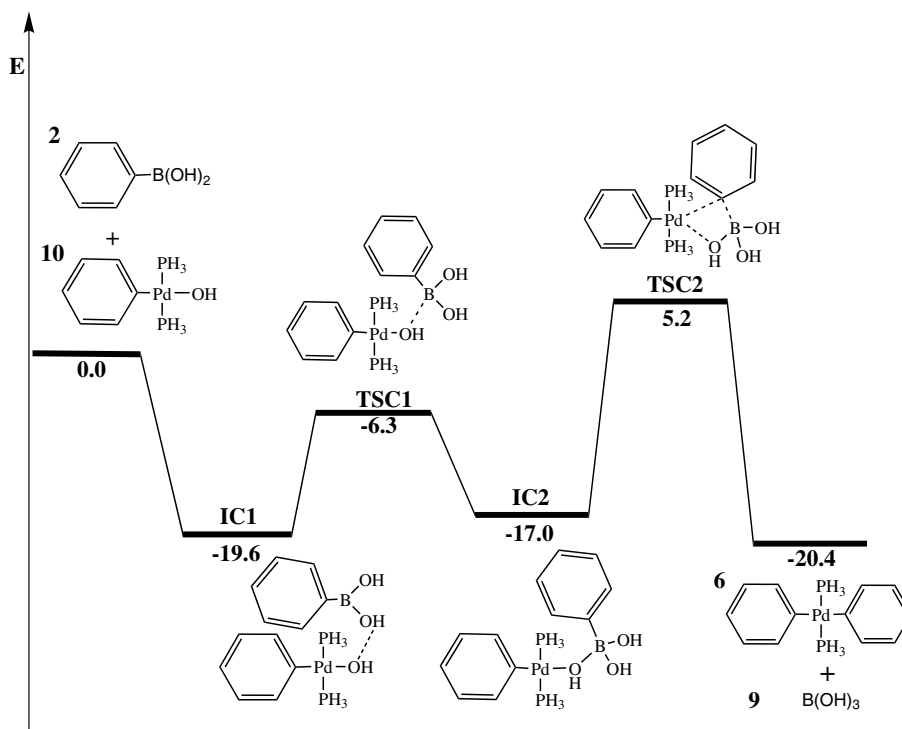


Fig. 6. Energy profile for transmetalation path C.

Thus, the overall reaction of this transmetalation process is exothermic, being 14.9 kcal/mol the difference between the energy of the reactants and products. The energy profile is smooth, with the highest energy (**TSA2**) being 10.8 kcal/mol above the reactants, and 26.7 kcal/mol above the lowest energy minimum. The latter value is similar to the 26.2 kcal/mol computed by Goossen, Thiel and co-workers for the transmetalation step involving acetic anhydride with phenylboronic acid [64].

*Path C:* The reaction here was carried out between the organoboronic acid **2** and the Pd(II)-oxo complex **10**. Figs. 5 and 6 present the selected optimized geometries and energy profile of path C. The process takes place in two stages. First, after the initial hydrogen-bond intermediate, the organoboronic acid binds through its B atom to the OH group of the Pd complex **10**.

The first intermediate, **IC1** (−19.6 kcal/mol), results from the interaction between complex **10** and the organoboronic acid **2**. The O...H distance was computed as 1.607 Å. After that, the B center binds to the OH group attached to Pd. This step going through the **TSC1** (1071 cm<sup>−1</sup>) transition state, produces the intermediate **IC2**. In the case of **TSC1** the breaking B–O distance was calculated as 2.553 Å and the Pd–O forming bond presented a distance of 2.100 Å. In the next intermediate (**IC2**) the B–O and Pd–O distances were computed as 1.568 and 2.166 Å, respectively. The energies of **TSC1** and **IC2** were calculated as −6.3 kcal/mol and −17.0 kcal/mol below the separated reactants, respectively. It is worth mentioning that the intermediates **IC2** (path C) and **IA2** (path A) are essentially equivalent, though in the latter the leaving bromide continues interacting with OH groups.

Structures of the transition states **TSC2** and **TSA2** are in turn also equivalent. Hence, the energy difference from the intermediate **IC2** to the transition state **TSC2** is the same value as that computed between **IA2** and **TSA2** (22.2 kcal/mol). The pattern of the energy profile obtained for path C reproduces in part the profile of path A.

#### 4. Discussion

The mechanism of the transmetalation process in Suzuki–Miyaura cross-coupling reactions of aryl groups has been studied by means of DFT calculations. The reaction studied consists of the coupling between phenylboronic acid, **2**, and the complex *trans*-Pd(Ph)(PH<sub>3</sub>)<sub>2</sub>Br, **5**. The main target of this work was to check whether the conclusions obtained in a previous computational study on the role of the base in the reaction of vinyl groups were still valid for the case of the more usual phenyl groups. Three different possible reaction paths were considered, A, C and 0 (Schemes 1 and 2). Path B, which was found not operative in the previous study on vinyl coupling, was not considered in this study.

The first path studied was the reaction in absence of a base, identified as path 0. In this hypothetical mechanism the organoboronic acid, **2**, reacts directly with the Pd complex **5**. The reaction is endothermic in 32.3 kcal/mol and takes place in only one step. The highest energy point is 48.7 kcal/mol above the reactants. These results are in good agreement with those of the previous study on vinyl. In the former case, the reaction was also endothermic (31.6 kcal/mol) and the highest energy point was 44.6 kcal/mol above the reactants. The main difference between the two systems is the existence in the vinyl case of an  $\eta^2$  intermediate where the organoboronic acid coordinates the Pd center through its double bond. This intermediate was separated from the reactant complex by a barrier of only 1.4 kcal/mol. It is thus not surprising that it does not exist when vinyl is replaced by the less coordinating phenyl group. In any case, this eventual intermediate is not relevant for the overall pathway, which remains forbidden because of its high barrier.

In path A, the base reacts initially with the organoboronic acid to afford the corresponding organoborate anion, which then reacts with the palladium complex. This was found to be the most efficient path for the reaction to take place in the case of the vinyl systems. As shown experimentally [44], the addition of base to a solution of R–B(OH)<sub>2</sub> is a reaction highly displaced to the formation of the R–B(OH)<sub>3</sub><sup>−</sup> species. In the case of the phenyl systems studied here, the pathway is also smooth. The reaction is exothermic by 14.9 kcal/mol, and the highest energy point is 10.8 kcal/mol above the reactants. This can be compared with the exothermicity of 17.4 kcal/mol and the highest energy of 4.2 kcal/mol obtained for the vinyl systems. As for path 0, there is an  $\eta^2$  intermediate that disappears when vinyl is replaced by the less coordinating phenyl group. Interestingly, this intermediate is directly connected to

the highest energy point of the path. The absence of this stabilizing interaction could explain why this point is 6.6 kcal/mol higher in the case of the phenyl reaction. The Pd–C distances (2.250 Å for vinyl, 2.295 Å for phenyl) give further support to this hypothesis. In any case, also in the case of phenyl, path A is smooth enough to explain the overall process that takes place experimentally.

A final set of calculations was carried out on path C. In this case, the transmetalation starts from the oxo-palladium complex which already contains the OH ligand, and no base is added. The overall reaction for the phenyl systems is exothermic (−20.4 kcal/mol) and the reaction evolves quite smoothly, with the highest energy point 5.2 kcal/mol above the reactants and 24.8 kcal/mol above the lowest energy minimum. These values are similar to those previously reported by Sakaki and co-workers for the reaction between Pd(OH)(Ph)(PH<sub>3</sub>)<sub>2</sub> and B<sub>2</sub>(eg)<sub>2</sub> (eg = −OCH<sub>2</sub>CH<sub>2</sub>O−), which were 6.9 and 24.0 kcal/mol, respectively [60]. The values were similar also in our previous study for vinyl (0.6, −21.0 kcal/mol), the only difference between both profiles being again the absence of an  $\eta^2$  intermediate in the case of phenyl.

#### 5. Conclusion

The role of the base in the transmetalation step of the Suzuki–Miyaura cross-coupling reaction between phenyl bromide and phenylboronic acid has been analyzed by means of theoretical calculations based on DFT methods. The resulting picture is very similar to that previously obtained in a similar study on the reaction between vinyl bromide and vinylboronic acid. In the absence of base, the reaction from the bromide complex is forbidden because of the high barrier, as shown in the process labeled as path 0. When a base is introduced, the reaction can take place smoothly through path A, where the base first attacks the organoboronic acid. The reaction can proceed smoothly in the absence of base if it starts from an oxo-palladium, which has been labeled as path C. The analysis of the energy profiles shows that in all cases, the transmetalation is a multistep process, and that the substitution of the halide seems to be critical for the process to take place.

The fact that the overall mechanism is the same for vinyl and phenyl substrates confirms previous experimental suggestions. It supports the idea that the base initially reacts with the boronate species, not depending on the organic substrate. It is furthermore an encouraging result for computational studies, which can in principle obtain results of general validity working with the less computationally demanding vinyl systems.

#### Acknowledgements

We acknowledge financial support from the ICIQ foundation and from the Spanish MEC through Projects CTQ2005-09000-CO1-01 (G.U., A.L.) and CTQ2005-09000-CO1-02 (A.A.C.B., F.M.). G.U. acknowledges the

Spanish MEC for financial support through the “Ramon y Cajal” program.

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