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DFT studies on the mechanisms of palladium-catalyzed intramolecular arylation of a silyl C(sp^3)–H bond† ‡

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Detailed mechanisms of the intramolecular C(sp^3)–C(sp^2) bond formation *via* C(sp^3)–H bond activation of a trimethylsilyl (TMS) substituent catalyzed by palladium(0) complexes have been investigated with the aid of density functional theory (DFT) calculations. The results reveal that the favorable catalytic cycle includes oxidative addition, ligand substitution, concerted metalation deprotonation (CMD) and reductive elimination steps. The CMD was found to be the rate-determining step with an overall free energy barrier of 26.4 kcal mol^{-1}. For the analogous CMe_3-substituted substrate, the C(sp^3)–H bond activation of the CMe_3 substituent was calculated to have a high free energy barrier of 29.9 kcal mol^{-1}. Our calculation results show that during the deprotonation process of the TMS C(sp^3)–H bond, the adjacent Si atom stabilizes the charge accumulated on the C(sp^3)–H carbon and facilitates the C(sp^3)–H bond activation due to the ability of Si to engage in Si–C hypervalent bonding.

Introduction

Palladium-catalyzed C–C cross coupling *via* direct functionalization of C–H bonds has been the subject of tremendous research activity over the past few years,[1,2] and has been extensively developed for synthetic applications to make new molecules for pharmaceuticals, natural products and organic materials.[3]

The majority of the research work done on the above-mentioned cross coupling reactions deals with functionalization of arene and heteroarene C(sp^2)–H bonds.[4] Relevant research work involving functionalization of C(sp^3)–H bonds has attracted wide attention in recent years. In 2006, Yu *et al.*[5] developed a catalytic protocol for C–C bond formation *via* nitrogen-containing group-directed Pd(II)-catalyzed alkylation of C(sp^3)–H bonds with either methylboroxine or alkylboronic acids. In 2008, Fagnou *et al.*[6] reported palladium-catalyzed alkylation of C(sp^2)–H and C(sp^3)–H of picoline N-oxide with aryl halides. Review papers devoted to palladium-catalyzed C(sp^3)–H activation/C–C cross coupling reactions can be found in the literature.[7]

Significant achievements have been realized in the C–C bond formation *via* C(sp^3)–H bond activation. However, the mechanistic understanding of these reactions remains limited. Clot *et al.*[8] have theoretically investigated the mechanism of the intramolecular C(sp^3)–H bond arylation of 2-bromo-*tert*-butylbenzene to form 1,2-dihydro-2,2-dimethylcyclobutabenzene using a Pd(0) catalyst. Daugulis *et al.*[9] have experimentally studied the mechanism of palladium-catalyzed arylation and alkylation of C(sp^2)–H and C(sp^3)–H bonds in carboxylic acid derivatives. Rousseaux *et al.*[10] have experimentally and theoretically investigated the mechanism of palladium-catalyzed intramolecular arylation of C(sp^3)–H bonds adjacent to amides and sulfonamides. All of these studies seem to suggest that the C–H bond activation is crucial and most likely rate-limiting.

Xi *et al.*[11] have recently reported palladium-catalyzed selective cleavage of a silyl C(sp^3)–H bond in a $SiMe_3$ group and consequent intramolecular silyl C(sp^3)–C(sp^2) bond formation. It was found that the silicon atom is important in the activation of the silyl C(sp^3)–H bond, because when the $SiMe_3$ group is substituted by a CMe_3 group, the reaction cannot take place under the same reaction conditions. In this paper, we will theoretically study the reaction mechanism with the aid of DFT calculations to understand the role of the Si atom in this intramolecular cross coupling reaction.

Computational methods

Molecular geometries of the reactants, intermediates, transition states, and products were optimized *via* density functional theory

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‡ Electronic supplementary information (ESI) available: Free energy profiles calculated for the palladium-catalyzed intramolecular C(sp^3)–C(sp^2) bond coupling reaction of CMe_3-containing substrates. See DOI: 10.1039/c3nj00531c

calculations using the hybrid Becke3LYP (B3LYP) method.[12] The reliability of the chosen method has been confirmed by previous work[13] and other theoretical studies of Pd-catalyzed reactions.[14] The 6-31g(d) basis set was used for C, O, and H atoms, while the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ)[15] were chosen to describe the Pd, Br, P, and Si atoms. In addition, polarization functions were added for Pd(ζ_f) = 1.472,[16] Br(ζ_d) = 0.389, P(ζ_d) = 0.340, Si(ζ_d) = 0.262.[17] Frequency analyses have been performed to obtain the zero-point energies (ZPE) and identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) on the potential energy surfaces (PES). Intrinsic reaction coordinate (IRC) calculations were also performed for the transition states to confirm that such structures indeed connect two relevant minima.[18] All calculations were performed using the Gaussian 03 software package.[19]

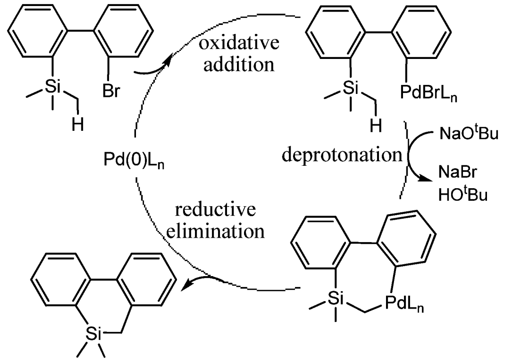
To consider solvent effects, a continuum medium was employed to do single point energy calculations for all of the optimized species, using UAHF radii on the conductor-like polarizable continuum model (CPCM).[20] Toluene was used as the solvent, according to the experimental reaction conditions. In this paper, solvation-corrected relative free energies were used to analyze the reaction mechanisms.

To examine the basis set dependence, we used 6-31++G(d,p) for C, O and H atoms instead to carry our single-point energy calculations for the most important steps **3** → **TS$_3$** and **3_C** → **TS$_{3\_C}$**. Using the 6-31++G(d,p) basis set, the electronic energy barriers for **3** → **TS$_3$** and **3_C** → **TS$_{3\_C}$** were calculated to be 28.3 and 31.5 kcal mol^{-1}, respectively, similar to those (27.0 and 30.8 kcal mol^{-1}) obtained using the 6-31g(d) basis set. Clearly, the basis set dependence is insignificant.

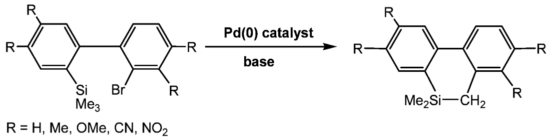
Results and discussion

Mechanism of the intramolecular C–C cross coupling reaction

Preliminary experimental results allowed Xi and coworkers to propose a mechanism (Scheme 1),[11] which consists of oxidative addition, deprotonation and reductive elimination, to account for the Pd-catalyzed selective cleavage of the silyl C(sp^3)–H bond in a SiMe$_3$ group and intramolecular C(sp^3)–C(sp^2) bond formation (eqn (1)). Herein, we perform DFT calculations to explore the mechanism in detail.



Scheme 1 A proposed catalytic cycle for the intramolecular silyl C(sp^3)–C(sp^2) bond coupling reaction shown in eqn (1).

 (1)

On the basis of the recent experimental studies,[11] we first consider the oxidative addition process. Experimentally, tri-*tert*-butylphosphine (*t*-Bu$_3$P) was used. Considering the bulkiness of the phosphine ligand, we expect that a monophosphine Pd(0) complex is the active species as found experimentally.[21] Therefore, we used complex **1** as the starting Pd(0) complex in the oxidative addition process (Fig. 1). From complex **1**, oxidative addition occurs to afford intermediate **2** (Fig. 1). The structures of **1** and the transition state **TS$_1$** with selected structural parameters are displayed in Fig. 2. As shown in Fig. 1, oxidative addition occurs directly *via* the three-membered transition state **TS$_1$** from **1** to form **2**, with a barrier of 7.5 kcal mol^{-1}. The C–Br, Pd–Br and C–Pd bond lengths in **TS$_1$** were calculated to be 2.258, 2.650 and 2.053 Å, respectively (Fig. 2).

Starting from intermediate **2**, two deprotonation pathways are possible, which are closely related to concerted metalation deprotonation (CMD) discussed in the literature.[22] Fig. 3 shows

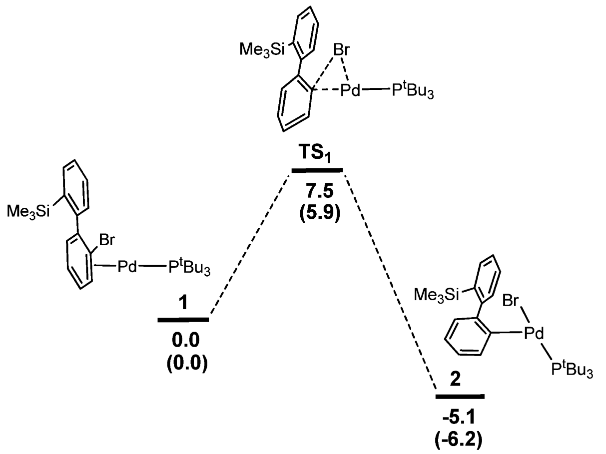


Fig. 1 The energy profile calculated for the oxidative addition step. The solvation-corrected relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

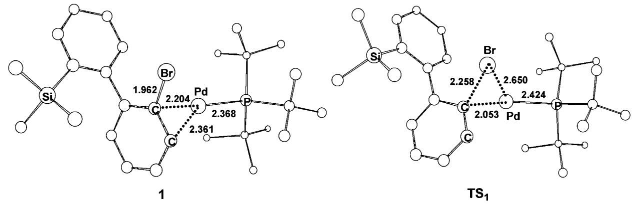


Fig. 2 Optimized structures for selected species involved in the oxidative addition step shown in Fig. 1.

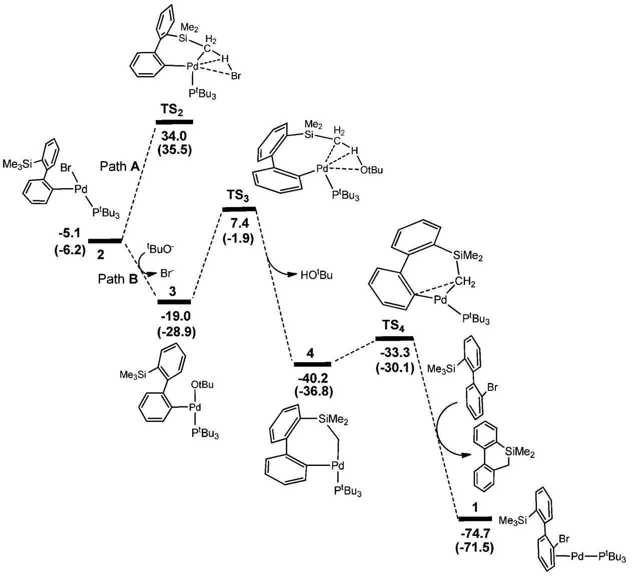


Fig. 3 The energy profile calculated for the deprotonation process starting from intermediate **2**. The solvation-corrected relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

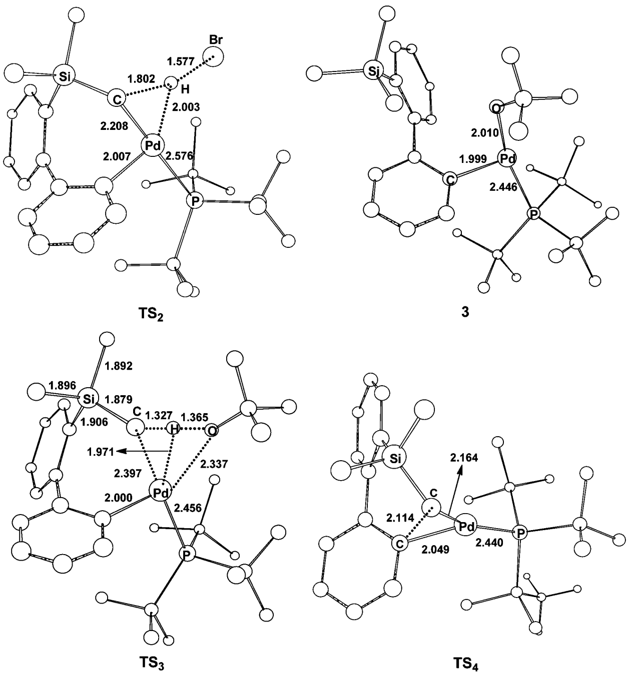


Fig. 4 Optimized structures for selected species involved in the deprotonation process calculated and shown in Fig. 3. The hydrogen atoms associated with P^{t}Bu$_3$, O^{t}Bu and the substrate RBr have been omitted for the purpose of clarity.

the free energy profiles calculated for the two possible pathways. Selected optimized structures are presented in Fig. 4.

Path A shown in Fig. 3 considers proton abstraction directly by the bromide ligand. Clearly, this pathway is energetically very unfavorable, suggesting that the bromide is not basic enough to facilitate the deprotonation process. Path B considers a ligand substitution of ^{t}BuO$^-$ for Br$^-$ prior to deprotonation, giving intermediate **3** in which ^{t}BuO$^-$ replaces Br$^-$. Path B has a barrier of 26.4 kcal mol^{-1}, leading to the formation of intermediate **4**.

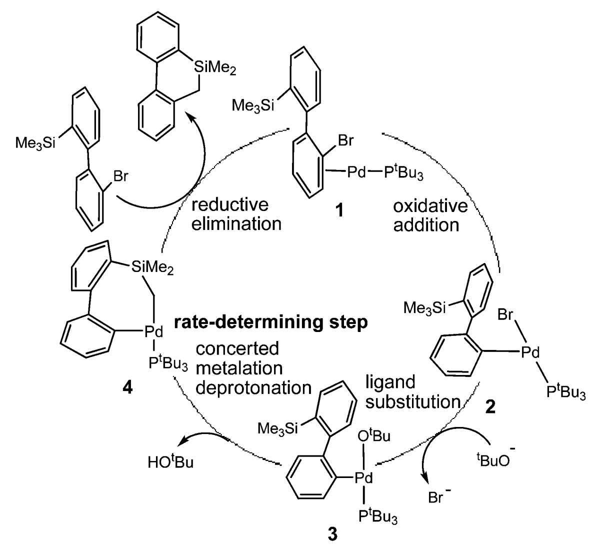


Fig. 5 A detailed catalytic cycle for the intramolecular C(sp^3)–C(sp^2) bond coupling reaction shown in eqn (1).

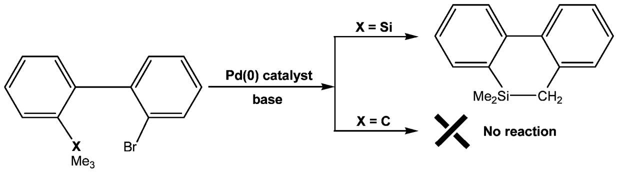
From intermediate **4**, reductive elimination with an intramolecular C(sp^3)–C(sp^2) bond coupling occurs with a barrier of 6.9 kcal mol^{-1}. Finally, re-coordination of substrates, accompanied by the release of the product molecule, regenerates the palladium(0) complex **1**.

Based on the calculation results discussed above, a detailed version of the catalytic cycle is given in Fig. 5. The reaction mechanism consists of four major parts: (1) oxidative addition of the C–Br bond to give an arylpalladium intermediate **2**; (2) ligand substitution of O^{t}Bu$^-$ for Br$^-$ to form intermediate **3** containing an O^{t}Bu$^-$ ligand; (3) a CMD step generates a seven-membered palladacycle intermediate **4**; (4) finally reductive elimination gives the six-membered silacycle product and regenerates the active species **1**. The CMD step is rate-determining and the overall rate-determining free energy barrier was calculated to be 26.4 kcal mol^{-1} (the energy of **TS$_3$** relative to **3** in Fig. 3). The rate-determining barrier of 26.4 kcal mol^{-1} is moderately high, consistent with experimental conditions of 120 °C.[11]

The role of Si in the intramolecular cross coupling reaction

As mentioned in the Introduction, when the SiMe$_3$ group in the substrate is substituted by a CMe$_3$ group, no cross coupling reaction was observed in the experiments (Scheme 2).[11] To investigate the role played by the Si atom of the SiMe$_3$ group in the intramolecular cross coupling reaction, we also calculated the free energy profile of the corresponding palladium-catalyzed C–C bond coupling reaction for the CMe$_3$-containing substrate. The complete free energy profile is given in the ESI.‡ Here, we only provide the energies associated with the rate-determining step (Fig. 6) and the calculated structures for the relevant species (Fig. 7).

Fig. 6 shows that the CMe$_3$-substituted substrate gives a rate-determining free energy barrier of 29.9 kcal mol^{-1} (the energy of **TS$_{3\_C}$** relative to **3_C**). The barrier difference (3.5 kcal mol^{-1})



Scheme 2 Importance of Si in the palladium-catalyzed intramolecular C(sp^3)–C(sp^2) cross coupling reaction.

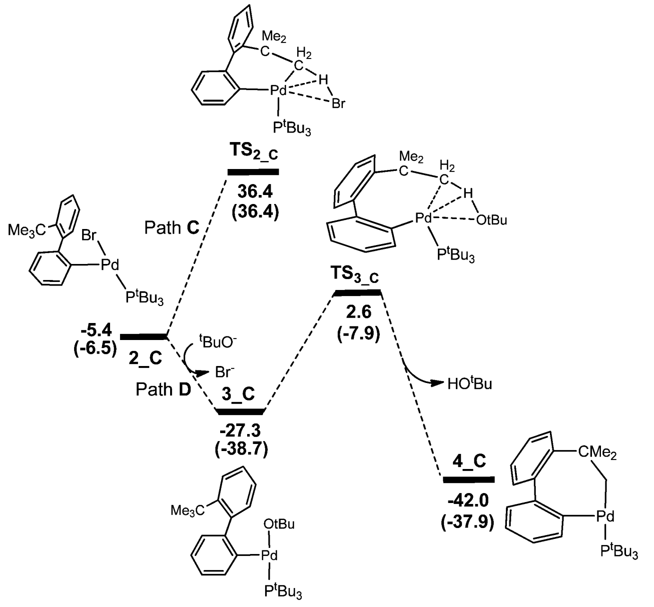


Fig. 6 The energy profile calculated for the CMD step in the palladium-catalyzed intramolecular C(sp^3)–C(sp^2) cross coupling reaction of the CMe$_3$-containing substrate. The solvation-corrected relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}.

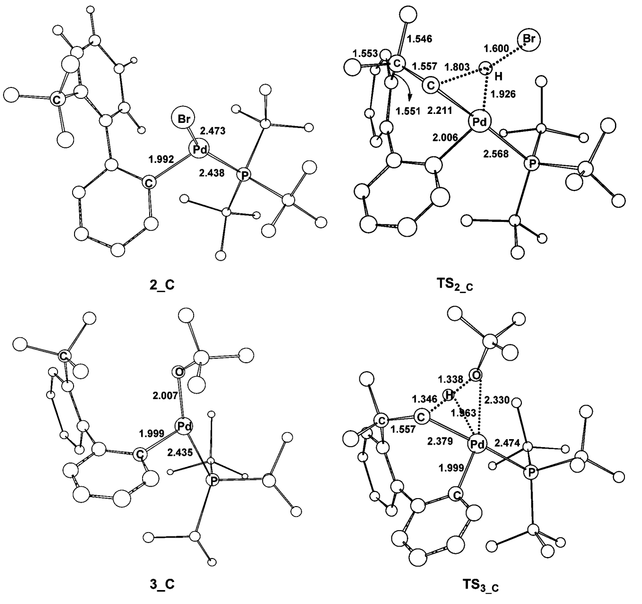


Fig. 7 Optimized structures for selected species involved in the deprotonation process calculated and shown in Fig. 6. The hydrogen atoms associated with P^{t}Bu$_3$, O^{t}Bu and the substrate RBr have been omitted for the purpose of clarity.

can give a multiplicative difference of about 10^2 in the reaction rate if we assume an Arrhenius expression for the rate constant and similar preexponential factors, explaining the experimental observation illustrated in Scheme 2. Experimentally, the reaction for the SiMe$_3$-substituted substrate took 12 hours to achieve a yield of 74%.[11] Given the difference in the reaction rate, we can understand that the corresponding reaction was not observed experimentally for the CMe$_3$-substituted substrate.

The next important question is why there is such a rate-determining barrier difference for the two different substrates. Examining the rate-determining transition structures **TS$_3$** (Fig. 4) and **TS$_{3\_C}$** (Fig. 7), we believe that the ability of Si to be hypervalent is the key to such a significant difference. The rate-determining transition states correspond to C–H deprotonation by the Bu^{t}O$^-$ ligand. Therefore, in the transition states, it is expected that the C–H carbon atom would accumulate negative charge. In the rate-determining transition structure **TS$_3$** for the coupling reaction of the SiMe$_3$-substituted substrate, the silicon atom is able to stabilize the negatively charged carbon atom through Si–C hypervalent bonding interaction. Indeed, the natural atomic charges on the C–H carbon atoms for **TS$_3$** and **TS$_{3\_C}$** were calculated to be −1.367 and −0.814, respectively, consistent with the hypervalent bonding interaction argument given above. Furthermore, the calculated transition state structural parameters (**TS$_3$**, Fig. 4) show clearly that the relevant Si–C bond (1.879 Å) is noticeably shorter than the other three Si–C bonds (1.892, 1.896 and 1.906 Å). In contrast, in the rate-determining transition structure **TS$_{3\_C}$** (Fig. 7) for the coupling reaction of the CMe$_3$-substituted substrate, where hypervalent interaction is not possible, the corresponding C–C bond (1.557 Å) is slightly longer than the other three C–C bonds (1.546, 1.553, 1.551 Å).

Conclusions

The detailed mechanisms of the palladium-catalyzed intramolecular C(sp^3)–C(sp^2) bond formation reaction *via* silyl C(sp^3)–H bond activation have been investigated with the aid of density functional theory calculations. The computational results are consistent with a catalytic cycle that includes: (1) oxidative addition of the C–Br bond to yield an arylpalladium intermediate, (2) ligand substitution of O^{t}Bu$^-$ for Br$^-$ to form the intermediate LPd(Ar)(O^{t}Bu), (3) concerted metalation deprotonation (CMD) to produce a seven-membered palladacycle intermediate, and (4) reductive elimination to give the six-membered silacycle product and regenerate the active species. The CMD was found to be the rate-determining step with an overall free energy barrier of 26.4 kcal mol^{-1}. The CMD process for the C(sp^3)–H bond of an analogous substrate having a CMe$_3$ substituent (instead of a trimethylsilyl substituent) was calculated to have a very high overall free energy barrier of 29.9 kcal mol^{-1}, consistent with the experimental results that the corresponding intramolecular C(sp^3)–C(sp^2) bond formation reaction for such a substrate did not occur. The ability of the Si atom to engage in Si–C hypervalent bonding is essential for the deprotonation of the TMS C(sp^3)–H bond, which can stabilize the transition state structure and facilitate the CMD process.

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