A Syn Outer-Sphere Oxidative Addition: The Reaction Mechanism in Pd/Senphos-Catalyzed Carboboration of 1,3-Enynes

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ABSTRACT:

We report a combined experimental and computational study of Pd/Senphos catalyzed carboboration of 1,3-enynes utilizing DFT calculations, ³¹P NMR study, kinetic study, Hammett analysis and Arrhenius/Eyring analysis. Our mechanistic study provides evidence against the conventional inner-sphere β-migratory insertion mechanism. Instead, a syn outer-sphere oxidative addition mechanism featuring a Pd-π-allyl intermediate followed by coordination-assisted rearrangements is consistent with all the experimental observations.
Introduction

Tetra-substituted alkenes are prevalent structural motif among bioactive compounds and natural products.[1] Representative examples include Illudol, Cassiabudanol A, Brasilenol and Tamoxifen. They also serve as synthetic intermediate for downstream functionalization.[2] However, synthesis of tetra-substituted alkenes[3] in a stereo-defined manner remains nontrivial. Among numerous methods developed to date, transition-metal-catalyzed difunctionalization of alkynes[4] has exhibited remarkable efficiency owing to the simultaneous introduction of two desired units across an alkyne, an inexpensive and readily available feedstock, and therefore has continuously drawn substantial attention. In this context, transition metal-catalyzed carboboration of internal alkynes[5] allows expedient synthesis of tetra-substituted alkenyl boronates[6] which are useful precursors to stereo-defined tetra-substituted alkenes. These alkenyl boronates have long been recognized as versatile building blocks[7] for their participation in Suzuki-Miyaura cross coupling[8] and in various derivative synthesis.[9] The carboboration approach features a diverse combination of carbon and boron moiety and all involve syn-selective addition of boron group and metal across a π-bond of an alkyne (Scheme 1). Suginome et al. pioneered nickel- or palladium-catalyzed intramolecular carboboration of alkyne tethered with chloroborane moiety (Scheme 1a).[10] Similarly, extensions to intermolecular carboboration with various carbon nucleophile sources (Scheme 1b) were achieved.[11] More recently, in copper catalyzed three-component coupling systems (Scheme 1c), carboboration has been accomplished by a copper-boryl migratory insertion process with an alkyne to give an alkenyl copper intermediate, which can then be quenched by various electrophilic carbon sources.[12] Despite these breakthroughs, regio- and diastereoselectivity issues for internal unsymmetrical alkynes remain generally challenging in stereoselective carboborations to produce tetra-substituted alkenes.[12a-e] Furthermore, enolate nucleophiles have not been demonstrated as reagents in carboboration reactions. In 2021, our group reported a new cis-selective enolate carboboration reaction (Scheme 1d) of internal 1,3-enynes accompanying the discovery of a new family of carbon-bound boron enolates (C-boron enolates) generated by a kinetically controlled halogen exchange between chlorocatecholborane and silylketene acetals.[13] These
unquaternized C–boron enolates\textsuperscript{[14]} are demonstrated to activate 1,3-enzyme substrates in the presence of a Pd\textsuperscript{0}/Senphos ligand complex. A remarkable feature is that this transformation provides access to the highly substituted dienyl boron building blocks in high site-, regio-, and diastereoselectivity.

**Scheme 1.** Regio- and Stereoselective Synthesis of Tetrasubstituted Alkenyl Boronates

The consistently high selectivity of the reaction and the underexplored carbon-bound boron enolates inspired our interest in understanding the reaction mechanism. In our recently reported
trans-hydroboration\cite{15} and trans-cyanoboration\cite{16} of 1,3-enynes catalyzed by a Pd\textsuperscript{0}/Senphos ligand complex, an unusual “outer-sphere” oxidative addition mechanism featuring a Pd-π-allyl intermediate is proposed.\cite{17,18} Our initial mechanistic hypothesis was analogous (Scheme 2a): the presence of Senphos ligand L enables (COD)Pd(CH\textsubscript{2}TMS)\textsubscript{2} to reductively eliminate 1,2-bis(trimethylsilyl)-ethane to form the active LPd\textsuperscript{0} species I,\cite{19} which then binds to the 1,3-ene. The resulting LPd\textsuperscript{0}-ene complex II is then activated by the Lewis acidic C-boron enolate to furnish the outer-sphere oxidative adduct III. An enolate equivalent then attacks Pd-π-allyl to yield the product with concomitant regeneration of LPd\textsuperscript{0} species I.\cite{20} Our initial hypothesis provided a plausible explanation for the observed high site-, regio-, and diastereoselectivity. However, many mechanistic details of the C-B bond cleavage of the C-boron enolate and the C-C and C-B bond formation in the product are vaguely defined. For example, mechanistic divergence arises as C-boron enolate could potentially approach the LPd\textsuperscript{0}-ene complex II either from the same side with respect to Pd complex (“syn” outer-sphere oxidative addition) or from the opposite side (“anti” outer-sphere oxidative addition, Scheme 2b). In addition, the conventional “inner-sphere” oxidative addition / β-migratory insertion / reductive elimination sequence (Scheme 2c) could not be ruled out completely, calling for new mechanistic evidence. We believe a detailed mechanistic investigation is therefore critical to clarify this mechanistic puzzle as well as to understand the origin of the selectivity and the behavior of carbon-bound boron enolates. In this article, we report our mechanistic study, starting with computational investigation (DFT calculations) which has been well correlated with \textsuperscript{31}P NMR study, kinetic study, Hammett analysis, Arrhenius analysis and Eyring analysis to obtain a more complete picture. Our mechanistic analysis does not support the inner-sphere mechanism and instead offers compelling evidence for Pd-π-allyl intermediacy as well as reveals full details for each elementary step of the new catalytic cycle, including a series of coordination-assisted rearrangements. Additionally, we also compare the ligand performance of Senphos and its carbonaceous version to probe the intrinsic effect of BN/CC isosterism. Collectively, the fundamental insights from this work should further expand the application of Senphos ligand toward new reaction development.
Scheme 2. Mechanistic Consideration

(a) Initial Working Hypothesis: “Outer-Sphere” Oxidative Addition

(b) Nuances of “Outer-Sphere” Oxidative Addition

(c) “Inner-Sphere” Oxidative Addition Mechanism

(d) Model Substrate and Catalyst Used throughout the Study
Results and Discussion

We selected 1 and 2 as model substrates (Scheme 2d) and performed DFT calculations to explore the mechanism at SMD(Toluene)-TPSS-D3(BJ)/SDD+f(Pd), 6-31G**(other atoms) level of theory (see ESI for computational details).[21][22] Given the observed selectivity of the reaction, different pathways leading to the cis-addition product have been considered theoretically. We first studied the inner-sphere mechanism involving direct oxidative addition of the C-boron enolate to the Pd(0)/Senphos complex. Upon oxidative addition, two approaches of C-boron enolate were considered leading to two products, with Bcat moiety cis (Path Ia, Figure 1, Ia-Int1) or trans (See Path Ib, Ib-Int1, Figure S1 in ESI) to the phosphorus atom of the Pd(II)/Senphos complex. Then, the 1,3-enyne coordinates to the Pd(II)/Senphos complex to form Ia-Int2. Compared to the initial reactants, this π-complex (Ia-Int2) is strongly uphill in energy (Path Ia, Figure 1, ΔG: 40.9 kcal/mol; Path Ib, Figure S1, ΔG: 36.5 kcal/mol (see ESI)), which may be due in part to the loss of the η2-BC coordination of the Senphos ligand on Pd. Consequently, the β-migratory insertion,

![Energy profile](image)

**Figure 1.** Energy profile (ΔG in kcal/mol) computed at SMD(Toluene)-TPSS-D3(BJ)/SDD+f(Pd), 6-31G**(other atoms) level of theory for the inner-sphere mechanism involving direct oxidative addition pathway of C-boron enolate to Pd. Path Ia is shown: Bcat moiety cis to phosphorus of the 1,4-azaborine-Senphos ligand. For Path Ib: Bcat moiety trans to phosphorus of the 1,4-azaborine-Senphos ligand, see ESI.
which is the rate-determining step, proceeds with an inaccessible activation barrier computed at 41.8 kcal/mol for Path Ia (Figure 1) and 38.2 kcal/mol for Path Ib (see ESI). Lastly, the activation barrier for the reductive elimination is energetically less demanding ($\Delta G^\ddagger$: 18.7 kcal/mol from starting materials, Path Ia (Figure 1); $\Delta G^\ddagger$: 32.8 kcal/mol, Path Ib (See ESI)) than the $\beta$-migratory insertion step. Overall, the inner-sphere mechanism is predicted to be energetically unfeasible and is not consistent with the reported relatively mild catalytic cis-carboboration reaction conditions.$^{[13]}$

We then examined the outer-sphere oxidative addition mechanism (Scheme 2a-2b), where the palladium center is not directly involved in the cleavage of the C-B bond of the C-boron enolate. As illustrated in Figure 2, this mechanism starts with the enyne coordinating to the palladium center. The C=C double bond of the enyne is coordinated in a quasi-symmetric fashion to the metal center (Pd···C distances: 2.183-2.202 Å). The formation of the $\pi$-complex (Pd-enzyme) is thermodynamically favorable by 19.1 kcal/mol compared to the initial reactants. Then, the C-boron enolate approaches this $\pi$-complex in a fashion syn to the Pd to engage in a syn outer-sphere oxidative addition (See ESI for the details for the anti outer-sphere oxidative addition). Calculations predict that the activation barrier for the syn outer-sphere oxidative addition step is $\Delta G^\ddagger$: 16.2 kcal/mol from the Pd-enzyme $\pi$-complex. The “activated” quaternized C-boron enolate in Int$_1$ then undergoes a coordination-assisted (Pd···O distance: 2.138 Å in the transition state TS$_2$) rearrangement to form a Pd-O-enolate (Int$_2$) with an activation barrier of 22.8 kcal/mol from the resting state. This coordination assistance in the syn outer-sphere oxidation pathway is responsible for a 17.2 kcal/mol lower overall rate-limiting energy barrier in comparison to the anti outer-sphere oxidative addition (or 25.1 kcal/mol lower energy barrier when directly comparing the C-B bond breaking step, see ESI for the anti energy profile). The O→Pd bonding in TS$_2$ is apparent in the NBO analysis (see ESI) as donor-acceptor interactions with a total stabilizing energy $\Delta E(2)$ of 43.9 kcal/mol ($\Sigma$O→Pd interaction). The natural localized molecular orbital (NLMO) associated with the main n$_O$ → Pd interaction shows a major contribution of the oxygen lone pair (77 %) mixed in with contributions from Pd (5.3%).
Figure 2. Energy profiles (ΔG in kcal/mol) computed at SMD(Toluene)-TPSS-D3(BJ)/SDD+f(Pd), 6-31G**(other atoms) level of theory for the outer-sphere oxidative addition mechanism, involving B-C bond cleavage with assistance of O→Pd interaction, Pd-O/B-O isomerization and reductive elimination (black path). Concerted reductive elimination (green path), and Pd-O/Pd-C isomerization prior to reductive elimination (blue path) were also considered.

From Int₂, a direct reductive elimination transition state (TS-concerted, green path, Figure 2) via a concerted 5-membered transition state (Pd-O distance: 2.373 Å and C···C distance: 2.477 Å) has been located with a barrier of ΔG‡: 59.1 kcal/mol from the resting state, suggesting that this C-C bond-forming step is unlikely to take place under the relatively mild reaction conditions. Thus, an isomerization was considered before the reductive elimination step. Two possibilities were examined: 1) Pd-O-enolate to Pd-C-enolate isomerization (blue path, Figure 2), and 2) Pd-O-enolate to B-O-enolate isomerization (black path, Figure 2). From the resting state, the barrier for the Pd-O-enolate to Pd-C-enolate isomerization to furnish Int-Pd-C-enolate (blue) was found to be ΔG‡: 54.4 kcal/mol whereas Pd-O-enolate to B-O-enolate isomerization (black) to form Int₃ is predicted to be barrierless.

From the isomerized B-O-enolate Int₃, “reductive elimination” proceeds with an activation barrier of ΔG‡: 12.5 kcal/mol, leading to Int₄, which is the cis-carboboration product bound to the Pd catalyst. Finally, the cis-carboboration product is released from the Pd catalyst, and a new
cycle can begin. The *cis*-carboboration product features an O→B interaction (B···O distance: 1.662 Å), in agreement with the observed $^{11}$B NMR signal of the product at 17 ppm.

Based on the computational study, the most favorable pathway to form the *cis*-carboboration product involves: i) a *syn* outer-sphere oxidative addition, ii) coordination-assisted B-C bond cleavage to form a Pd-O-enolate, iii) Pd-O-enolate to B-O-enolate isomerization, and iv) reductive elimination via an enolate attack to a Pd-π-allyl species. Overall, DFT calculations predict the Pd-enzyme complex (Pd-enzyme) to be the resting state and the reductive elimination (TS$_3$) to be the rate-limiting step with an overall rate-limiting barrier of 23.1 kcal/mol. It is worth noting that TS$_2$ (B-C to Pd-O isomerization, overall barrier of 22.8 kcal/mol from the resting state) is very close in energy with TS$_3$.[23] The assistance of an O→Pd interaction between CO$_2$Me moiety and the Pd metal center in the *syn* outer-sphere oxidative addition pathway is critical in lowering the overall activation barrier to allow for sufficient reactivity under mild conditions.[24]

To validate the conclusion of computational study, we performed the following experimental studies: 1) resting state determination via $^{31}$P NMR, 2) initial-rate kinetics to obtain reaction orders of the reactants and the catalyst, 3) Hammett analysis, 4) determination of activation parameters. We began with $^{31}$P NMR characterization of the reaction mixture to determine the likely resting state of the catalyst. The toluene-$d_8$ solution of 1:1 mixture of (COD)Pd(CH$_2$TMS)$_2$ and L showed two broad signals ($\delta_P = 53.2$ and $\delta_P = 33.3$ ppm) and one sharp signal ($\delta_P = 52.7$ ppm) (Scheme 3, A). Next, the addition of 20 equiv. of enyne 1 to this solution, as a simulation of real catalytic reaction condition, resulted in the observation of a sharp resonance ($\delta_P = 39.9$ ppm, Scheme 3, B), which we tentatively assign as the enyne-bound Pd complex (Pd-enzyme). On the other hand, the addition of 40 equivalents of C-boron enolates 2 to the 1:1 mixture of Pd precursor and L generated three additional signals ($\delta_P = 66.0$, $\delta_P = 43.1$, and $\delta_P = 38.5$ ppm) with two broad signals remaining as major peaks (Scheme 3, C). Under standard condition for catalytic reaction, the $^{31}$P NMR spectrum exhibited a major sharp peak ($\delta_P = 40.4$ ppm) that matches nicely the signal observed for enyne bound Pd π-complex (Scheme 3, D). This peak
**Scheme 3.** $^{31}$P NMR Experiments for the Detection of the Resting State of the Catalyst

Persisted throughout the course of the reaction for ca. 4 hours and disappeared when the starting material was consumed. Thus, the observed $^{31}$P data is consistent with the Pd-enzyme being the resting state of the catalytic cycle, which is in agreement with the DFT calculations (Figure 2).

To probe the effect of each reaction component on the catalytic reaction, we then determined the kinetic orders in 1,3-enzyme [1], C-boron-enolate [2] and [Pd/L<sub>total</sub>], by measuring the initial rate over time in toluene-d<sub>8</sub> solutions via $^1$H NMR spectroscopy. Plotting the log(-d[I]/dt) vs. log ([2]) (Scheme 4, A), log(-d[I]/dt) vs log([Pd/L<sub>total</sub>]) (Scheme 4, B) fitted two lines with slope 1.00 and 1.01, respectively, implying first order dependence on both C-boron-enolate [2] and [Pd/L<sub>total</sub>]. Varying the concentration of enzyme [1] did not influence the reaction rate (Scheme 4, C), suggesting saturation kinetics (zero order dependence) with respect to [1]. Together with the conclusions from $^{31}$P NMR study, the reaction order determination is consistent with the
proposed *syn* outer-sphere oxidative addition pathway in Figure 2 where the **Pd-enyne** complex is the resting state and the B-C bond cleavage (**TS*2*) and/or reductive elimination (**TS*3*) being the rate-limiting transition state.

**Scheme 4. Initial-Rate Kinetic Analysis**
We then investigated the electronic effect of the aryl group in the 1,3-enyne on the reaction rate of the carboxaboration (Scheme 5). The Hammett analysis reveals that a 1,3-enyne bearing an electron-donating substituent reacts faster than an unsubstituted 1,3-enyne. A linear fit with reported $\sigma_p^+$ constants is observed whereas less linear fit was be obtained with $\sigma_p$ or $\sigma_p^-$ constants, respectively.\cite{25} The $\rho$ value determined from the Hammett plot (from $\sigma_p^+$ values) was $-0.61$, implying the development of some positive charge in the 1,3-enyne substrate during the transition from the resting state to the rate-limiting transition state. Considering the multiple elementary processes involved (i.e., see Figure 2, (i) syn outer-sphere oxidative addition (developing positive charge), (ii) coordination-assisted B-C bond cleavage to form a Pd-O-enolate (reduction of positive charge), (iii) Pd-O-enolate to B-O-enolate isomerization (development of positive charge), and (iv) reductive elimination (reduction of positive charge), the relatively small magnitude of $\rho$ value could be interpreted as a net result of these opposing charge-generating processes.

Scheme 5. Hammett Analysis
We also obtained the activation parameters of the carboboration by measuring the reaction rate in the temperature range of 25-50 °C. The Arrhenius plot (Scheme 6A) exhibited excellent linearity, with activation energy $E_a = 5.21 \pm 0.14 \text{ kcal/mol}$, and preexponential factor $A = 4.10 \pm 0.96 \text{ M}^{-1}\text{s}^{-1}$. Such a relatively small A value is consistent with a quite negative activation entropy for this reaction.\textsuperscript{[26]} We also performed an Eyring analysis (Scheme 6B) while acknowledging that the Eyring equation is theoretically only applicable to a single-step elementary reaction.\textsuperscript{[27]} The activation parameters determined via Eyring analysis are $\Delta H^\ddagger = 4.59 \pm 0.15 \text{ kcal/mol}$, $\Delta S^\ddagger = -58 \pm 1 \text{ e.u.}$, and $\Delta G^\ddagger = 23.25 \pm 0.22 \text{ kcal/mol}$. While the exact values of the activation parameters should be interpreted with caution, the magnitude of the activation parameters is consistent with the prediction from the computational study (see Figure 2, predicted $\Delta H^\ddagger = 4.5 \text{ kcal/mol}$, $\Delta S^\ddagger = -62.3 \text{ e.u.}$, $\Delta G^\ddagger = 23.1 \text{ kcal/mol}$).

**Scheme 6.** Arrhenius and Eyring Analysis
Achieving the rate-limiting transition state $\text{TS}_3$ from the **Pd-enzyme** resting state involves a bimolecular outer-sphere oxidative addition step and a highly conformationally organizing reductive elimination step. The very limited degrees of freedom in the rate-limiting $\text{TS}_3$ (or in the energetically similar $\text{TS}_2$) relative to the resting state are consistent with the predicted and experimentally observed Arrhenius preexponential factor $A$ and activation entropy $\Delta S^\ddagger$ values.

Finally, we compared the performance of Senphos ($L$) and its carbonaceous version ($L_{CC}$ ligand) under otherwise identical conditions by following the disappearance of the 1,3-enzyme substrate over time via $^1$H NMR analysis. As can be seen from Scheme 7, the initial rate of the reaction is similar when either $L$ (BN) or $L_{CC}$ ligand is used. However, the reaction stopped at $\sim$50% conversion after ca. 1.5 hours when the $L_{CC}$ ligand was employed while the Senphos $L$ ligand enabled the reaction to go to completion over a period of 4 hours.

**Scheme 7. BN vs CC: Ligand Performance Comparison**
The 4 hours reaction time correlates with the duration of where the corresponding resting-state **Pd-enyne** signal is observed by $^{31}$P NMR (See ESI). These results suggest the Senphos ligand $L$ generates a more long-lived Pd/L catalyst than the $L_{CC}$ ligand does and is consistent with the proposed unique $\kappa^2,\eta^2$-BC coordination mode of the ligand and the electron-donating borataalkene electronic structure of the BN-heterocyclic portion of the Senphos ligand.[28]

**Conclusion**

We have conducted a combined experimental and computational mechanistic investigation of the Pd/Senphos-catalyzed stereoselective carboboration reaction of internal 1,3-enynes with C-boron enolates. DFT calculations, spectroscopic characterization of reaction intermediates, initial-rate kinetics, linear free energy relationship analysis, and Arrhenius/Eyring analysis are inconsistent with an inner-sphere mechanism that is initiated by an oxidative addition of the C-boron enolates to the Pd(0)/L catalyst and followed by alkyne $\beta$-migratory insertion and reductive elimination. Instead, our experimental and computational results are consistent with an outer-sphere oxidative addition mechanism where a Pd(0)/L-enyne complex is cooperatively activated by the Lewis acidic C-boron-enolate to furnish a zwitterionic Pd(II)/L $\pi$-allyl species. In contrast to previously reported outer-sphere oxidative addition mechanism for the trans-selective hydroboration reaction where the Lewis acidic H-Bcat activator approaches the enyne anti to the Pd complex, the C-boron enolate activator approaches the enyne syn to the Pd complex. This syn outer-sphere oxidative addition pathway enables a critical coordination assisted rearrangement to form a Pd-O-enolate which then further rearranges to a B-O-enolate before the product-forming reductive elimination. Due to the lack of coordination-assisted Pd-O-enolate formation, the anti outer-sphere oxidative addition pathway is predicted to be more unfavorable than the syn outer-sphere oxidative addition mechanism by 17.2 kcal/mol. Our experimental and computational data are consistent with the Pd-enyne complex being the resting state and the reductive elimination being the rate-determining step of the catalytic cycle. Furthermore, we establish that the BN heterocyclic Senphos ligand generates a significantly
longer-lived active Pd catalyst species than its carbonaceous ligand does. Overall, this work highlights the mechanistic nuances associated with the emerging outer-sphere oxidative addition mechanism to leverage the versatile Pd-π-allyl intermediate for new catalytic bond-forming reactions. We also hope to take advantage of the stabilizing ability of the Senphos ligand family to develop new efficient catalytic processes.

Associated Content
Experimental procedures, compound characterization data, computational information (PDF)

  Optimized cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

Acknowledgments.

Research reported in this publication was supported by the National Institute of General Medical Sciences of the National Institutes of Health under Award Number R01GM136920, the Excellence Initiative of Université de Pau et des Pays de l’Adour I-Site E2S UPPA, and by Boston College start-up funds. The “Direction du Numérique” of the Université de Pau et des Pays de l’Adour, CINES under allocation A011080045 made by Grand Equipment National de Calcul Intensif (GENCI) and Mésocentre de Calcul Intensif Aquitain (MCIA) are acknowledged for the support of computational facilities. Z.W. was supported as a LaMattina Graduate Fellow in Chemical Synthesis. W.L. was funded as a postdoctoral fellow by I-Site E2S-UPPA. We also acknowledge the NIH-S10 (award: 1S10OD026910-01A1) and the NSF-MRI (award: CHE-2117246) for the support of Boston College’s NMR facilities. We thank Prof. Anna Chrostowska and Dr. Jean-Marc Sotiropoulos at UPPA for helpful discussions.
References


24) The carboboration reaction when conducted at room temperature under otherwise identical conditions has a half-life of ca. 4 hours.


27) For an example of the application of the Eyring analysis to a multistep transition-metal catalyzed reaction, see: O. P. Schmidt, D. G. Blackmond, ACS Catal. 2020, 10, 8926-8932.