



Computational catalysis

Trans effects in the Heck reaction—A model study

Carina Bäcktorp, Per-Ola Norrby*

Department of Chemistry, University of Gothenburg, SE-412 96 Göteborg, Sweden

ARTICLE INFO

Article history:

Received 3 March 2010

Received in revised form 4 June 2010

Accepted 4 June 2010

Available online 11 June 2010

Keywords:

Heck couplings

Density functional calculations

Homogeneous catalysis

Palladium

Reaction mechanisms

ABSTRACT

The selectivity-determining step in Heck arylation of styrene, the migratory insertion, has been modeled by DFT. In particular, the regio-selectivity has been studied as a function of the trans effect of several sets of small model ligands with different σ -donor and π -accepting abilities. It has been shown, both by analyzing the geometries and comparing the activation energies, that the TS for branched product formation is more sensitive than the TS leading to linear product, although most ligand combinations give a preference for the linear product. The branched TS is strongly destabilized by any strong ligand in a position trans to the alkene in the pre-insertion intermediate. For the ligand trans to the migrating group, a strong trans effect accelerates the reaction, more for the branched than for the linear product formation. On electronic grounds, the regio-selectivity and rate can be adjusted by considering not only the trans effect of a ligand, but also by controlling the position they will have in the migratory insertion step. Very importantly, the trans effect change in the selectivity-determining TS will be expected to give rise to Halpern-type selectivity, with the consequence that product distributions cannot be reliably predicted from observable intermediates.

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1. Introduction

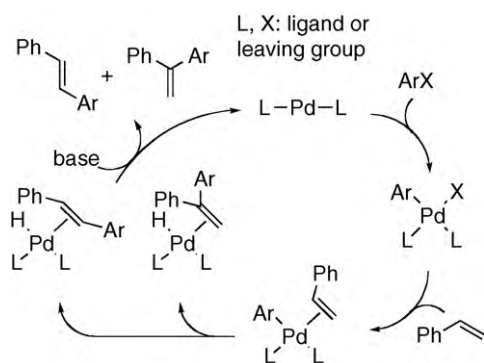
Palladium-catalyzed arylation and vinylation of alkenes has been used for more than 30 years in organic synthesis. This methodology is known as the Mizoroki–Heck reaction [1], or sometimes just the Heck reaction, and since its discovery, it has become one of the most important tools for complex building in organic chemistry [2,3]. It allows formation of new carbon–carbon bonds under relatively mild conditions, and with a high functional group tolerance. Furthermore, it is formally a C–H activation, and as such, more atom economical than most other Pd-catalyzed coupling reactions. However, like many other C–H activations [4], the selectivity can be a problem in the Heck reaction. Depending on the substrate, selectivity issues can include regiochemistry of the newly formed C–C bond, position and stereochemistry of the product alkene, and possibly also stereochemistry of newly formed asymmetric centers.

The scope and mechanism of the Heck reaction have been thoroughly studied [5]. The basic steps are schematically exemplified in Scheme 1. In particular the investigations by Cabri in the 90s have outlined empirical rules for selecting appropriate reaction conditions with various substrate combinations [2]. The experimental observations have also been augmented by detailed computational studies that help aid the understanding of the reaction at an atomic level [6–9].

The Heck reaction can broadly be divided into two classes. When the reaction is run with monodentate ligands (e.g., PR_3) in the presence of coordinating anions like halides, the alkene substrate will substitute a neutral ligand, leading to an overall neutral intermediate and subsequent transition state for the selectivity-determining carbopalladation step. In this mode, the so-called neutral Heck, the insertions tend to favor linear products [2]. On the other hand, the Heck reaction can be run in cationic mode by using bidentate neutral ligands (usually bis-phosphines), and excluding coordinating anions by using, for example, triflates as leaving groups. In this case, the pre-insertion square planar complex and the insertion TS will be cationic, with two neutral ligands, the alkene, and an aryl group coordinating to Pd^{II} . When the substrates are very electron rich alkenes, like vinyl ethers, the cationic Heck reaction frequently yields good selectivity for branched products [2]. However, the inherent regio-selectivity is not very strong, and the final product distribution is easily influenced by other factors, like solvent, steric repulsion [9], substrate electron density [10], subtle changes in ligand structure [11], ligand bite angle [12], or intramolecular geometry constrains [13].

We have recently undertaken computational and experimental studies of the reaction mechanism of the Heck reaction [7–10], aimed at increasing our understanding of the factors influencing product selectivity, and thereby facilitating the choice of reaction conditions for any substrate. In particular, it has been shown that DFT calculations can explain the observed product distribution from competing β -hydride elimination [7] and elimination–readdition [9] pathways, and also that the stereose-

* Corresponding author. Tel.: +46 31 7869034; fax: +46 31 7723840.
E-mail address: pon@chem.gu.se (P.-O. Norrby).



Scheme 1. A schematic representation of Heck arylation of styrene.

lectivity in asymmetric Heck can be rationalized at the same level of theory [8]. As the next step in our continuing investigations, we here return to the fundamental level of ligand electronic influence on the carbopalladation, the selectivity-determining step in many applications of the Heck reaction. In order to aid future reaction design, we want to separate the effects influencing the selectivity, and here we have chosen to neglect steric factors in order to clarify the purely electronic effects. We have therefore selected to study only small ligand models, where the steric repulsions have been eliminated. When the underlying electronic effects are clarified, suitable experimental systems can then be designed by also considering steric factors.

The electronic properties of a ligand are mainly manifested as trans influences or trans effects in metal complexes [14,15]. In square planar or octahedral complexes, the trans influence (sometimes called the steric trans effect) is understood as the elongation of a particular coordination bond caused by the ligand in a trans position, whereas the trans effect (or the kinetic trans effect) is a weakening of the same coordination, manifested as a lower barrier to substitution. From here on, we will use the term “trans effect” also for structural effects in transition states. In structurally similar situations, longer bonds are usually weaker, and therefore the trans influence and effect are closely correlated, but not identical. However, both can be most easily understood in terms of the 3-center-4-electron bond (ω -bond) [16]. Two ligands in a trans relationship σ -donate to the same metal-centered ds -hybrid orbital [17] (similar in shape to the familiar d_{z^2} orbital, Fig. 1), and any increase in bonding to one ligand must therefore be accompanied by a bonding decrease with the trans ligand. Thus, strong trans effects result from very basic lone pairs, like in alkyl groups which need a strong overlap with the central metal to stabilize the localized carbanion, or from lone pairs in orbitals of optimum size for maximizing the overlap with the metal, like phosphines. Attenuating factors include the ability of the ligand to accept π -backbonding, like in CO and to a lesser extent in phosphines, where the backdonation allows a stronger σ -donation without causing charge separation. Two strongly π -accepting ligands in a trans relationship will of course also compete for the same filled orbital on the metal, but this factor is probably less important than the σ -

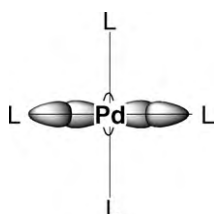


Fig. 1. Two ligand lone pairs competing for the same orbital on Pd, an ω -bond.

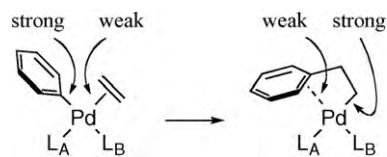


Fig. 2. Trans effect changes in the carbopalladation step.

donation, and it is not obvious that only ligands in trans positions will compete.

The trans effect is usually seen as a property of an isolated ligand, but in reality it is a pair function; a strongly trans influencing ligand will reduce the influence of a second ligand trans to itself, and vice versa [15]. In terms of stability, when two strong ligands are trans to each other, the complex will be destabilized, and thus be disfavored in equilibria with geometries where only weak ligands are trans to strong ones. However, it should be realized that in Curtin–Hammett situations [18], where all complexes are in rapid equilibrium compared to the rate of subsequent reactions, the destabilized complexes could still be important, since they also have a much higher reactivity. In fact, it was recently shown in the asymmetric Heck reaction that most of the observed product arose from the unstable and unobservable isomer intermediate [8]. This is an example of Halpern selectivity [19], that is, that the major product arises from a preceding minor intermediate.

The Halpern selectivity in the asymmetric Heck reaction can be understood in terms of how the trans effect changes during the course of the reaction. Fig. 2 illustrates this change in a selectivity-determining step of the Heck reaction, the carbopalladation (or migratory insertion). It is easily seen that a strong ligand in any position must destabilize either the reactant or the product. Since the transition state is somewhere between these two states, it is not self-evident what the total effect on the barrier will be. In the previously studied case [8], it turned out that, from the aspect of trans effects, the TS was more product-like, despite the strong exothermicity of the step. This is an indication that the TS is asynchronous, with the different bonds formed to unequal degree at the TS. From Fig. 2, it is obvious that for any case where the TS is product-like, the reaction will show Halpern selectivity, that is, the destabilized and less populated isomer of the intermediate will give rise to most of the observed product. However, it is by no means certain that the earlier result can be generalized to other types of systems. We have therefore embarked upon a study of how the regio-selectivity of both the cationic and neutral versions of the Heck reaction will be expected to vary with ligands of different trans-inducing power. As a model system, we have chosen to work with an experimentally well-studied reaction, phenylation of styrene. The system is interesting because the trans influences in the two carbopalladated intermediates leading to the regioisomeric products will be quite different (Fig. 3). In the intermediate leading to the linear product, the alkyl group is stabilized by conjugation with the styrene phenyl, giving a moderate trans influence, whereas in the intermediate leading to the branched product, the unstabilized alkyl group is a very strong σ -donor. Thus, we can expect sensitivity to the nature of the ligand. In any experimental system, the analysis

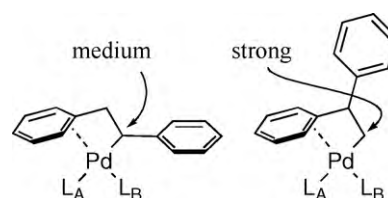


Fig. 3. Alkyl trans influence in carbopalladation products from styrene.

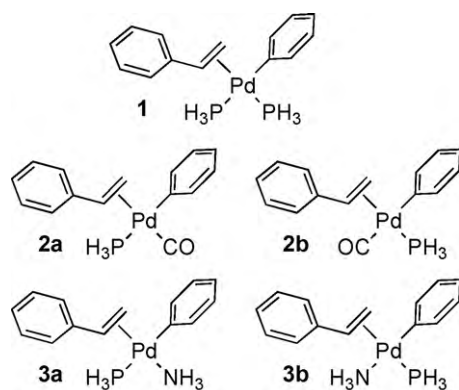


Fig. 4. Cationic pre-insertion intermediates.

will be complicated by the fact that we cannot *a priori* know which ligand is preferred in which position in the TS, but in a computational study, all preferences can be easily separated. In line with the earlier study [8], we will assume Curtin–Hammett conditions. In computational terms, this means that no intermediates have to be calculated since all selectivities are obtained directly from the TS energies.

2. Methods

2.1. Presentation of model systems

The purpose of the present study is to elucidate how the trans effect of the ligand affects the regio-selectivity in the Heck reaction. Therefore, we want to exclude other factors that influence the regio-selectivity as much as possible. It is obvious that steric effects will have an important influence on the regio-selectivity. Therefore, we have chosen as small ligands as possible – still with significant differences in trans effects – to exclude the steric effects as a factor of regio-selectivity. Also, the ligands should have similar sizes so that the interchange of two ligands will not affect the palladium complex from a structural point of view. We also desire a system that has a limited number of possible conformations, in order to minimize the necessary conformational scanning.

As our model system, we have chosen a well-studied reaction, phenylation of styrene, Scheme 1. The investigation includes both the cationic and neutral Heck reaction, and we concentrate on small systems that can be seen as models of bidentate ligands. For the cationic system, we have selected a series of three different ligands with different trans influencing capacities: phosphine (PH₃), carbon monoxide (CO) and ammine (NH₃). PH₃ is a relatively strong σ donor and a modest π acceptor, that is, a relatively strong trans influencing ligand. CO is a strongly π -accepting ligand but a modest σ donor; generally, it shows strong trans effects. NH₃ is the weakest ligand, with relatively poor σ -donating and negligible π -accepting ability [15]. The square planar pre-insertion intermediate for all cationic systems is depicted in Fig. 4. Experimentally, the most frequently used ligands are phosphines. Structure 1 is used as a model for bidentate phosphines as well as for an excess of monodentate phosphines in the absence of coordinating anions. Structure 2 simulates replacing one of the phosphines with a neutral carbenoid, like the popular N-heterocyclic carbene ligands [20], whereas 3 represents the frequently employed PN-ligands [8].

In the neutral Heck reaction, one neutral and one formally anionic ligand coordinates to Pd in the insertion step. We have herein investigated the case of cyanide (CN⁻) and alkyl (CH₃⁻) as the negatively charged ligand. These anionic ligands were combined with the same series of ligands as in the cationic Heck reaction (CO, PH₃ and NH₃). The cyanide can be seen as an anionic analogue

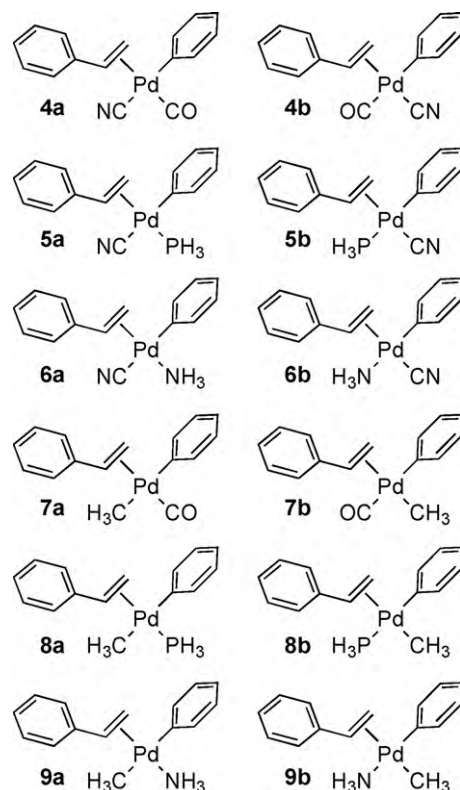


Fig. 5. Neutral pre-insertion intermediates.

of CO, exhibiting a somewhat stronger σ -donating but slightly weaker π -accepting capacity (4–6). In contrast, CH₃⁻ is a very strong σ -donor, with no π -accepting ability (7–9) [15]. In particular, the combination of CH₃⁻ with PH₃ (8) can be seen as a model of cyclometallated phosphine ligands [21].

2.2. Computational method

All calculations herein were performed with Jaguar [22] using the hybrid functional B3LYP [23] in combination with the LACVP* basis set [24]. All optimized geometries were characterized and saddle points were verified by frequency calculation. Harmonic vibrational frequencies have been used to calculate the thermodynamic contributions to the enthalpies and free energies.

3. Results and discussion

The migratory insertion step in the cationic and neutral Heck reactions has been investigated for 17 different model systems (Figs. 4 and 5). The bond lengths and the full geometries can be found in Supporting Information. Starting with system 1 (Fig. 4), the symmetrically substituted intermediate where both ligands are PH₃, the transition states leading to branched and linear products are shown in Fig. 6.

It can be seen from Table 1 that the two transition states are very similar in energy. This agrees well with the observation that phenylation of styrene is relatively unselective when sterically unencumbered phosphines (e.g., dppp) are employed [2,10]. When analyzing the geometries in Fig. 6, we notice that the length of the developing Pd–C bond differs substantially. In the branched case, the new bond is forming to the β -carbon, where a free negative charge would be very unstable, and as a result the interaction with Pd is strong. In the linear TS, the forming negative charge on the α -carbon can be stabilized by conjugation, and therefore the

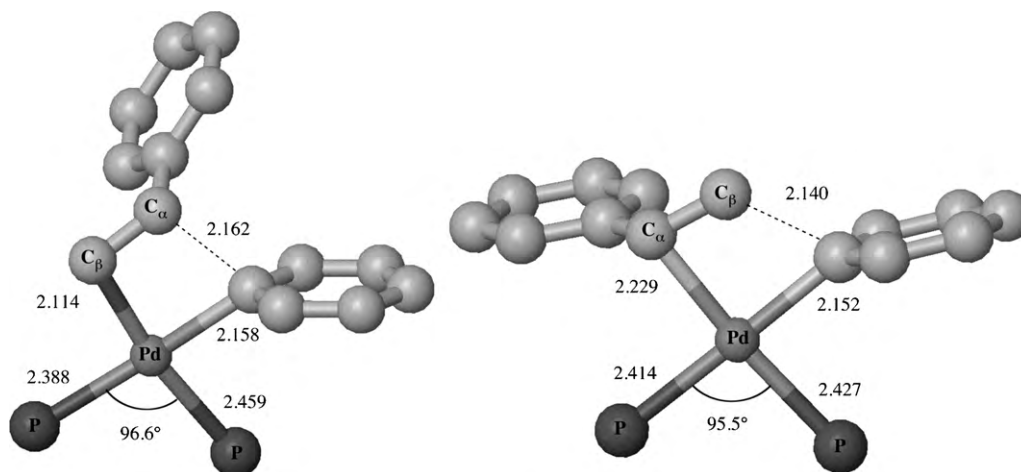


Fig. 6. Branched and linear TS from cationic **1**. Hydrogens are hidden for clarity.

Table 1

Differential activation energies (kJ mol^{-1}) for cationic systems, relative to the lowest energy TS for each ligand combination (**1**, **2**, or **3**).

Intermediate	Variable ligand	ΔE		ΔG	
		Linear	Branched	Linear	Branched
1	PH_3	0	3	0	1
2a	CO	5	3	7	0
2b	CO	0	0	0	2
3a	NH_3	0	1	0	3
3b	NH_3	1	13	3	11

interaction with Pd is weaker and the forming bond is longer by 0.115 Å.

We also see that the Pd–P bond trans to the forming Pd–C bond is longer in the branched TS (by 0.032 Å), in good agreement with the qualitative picture in Fig. 3. On the other hand, the breaking bond between Pd and the phenyl group is very similar in the two cases, only longer by 0.006 Å in the branched form. Despite this, the Pd–P bonds trans to the phenyl differ by 0.026 Å, indicating that more of the negative charge has been transferred to the alkene in the branched TS. Qualitatively, the differences between branched and linear TS seen in Fig. 6 can be found in all transition states analyzed here, for both the cationic and neutral pathways; only a few examples will be shown (*vide infra*), but all structures are available in Supporting Information.

Exchanging one phosphine for CO (intermediate **2**), we can see that the two products still can be formed via low energy pathways, but interestingly enough, for the linear TS, the geometry with CO trans to the phenyl (**2b**) is strongly preferred. In the branched TS, there is little free energy difference between the two coordination geometries. Viewed from a synthetic perspective, if geometry **2b** could be selectively disfavored by sterically demanding substituents, it should be possible to achieve a strong preference (>10:1) for the branched product. However, in a Curtin–Hammett situation without steric demands, the results with a CO-type ligand should closely mirror those obtained with only phosphines.

In the PN-model, **3**, we can see an inherent preference for transition states with the strong phosphine ligand trans to the phenyl group. This result, already seen in a study of the asymmetric Heck reaction [8], shows that from an electronic viewpoint, the TS can be characterized as “late”, despite the strong exergonicity. Obviously, enough electron density has been transferred from the phenyl group so that the forming Pd–C bond dominates the trans effect, and thus prefers the ammine in a trans position. Interestingly enough,

Table 2

Differential activation energies (kJ mol^{-1}) for neutral systems with one cyanide ligand, relative to the lowest energy TS for each ligand combination (**4**, **5**, or **6**).

Intermediate	Neutral ligand	ΔE		ΔG	
		Linear	Branched	Linear	Branched
4a	CO	0	2	0	0
4b	CO	13	21	13	21
5a	PH_3	0	6	0	4
5b	PH_3	13	27	14	27
6a	NH_3	0	4	0	4
6b	NH_3	17	40	20	36

the PN-system shows a preference for linear products. Synthetically, this effect could be maximized by favoring geometry **3b**, which shows a large linear preference of 8 kJ mol^{-1} .

The neutral Heck reaction has been modeled with two simple anionic ligands, cyanide and methyl. Transition states for an example model system, **5a**, are shown in Fig. 7. Overall, it can be seen that the geometries are very similar to those of the cationic system in Fig. 6, but the transition states are “later”; the forming C–C and Pd–C bonds are shorter, and the breaking Pd–C bond is longer for both structures in Fig. 7 compared to their counterparts in Fig. 6.

The relative energies for the migratory insertion transition states for all cyanide-containing systems are shown in Table 2. The most obvious trend is that the strong cyanide ligand prefers a position trans to the migrating phenyl group. Again, this is not what would have been expected from the pre-insertion intermediate, where a trans position of the two strong ligands phenyl and cyanide should be disfavored, but it agrees well with the effect seen in the cationic case (*vide supra*), especially for the PN-system **3** [8]. It is also clear from Table 2 that the preference for the weak ligand trans to the forming Pd–C bond is much stronger for the branched TS. In the linear TS, the developing negative charge on the β -carbon is stabilized by the aromatic substituent, somewhat mitigating the effect. Another way to view the same effect is that the branched TS is “later” than the linear TS, and thus has a more marked preference for the strong ligand trans to the phenyl, which has lost much of its trans effect thanks to charge transfer to the alkene.

It can also be seen that the observed linear preference for the neutral Heck reaction [2] is reproduced by the calculations, at least for the two cases where the neutral ligands are substantially weaker than the cyanide, **5** and **6**. We note that system **5** is the one most closely reminiscent of the “classical” neutral Heck system, a monodentate phosphine together with an anionic ligand. We also see

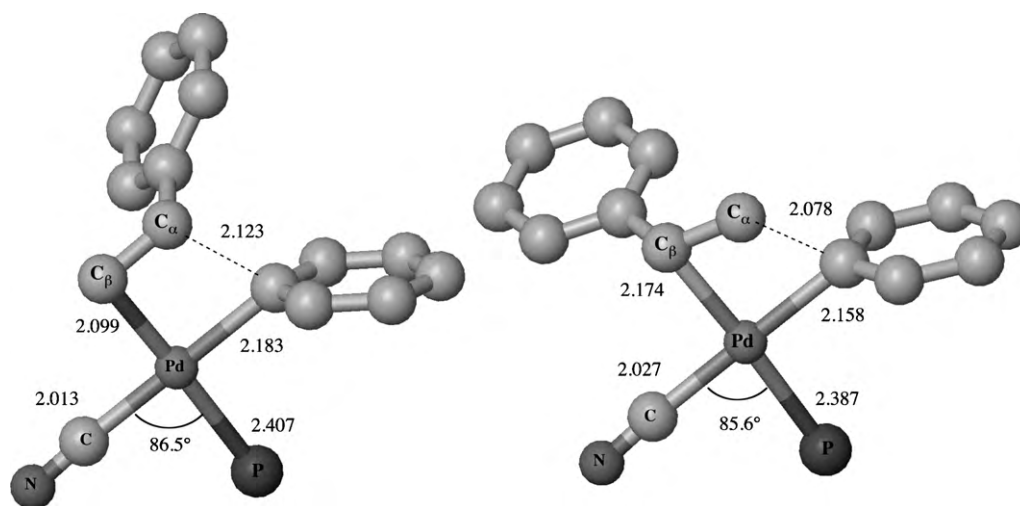


Fig. 7. Branched and linear TS from neutral **5a**. Hydrogens are hidden for clarity.

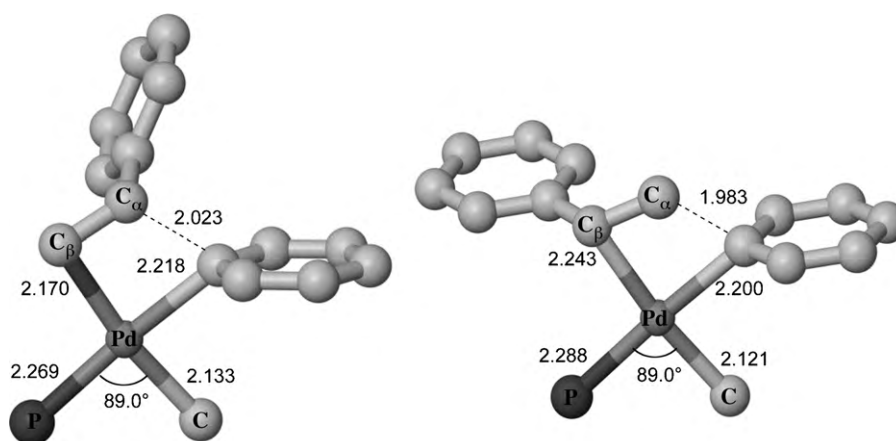


Fig. 8. Electronically disfavored branched and linear TS from neutral **8b**. Hydrogens are hidden for clarity.

that the linear preference will be much stronger in cases where path **b** can be favored. This could happen in specific cases due to steric interactions, but also for any reaction that does *not* obey Curtin–Hammett kinetics. The latter would occur in experiments where the oxidative addition is rate limiting and shows a preference for the most stable intermediate (e.g., **5b**), and where no *cis/trans*-isomerization path is open to the intermediate.

For the systems with a very strong methyl ligand (**7–9**), we have chosen to illustrate the disfavored path **b**, where the methyl group is *trans* to the developing Pd–C bond (Fig. 8). We can see a few important differences from the favored path **a** in Fig. 7. First of all, the developing Pd–C bond is much longer than in any of the previously depicted transition states. This is not due to “earlier” TS, but rather to the very strong *trans* effect of the methyl group. In fact, the length of the developing C–C bond indicates that the TS is “later”, as would be expected according to the Bell–Evans–Polanyi relationship when the product is destabilized [25]. This is verified also by the breaking Pd–C bond, which is substantially longer in **8b** compared to either **1** (Fig. 6) or **5a** (Fig. 7), despite having only a phosphine in the *trans* position.

The relative migratory insertion barriers for all systems with a methyl ligand (**7**, **8**, and **9**) are shown in Table 3. Compared to the values obtained for the cyanide ligand (Table 2), we can see that the trends correlate, but the linear preference is substantially larger, even for the favored path **a**. In fact, the linear preference obtained for **8a** (ca. 20:1) is close to the experimental preference seen with

Table 3

Differential activation energies (kJ mol^{-1}) for neutral systems with one methyl ligand, relative to the lowest energy TS for each ligand combination (**7**, **8**, or **9**).

Intermediate	Neutral ligand	ΔE		ΔG	
		Linear	Branched	Linear	Branched
7a	CO	0	7	0	2
7b		8	26	7	26
8a	PH ₃	0	10	0	8
8b		11	35	12	36
9a	NH ₃	0	9	0	8
9b		19	59	20	56

a phosphapalladacycle ligand [21], the closest experimental analog to **8a**.

Like in the cyanide case, the linear preference would become huge if the experimental system could be constrained to follow path **b**. How to do this is not easily envisioned, since the preference for path **a** is strong, but bidentate ligands like the aforementioned palladacycle, decorated with selective steric bulk could offer a possible way to accomplish this.

4. Summary and conclusions

DFT has been utilized to investigate the influence of the *trans* effect of ligands for the migratory insertion selectivity in the

cationic and neutral Heck reaction. Small model systems have been utilized to exclude interference of any other factors that may affect the insertion selectivity. The geometries and activation energies of the transition state for the branched and linear forms have been investigated and compared. The following general trends have been observed in the systems investigated here.

- (i) Due to the product-like electronic nature of the migratory insertion TS, the favored TS will frequently arise from the least favored intermediate, leading to Halpern-type selectivity [19,8]. Thus, the selectivity *cannot* be reliably predicted from observable intermediates.
- (ii) The TS is very sensitive to the trans effect of the ligand in a position trans to the migrating aryl moiety. A strong ligand in this position will accelerate the reaction, more so for the branched TS, but rarely to a point where the branched product is favored.
- (iii) The forming Pd–C bond is generally shorter in the branched than in the linear TS, implying a stronger interaction. This is a result of the lower basicity of the α -carbon due to stabilization of the forming negative charge by the neighboring aryl group.
- (iv) A related observation is that the bond length of palladium and the ligand trans to the forming Pd–C bond is more elongated in the branched form compared to the linear form. This is true no matter if the ligand has a strong or weak trans effect. This can be traced to the more σ donating nature of the β -carbon atom in the branched form. In the linear form the negative charge can be distributed into the π system turning the α -carbon into a weaker σ donor. We conclude that the branched product formation would benefit from a less competitive ligand opposite to the alkene in the pre-insertion intermediate. The effect is clearly seen in the bond lengths, and we also observe a minor difference in activation energy in the cationic system going from a weak, to a moderate σ donating group.
- (v) The Pd–L bond trans to the migrating phenyl group is always shorter in branched than in linear transition states, implying that the trans effect of the phenyl group has decreased more in the branched TS, and that this therefore is “later” than the linear TS. Similarly, the breaking Pd–C bond to the phenyl group is always slightly longer in the branched TS, for the same reason, but this effect is much smaller.

Acknowledgements

The current project is supported by the Swedish Research Council. The computations were performed on C3SE computing resources in Gothenburg. We are grateful to AstraZeneca for generous support, including funding the position for CB.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.06.007.

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