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Understanding Sulfone Behavior in Palladium-Catalyzed Domino Reactions with Aryl Iodides

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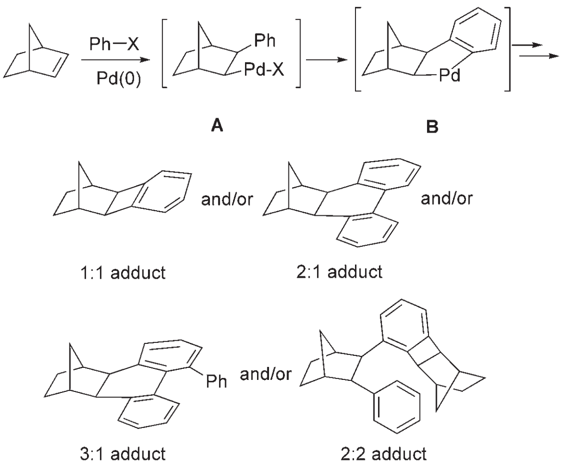
Abstract: Unlike traditionally used acyclic 1,2-disubstituted alkenes, the reaction of α,β-unsaturated phenyl sulfones with aryl iodides under Heck reaction conditions takes place mainly by means of a four-component domino process, involving one unit of the alkene and three units of the aryl iodide, affording substituted 9-phenylsulfonyl-9,10-dihydrophenanthrenes. We report here the results of a computational study on the mechanism of this domino arylation reaction. Based on these results we can explain why vinyl sulfones, unlike other electron-deficient alkenes such as enones, preferentially follow this domino pathway instead of the usual Heck pathway. The key step is a C−H activation process in which a five-membered palladacycle is formed. The greater ability of vinyl sulfones, relative to enones, to reach the transition state that leads to the formation of the initial palladacycle makes the difference.

Keywords: C−H activation · density functional calculations · domino reactions · Heck reaction · sulfones

Introduction

Among the numerous palladium-catalyzed processes for C−C bond formation,[1] the Heck reaction is one of the most versatile and widely used methods in modern organic synthesis.[2] The mechanism of this reaction is accepted to proceed according to a Pd^0/Pd^{II} cycle through oxidative addition/*syn*-carbopalladation/*syn*-β-hydride elimination as the main steps.[3] On the other hand, additional C−C bonds can be formed if, after the carbopalladation step, the *syn*-β-dehydropalladation is structurally not feasible or energetically unfavorable. In this case the resulting σ-alkylpalladium(II) intermediate undergoes further intra- or intermolecular carbopalladation[4] or intramolecular C−H activation processes to give palladacycle intermediates.[5] This latter domino process has been widely studied in the palladium-catalyzed reaction of aryl halides with norbornene,[6] because in this rigid bicyclic alkene the *syn*-β-dehydropalladation step is not possible. Thus, in this case the insertion step generates the long-lived σ-alkylpalladium intermediate (**A**) that, being unable to undergo β-hydrogen elimination, suffers an intramolecular aromatic C−H activation process with the formation of the key five-membered palladacycle intermediate (**B**). Depending on experimental conditions 1:1, 2:1, 3:1 or 2:2 coupling products are finally isolated[7] (Scheme 1).



Scheme 1. Palladium-catalyzed arylation of norbornene.

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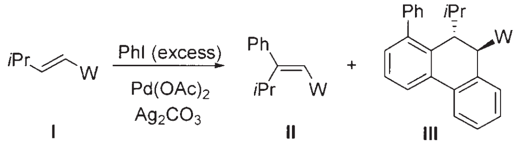
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The Supporting Information contains cartesian coordinates for all optimized structures and their absolute energies, as well as ZPE and free energy.

We recently reported the first example of a polyarylation process of an acyclic alkene (in which the β-dehydropalladation step is not precluded for structural reasons) under typical Heck reaction conditions. In particular, we found that the intermolecular palladium-catalyzed reaction of β-substituted α,β-unsaturated sulfones **I** with a large excess of iodobenzene (or *p*-substituted iodoarenes), in the presence of Ag_2CO_3 as base, occurs mainly through a domino reaction in which three molecules of iodobenzene and one molecule of vinyl sulfone are involved, affording 9,10-dihydrophenanthrenes **III**, instead of the expected Heck trisubstituted olefin **II**[8] (Table 1, entry 1). Moreover, although less favored than in the case of the arylation of α,β-unsaturated sulfones, related substituted 9,10-dihydrophenanthrenes were obtained in the case of α,β-unsaturated sulfonamides (entry 2), α,β-unsaturated phosphine oxides (entry 3), and phosphonate esters (entry 4). To our surprise, the corresponding dihydrophenanthrenes were also detected in the reaction of α,β-unsaturated esters and ketones (entries 5 and 6),[8a] although in these two cases the Heck product largely predominated.

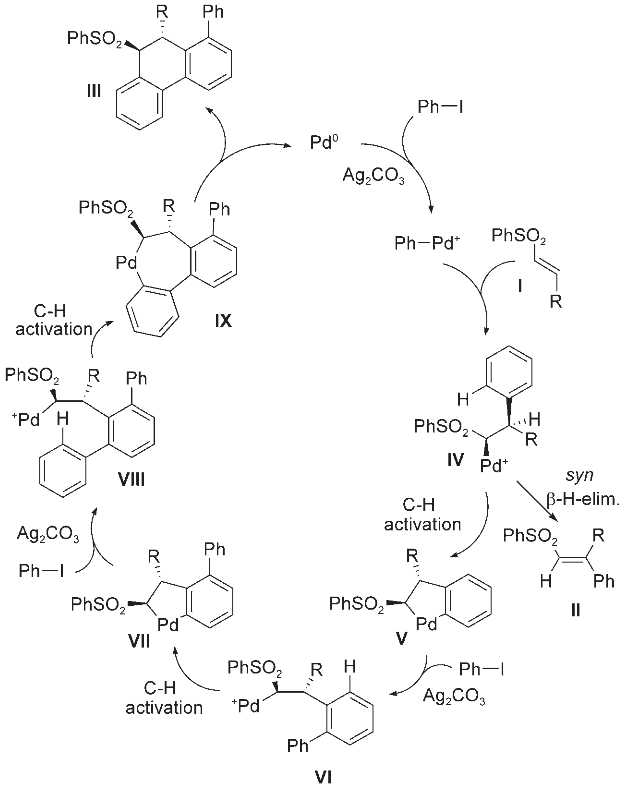
Table 1. Palladium-catalyzed reaction of electron-deficient alkenes with iodobenzene.[8a]



Entry	W	II:III
1	SO_2Ph	5:95
2	SO_2NEt_2	21:79
3	$P(O)Ph_2$	53:47
4	PO_3Et_2	65:35
5	CO_2Et	82:18
6	COPh	91:9

Abstract in Spanish: *Al contrario que los alquenos acíclicos 1,2-disustituidos tradicionalmente utilizados, la reacción de fenil sulfonas* α,β-*insaturadas con yoduros de arilo bajo condiciones de reacción de Heck tiene lugar mayoritariamente a través de un proceso dominó de cuatro componentes, en el que participan una unidad de alqueno y tres unidades de yoduro de arilo, dando lugar a 9-fenilsulfonil-9,10-dihidrofenantrenos sustituidos. Aquí se presentan los resultados de un estudio computacional sobre el mecanismo de esta reacción de arilación dominó. De acuerdo con estos resultados se puede explicar por qué en el caso de las vinil sulfonas este camino de reacción predomina sobre la reacción de Heck, al contrario que en el caso de otros alquenos pobres en electrones como las enonas. La etapa clave es un proceso de activación C–H en el que se forma un paladaciclo de cinco miembros. La mayor capacidad de las vinil sulfonas en comparación con las enonas para alcanzar el estado de transición que conduce al paladaciclo es la causa fundamental de este comportamiento diferencial.*

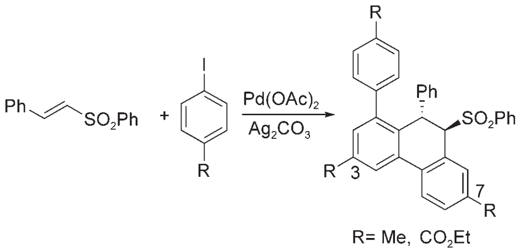
The formation of the 3:1 coupling product **III**, in which four C–C bonds are formed in a single synthetic step, indicates that *ortho*-C–H activation processes can favorably compete with the expected Heck reaction. According to the existing precedents on the polyarylation of norbornene,[7] we proposed a tentative simplified mechanistic hypothesis (Scheme 2).[8] Oxidative addition of iodobenzene to the Pd^0 catalyst in the presence of Ag_2CO_3 could give a highly electrophilic phenylpalladium species that would undergo regioselective *syn*-insertion into the C–C double bond of **I** to form the sulfonylalkylpalladium intermediate **IV**. Unlike the usual behavior of other types of acyclic alkenes, which cleanly afford Heck-type products (**II**), complex **IV** would evolve faster through a C–H activation process, to give the five-membered palladacycle **V**. This intermediate could further react with iodobenzene to give the σ-alkylpalladium intermediate **VI**. Two different mechanisms can be envisaged for this step: an oxidative addition/reductive elimination pathway via a Pd^{IV} palladacycle intermediate[9] or a ligand exchange reaction between two Pd^{II} complexes.[10] The repetition of the same mechanistic sequence at the next available *ortho*-position would lead to the sequential formation of the



Scheme 2. Mechanistic proposal for the palladium-catalyzed domino reaction of vinyl sulfones with iodobenzene (ligands at palladium atom have been omitted for clarity).

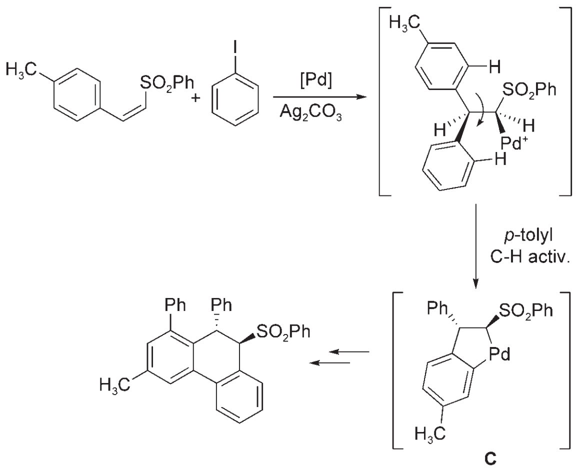
intermediates **VII** and **VIII**. Finally, a third C–H activation process would give the seven-membered palladacycle **IX**, which would afford the main product **III** after reductive elimination.

In agreement with the sequence of formation of C–C bonds depicted in Scheme 2, the palladium-catalyzed reaction with *para*-substituted iodoarenes, such as *p*-iodotoluene and ethyl *p*-iodobenzoate, led exclusively to the dihydrophenanthrenes bearing substitution at C-3 and C-7 positions[8a] (Scheme 3).



Scheme 3.

Moreover, as an additional experimental argument in favor of the *trans*-substituted five-membered palladacycle intermediates, in the reaction of a *cis*-substituted β-(*p*-tolyl)-α,β-unsaturated sulfone (Scheme 4) we obtained the dihydrophenantrene, in which the C–H activation process had taken place in the *p*-tolyl unit instead of the phenyl ring introduced after the *syn*-carbopalladation step.[8a] This result can be easily explained assuming the formation of the key *trans*-substituted five-membered palladacycle **C**.



Scheme 4.

To shed some light to the intriguing findings on the selectivity of the Heck/polyarylation reaction of electron-deficient disubstituted alkenes and the spectacular results found for sulfones, a theoretical analysis of the palladium-catalyzed arylation process has been carried out. As described herein, this study provides a plausible mechanistic explanation that is consistent with the available experimental results. Additionally, our theoretical study reveals the crucial effect of acetate ion acting as a basic ligand during the C–H activation process. This effect could presumably operate in analogous $Pd(OAc)_2$-catalyzed process reported by other authors.[4a,6,7]

Computational Methods

All calculations were performed by using hybrid density functional theory (B3LYP).[11] Geometries were fully optimized by using the 6–31G(d) basis set for all the atoms except Pd and I, for which the LANDL2Z basis set supplemented with a d function of exponent 0.289 were used.[12] Frequencies and zero-point energies (ZPE) were also computed at the same level of theory. Final energies were obtained by using the more extended 6–311+G(2df,2p) basis set for all atoms. For I and Pd basis set of similar quality with the Stuttgart effective core potentials (ECP) were used.[13] Relative free energies (in $kcal\,mol^{-1}$) were evaluated at the B3LYP/6–311+G(2df,2p) level with entropy correction evaluated at 298 K by using the frequencies previously calculated at B3LYP/6–31G(d) level. All calculations were performed by using the Gaussian 03 program[14] and the AIMPAC program provided by J. Cheeseman and R. F. W. Bader for AIM analysis.

Results and Discussion

To gain insight into the factors controlling the different trends shown by α,β-unsaturated sulfones with respect to other electron-deficient alkenes, such as enones, we carried out the theoretical characterization of the main intermediates and transition states that may be present when both processes, Heck and domino, take place. As model alkenes for this study we chose *trans*-1-propenyl methyl sulfone (**Ia**) and *trans*-3-penten-2-one (**Ib**; Figure 1). Taking into account

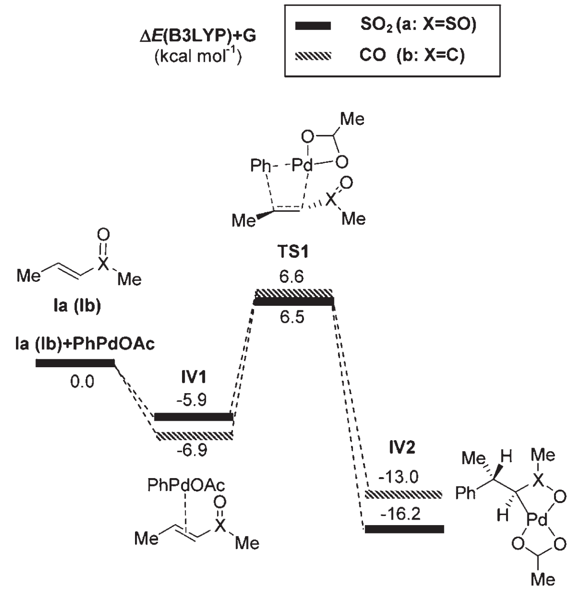


Figure 1. Energy profile for the coordination-insertion step of sulfone **Ia** and ketone **Ib**.

recent studies on the mechanism of the oxidative addition of aryl halides to Pd^0 species generated from $Pd(OAc)_2$,[15] which strongly support that one acetate ligand remains bound to palladium and influences its reactivity,[3a] we used PhPdOAc as the catalyst model. In this case, as well as in the intermediates of the Heck reaction, in the absence of strong donating ligands the acetate ion occupies two coordination sites of the metal.[16]

The intermediates have been further named with a prefix that indicates the approximate situation in the simplified mechanistic proposal shown in Scheme 2. For simplicity reasons, only the most relevant transition states (TS) have been included in the figures. Additionally, intermediates are differentiated by a letter: **H** for intermediates involved in the Heck reaction and **D** for those in the domino process.

Coordination–insertion step: As shown in Figure 1, a first intermediate (**IV1**) was identified after the initial coordination of the C–C double bond to PhPdOAc. This complex leads, through **TS1**, to the insertion intermediate **IV2**, which actually can be regarded as the starting point from which both pathways, Heck and domino, diverge (vide infra). For both, ketone and sulfone substrates, intermediate **IV1** and **TS1** are quite similar regarding their energy content and the orientation of the carbonyl or sulfonyl group as none of them is coordinated to the metal. However, once the phenyl group has been inserted in the double bond, giving rise to intermediate **IV2**, the coordination site left vacant is occupied by an oxygen atom from the carbonyl or sulfonyl groups. At this point structural differences begin to appear. While the sulfone[17] is coordinated exclusively through electron pairs located on the oxygen atom, in the case of the ketone an oxa-π-allyl arrangement is shown[18] (Figure 2). As can be observed, the sulfonyl intermediate **IV2a** is around 3 kcal mol^{-1} more stable than the carbonyl analogue **IV2b**. This can be ascribed, at least in part, to the loss of the thermodynamically stabilizing effect of the π-conjugation in the starting enone **Ib**.

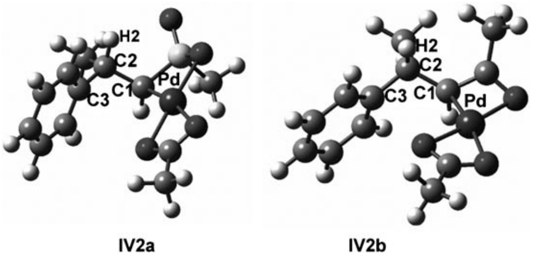


Figure 2. Molecular structures of intermediates **IV2**. Dihedral angle H2-C2-C1-Pd: 63.2° for **IV2a** and 52.3° for **IV2b**; angle C3-C2-C1-Pd: −54.0 for **IV2a** and −65.8° for **IV2b**.

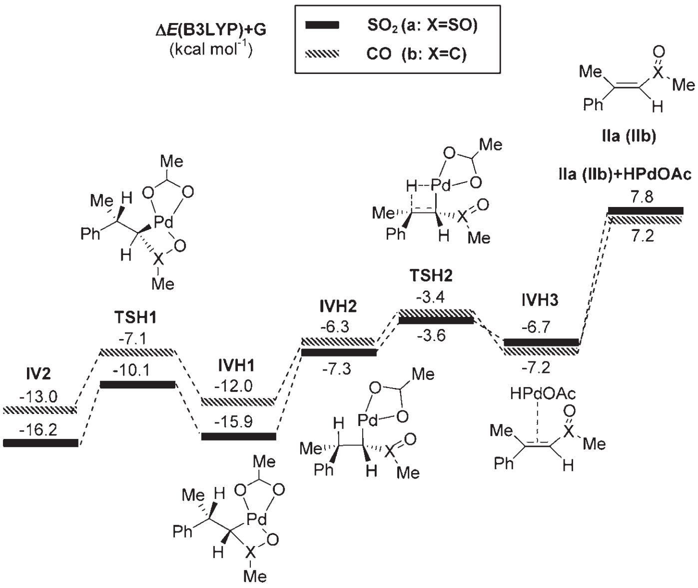


Figure 3. Energy profile for the Heck reaction of sulfone **Ia** and ketone **Ib**.

Heck reaction pathway: In this pathway (Figure 3), intermediate **IV2** may suffer a rotation through the C1–C2 bond (via **TSH1**) to afford **IVH1**, an intermediate that shows the phenyl group in a complete *anti* arrangement with respect to the palladium atom (compare dihedral angle values in Figures 2 and 4). Thus, no interactions between palladium and the aromatic ring can exist (unlike the case of the domino process) and β-hydride elimination occurs. This step takes place from **IVH2**, in which an agostic interaction between palladium and the hydrogen to be eliminated was found[19] (Figure 4: distance Pd–H2 = 1.90 and 1.84 Å; C2–H2 = 1.18 and 1.19 Å for the sulfone and the ketone intermediates, respectively). Further β-hydride elimination through the four-membered transition state **TSH2** affords **IVH3**. Finally, a highly endothermic decomplexation leads to the Heck product **II**.

As it can be seen in Figure 3, **TSH1** and **IVH1** show the same coordination pattern indicated for **IV2**. Thus, as in the case of **IV2**, the difference in energy content between the sulfone and ketone intermediates is around 3 kcal mol^{-1}. Nevertheless in the final intermediates **IVH3**, as well as in the Heck products, there is a reversion in the relative thermodynamic stability of sulfone and ketone compounds, being somewhat more stable for the carbonyl partners. This fact can be attributed to the recovery of the C–C double bond in these species, and consequently the favorable π-conjugation with the carbonyl in the case of the ketone derivatives.[20] On the other hand, according to the energy profile shown in Figure 3 it can be said that the intermediate steps in the Heck process are reversible (**IV2**/**IVH1** and **IVH2**/**IVH3**).

Domino reaction pathway: Several complexes that imply the displacement of an oxygen atom of the acetate ligand by a π bond from the previously inserted aromatic ring have been found from **IV2**. However, the most plausible complex to trigger the alternative domino mechanism is complex

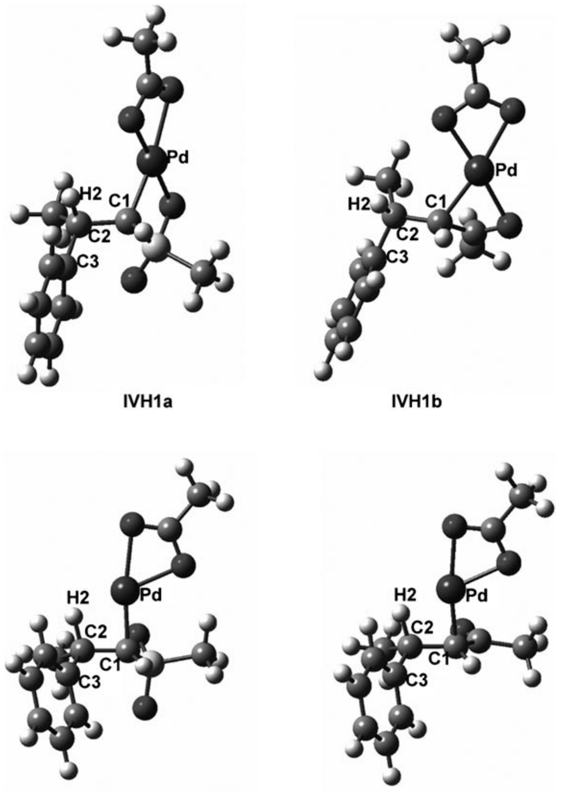


Figure 4. Molecular structures of intermediates **IVH1** and **IVH2**. Dihedral angle H2-C2-C1-Pd: −55.0° for **IVH1a**, −68.4° for **IVH1b**, −1.1° for **IVH2a** and 5.7° for **IVH2b**; C3-C2-C1-Pd: −168.3° for **IVH1a**, 177.7° for **IVH1b**, −113.7° for **IVH2a** and −107.0° for **IVH2b**.

IVD1 (see Figure 5). In this structure a σ-C–H bond is associated to palladium (distances: Pd–C = 2.35 and 2.40 Å, Pd–H = 2.26 and 2.37 Å for the sulfone and ketone species, respectively). The coordinated C–H bond is oriented in an orthogonal fashion with respect to the coordination plane of the metal. Its activation through **TSD1**, in which the simultaneous C–H breaking and C–Pd and O–H bond formation or "σ-bond metathesis" take place,[21] will lead to the five-membered palladacycle **VD2**. This is the energetically key step that determines whether the reaction proceeds through the domino mechanism or leads to the Heck product. In the case of the sulfone, the energy required to form **TSD1** is slightly lower than the energy for the Heck product (7.0 vs. 7.8 kcal mol^{-1}), while in the case of the ketone the energy of **TSD1** is much higher than that corresponding to the Heck product (12.1 vs. 7.2 kcal mol^{-1}). Thus, the high energy for **TSD1** in the case of the ketone prevents the domino mechanism from occurring and would be consistent with the usual behavior of enones in Heck reactions.

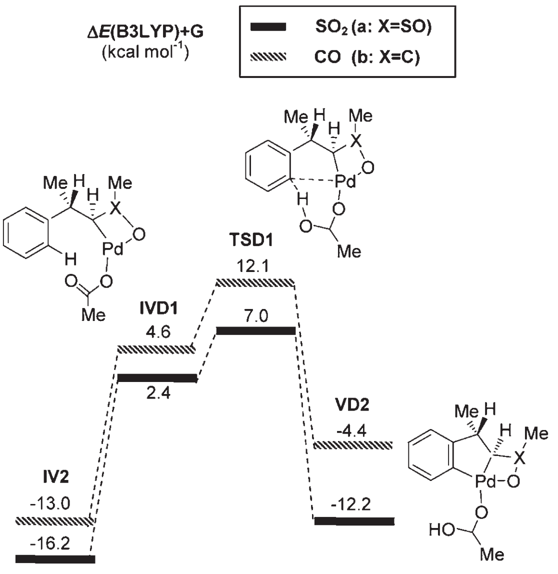


Figure 5. Energy profile for the formation of the five-membered palladacycle in the palladium-catalyzed domino arylation of sulfone **Ia** and ketone **Ib**.

Once the palladacycle **VD2** is formed, the following step (**V**→**VI** according to Scheme 2) is much more complex, and taking into account the size of the models employed, a detailed analysis exceeds the scope of this study. Additionally, considering that the repetition of the C–H activation at the next available *ortho*-position would afford quite similar intermediates, and would considerably increase the size of the models, we decided to study on **VI** the last C–H activation process leading to the dihydrophenanthrene-type product **III′** (Figure 6). As in **IVD1**, in **VID3** it was also observed that a σ-C–H bond is associated with the palladium atom (distances: Pd–C = 2.28 and 2.31 Å, Pd–H = 2.45 and 2.39 Å

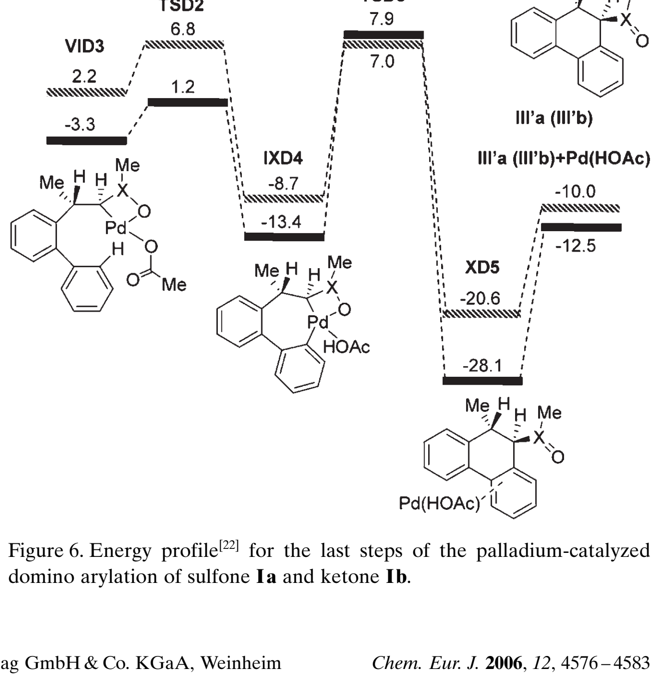


Figure 6. Energy profile[22] for the last steps of the palladium-catalyzed domino arylation of sulfone **Ia** and ketone **Ib**.

for the sulfone and the ketone, respectively). Then, the C−H activation takes place through **TSD2** affording the seven membered palladacycle **IXD4**. From this point a reductive elimination takes place (**TSD3**) giving rise to complex **XD5**, which after a decomplexation step leads to dihydrophenanthrene **III′** (lacking the phenyl group at C-1 with respect to **III**).

From a global mechanistic point of view, both ketone and sulfone starting compounds **I** must overcome a first activation barrier for the insertion step (**TS1**) before the Heck or domino competitive process occur. This is in agreement with the fact that the reaction only takes place by heating (120 °C). After this common step, the more energetically demanding steps are the final decomplexation (to afford the Heck product) and the initial C−H activation process in the domino pathway. All the intermediate steps in the Heck process are reversible (**IV2**/**IVH1** and **IVH2**/**IVH3**), whereas in the domino process, once **VD2** has been formed the following steps are highly exothermic (**VID3**→**IXD4**→**XD5**). Therefore, the relative energies of the Heck product and **TSD1** determine the preferred pathway trend. In other words, the Heck product is much more stable (in comparison with **TSD1**) for ketones and should be the main product formed; this observation is in agreement with experimental evidence. However, for sulfones, although evolution through **TSD1** is only slightly more favorable than the Heck product formation, the domino process is thermodynamically much more favorable and can effectively compete with the Heck process.

The nature of the intermediates that would connect **VD2** and **VID3** in Figures 5 and 6 is a controversial issue. Although a detailed study was not possible due to the size of these models, the final presumed intermediates involved in the two mechanisms usually proposed [oxidative addition via Pd^{IV}[9] (**PdIV**) or ligand exchange reactions between two Pd^{II} complexes[10] (**PdLE**) have been characterized (Figure 7). The latter case implies a bimolecular reaction and appropriate kinetic experiments have not been undertaken. However, although the reaction is conducted under catalytic conditions,[24] the concentration of PhPdOAc could be enough for the reaction to proceed through a bimolecular pathway. It is important to note that the intermediate **PdLE** (resulting from a ligand exchange) is by far much more stable (19–20 kcal mol^{-1}) than the hypothetical Pd^{IV} intermediate **PdIV**. In fact, the participation of these Pd^{IV} intermediates would make the domino pathway unfeasible.

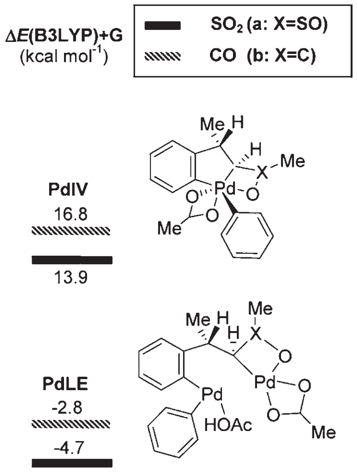


Figure 7. Relative energies[23] and structures of the hypothetical intermediates **PdIV** and **PdLE** allowing the step process **VD2**→**VID3**.

Structural differences between sulfonyl and carbonyl palladium-coordinated species: An interesting observation from the energy profiles on Figures 1, 3, 5, and 6 is the higher stability of complexes and transition states in which the sulfonyl group is coordinated to the palladium atom instead of the carbonyl group (from **IV2** to **IVH1** in the Heck pathway and in **IVD1**→**VD2**→**VID3**→**IXD4** and in **XD5** in the domino pathway). In contrast, the sulfone versus carbonyl differences in the stability of the complexes are lower or even inverted when the coordination with the palladium atom is not present (species **IVH2**, **TSH2**, **IVH3** and **TSD3**). These results are noteworthy, since sulfones are not usually considered as highly metal-coordinating groups. However, the inspection of the electronic densities[25] shows the formation of very similar bonds between the Pd atom and the carbonylic or the sulfonylic oxygen atoms. Complexes formed in the reaction of the enone **Ib** show a well-established oxa-π-allyl coordination,[18] whereas in complexes derived from sulfone **Ia** only the carbon atom at the α-position (C1) and one of the sulfonylic oxygen atoms[17] are involved in the coordination to the metal. Spatial arrangements of the key intermediates **TSD1** showing these modes of coordination are depicted in Figure 8.

An inspection of the electronic densities between Pd and its coordinating atoms shows that the electronic effects are very similar in both sulfone and ketone intermediates. The carbon atom C1 is slightly better donor in the case of the sulfone, and the bond between Pd and O6 presents the same characteristics regardless of its carbonyl or sulfonyl nature.

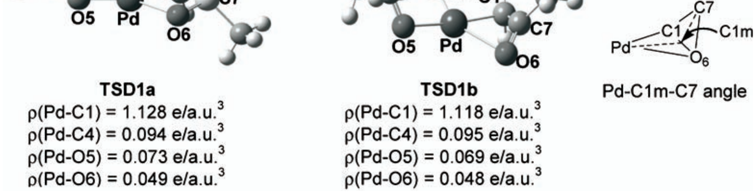


Figure 8. Spatial representation of intermediates **TSD1**. The values of the electronic density at the bond critical points[25] located around Pd are indicated.

The main differences between both complexes emerge from the different coordination modes. As it is depicted in Figure 8, **TSD1a** shows a conformation almost free of steric interactions. Due to the existence of two oxygen atoms on the sulfonyl group the coordination is established between Pd and O6 (and not O8), in such a way that the methyl sulfonyl group can be located far from carbon atoms C2 and C3. However, in the case of the carbonyl species, there is an important steric interaction between the methyl ketone group (C8) and the benzylic position (atoms C2 and C3) on **TSD1b**. This repulsive interaction forces the oxa-π-allyl moiety to deviate from the usual perpendicular arrangement with respect to the coordination plane of the palladium atom. As in π-allyl coordination, the angle Pd-C1m-C7 (in which C1m is the midpoint of the C1–O6 bond; see Figure 8) should be close to 90° in order to reach the highest degree of stabilization. The deviation from the perpendicular plane can be directly related with the differences in the stability for ketone and sulfone intermediates. Thus, as shown in Table 2 for the key intermediates **IVD1** and **VD2** and the transition state **TSD1** leading to the five-membered palladacycle, the higher the difference in stability between sulfone and carbonyl species, the higher the angle Pd-C1m-C7 observed in the oxa-π-allyl unit. The increase of the value of this angle also produces a decrease in the corresponding orbital interactions (last column in Table 2).

Table 2. Correlation between energy differences in sulfonyl/carbonyl complexes and oxa-π-allyl moiety orientation in carbonyl complexes (**b**).

	Energy content[a]	Energy difference	Angle (Pd-C1m-C7)	Orbital interactions[b] [kcal mol^{-1}]	
IVD1a	2.4		–		–
IVD1b	4.6	2.2	115.0	σ(Pd–C1)→π*(C7–O6)	42.1
				Pd→π*(C7–O6)	10.9
				π(C7–O6)→σ*(Pd–C1)	21.9
				π(C7–O6)→Pd*	8.6
TSD1a	7.0		–		–
TSD1b	12.1	5.1	126.8	σ(Pd–C1)→π*(C7–O6)	23.2
				Pd→π*(C7–O6)	3.1
				π(C7–O6)→σ*(Pd–C1)	11.5
				π(C7–O6)→Pd*	7.0
VD2a	−12.2		–		–
VD2b	−4.4	7.8	131.6	σ(Pd–C1)→π*(C7–O6)	20.4
				Pd→π*(C7–O6)	1.4
				π(C7–O6)→σ*(Pd–C1)	1.2
				π(C7–O6)→Pd*	0.8

[a] Relative energy values with respect to **I+PhPdOAc** (from Figure 5). [b] Evaluated by means of a second-order perturbational analysis of the Fock matrix on the NBO basis.

Conclusion

In summary, DFT calculations provide a plausible mechanism for the domino arylation reaction observed in the Pd(OAc)$_2$-catalyzed reaction of α,β-unsaturated sulfones with iodoarenes and its great predominance over the expected Heck reaction. We have found that the acetate ligand is essential in the key C–H activation process leading to palladacycles intermediates. We have also found that the different palladium coordination modes shown by sulfones and ketones could be at the origin of the opposite reactivity of enones (Heck reaction pathway) and α,β-unsaturated sulfones (polyarylation domino pathway) under the same palladium-catalyzed reaction conditions. Moreover, the theoretical results presented here suggest that the ability of sulfonylic oxygen atoms to coordinate palladium should be carefully considered when using this functional group in metal-catalyzed reactions.

Acknowledgements

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