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Aryl Transfer between Pd(II) Centers or Pd(IV) Intermediates in Pd-Catalyzed Domino Reactions

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Abstract: A computational study has been performed to determine the mechanism of the key steps of Pd-catalyzed domino reactions in which $C(sp^2)-C(sp^2)$ are formed from aryl and alkenyl halides. DFT calculations were done on model complexes of the proposed intermediates, with PH_3 and H_2O as ancillary ligands, to explore two possible mechanisms: the oxidative addition of aryl or alkenyl halides to palladacycles to give Pd(IV) intermediates, and the transmetalation-type reaction of aryl or alkenyl ligands between two Pd(II) centers, a palladacycle, and a Pd(II) complex formed by oxidative addition of aryl or alkenyl halides to Pd(0). We have shown that oxidative addition of iodoethylene to Pd(0) precursors is more favorable than oxidative addition to Pd(II) palladacycles, whereas transmetalation-type reactions between Pd(II) complexes are facile. Similar results were obtained with iodobenzene instead of iodoethylene and formamide as the ancillary ligand. These results suggest that Pd(IV) intermediates are not involved in these reactions.

Introduction

Palladium-catalyzed reactions of synthetic interest usually involve Pd(0) and Pd(II) complexes in the catalytic cycles.[1] However, there is strong evidence for the formation of Pd(IV) intermediates by oxidative addition of alkyl halides to Pd(II) complexes by S_N2 processes.[2−4] Other d^8 organometallic compounds such as Vaska's complexes $[IrCl(CO)L_2]$[5] and certain Pt(II) complexes also react readily with alkyl halides by oxidative addition.[6,7] Activation of $C(sp^2)-X$ electrophiles, such as aryl halides, by oxidative addition has been reported in the case of Ir(I)[8] and Pt(II)[9] complexes, but such a process has not been observed for Pd(II) derivatives. Indeed, there is no clear-cut experimental evidence for the oxidative addition of $C(sp^2)-X$ electrophiles to Pd(II) complexes,[10,11] although Pd(IV) complexes $[PdArX_3(L-L)]$ ($Ar = C_6F_5$; $X = Cl, Br$) are obtained by oxidative addition of X_2 to $[PdArX(L-L)]$.[12] In addition, reaction of $[Ph_2I]OTf$ with Pd(II) and Pt(II) has recently been reported to give metal(IV) species by formal transfer of Ph^+.[13,14] Comparison between calculated activation barriers for the oxidative addition of iodobenzene to Pd(0) and Pd(II) precursors show that the former process is more favorable.[15]

Certain cross-coupling reactions and Heck alkenylations were proposed to involve Pd(IV) species as intermediates.[16,17] This proposal was based on the fact that several palladacycles[18−20] act as catalysts in Heck alkenylation and cross-coupling reactions. However, strong evidence has been accumulated indicating that the palladacycles actually act as a reservoir of

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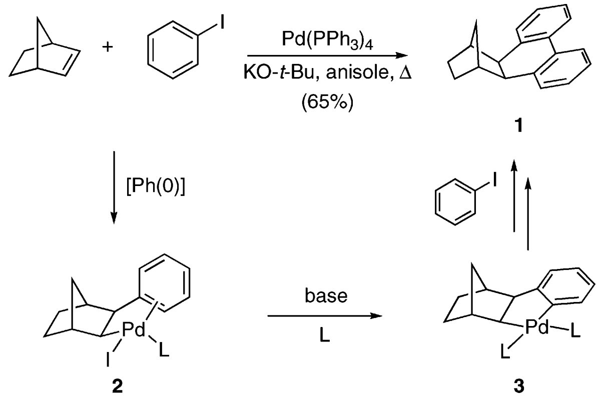
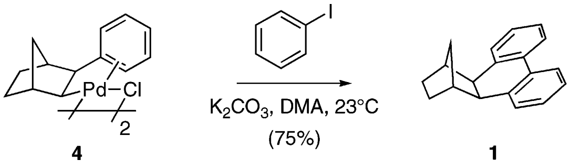
10.1021/ja056661j CCC: $33.50

Pd(II) that is reduced to Pd(0) to enter the catalytic cycle.[21−30] It is known that stabilized metallic palladium particles are catalytically very active at low catalyst loading.[31−33] The formation of Pd(IV) complexes by oxidative addition of C−H bonds has been invoked in other catalyzed reactions.[34] However, recent computational studies on cyclocarbopalladations have shown that a more favorable mechanistic alternative exists that avoids the involvement of Pd(IV) intermediates.[35,36]

Scheme 1



The reaction of norbornene with iodobenzene or bromobenzene in the presence of [$Pd(PPh_3)_4$] as the catalyst at high temperature leads to pentacycle **1** (Scheme 1). This reaction has been most extensively studied by Catellani and co-workers and by others.[37,38] The reaction proceeds by insertion of the phenylpalladium(II) complex into the double bond of norbornene to give (η^2-phenyl)norbornyl palladium(II) complex **2**,[39] which undergoes intramolecular C−H activation to form palladacycle **3**. Further reaction of this intermediate with iodobenzene leads to **1**. Some other polycyclic compounds have also been isolated in this and related reactions.[40−44] In general, these reactions usually proceed in coordinating solvents such as DMF and DMA, and in the absence of phosphines. For example, in sharp contrast with the catalytic reaction shown in Scheme 1, the stoichiometric reaction of complex **4** with iodobenzene and base in the absence of phosphines and in DMA as the solvent affords **1** under very mild conditions (eq 1).[45]



(2)

Dyker has reported related reactions leading to polycycles such as **5**, in which the intermediacy of palladacycles **6** has

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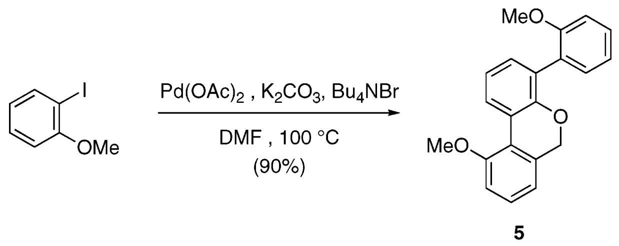
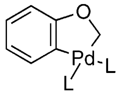
Scheme 2





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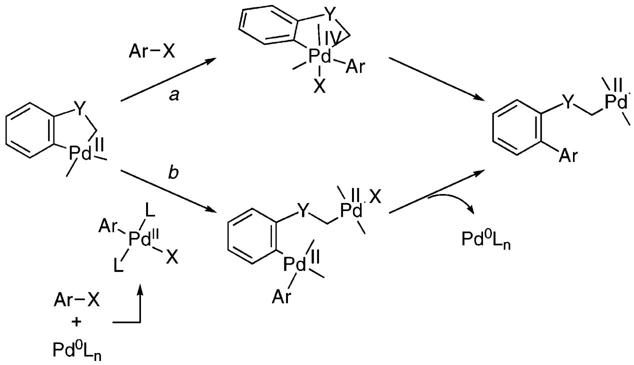
Scheme 3 [a]



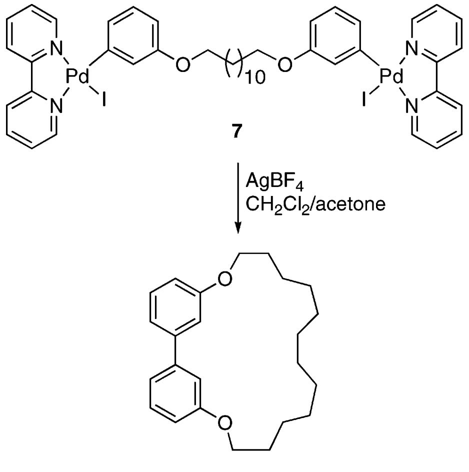
[a] Ligands on Pd are omitted for clarity.

also been proposed (Scheme 2).[46] Stabilized versions of complexes **3** and **6** have been isolated by using suitable ligands,[4,40] and there is little doubt about their participation in the catalytic cycle. Reaction of these palladacycles with alkyl, allyl, and benzyl halides takes place easily,[2−4] and as a consequence, new synthetic methods for the formation of several C−C bonds have been recently developed.[47,48]

However, it is not yet clear how these palladacycles react with $C(sp^2)-X$ electrophiles to form the $C(sp^2)-C(sp^2)$ bonds present in the final products.[49] Although processes involving the oxidative addition of PhX (X = Br, I) to palladacycles **3** and **6** have been usually invoked,[37−44] a mechanistic alternative consists on a transmetalation-type exchange of aryl ligands between different Pd(II) centers. Both possibilities are shown in Scheme 3 (pathways *a* and *b*, respectively).

Exchange of carbon ligands between two Pd(II) centers[50] or between Pd(II) and Pt(II)[51] have been reported. A particularly illustrative example has been reported by the group of Osakada

Scheme 4



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(Scheme 4). Thus, reaction of dinuclear arylpalladium complex **7** with $AgBF_4$ gives rise to macrocyclic biaryl **8** via a Pd(II)/Pd(II) transmetalation-like reaction.[52]

Due to the lack of evidence on the oxidative addition of aryl or alkenyl halides to Pd(II) complexes, we have explored the feasibility of this second mechanistic alternative for the formation of $C(sp^2)-C(sp^2)$ bonds in the context of domino reactions, catalyzed by Pd complexes, summarized in Schemes 1 and 2. We chose to study systems such as that shown in Scheme 3 in which palladacycles bear $Pd-C(sp^2)$ and $Pd-C(sp^3)$ as models for the palladacycles involved in important domino reactions developed by Catellani (Scheme 1 and eq 1) and Dyker (Scheme 2). Our aim was to find a plausible reaction pathway for the activation of aryl and alkenyl halides to give C−C bonds, comparing the more probable mechanisms involving oxidative addition either to Pd(0) or Pd(II) complexes.

Computational Methods

Calculations were performed with Gaussian 98 at DFT level.[53] The geometries of all complexes here reported were optimized at the generalized gradient approximation using the B3LYP hybrid functional.[54] Optimizations were carried out using a basis set we refer to as B_1. It consists of the standard 6-31G(d) basis set for C, H, O, and P. The LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt and employs a split-valence (double-ζ) basis set, was used for Pd and I.[55] For more accurate energy values, single-point calculations were performed on the optimized geometries using a larger basis set (B_2), essentially a valence triple-ζ one. *The corresponding energies are labeled as E′ in the Schemes.* For Pd, the Stuttgart RSC ECP was utilized. The (8s7p6d) primitive set was

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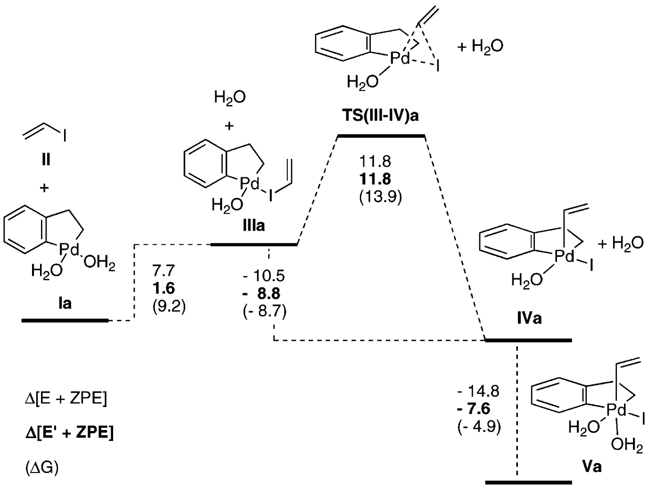
(55) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5653. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

Scheme 5. Reaction Pathway and Energies for the Oxidative Addition of **II** to Palladacycle **Ia** (kcal/mol; Δ(*E*+ZPE) in lightface, Δ(*E*′+ZPE) in boldface, and Δ*G* in brackets)



Scheme 6. Reaction Pathway and Energies for the Oxidative Addition of **II** to Palladacycle **Ib** (kcal/mol; Δ(*E*+ZPE) in lightface, Δ(*E*′+ZPE) in boldface, and Δ*G* in brackets)

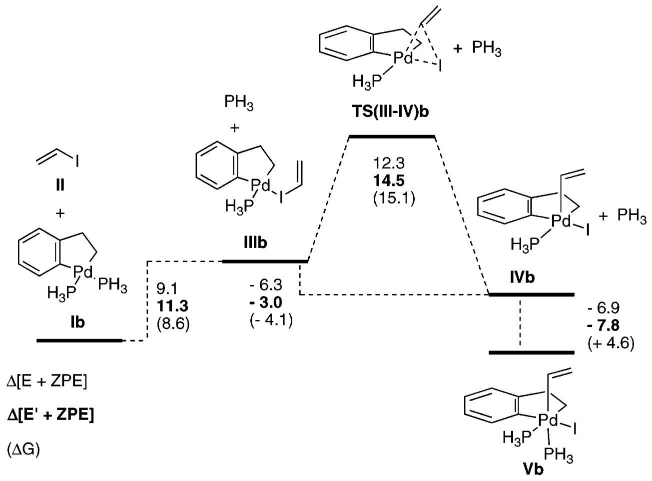


Table 1. Relative Energies (kcal/mol) for the Pd(II)−Pd(IV) Pathways of Schemes 5 and 6[a]

	Δ(*E* + ZPE)	Δ*E*′	Δ(*E*′+ZPE)	Δ*G*
		L = H_2O		
Ia +**IIa**	0	0	0	**0**
IIIa + H_2O	7.7	3.2	1.6	**9.2**
TS(III−IV)a	19.5	15.7	13.4	**23.1**
IVa	−2.8	−6.2	−7.2	**0.5**
Va	−17.6	−16.5	−14.8	**−4.4**
		L = PH_3		
Ib +**IIb**	0	0	0	**0**
IIIb + PH_3	9.1	13.0	11.3	**8.6**
TS(III−IV)b +PH_3	21.4	27.9	25.8	**23.7**
IVb + PH_3	2.8	9.3	8.0	**4.5**
Vb	**−4.1**	**−0.9**	**0.2**	**9.1**

[a] *E*: electronic energy calculated with basis set B_1. *E*′: electronic energy calculated with basis set B_2. ZPE and Δ*G* calculated with B_1.

contracted to [6s5p3d], and was supplemented with two f and one g polarization functions ($\zeta_f = 0.6122, 2.1857$; $\zeta_g = 1.3751$).[11] For I, the Stuttgart RLC ECP was used. For the valence shell, the [2s,3p] pattern was uncontracted to (4s,5p), and the basis set was supplemented with one s and one p diffuse functions ($\zeta_s = 0.0405$; $\zeta_p = 0.0328$); and two d and one f polarization functions ($\zeta_d = 0.414, 0.184$; $\zeta_f = 0.434$) according to the literature.[56] The standard 6-311+G(2df,2p) basis set was used for C, H, O and P. Harmonic frequencies were calculated at the same level with basis set B_1 to characterize the stationary points and to determine the zero-point energies (ZPE). Energies calculated with basis sets B_1 and B_2 were both corrected with these ZPEs without scaling. The starting approximate geometries for the transition states (TS) were graphically located. Intrinsic reaction coordinate (IRC) studies were performed to confirm the relation of the transition states with the corresponding minima. The bonding characteristics of the different stationary points were analyzed by means of two different partition techniques, namely, the atoms in molecules (AIM) theory of Bader[57] and the natural bond orbital (NBO) analysis of Weinhold et al.[58] The first approach is based in a topological analysis of the electron charge density, $\rho(\mathbf{r})$ and its Laplacian $\nabla^2\rho(\mathbf{r})$. More specifically, we have located the so-called bond critical points (bcp), i.e., points where $\rho(\mathbf{r})$ is minimum along the bond path and maximum in the other two directions. These points are associated with the positions of the chemical bonds. Then, at the bcp, $\rho(\mathbf{r})$ presents one positive curvature (λ_3) and two negative ones (λ_1, λ_2). The NBO technique permits describing the different bonds of the system in terms of the natural hybrid orbitals centered on each atom and provides also useful information on the charge distribution of the system.

Results and Discussion

1. Reaction of Palladacycles with C(sp^2)−X electrophiles. Palladacycles of type **I** were chosen since they share the common features shown by the proposed intermediates in the above-mentioned domino reactions (**3** and **6**): Pd atom is coordinated to one C(sp^2) and one C(sp^3) in a cis arrangement. Iodoethylene (**II**) was used as a model for iodoarenes in the oxidative addition to palladacycles **I** (Scheme 5). Two types of ancillary ligands, H_2O and PH_3, have been used in the model structures. Water has been chosen as a model for DMA or DMF, the usual solvents for these reactions, which are usually said to proceed under "ligandless" conditions.[28] Similar results were found using formamide as a more realistic model for these solvents as well as by using iodobenzene instead of **II** (see below). On the other hand, phosphine ligands might facilitate transmetalation-type process of organic groups between two Pd atoms. Thus, aryl−Pd(II) complexes Ar_2PdL_2 have been observed to exchange aryl groups with $MePdL_2I$ (L = PEt_2Ph) species.[50]

The calculated free energy profiles for the oxidative addition of **II** to **Ia** and to **Ib** are shown in Schemes 5 and 6, respectively. Relative energies at different levels are shown in Table 1. Structures of complexes **IIIa** and **IVa** were reoptimized using triple-ζ basis set B_2 (see Supporting Information). The energy difference is almost identical to the value found at B3LYP/B2//B3LYP/B_1 level (8.7 vs 8.8 kcal/mol^{-1}). Therefore, the energy values obtained from single-point calculations with B_2 on the molecules optimized with B_1 are reliable.

Transition states for these reactions **TS(III−IV)a−b** are reached from complexes **IIIa−b**, respectively, in which one of the non-carbon ligands have been replaced by **II**, which is coordinated through iodine. Activation energies are moderate (11−15 kcal/mol), and similar for both types of ancillary ligands. Since ligand exchange is endothermic, these transition states lye far above the entry channel. Binding of an additional ligand

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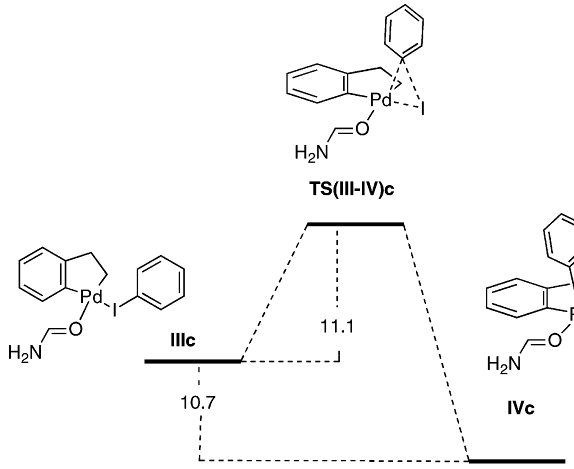
(56) The most diffuse p function ($\zeta_p = 0.032641$) of the Stuttgart (4s,5p) scheme was replaced with the p function ($\zeta_p = 0.0328$) given with the above-mentioned diffuse s and polarization d and f functions in: Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995** *103*, 1878−1885.

(57) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, 1990.

(58) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

Scheme 7. Reaction Pathway and Energies for the Oxidative Addition on **III** (kcal/mol; Δ(*E*+ZPE) Calculated with Base B_1



to pyramidal five-coordinate complexes affords octahedral derivatives **Va−b**. This process should present low activation energies, and it is thermodynamically favored in the case of complexes **a** (−7.6 kcal/mol for Δ(*E*′+ZPE), and − 4.9 kcal/mol for Δ*G*, see Table 1). For the PH_3 derivatives, instead, entropic factors account for a positive Δ*G* at 298 K (+ 4.6 kcal/mol, vs Δ(*E*′+ZPE) = −7.8 kcal/mol). We could not find octahedral transition states for the direct reaction between complexes **Ia−b** and iodoethylene, which is in accord with the reductive elimination from pyramidal Pd(IV) complexes previously reported.[2a] Oxidative addition from **IIIa** is slightly more favorable compared with that from **IIIb**, although it is usually stated that phosphine ligands favor oxidative addition processes. This may be due to the lower ability of water (a pure σ-donor) to release electron density from the electron-rich Pd(II) center in complex **Ia**, which destabilizes the reagent. In fact, NBO analysis of **Ia** and **Ib** shows a lower natural charge for Pd in the latter (+0.38 and +0.27 for **Ia** and **Ib**, respectively) due to back-donation from Pd to antibonding σ(P−H) orbitals. In the transition states leading to Pd(IV) complexes, this effect of ligands is less important, as indicated by the more similar natural atomic charges for Pd (+0.52 and +0.47 for **TS(III−IV)a** and **TS(III−IV)b**, respectively).

The oxidative addition process was also studied with model **IIIc** with iodobenzene instead of iodoethylene and formamide as a ligand for Pd (Scheme 7). The results are similar to that found for **3a** (Scheme 5).

2. Transmetalation between Pd Complexes. To study the transmetalation pathway between two Pd complexes, we first considered the oxidative addition of **II** to coordinatively unsaturated Pd(0) species (Scheme 8).

This process begins with coordination of **II** to PdL_2, so that it can be compared with the mechanism discussed above. Coordination of **II** to $Pd(H_2O)_2$ makes one of the water molecules to dissociate along the optimization process and remain hydrogen bonded. Regardless of the type of ancillary ligand, binding of **II** to PdL_2 to give **VIa−b** is significantly exothermic, especially for the water derivative. In contrast to complexes **IIIa−b**, iodoethylene binds to Pd(0) in the usual fashion for this oxidation state, through the C−C double bond to give **VIa−b**. The unfavorable entropic balance makes the formation of **VIb** only slightly exergonic at 298 K. Oxidative addition takes place from complexes **VIa−b**. Activation energies are very similar to those computed for the oxidative addition to give Pd(IV) species when Δ*G* is considered and are somewhat higher in this case for the H_2O derivative when entropy is not considered. The initially formed oxidative addition cis complexes **VIIa−b** would rapidly equilibrate with the corresponding trans stereoisomers.[59] This transformation is exothermic for PH_3 derivatives and endothermic for the H_2O analogues.

The reaction profiles, including the entry channels, for the processes involving carbon ligand exchanges between Pd centers (transmetalation-type process), are depicted in Schemes 9 and 10 for H_2O and PH_3 derivatives, respectively. Relative energies for the stationary points are depicted in Table 2.

The transmetalation-type process was also studied with a more complete model **VIIIc** where phenyl replaces the alkenyl and formamide is used as the ligand as a model for the commonly used amide solvents such as DMF or DMA (Scheme 11). The Pd−Pd transmetalation process is similar to that shown in Schemes 9 and 10 and proceeds with a moderate activation energy of 5.4 kcal/mol.

Association between metallacycles **Ia−b** and oxidative addition complexes **VIIa−b** may lead to dinuclear species in which both Pd centers become bridged by iodine. Gathering of both metal fragments would favor a transmetalation-type reaction of an organic ligand from the complex containing two Pd−C bonds which would be the most nucleophilic one to the other metal atom. Indeed, we have experimentally observed that addition of LiCl or LiI favors the formation of aryl−aryl bonds in this context.[45] Therefore, complexes **VIIIa−b** were optimized (Figure 1). Phenyl ligand, which is bound to one Pd through a usual $C(sp^2)$−Pd σ-bond (Pd−C distances: 2.063 and 2.114 Å, for **VIIIa** and **VIIIb**, respectively), is also coordinated to the second metal atom by the *ipso* carbon through the π-cloud (Pd−C distances: 2.241 and 2.331 Å, for **VIIIa** and **VIIIb**, respectively). This interaction forces the aryl ring out of coplanarity with the coordination plane of the metalacycle. Bader analysis[58] of **VIIIa** and **VIIIb** shows the existence of bond critical points between the phenyl carbon and both Pd atoms. In the case of **VIIIa**, NBO analysis[59] shows similar natural bond orbitals between C and both Pd atoms, although second-order perturbation theory reveals different character for each bond, since an important donor−acceptor interaction takes place from the Pd−C bonding orbital of the donor carbon ligand to the antibonding Pd−C orbital of the metal that is accepting the phenyl ligand in the transmetalation-type process. Only one Pd−C bond is observed in the NBO analysis of **VIIIb**, in which Pd−C bond distances are longer compared with those in **VIIIa** due to the higher trans influence exerted by phosphine ligands compared with H_2O. Bridging phenyl interaction is strong enough to force small Pd−I−Pd angles (56.0° and 59.5° for **VIIIa** and **VIIIb**, respectively).

Transfer of phenyl takes place with concomitant coordination of an additional ancillary ligand, resembling an associative ligand exchange typical of d^8 metal complexes. The incoming ligand coordinates the metal atom from which the organic ligand is transferred, which is the more electron-rich one, according to the computed natural charges (+ 0.33 vs + 0.39 for **VIIIa**; and +0.42 vs +0.53 for **VIIIb**). In **TS(VIII−IX)a**, the phenyl group has been completely transferred (Pd−C bond distance

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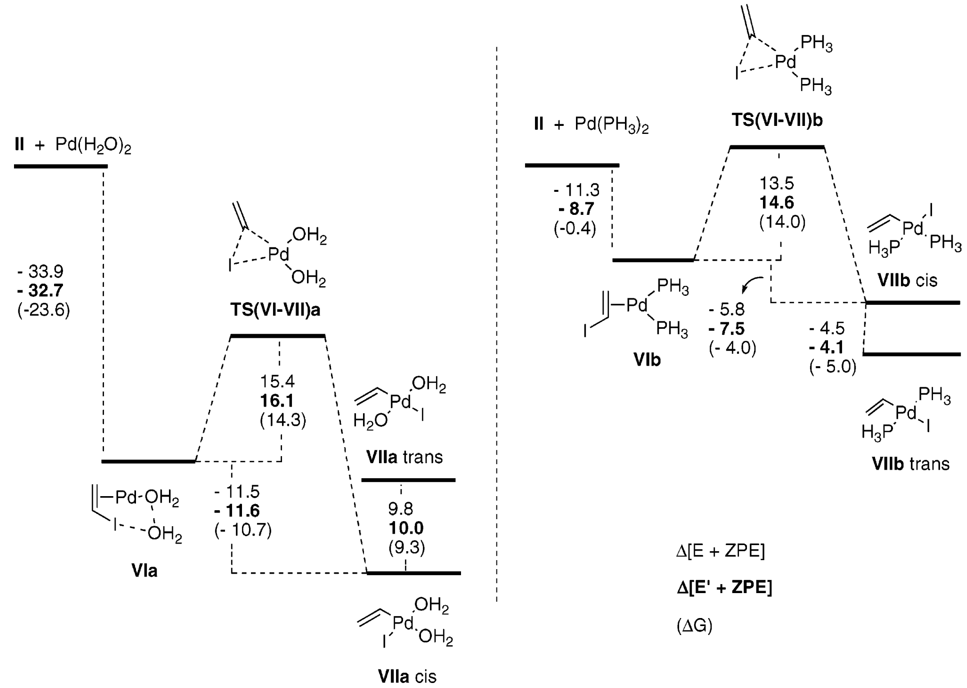
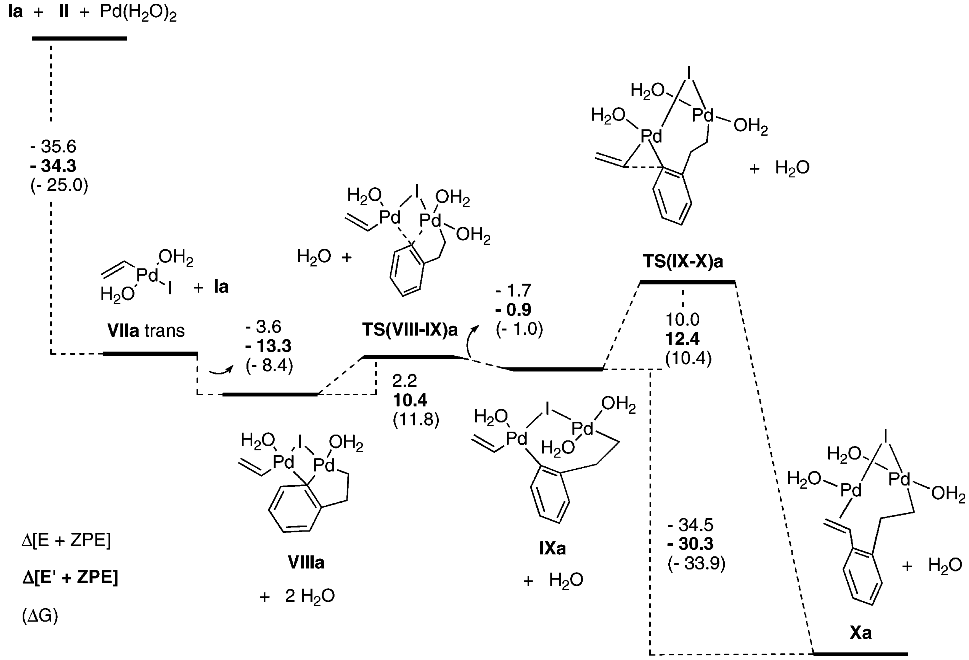
(59) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954−959 and references therein.

Scheme 8. Reaction Pathways for the Oxidative Addition of **II** to PdL_2 (L = H_2O on the left, L = PH_3 on the right) Showing Reaction and Activation Energies (kcal/mol; Δ(*E*+ZPE) in lightface, Δ(*E*′+ZPE) in boldface, and Δ*G* in brackets)



Scheme 9. Reaction Pathway and Energies Involving Pd−Pd Transmetalation and Reductive Elimination for H_2O-Containing Model Complexes (kcal/mol; Δ(*E*+ZPE) in lightface, Δ(*E*′+ZPE) in boldface, and Δ*G* in brackets)



corresponding to the donating metal is 2.819 Å, the other one being 2.026 Å), whereas in **TS(VIII−IX)b** Pd−C bond distances are more similar (2.137 and 2.474 Å). Bader analysis shows that both Pd−C bonds are still present in the latter transition state.

Formation of dinuclear complexes **IXa−c** is endothermic. Square planar geometry for both Pd atoms is observed in these complexes. Reductive elimination from **IXa−b** to **Xa−b** proceeds with similar activation energy compared with the transmetalation-type process for the PH_3 complexes (8.9 kcal/mol), and is a little higher for the H_2O derivatives (12.4 kcal/mol). Since these activation energies can be easily overcome,[60] we did not study the possibility of concomitant ligand coordination along the reductive elimination reaction coordinate, which would probably lower the energy of the transition states.[61] In no case would C−C reductive elimination be rate determining.

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[60] Recent studies on C−C reductive elimination: (a) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839−2852. (b) Culkin, D. A.; Hartwig, J. F. *Organometallics* **2004**, *23*, 3398−3416. (c) Baylar, A.; Canty, A. J.; Edwards, P. G.; Slelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 3325−3330. (d) Reid, S. M.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2001**, *123*, 4081−4082. (e) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115−6128.

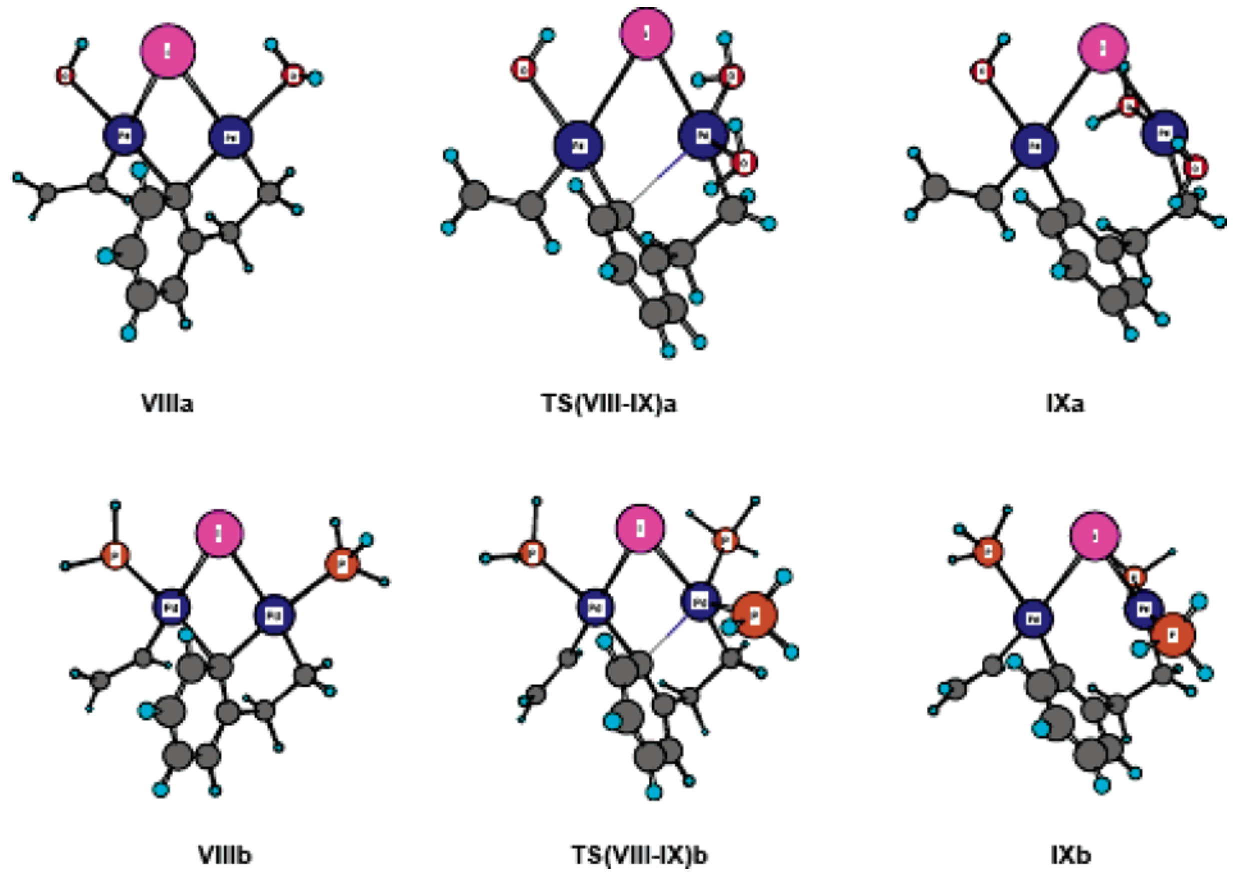
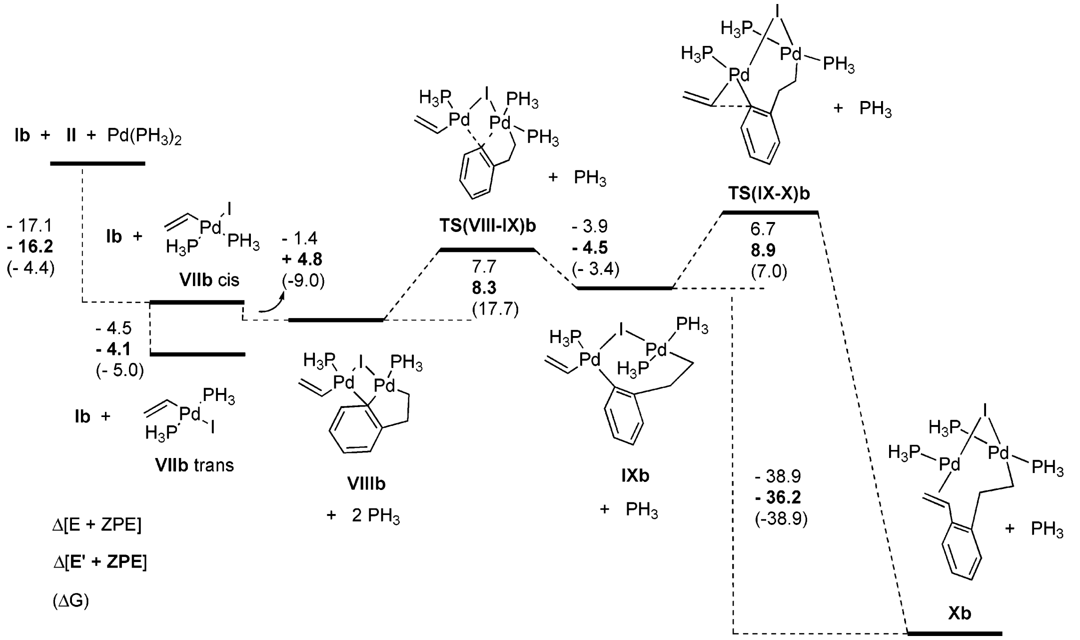


Figure 1. Optimized molecular structures for complexes involved in the Pd−Pd transmetalation.

Scheme 10. Reaction Pathway and Energies Involving Pd−Pd Transmetalation and Reductive Elimination for PH_3-Containing Model Complexes (kcal/mol; Δ(*E*+ZPE) in lightface, Δ(*E'*+ZPE) in boldface, and Δ*G* in brackets)



Computational results support the reaction pathway in which participation of Pd(IV) complexes is not necessary. Under the usual conditions for Pd-catalyzed domino reactions (absence of phosphine ligands, amide-type solvents, presence of halide), the theoretical results indicate that Pd(0) complexes with weakly coordinating ligands readily react with organic halides (**II** in our model) by a previous highly exothermic coordination, to give the usual Pd(II) complexes containing a Pd−C bond. The alternative pathway requires an endothermic ligand substitution reaction, followed by oxidative addition to Pd(IV). Noticeably,

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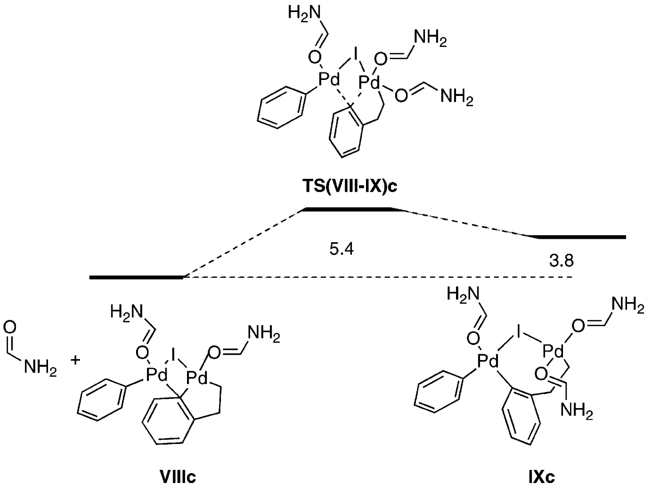
(61) (a) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B. *Chem. Eur. J.* **2001**, *7*, 2481−2489. (b) Kurosawa, H.; Kajimaru, H.; Miyoshi, M. A.; Ohnishi, H.; Ikeda, I. *J. Mol. Catal.* **1992**, *74*, 481−488. (c) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1987**, *109*, 6333−6340.

Table 2. Relative Energies (kcal/mol) for the Transmetalation-Type Pathways[a]

	Δ (*E* + ZPE)	Δ*E′*	Δ (*E′*+ZPE)	Δ*G*
	$L = H_2O$			
Ia +**II** + $Pd(H_2O)_2$	0	0	0	**0**
VIa + **Ia**	−33.9	−34.4	−32.7	**−23.6**
TS(VI−VII)a + **Ia**	−18.5	−16.2	−16.6	**−9.3**
VIIa cis + **Ia**	−45.4	−45.9	−44.3	**−34.3**
VIIa trans + **Ia**	−35.6	−35.9	−34.3	**−25.0**
VIIIa + 2 H_2O	−39.2	−45.0	−47.6	**−33.4**
TS(VII−IX)a + H_2O	−37.0	−36.8	−37.2	**−21.6**
IXa + H_2O	−38.7	−39.1	−38.1	**−22.6**
TS(IX-X)a + H_2O	−28.7	−25.9	−25.7	**−12.2**
Xa + H_2O	−73.2	−71.2	−68.4	**−56.5**
	$L = PH_3$			
Ib +**II** + $Pd(PH_3)_2$	0	0	0	**0**
VIb + **Ib**	−11.3	−9.7	−8.7	**−0.4**
TS(VI−VII)b + **Ib**	2.2	6.2	5.9	**13.6**
VIIb cis + **Ib**	−17.1	−17.8	−16.2	**−4.3**
VIIb trans + **Ib**	−21.6	−22.0	−20.3	**−9.4**
VIIIb + 2 PH_3	−18.6	−9.7	−11.4	**−13.3**
TS(VII−IX)b + PH_3	−10.9	−0.8	−3.1	**4.4**
IXb + PH_3	−14.8	−6.7	−7.6	**1.0**
TS(IX-X)b + PH_3	−8.1	2.1	1.3	**8.0**
Xb + PH_3	**−53.7**	**−45.0**	**−43.8**	**−39.9**

[a] *E*: electronic energy calculated with basis set B_1. *E′*: electronic energy calculated with basis set B_2. ZPE and Δ*G* calculated with B_1.

Scheme 11. Reaction Pathway and Energies Involving Pd−Pd Transmetalation for Formamide Containing Model Complexes (kcal/mol; Δ(E+ZPE) with Base B_1



oxidative addition of $C(sp^2)-I$ bond of **II** to metallacycle **Ia**, shows significantly lower activation energies compared with the previously calculated oxidative addition of iodobenzene from complex $(PhI)Pd(CH_2{=}CH_2)(H_2PCH_2CH_2PH_2)$ (ca. 20 kcal/mol),[15] probably due to the presence of strong donor ligands and the absence of acceptors in **Ia**. Even so, oxidative addition of $C(sp^2)-X$ electrophiles to Pd(II) complexes is *not* the preferred pathway in the presence of Pd(0) species, since oxidative addition to Pd(0) derivatives is strongly favored, especially in the absence of phosphines.

Conclusions

We have found a feasible Pd−Pd transmetalation-type process that accounts for the observed products and shows lower activation energies, at least for complexes bearing oxygen ligands. In the case of phosphine derivatives, entropic factors make associative transmetalation-type reaction the most difficult step, but the intermediates involved in the formation of Pd(IV) species still show the highest energies. Computational results are also in accord with the poorer results obtained in Pd-catalyzed domino reactions in the presence of phosphines.[62]

Our results suggest that the formation of $C(sp^2)-C(sp^2)$ bonds in Pd-catalyzed reactions probably takes place without the intermediacy of Pd(IV) complexes. Calculations show that alkenyl and aryl electrophiles react more easily with unsaturated Pd(0) complexes than with Pd(II) metallacycles. Coordination previous to oxidative addition is significantly exothermic for the former and endothermic for the latter, whereas the formation of the new bonds shows similar energies for both cases. The easy formation of bridged dinuclear complexes allows a facile intramolecular transmetalation-type process of organic ligands between two Pd centers, leading to diorganopalladium intermediates that evolve by reductive elimination. Whereas formation of Pd(IV) species in the Catellani reaction involving $C(sp^3)-X$ electrophiles is strongly supported by other experimental work,[2−4] our results indicate that, in contrast, Pd(IV) species are unlikely to be actual intermediates in the formation of $C(sp^2)-C(sp^2)$ bonds in Pd-catalyzed domino reactions involving $C(sp^2)-X$ electrophiles.

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Supporting Information Available: Atomic coordinates and energy values for all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

JA056661J

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