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Cyclocarbopalladation Involving an Unusual 1,5-Palladium Vinyl to Aryl Shift as Termination Step: Theoretical Study of the Mechanism

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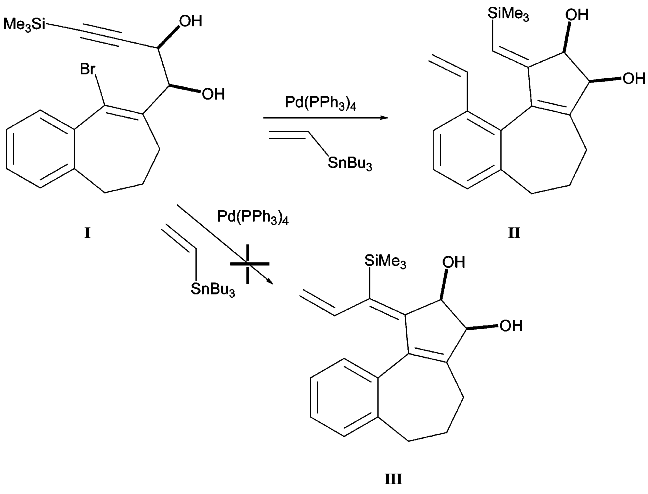
Abstract: A DFT/B3LYP model study has been carried out on the cyclocarbopalladation and on an unusual 1,5 vinyl to aryl palladium shift which are the two first steps of a cyclocarbopalladation-Stille coupling tandem reaction of various γ-bromopropargylic-1,2 diols with alkenyls or alkynyl stannanes catalyzed by $Pd(PPh_3)_4$. From the calculations, the active intermediates in the catalytic process appear to bear a single phosphine ligand, the palladium(II) center keeping in all cases a square-planar coordination pattern either through intramolecular binding of the triple bond or via an intramolecular Pd$\cdots$C$_{\text{phenyl}}$ interaction. The computation of the various transition states and intermediates for the 1,5 vinyl to aryl palladium shift reveals that the intimate mechanism of this pathway corresponds to a one-step hydrogen transfer between the two negatively charged carbon atoms of the vinyl and phenyl groups. A two-step pathway involving a Pd(IV) intermediate is not likely to occur. This conclusion may apply to other 1,*n*-palladium shifts which have been experimentally observed in various organometallic transformations.

Introduction

C−C coupling reactions catalyzed by palladium complexes form a class of reactions that is presently thoroughly investigated with the aim of getting organic compounds of increasing complexity.[1] The cyclocarbopalladation process (the intramolecular Heck reaction) of enynes has been used in organic synthesis to obtain cyclic natural products, most often five-, six-, and seven-membered exocyclic alkenes.[2−5] This process can then be coupled to a termination cross-coupling reaction, if the alkenylpalladium(II) intermediate is not prone to or cannot undergo a β-hydride elimination.[6−9]

Two of us recently reported such tandem reactions of various γ-bromopropargylic-1,2 diols (in which the triple bond is substituted by a trimethylsilyl group) with alkenyl or alkynyl stannanes.[10] Quite unexpectedly the tandem reaction of **I** with tributylvinyltin, catalyzed by $Pd(PPh_3)_4$ (see Scheme 1), led to the coupling of the vinyl moiety with the phenyl ring rather than with the exocyclic double bond.[11] This points to some 1,5 vinyl to aryl shift of the metal moiety in the product of the cyclocarbopalladation reaction, akin to the 1,4 Pd shifts that have been evidenced in various organopalladium compounds.[12−17]

Scheme 1. Cyclocarbopalladation-Stille Coupling Tandem Reaction on the γ-Bromopropargylic-1,2 Diol **I**



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(1) For a recent review, see: Bräse, S.; Meijere, A. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 5, pp 217−317.

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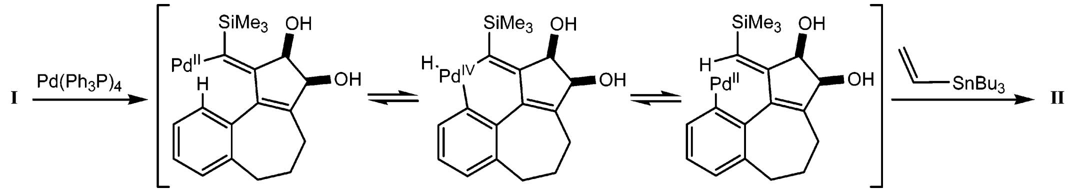
Scheme 2. Presumed Catalytic Process for the **I** → **II** Conversion

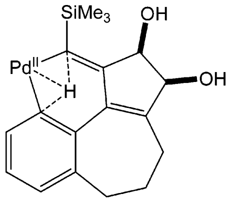


A possible mechanism that could account for the experimental findings is shown in Scheme 2. It involves, after the cyclocarbopalladation step that yields the vinyl palladium(II) derivative, an intramolecular oxidative addition of the phenyl C−H bond to the Pd atom. The resulting hydridophenylvinyl palladium(IV) intermediate subsequently undergoes a (vinyl)(H) reductive elimination that leads to the phenyl palladium(II) intermediate, thus completing a formal Pd/H exchange.[18] This exchange is then followed by the Stille coupling[19] that ultimately yields the observed product.

Because of its importance and its versatility in synthetic organic chemistry, the Heck reaction has been the subject of numerous mechanistic studies, either experimentally or theoretically. The theoretical studies that have been carried out thus far have addressed several issues: the nature of the intermediate species that are active in the reaction, either cationic, neutral, or anionic;[20−22] whether the mechanism involves a Pd(0)/Pd(II) or a Pd(II)/Pd(IV) redox system;[23] the coordination sphere around the palladium atom, and in particular the number of phosphine ligands involved;[22,24] the regioselectivity and the enantioselectivity;[25−27] or the use of nickel as a possible catalyst.[28] All these studies but one have considered the intermolecular Heck reaction, the only exception being the recent study by Ziegler et al. on polyene cyclization by a double intramolecular tandem reaction.[29]

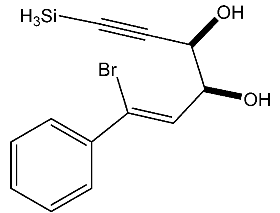
In the present article we wish to address, through DFT calculations, the validity of the mechanism shown in Scheme 2 and more particularly to assess the intimate nature of the Pd/H exchange. We first look at the intramolecular Heck reaction (viz. cyclocarbopalladation) that leads to the vinyl palladium(II) intermediate, paying some attention to the coordination sphere around the palladium center in this reaction. Next we focus on the possible involvement of a Pd(IV) intermediate and then show that a one-step process, in which a *direct* hydrogen transfer from the phenyl to the vinyl takes place, is more feasible (Scheme 3). This implies that Pd(II) complexes rather than Pd(IV) complexes, which turn out to be energetically much more unfavorable, are implicated throughout the whole tandem reaction.

Scheme 3. Direct Hydrogen Transfer Process



Computational Details

The calculations were carried out at the DFT-B3LYP level[30−32] with the Gaussian 03 program.[33] We used as a model for the bromo derivative **I** the system **1**, in which the seven-membered ring has been removed and the trimethylsilyl group $SiMe_3$ has been replaced by SiH_3. Since the seven-membered ring is known to be conformationally flexible, its removal should not significantly alter the results.



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The replacement of $SiMe_3$ by SiH_3 is probably valid, since no spurious metal···Si−H agostic interactions were obtained in the geometry optimization steps.[34] Moreover, DFT calculations on the $[\eta^2\text{-}(HC{\equiv}C{-}SiH_3)M^+]$ system ($M^+{=}Cu^+$ or Ni^+) have shown that the enhancement of the interaction energy between the metal cation and the triple bond brought by the substitution of a hydrogen atom by a methyl is relatively marginal, less or equal to 1.5 kcal mol^{-1}.[35,36] The triphenylphosphine ligand PPh_3 was modeled by PH_3. The geometries were fully optimized by the gradient technique with the following basis: For Pd the LANL2DZ basis set is modified following the

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prescription of Couty and Hall.[37] In this modified basis, the innermost core electrons (up to 3d) are described by the relativistic orbital-adjusted effective core potential of Hay and Wadt,[38] and the remaining outer core and valence electrons are described by a [341/541/31] basis set where the two outermost 5p functions of the standard LANL2DZ basis set have been replaced by a [41] split of the 5p function optimized by Couty and Hall. For the Br atom, the quasi relativistic energy-adjusted spin-averaged effective core potential was taken from the work of the Stuttgart group, together with their [31/31] basis set,[39] to which s and p diffuse functions (with exponents of 0.0493 and 0.0363, respectively), and a d polarization function (of exponent 0.381) were added, following Radom et al.[40] The carbon, oxygen, and hydrogen atoms[41] were described by the standard 6-31G basis set, whereas we used for the phosphorus and silicon atoms the polarized 6-31G* basis set.[42] We refer to this basis set as BS-I. The nature of the optimized structures, either transition states or intermediates, was assessed through a frequency calculation, and the changes of Gibbs free reaction energies (ΔG values) were obtained by taking into account zero-point energies, thermal motion, and entropy contribution at standard conditions (temperature of 298.15 K, pressure of 1 atm). The geometrical parameters obtained with this basis set are in agreement with related experimental structures of bromo palladium complexes:[43−45] for instance, in the **2c** system (vide infra) the computed Pd−Br and Pd−P bond lengths are 2.572, 2.339, and 2.328 Å, to be respectively compared to 2.532, 2.304, and 2.311 Å in the (Xantphos)Pd(4-cyanophenyl)(Br) complex reported recently.[44] The Pd−C(phenyl) bond that is trans to Br in **6-*trans*-OF** and **6-*trans*-SF** (vide infra) amounts to 2.055 and 2.062 Å, respectively, and the experimental value in the (Xantphos)-Pd(4-cyanophenyl)(Br) complex is 1.996 Å. The effect of a larger basis set (hereafter referred to as BS-II) was tested by single-point energy calculations on the BS-I optimized geometries. In BS-II, the innermost core electrons of palladium atom are described by the quasi relativistic energy-adjusted spin−orbit averaged effective core potential from the Stuttgart group and the remaining outer core and valence electrons are described by the associated triple-ζ basis set,[46] to which an f polarization function of exponent 1.472 is added.[47] The standard 6-311G** basis set is used for C, O, P, Si, and H,[48] while keeping the above-described basis set and pseudo potential for Br. Since the ΔE values results obtained with BS-I and BS-II basis sets turned out to be very similar (see Tables S1−S3 in the Supporting Information), we will concentrate our discussion on the BS-I results and the corresponding enthalpy values.

Results and Discussion

1. The Cyclocarbopalladation Step. We shall not fully address here the mechanism of the first step, namely the oxidative addition of the aryl bromine bond of **1**. Several studies have been recently devoted to the oxidative addition of the carbon−bromine bond to palladium, both theoretically[49,50] and experimentally.[7,43,51−58] Let us simply mention that the oxidative addition of **1** to $Pd(PH_3)_4$ leading to the *cis*-$Pd(PH_3)_2(Br)(vinyl)$ complex **2b** (see Scheme 1) + 2 PH_3 is exothermic by −12.8 kcal mol^{-1}. The corresponding ΔH and ΔG values are −13.6 and −17.9 kcal mol^{-1}, respectively.[59]

Table 1. Energies (ΔE), Enthalpies (ΔH), and Free Energies (ΔG) of the Various Monophosphine and Bisphosphine Pd(II) Vinyl Intermediates That Can Result from the Oxidative Addition of **1** to $Pd(PH_3)_4$[a,b]

system	ΔE	ΔH	ΔG
3a-*trans*-SF + PH_3	0.0	0.0	0.0
3a-*cis*-SF + PH_3	+2.1	+1.7	+0.5
3a-*trans*-OF + PH_3	+2.6	+2.4	+1.8
3a-*cis*-OF + PH_3	+9.0	+8.4	+7.1
3b-*trans*-6 + PH_3	−5.2	−5.6	−5.5
3b-*cis*-6 + PH_3	+5.2	+4.9	+1.8
3b-*trans*-5 + PH_3	−3.4	−3.1	−5.7
3b-*cis*-5 + PH_3	+6.4	+6.2	+3.8
2a	−12.2	−10.1	−0.3
2b	−13.3	−11.2	−2.0
2c	−12.9	−11.4	−0.6

[a] The values are in kcal mol^{-1}. [b] The B3LYP/BS-I total energies (in au) of **3a-*trans*-SF** + PH_3 are: $E = -1731.27263$, $H = -1730.97659$, $G = -1731.07748$.

We will instead focus on the product of this oxidative addition, for which various structures can be anticipated, either four-coordinated or five-coordinated. The most obvious choice is a four-coordinated bisphosphine Pd(II) bromo vinyl complex. But one can also think to intermediates in which one additional phosphine is dissociated,[45,51,56,57,60−63] and either the triple bond or one hydroxyl group is bound to the palladium atom. The structures corresponding to these possibilities are depicted in Scheme 4, and their relative stabilities are given in Table 1.

2a and **2b** are bisphosphine rotamers in which the two phosphine ligands are cis to each other, but differ by the position of the Br atom. In **2c**, the two phosphine ligands are trans to each other. In the monophosphine complexes **3** either the triple bond (**3a**) or one hydroxyl group (**3b**) is bound intramolecularly to the metal. In addition, there are four possible stereoisomers for each of these two isomers. In **3a**, the Br atom can be either cis or trans with respect to the covalently bound organic moiety, and the Pd atom lies either on the same face (SF) or on the opposite face (OF) with respect to the hydroxyl groups. In **3b**, the Br atom can again be either cis or trans with respect to the organic moiety, and the binding of the hydroxyl groups can

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(59) The ΔE value of −12.8 kcal mol^{-1} is somewhat larger than the value of −3.3 kcal mol^{-1} computed by Senn and Ziegler for the oxidative addition of C_6H_5Br to $Pd(dmpe)_2$ (dmpe = dimethylphosphinoethane); see ref 50. For the oxidative addition of bromoethyne ($BrC{\equiv}CH$) to $Pd(PH_3)_2$, Jakt et al. have reported a ΔE value of −21.8 kcal mol^{-1} at the B3LYP/DZVP level; see ref 49. For the sake of comparison with our value, which refers to the $Pd(PH_3)_4$ system, one should of course add the energy of dissociation of two PH_3, which in our case amounts to +16.5 kcal mol^{-1}.
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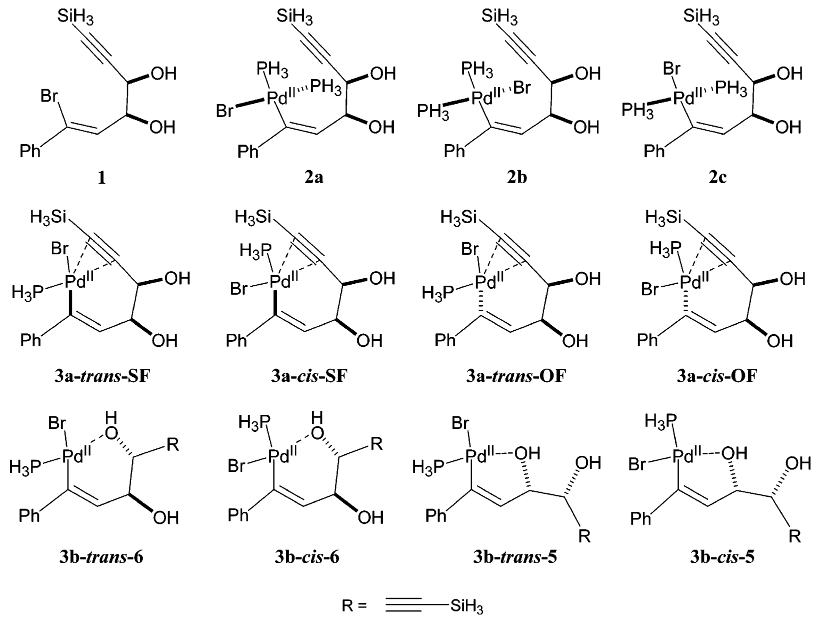
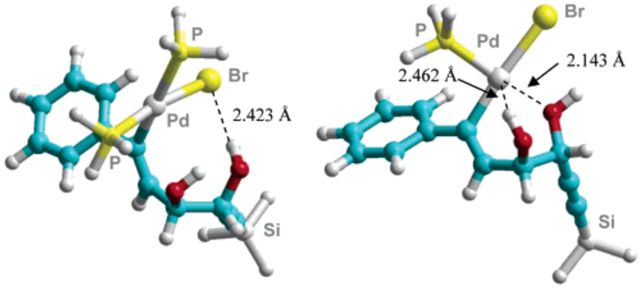
Scheme 4. Schematic Representations for the Structures **1**, **2**, and **3**



lead either to a five- or a six-membered ring, depending on which hydroxyl is bound. From Table 1 it is clear that the dissociation of one phosphine ligand from isomer **2** is energetically disfavored, but entropically favored: the monophosphine isomers are either more stable or only slightly less stable than the bisphosphine isomers (ΔG values), the largest stabilization being found for the **3b-*trans*** isomers (i.e., monophosphine complexes having one coordinated hydroxyl group and the Br atom trans to the organic moiety). One should keep in mind, however, that entropic effects are exaggerated in the gas phase (these calculations) with respect to solution. At this stage, it should be mentioned that all our attempts to optimize five-coordinated bisphosphine intermediates in which the triple bond and a second phosphine were coordinated together to the palladium atom led invariably to one of the four geometries **3a**, thus with a single phosphine ligand. A similar situation has been encountered by Goossen et al. who could not, in their DFT study of the oxidative addition of C_6H_5I to $[Pd(PMe_3)_2(OAc)]^-$, find any energy minimum corresponding to a five-coordinate $[Pd(PMe_3)_2(OAc)(C_6H_5)(I)]^-$ intermediate.[22]

One does not need, however, to consider all the above-mentioned structures as possible *active* intermediates in the overall reaction: for the cyclocarbopalladation (i.e., the intramolecular insertion of the triple bond into the Pd−C bond) to proceed, the triple bond and the Pd−C bond should be cis to each other. This is not the case for the **3b** isomers. In these isomers, the triple bond lies far away from the Pd−C bond; see for instance in Figure 1 the structure of **3b-*trans*-6**. Finally, it turns out that for the Pd/H exchange step that follows the intramolecular insertion of the triple bond, bisphosphine intermediates are also rather unlikely (vide infra). We shall therefore focus our attention on the monophosphine isomers **3a**, considering first this intramolecular insertion of the triple bond.



2b **3b-*trans*-6**

Figure 1. Optimized structures for **2b** and **3b-*trans*-6** intermediates.

The structures of the corresponding intermediates and transition states are shown in Figure 2, including some salient distances. Note that the **4-*trans*** and **4-*cis*** products originate from the **3a-*cis*** and **3a-*trans*** complexes in the starting materials, respectively. In **4**, the fourth coordination site is filled via a Pd···C_{phenyl} interaction, which is quite strong; see the values of the Pd···C distance, for example, 2.433 Å in **4-*cis*-SF**. This interaction clearly involves the π system of the phenyl, since the Pd atom lies above the *ortho*-carbon atom, almost perpendicularly to the phenyl plane. The situation here is different from the one encountered in the monophosphine T-shaped aryl palladium halide complexes which are stabilized by a weak agostic interaction of the metal with a C−H bond located on the single phosphine ligand.[45] It is more like the one found in structurally characterized cases of three-coordinated palladium complexes displaying a π,η^1 coordination of the phenyl ring with the *ipso*-carbon atom.[64−71]

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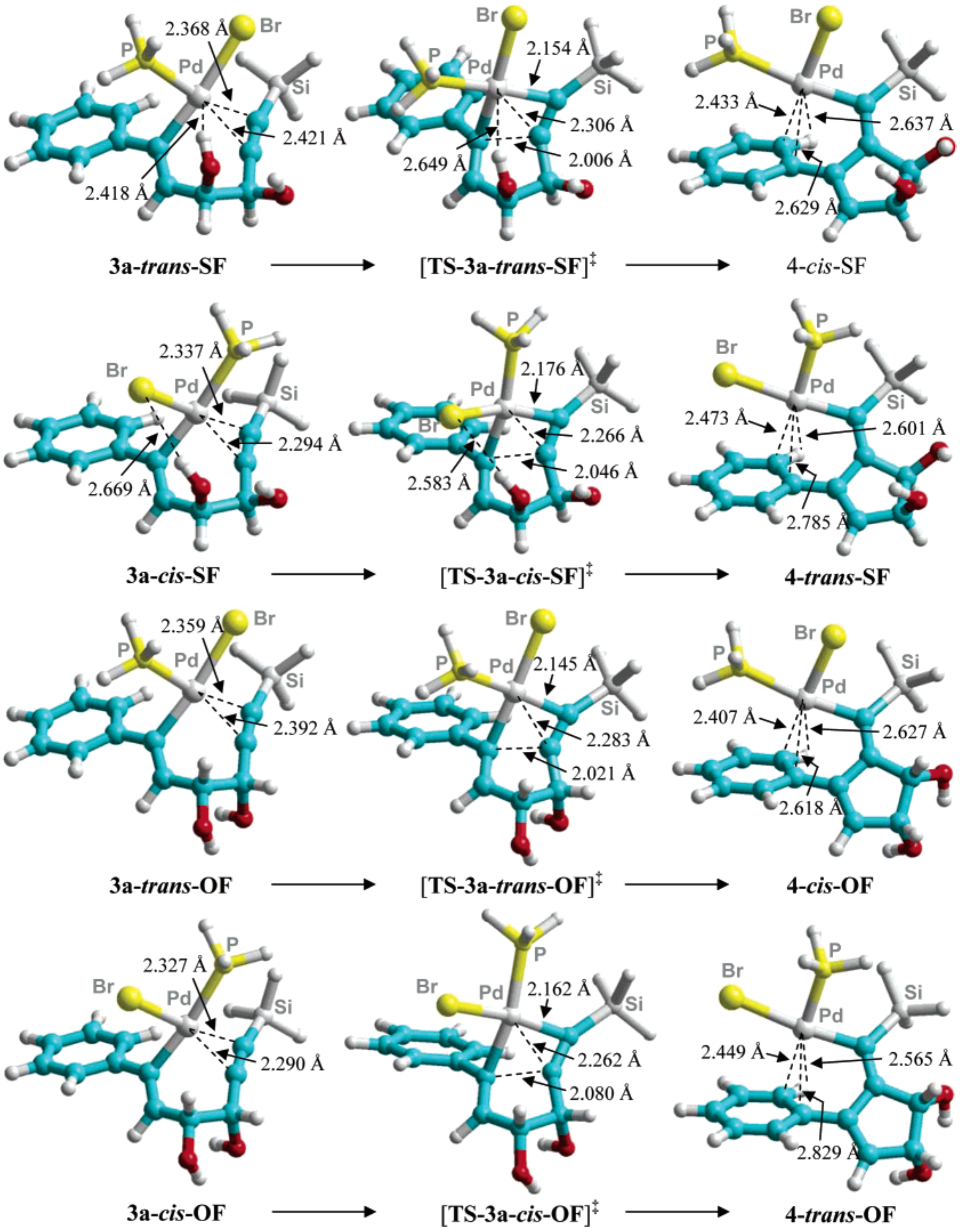

Figure 2. Optimized structures of the intermediates and transition states originating from the structures **3a** for the cyclocarbopalladation step.

The transition states are six-membered cycles with a flat boat conformation, and the interatomic distance between the two carbon atoms that form the new C−C bond of the five-membered ring ranges between 2.00 and 2.10 Å, depending on which isomer is considered. The corresponding energy barriers and the exothermicities of the reaction are given in Table 2. They point to a rather easy process for any of the four **3a** isomers: the barriers for this insertion reaction that leads to the five-membered intermediates **4** amount to less than 20 kcal mol^{-1}, and the process is exothermic.[72] Yet, there seems to be some preference for the **3a-*cis*-SF** and **3a-*trans*-SF** isomers. These two isomers are more stable and have transition states that are 4 kcal mol^{-1} or more lower in energy than the transition states arising from the **3a-*cis*-OF** and **3a-*trans*-OF** isomers (Figure 3 summarizes the energetics of the overall process). We trace this feature to an additional hydroxyl hydrogen and either the metal center or the bromine atom; see the short H···Pd and H···Br distances reported in Figure 2.[73] The interaction of an acidic hydrogen atom with either the metal or a halogen ligand is a feature that is now quite well-documented in square-planar

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(72) Similar values were found in our previous CASSCF-MRSDCI study of the insertion of C_2H_2 into the Pd−CH_3 bond of the [PdCl(NH_3)(CH_3)(C_2H_2)] model system. See: de Vaal, P.; Dedieu, A. *J. Organomet. Chem.* **1994**, *478*, 121.

(73) In the **3a-*cis*-SF** derivative one also finds, in addition to the short interatomic distance of 2.669 Å between the hydrogen atom and the bromine atom, a short distance of 2.711 Å between the hydrogen atom and the palladium atom.

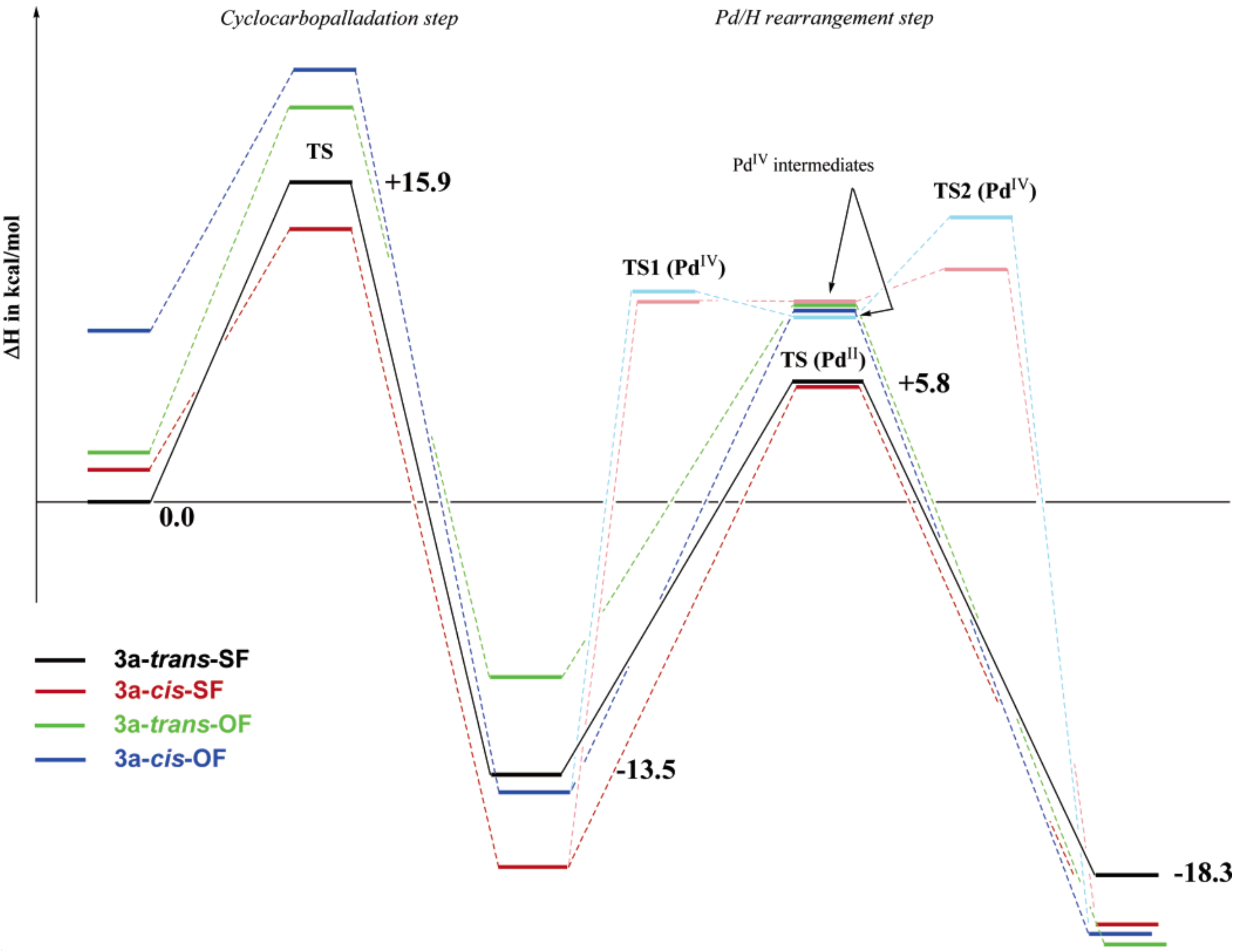

Figure 3. Energy profiles of the cyclocarbopalladation and of the subsequent Pd/H rearrangement processes originating from the **3a** structures. The zero of energy corresponds to the **3a-*trans*-SF** structure (in black). Pd^{IV} intermediates **5c** (light red) and **5d** (light blue) come from **4-*trans*-OF** (blue) and **4-*trans*-SF** (red), respectively.

Table 2. Energy Barriers, Energies of Reaction ($\Delta E^{\ddagger}$, ΔE), Enthalpy Barriers, Enthalpies of Reaction ($\Delta H^{\ddagger}$, ΔH), and Free Energy Barriers, Free Energies of Reaction ($\Delta G^{\ddagger}$, ΔG) for the Cyclocarbopalladation Step **3** → **4**, for the Four **3a** Isomers[a−c]

system	$\Delta E^{\ddagger}$, ΔE	$\Delta H^{\ddagger}$, ΔH	$\Delta G^{\ddagger}$, ΔG
3a-*trans*-SF	+17.2, −13.8	+15.9, −13.5	+16.6, −12.1
	(+17.2, −13.8)	(+15.9, −13.5)	(+16.6, −12.1)
3a-*cis*-SF	+12.7, −20.8	+11.9, −19.6	+13.5, −16.5
	(+14.8, −18.7)	(+13.6, −17.9)	(+14.0, −16.0)
3a-*trans*-OF	+18.6, −11.5	+17.3, −11.1	+18.3, −10.0
	(+21.2, −8.9)	(+19.7, −8.7)	(+18.8, −9.5)
3a-*cis*-OF	+13.8, −24.4	+13.1, −23.0	+14.5, −20.3
	(+22.8, −15.4)	(+21.5, −14.6)	(+15.0, −19.8)

[a] The values are in kcal mol^{-1}. [b] The values in parentheses refer to the corresponding energy value taking **3a-*trans*-SF** as zero reference. [c] The B3LYP/BS-I total energies (in au) of **3a-*trans*-SF** are: $E = -1388.13482$, $H = -1387.86686$, $G = -1387.94287$.

platinum or palladium complexes.[74−79] For instance, the hydroxyl group in ethanol intramolecularly hydrogen bonds to the bromide ligand in the crystal structure of the [PdBr{$C_6H_4(CH_2CH_2OH)$-2}(tmeda)] complex.[80,81]

2. The Pd/H Rearrangement Step. Since the ultimate product of the tandem reaction of Scheme 1 corresponds to the metal-mediated coupling of the vinyl moiety of tri(*n*-butyl)vinyltin with the phenyl group, a through-space relocation of the metal moiety between the internal vinyl and the phenyl groups (Scheme 5) has to take place in **4**. This formal 1,5-Pd shift that will lead to **6** has been experimentally evidenced in the case of 1,4-Pd shifts in various organopalladium compounds,[12,14−17] but their mechanisms have not been ascertained. One can think of two possible pathways for this migration (Scheme 5): (i) either a two-step process that goes via a phenyl C−H oxidative addition on the palladium atom to yield a hydridophenylvinyl Pd(IV) intermediate **5**, which subsequently undergoes a C−H reductive elimination that leads to the phenyl Pd(II) complex **6**[14−16] or (ii) a one-step process in which the oxidation state +2 of the palladium atom is retained. In this

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(81) A metal H···O interaction has also been proposed on the basis of IR spectra between CpIr(CO)$_2$ and a number of fluorinated alcohols. See: Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069.

Scheme 5. Pd(II) and Pd(IV) Routes for the Pd/H Interchange Process

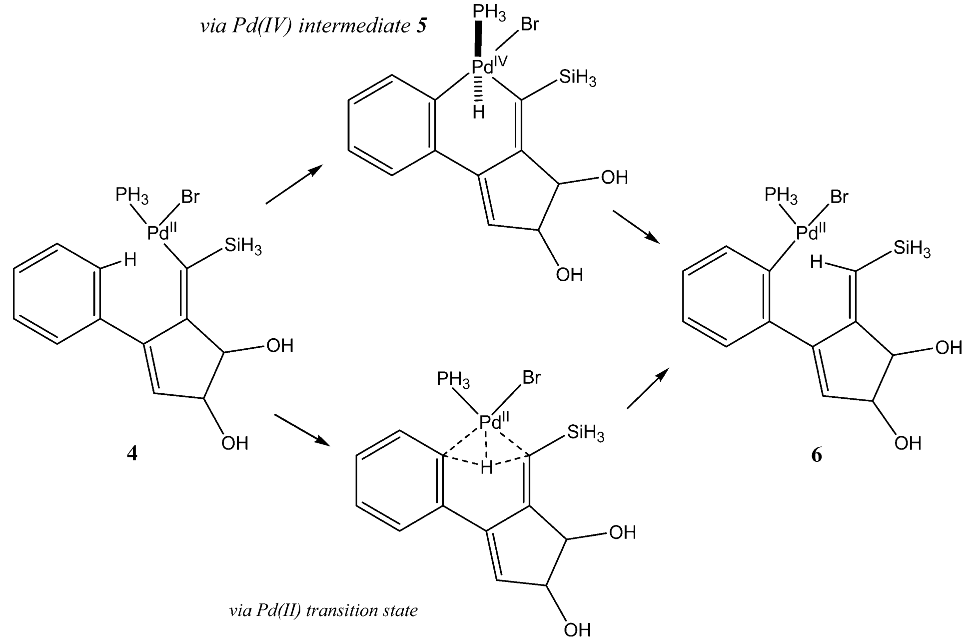

Table 3. Energies (ΔE), Enthalpies (ΔH), and Free Energies of Reaction (ΔG) for the Stable Pd(IV) Isomers **5** with Respect to **4-*cis*-SF** (**4** → **6** Pd^{IV} Pathway)[a–d]

system	ΔE	ΔH	ΔG
5a	+37.0, (+18.6)	+34.4, (+16.1)	+35.2, (+18.6)
5b	+42.5, (+24.1)	+39.9, (+21.6)	+40.0, (+23.4)
5c	+31.3, (+12.9)	+28.3, (+10.0)	+29.3, (+12.7)
TS1-5c	+31.7, (+13.3)	+28.3, (+10.0)	+28.6, (+12.0)
TS2-5c	+33.4, (+15.0)	+30.0, (+11.7)	+30.6, (+14.0)
5d	+29.9, (+11.5)	+27.4, (+9.1)	+26.8, (+10.2)
TS1-5d	+32.2, (+13.8)	+28.8, (+10.5)	+29.2, (+12.6)
TS2-5d	+34.9, (+16.5)	+31.4, (+13.1)	+31.4, (+14.8)
5e	+51.5, (+33.1)	+48.4, (+30.1)	+48.1, (+31.5)
5f	+50.2, (+31.8)	+47.1, (+28.8)	+46.7, (+30.1)

[a] The values are in kcal mol^{-1}. [b] The values in parentheses refer to the corresponding energy value taking **3a-*trans*-SF** as zero reference. [c] The B3LYP/BS-I total energies (in au) of **4-*cis*-SF** are: $E = -1388.15687$, $H = -1387.88835$, $G = -1387.96217$. [d] For **TS-5c** and **TS-5d**, ΔE, ΔH, and ΔG mean activation energies.

Table 4. Energy Barriers, Energies of Reaction ($\Delta E^{\ddagger}$, ΔE), Enthalpy Barriers, Enthalpies of Reaction ($\Delta H^{\ddagger}$, ΔH), and Free Energy Barriers, Free Energies of Reaction ($\Delta G^{\ddagger}$, ΔG) for the Four Isomers (**4** → **6** Pd^{II} Pathway)[a–c]

system	$\Delta E^{\ddagger}$, ΔE	$\Delta H^{\ddagger}$, ΔH	$\Delta G^{\ddagger}$, ΔG
4-*cis*-SF	+22.8, −4.6	+19.3, −4.8	+20.2, −4.5
	(+9.0, −18.4)	(+5.8, −18.3)	(+8.1, −16.6)
4-*trans*-SF	+27.4, −2.4	+23.5, −2.9	+23.7, −2.5
	(+8.7, −21.1)	(+5.6, −20.8)	(+7.7, −18.5)
4-*cis*-OF	+21.9, −13.7	+18.5, −13.5	+19.9, −12.1
	(+13.0, −22.6)	(+9.8, −22.2)	(+10.4, −21.6)
4-*trans*-OF	+28.1, −6.2	+24.2, −6.7	+24.9, −6.3
	(+12.7, −21.6)	(+9.6, −21.3)	(+5.1, −26.1)

[a] The values are in kcal mol^{-1}. [b] The values in parentheses refer to the corresponding energy value taking **3a-*trans*-SF** as zero reference. [c] The B3LYP/BS-I total energies (in au) of **4-*cis*-SF** are: $E = -1388.15687$, $H = -1387.88835$, $G = -1387.96217$.

case it could be considered either as a metathesis reaction of the C−H σ bond with the Pd−C bond or as a concomitant 1,5 shift of both the hydrogen and the palladium atoms.

(i) The Two-Step Process via a Pd(IV) Intermediate. In the Pd(IV) intermediate of the two-step mechanism, the metal atom is attached simultaneously to two carbon atoms, thus forming a six-membered ring. Of all possible isomers, either with a square pyramidal or with a trigonal bipyramidal structure, only six (**5a**−**5f**) shown in Figure 4 were found to be conformationally stable. They are, however, quite high in energy, being destabilized with respect to **4**-*cis*-SF by about 30 kcal mol^{-1} or more; see Table 3. The transition states of the phenyl C−H oxidative addition **4** → **5**, **TS1-5**, and of the subsequent C−H reductive elimination **5** → **6**, **TS2-5**, should be even higher. In fact, such transition states can be obtained only in the case of **5c** (connecting **4a-*trans*-SF** and **6-*cis*-SF** via **TS1-5c** and **TS2-5c**) and **5d** (connecting **4a-*trans*-OF** and **6-*cis*-OF** via **TS1-5d** and **TS2-5d**), these two isomers being the most stable Pd(IV) structures (see Table 3). Yet the rather high energy of **5c** and **5d** and of their associated transition states led us to investigate another pathway, viz. a one-step pathway that would instead retain the +2 oxidation state of palladium.

(ii) The Single-Step Pd/H Interchange. Table 4 summarizes the energetics of this process **4** → **6** for the four isomers of **4**. The corresponding geometries are shown in Figure 5. Note again that the **4-*cis*** and **4-*trans*** structures give rise to the **6-*trans*** and **6-*cis*** structures, respectively. The net result is that the trans stereochemistry is kept between **3** and **6**, and the same applies for the cis stereochemistry. In all instances the process is computed to be exothermic, the largest exothermicity being for the **4-*cis*-OF** isomer. The exothermicity of the process can be traced to the greater strength of the η^2-binding of palladium with the vinyl group in **6** compared to the strength of its interaction with the phenyl group in **4**.[82] The energy barriers are relatively low: the transition states are between 18 and 24 kcal mol^{-1} above their parent structure **4**.

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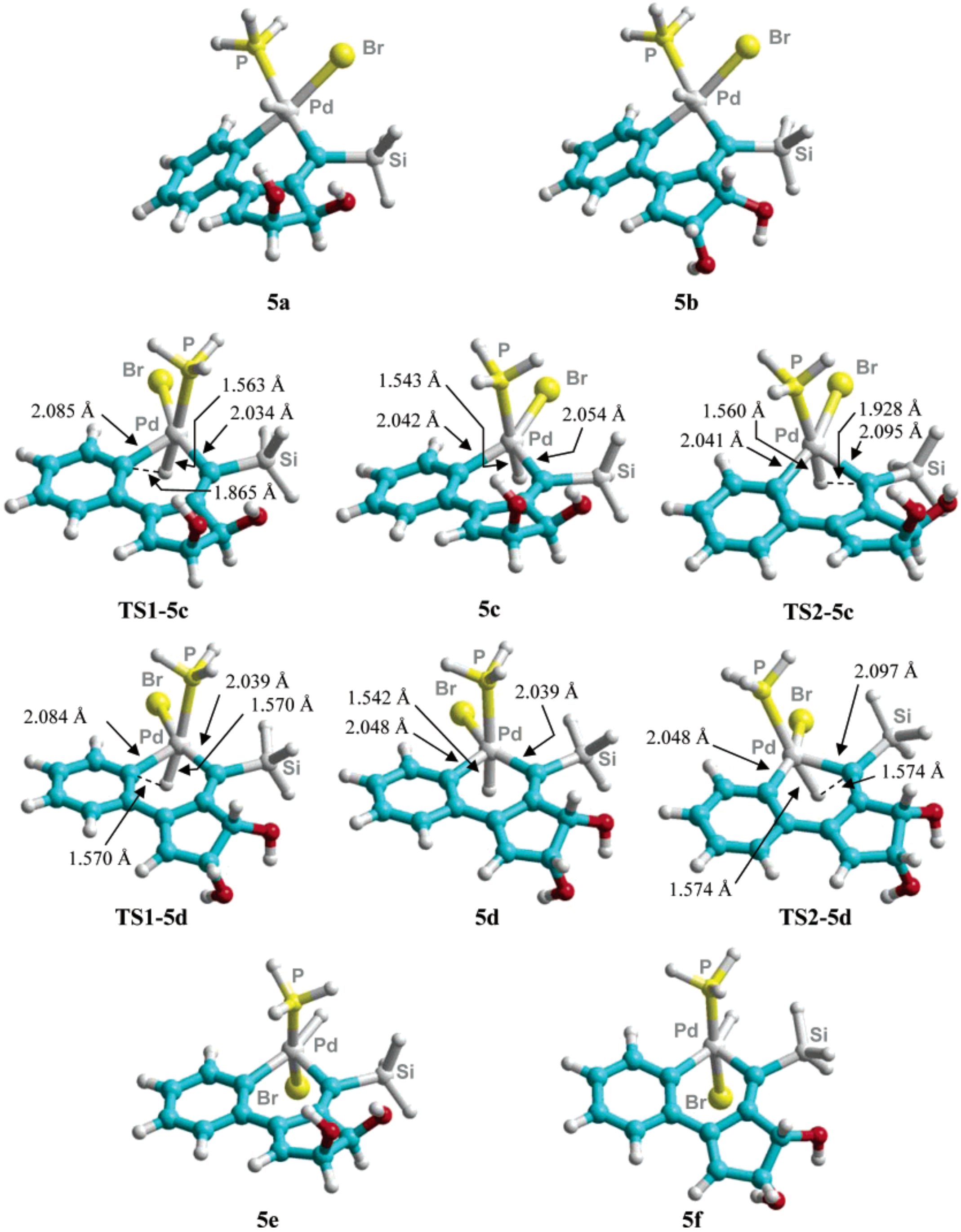
(82) This cannot be traced to a difference in the intrinsic strength of the Pd−C bond in **4** (the Pd−vinyl bond) and in **6** (the Pd−phenyl bond): pilot calculations carried out on the $[Pd(PH_3)_2(Br)((E)\text{-}2'\text{-phenylvinyl})]$ and $[Pd(PH_3)_2(Br)((4'\text{-vinylphenyl})]$ complexes yielded energies that are the same within 2 kcal mol^{-1}, either for the pair of cis isomers or for the pair of trans isomers.



5a **5b**

TS1-5c **5c** **TS2-5c**

TS1-5d **5d** **TS2-5d**

5e **5f**

Figure 4. Optimized structures of the **5a**−**f** isomers (stable Pd^{IV} forms) and the corresponding **5c** and **5d** transition states.

The transition states all adopt a geometry that is akin to the geometry of the corresponding Pd(IV) intermediates (compare for instance Figures 4 and 5), that is, a six-membered ring with a half chairlike conformation, and a geometry of the [Pd(Br)-(P)C_2] unit that is roughly square-planar. The two Pd···C distances are now quite similar and in the range of typical Pd−C bonds: for **TS-4-*cis*-SF** they amount to 2.159 and 2.191 Å for Pd···C_{phenyl} and Pd···C_{vinyl}, respectively. *The most striking feature of the transition state, however, is that the transferred hydrogen atom is no longer above the PdBrPC_2 plane but that it lies roughly in the C_{phenyl}PdC$_{vinyl}$ plane, at equal distance from the two carbon atoms*: the dihedral angle of the Pd−H bond with the $C_{phenyl}PdC_{vinyl}$ plane amounts to 23° only, and the hydrogen atom sits at 1.408 and 1.483 Å from the carbon atoms of the phenyl and the vinyl group, respectively. Moreover, the single imaginary vibrational mode (the frequency of which is 1299*i* cm^{-1}) involves almost exclusively the transferred hydrogen (see the Supporting Information). Thus, although this interchange process formally corresponds to a σ bond metathesis process of the C_{phenyl}−H bond with the Pd−C_{vinyl} bond, it can be better viewed as a proton transfer between the two negatively charged carbon atoms of the phenyl group on one hand, and of the vinyl group on the other hand: the computed charges from the NBO analysis[83] are +0.28e, −0.27e, and −0.66e for H, C_{phenyl}, and C_{vinyl} atoms, respectively. Here it is worth mentioning the calculations that have been carried out for the CH_3

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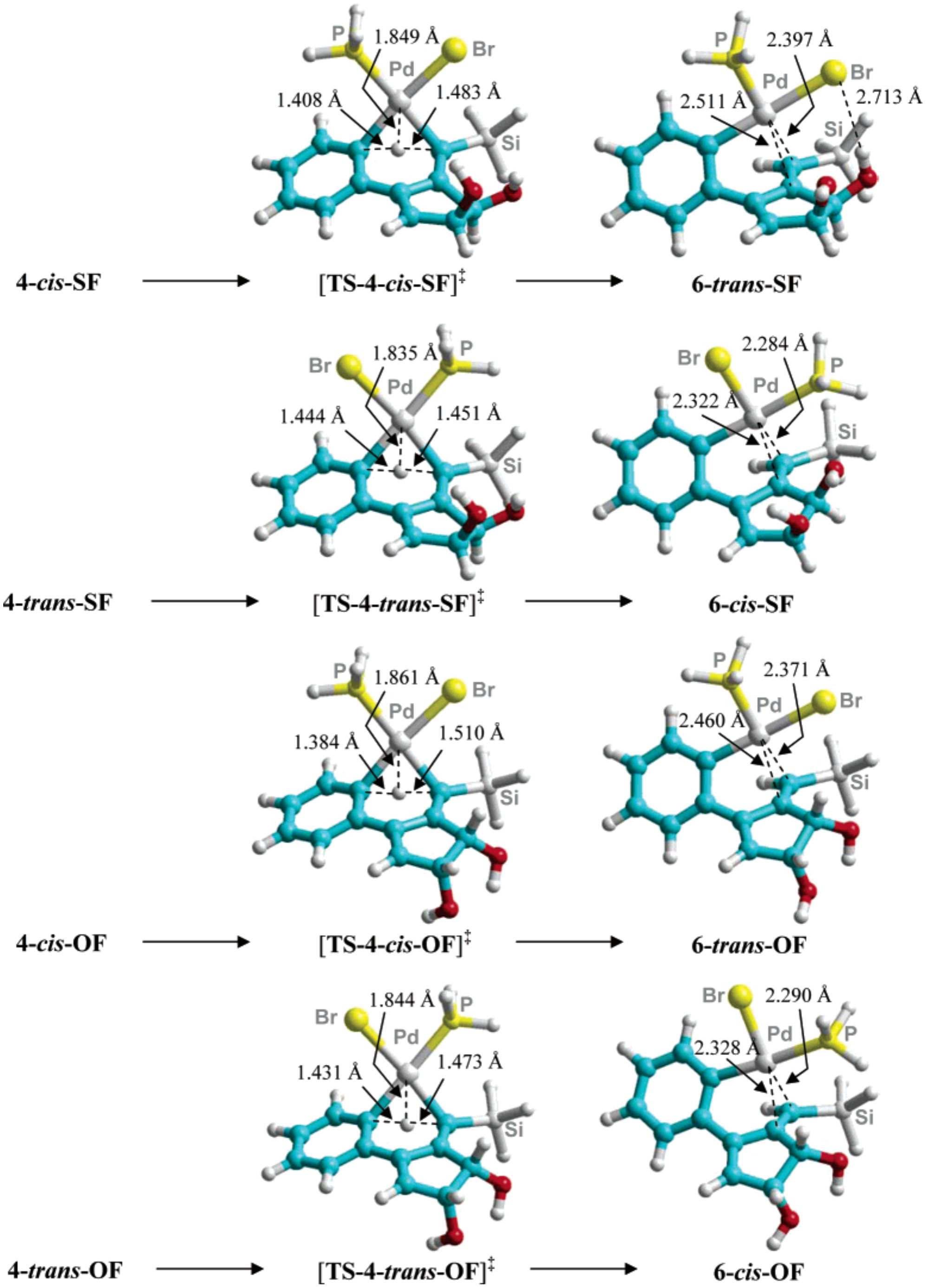

Figure 5. Optimized structure of the intermediates and transition states originating from the 1,5 vinyl to phenyl palladium transfer.

exchange model reaction $Cl_2LnCH^*_3 + H-CH_3 \rightarrow Cl_2LnCH_3 + H-CH^*_3$ (Ln being a lanthanide of the entire series La–Lu).[84] This reaction is formally a σ bond metathesis reaction. The corresponding transition state, however, displays an almost linear structure of the $C_{methyl}\cdots H\cdots C_{methyl}$ unit and has also been characterized as involving a proton transfer between two CH_3^- groups in the vicinity of a lanthanide cation.[84] Quite interestingly too, we can relate the Pd/H interchange to the hydrogen scrambling process in CH_5^+ by using the isolobal analogy[85,86] between the d^9 C_{2v} $Pd(PH_3)Br$ unit and CH_2^+. If one now replaces the phenyl and the vinyl groups bound to Pd by two hydrogen atoms, one gets a geometry of the transition state of the Pd/H interchange that is akin to the one of the C_{2v} transition state for hydrogen scrambling in CH_5^+.[87-89] It is therefore not too surprising that the energy barrier is relatively low. The isolobal analogy proposal is supported by the results of calculations that we carried out for the hydrogen transfer in the model system depicted in Scheme 6, where the $Pd(PH_3)Br$ unit is replaced by CH_2^+: here too, the transfer is relatively easy,

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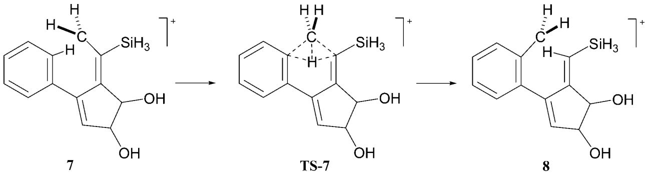
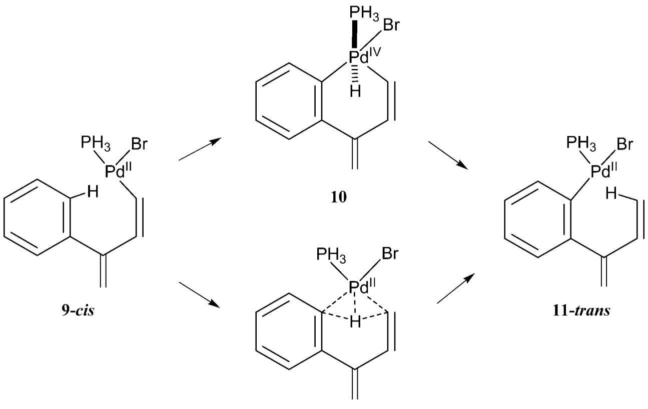
Scheme 6. 1,5-CH_2^+ Vinyl to a Aryl Migration Following the Isolobal Analogy Principle



7 **TS-7** **8**

Scheme 7. Schematic Representation of the **9** → **11** Possible Transformations for the More Generalized Model (Only the **9**-*cis* Isomer Is Presented in the Case of the Pd^{II} Route)



10

9-*cis* **11-*trans***

TS-9-*cis*

Table 5. Energy Barriers, Energies of Reaction ($\Delta E^‡$, ΔE), Enthalpy Barriers, Enthalpies of Reaction ($\Delta H^‡$, ΔH), and Free Energy Barriers, Free Energies of Reaction ($\Delta G^‡$, ΔG) for the Pd/H Interchange Step **9** → **11**, for the Two Isomers **9**, Pd^{II} and Pd^{IV} Pathways[a–c]

system	$\Delta E^‡$, ΔE	$\Delta H^‡$, ΔH	$\Delta G^‡$, ΔG
9-*trans* → **11-*cis*** (Pd^{II})	+30.7, −4.2 (+30.7, −4.2)	+26.8, −4.5 (+26.8, −4.5)	+27.6, −4.2 (+27.6, −4.2)
9-*cis* → **11-*trans*** (Pd^{II})	+26.6, −11.4 (+30.1, −7.9)	+23.1, −11.0 (+26.2, −7.9)	+24.1, −10.2 (+26.9, −7.4)
9-*cis* → **10** (Pd^{IV})	+37.9, +35.5 (+41.4, +39.0)	+34.5, +33.0 (+37.6, +36.1)	+34.9, +31.8 (+37.7, +34.6)
10 → **11-*trans*** (Pd^{IV})	+0.5, −46.9 (+39.5, −7.9)	−0.4, −44.0 (+35.7, −7.9)	+1.1, −42.0 (+35.7, −7.4)

[a] The values are in kcal mol^{-1}. [b] The values in parentheses refer to the corresponding energy value taking **9-*trans*** as zero reference. [c] The B3LYP/BS-I total energies (in au) of **9-*trans*** are: $E = -869.690863$, $H = -1387.487231$, $G = -187.547475$.

the computed enthalpy of activation being 26.6 kcal mol^{-1}, and the geometry of the transition state is also similar to the one of **TS-4-*cis*-SF**. It is noteworthy that the **7** → **8** process is not thermodynamically favored ($\Delta H = +10.3$ kcal mol^{-1}), underlining the valuable behavior that palladium displays for this striking pathway in the catalyzed process.

(iii) The Role of the Substituents. At this stage, one might ask whether the substituents, viz. the silane and the hydroxyl groups, do play a role for the ease of the Pd/H rearrangement. To this end, we carried out calculations on another model of **4**, see **9** and Scheme 7, in which the SiH_3 was replaced by H and only the C═C double bond of the dihydroxycyclopentene was retained. **9** can be seen as a generalized model for the 1,5 rearrangement studied above. The energetics of both pathways, the Pd(IV) pathway **9** → **10** → **11** and the Pd(II) 1,5 hydrogen transfer pathway **9** → **TS-9** → **11**, is reported in Table 5 for both isomers **9-*cis*** and **9-*trans*** corresponding to Br being either cis or trans with respect to the covalently bound organic moiety.[90] The corresponding energy profiles are displayed in Figure 6.[91] The values quoted in Table 5 are rather similar to the ones of Tables 3 and 4 obtained for the **4** → **TS-4** → **6** process. Thus the key factor for the ease of the Pd(II) 1,5 hydrogen transfer pathway is indeed the mediation provided by a d^9 C_{2v} PdL(X) unit and not the presence of substituents such as TMS or OH. Figure 6 also clearly points to the fact that the Pd(IV) pathway is quite unfavorable in the absence of the silane and OH substituents, as in the case of the SF-type isomers, which energetically perform the best along the whole reaction (see below).

3. The Overall Process. We have already referred to Figure 3 that summarizes the overall process that starts from the isomers **3a**. From this figure, it is clear that the transition states for the cyclocarbopalladation step are intrinsically higher in energy than the transition steps for the Pd/H interchange process. These two steps are, however, rather facile, their energy barrier being of the order of 20 kcal mol^{-1} or less. Note that the barrier for the Pd/H interchange in **4** is in general somewhat larger than the one for the cyclocarbopalladation step. The two steps are also exothermic. As a result the overall process is quite exothermic, by 20 kcal mol^{-1} or more. At this point, we may underline the validity of these BS-I basis set results, since by carrying out single-point calculations with the BS-II basis set on the BS-I optimized geometries, values that are close to the BS-I ones were obtained; see Tables S1−S3 in the Supporting Information.

Although the energy profiles are quite similar for the four isomers (since they only differ by a few kcal mol^{-1}) it is clear that the overall process is kinetically favored for the SF-type isomers. The **3a-*trans*-SF** or the **3a-*cis*-SF** isomers are the lowest ones, and the corresponding transition states for both the cyclocarbopalladation step and the Pd/H rearrangement step via the Pd(II) 1,5 hydrogen transfer pathway are also the lowest ones. Thus, for these SF isomers the Pd(IV) route is clearly unfavorable. Should the OF-type isomers be considered, then one might think that it can be competitive with the Pd(II) 1,5 hydrogen transfer pathway since the **5c** and **5d** Pd(IV) intermediates lie at the same energetic level as **TS-4-*cis*-OF** and **TS-4-*trans*-OF**. However, the **TS2** transition states arising from **5c** and **5d** lie well above the most favorable Pd(II) SF-type transition states by ca. 6 kcal mol^{-1} (**TS2-5c**) and ca. 8 kcal mol^{-1} (**TS2-5d**), making this Pd(IV) pathway notably unlikely.[92]

One cannot of course exclude some additional isomerization between the intermediates. This isomerization could proceed via either a dissociative mechanism or an associative mechanism with a second phosphine ligand. Its full analysis lies beyond the scope of the present study. We only computed the free energy for the dissociation of the single phosphine ligand in **3a-*trans*-SF**. The corresponding value, +2.0 kcal mol^{-1}, is of the same order of magnitude as the energy difference between **2** and **3** + PH_3. On the other hand, we have previously

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(90) Note that **10** is the only stable Pd(IV) structure that could be obtained, and that it has a geometry similar to **5c** or **5d**.

(91) One may notice that the transition states that connect **9** to **10**, **TS1−10**, and **10** to **11**, **TS2−10**, are energetically rather close to **10**, in agreement with the Hammond postulate. This is especially true for **TS2−10**, which is only 0.5 kcal mol^{-1} higher in energy than **10** ($\Delta E^‡$ value). It is therefore not surprising that the corresponding $\Delta H^‡$ value is computed to be slightly negative (−0.4 kcal mol^{-1}) since a maximum on a ΔE potential energy surface (which is computed here) and a maximum on the ΔH potential energy surface may well be at slightly different positions.

(92) Moreover, **5c** connects SF-type isomers and not OF-type isomers. One should also note that **5d** comes from **4a-*trans*-OF**, which itself derives from **3a-*cis*-OF** via a transition state (**TS-3a-*cis*-OF**), which is energetically the highest.

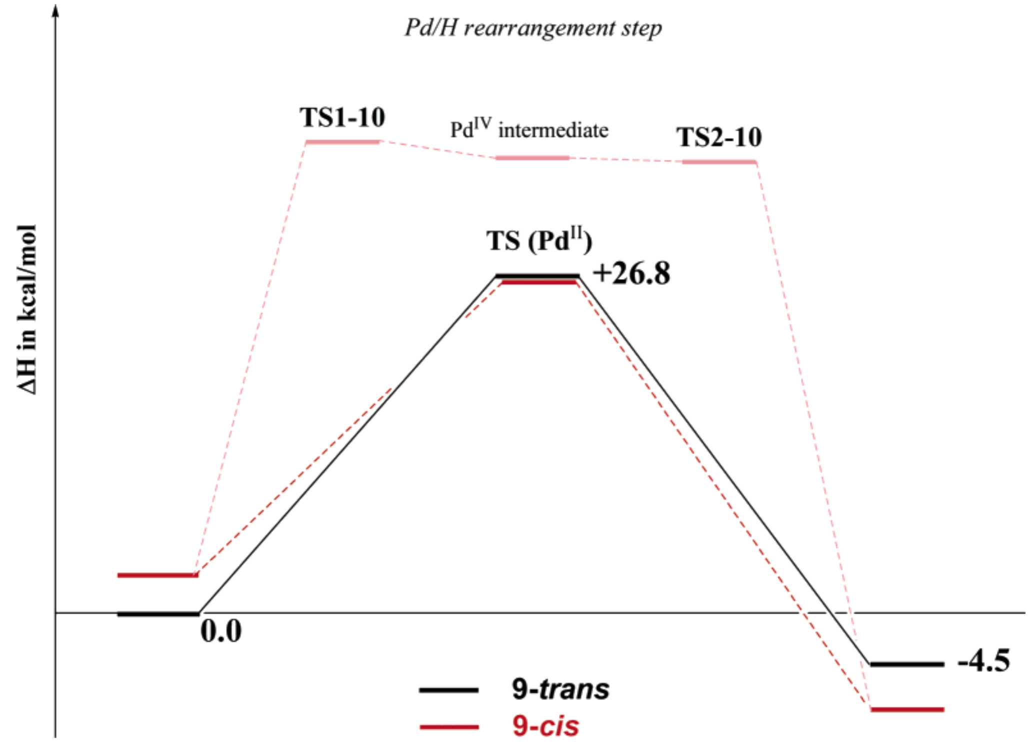

Figure 6. Energy profiles of the Pd/H rearrangement processes originating from the structures **9**. The zero of energy corresponds to **9a-*trans*** (in black). PdIV intermediate **10** (light red) comes from **9-*cis*** (red).

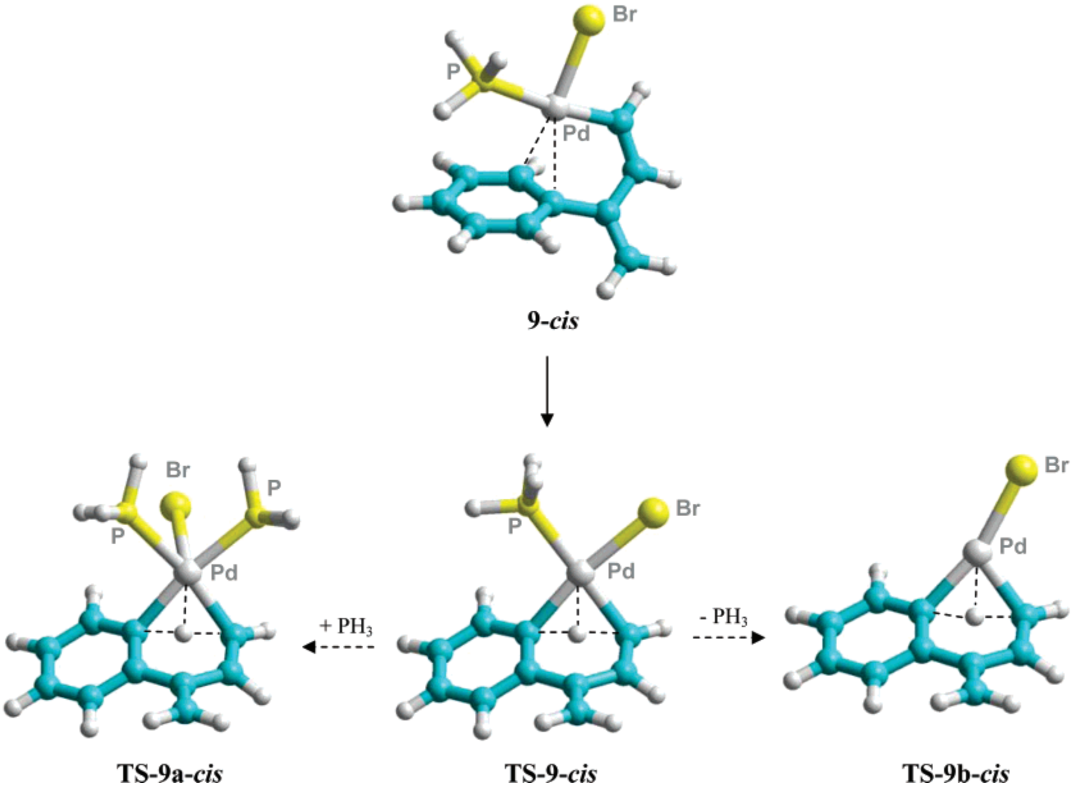

Figure 7. Optimized structures of the possible transition states than can originate from **9-*cis***, depending on the number of phosphine ligands.

mentioned that our attempts to optimize a five-coordinate *intermediate* that would result from the coordination of a second phosphine ligand in **3a** failed. Similar attempts to optimize a five-coordinated species as a transition state for phosphine exchange were also unsuccessful. This indicates that an associative mechanism that would go through such a five-coordinated intermediate or transition state is unlikely, and that any isomerization process between the intermediates **3** would most likely involve a dissociative type mechanism. As for the Pd/H rearrangement step, we checked whether a bisphosphine complex might be also involved. To this end, we used the somewhat simplified model **9** mentioned above. Adding a phosphine ligand to **TS-9-*cis*** led to a new transition state **TS-9a-*cis***; see Figure 7. **TS-9a-*cis*** also corresponds to the H migration, but it is much higher in energy than **TS-9-*cis***, especially when the entropy effects are considered: the corresponding $\Delta E^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ values from **9-*cis*** + PH_3 are +31.9, +30.4, and +42.1 kcal mol^{-1}, to be compared to +26.6, + 23.1, and +24.1 kcal mol^{-1} for **TS-9-*cis***. The assistance of the Pd/H rearrangement process by one extra phosphine ligand appears therefore quite unlikely. Interestingly, the loss of a phosphine ligand from **TS-9-*cis*** does not provide any assistance either, since for **TS-9b-*cis*** the corresponding $\Delta E^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ values from **9-*cis***$-PH_3$ are +48.2, +42.7, and +32.1 kcal mol^{-1} (i.e., again larger than the values for **9-*cis*** → **TS-9-*cis***). Thus, in agreement with the isolobal analogy argument mentioned above, the occurrence of only one phosphine ligand seems to be the optimal situation for the Pd/H rearrangement process.[93]

Conclusion

We have investigated through this study, based on DFT-B3LYP calculations, the intimate mechanism of the cyclocarbopalladation and of the 1,5 vinyl to aryl palladium shift steps that form the first part of a tandem reaction of various γ-bromopropargylic-1,2 diols with alkenyl or alkynyl stannanes.[10] From our calculations, the active intermediates in the catalytic cycle appear to have a single phosphine ligand. More importantly, we have shown that the intimate mechanism of the 1,5 vinyl to aryl palladium shift best corresponds to a proton transfer between the two formally negatively charged carbon atoms of the vinyl and the phenyl groups that are bound to the palladium atom in the transition state. As a consequence, the palladium center retains its +2 oxidation state throughout the tandem reaction. We believe that this conclusion can also apply to the 1,4-palladium shifts that have been experimentally observed thus far.[12-17] Work along these lines is now in progress.

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Supporting Information Available: Tables containing single point BSII//BSI relative energies of various monophospine and bisphosphine Pd(II) vinyl intermediates, energy barriers and energies of reaction for the cyclocarbopalladation step **3** → **4** for the four **3a** isomers, and energy barriers and energies of reaction for the Pd/H interchange step **4** → **6** for the four **4** isomers. Complete ref 33, **TS-4-*cis*-SF** imaginary normal mode representation, and Cartesian coordinates for all the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(93) That neither the d^9 three-coordinated fragment $Pd(PH_3)_2Br$ in **TS-9a-*cis*** nor the PdBr fragment in **TS-9b-*cis*** can be considered as being isolobal to CH_2^+ can be rationalized in the following way: A d^{10} ML_3 fragment is isolobal to CH_2, and hence the d^9 ML_3^+ fragment is isolobal to CH_2^+, if the ML_3 skeleton is derived from a trigonal bipyramid by removing one axial and one equatorial ligand (see page 407 of ref 86). This is not the case for the $Pd(PH_3)_2Br$ fragment in **TS-9a-*cis***, since its geometry is best viewed as originating from a ML_5 square pyramid (with Br in the apical position). In the PdBr fragment, the hybridized $4d_{z^2}$ and either the $5p_x$ or $5p_y$ orbital are separated by several electronvolts. In contrast, the σ and π orbitals of CH_2^+ are very close in energy. Thus, the prescription of having similar approximate energy of the frontier orbitals for two isolobal fragments is not fulfilled when one compares PdBr to CH_2^+.