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Employment of Palladium Pincer-Complexes in Phenylselenylation of Organohalides

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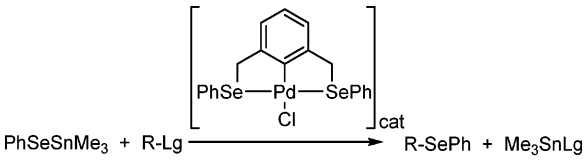

Palladium pincer-complex-catalyzed selenylation of propargyl-, allyl-, benzyl-, and benzoyl halides could be achieved under mild reaction conditions employing trimethylstannylphenylselenide as selenylating agent. This reaction has a high functional group tolerance as carbmethoxy, tosylamino, nitro, aryl bromide, and unprotected hydroxy groups are tolerated. Mechanistic studies indicate that the catalytic cycle is initiated by formation of a selenium-coordinated palladium pincer-complex, which subsequently reacts with the electrophilic substrate. DFT calculations were performed to explore the mechanism of the transfer of the organoselenium group from palladium to the substrate. These modeling studies revealed some interesting differences between the mechanism of the organoselenium group transfer and (the previously published) organostannane transfer reactions.

1. Introduction

The structural properties and catalytic reactivity of palladium pincer-complexes (e.g., **1a**−**c**) have attracted considerable attention in inorganic and, more recently, in organic chemistry.[1−6] We have previously shown that in the presence of dimetallic organotin reagents palladium pincer-complexes (**1a**,**b**) can be employed as efficient catalysts for synthesis of allenyl stannanes,[7,8] allenyl silanes,[8] and allyl stannanes.[9] In these reactions, palladium pincer-complex catalysts have been employed to transfer various organometallic groups from a dimetallic tin reagent (i.e., $(Me_3Sn)_2$ or $Me_3SnSiMe_2Ph$) to propargylic and allylic substrates. It was shown[7,8] that the reactivity of pincer-complexes is completely different from the reactivity of commonly used palladium-catalysts such as $Pd(PPh_3)_4$ and $Pd_2(dba)_3$. Employment of pincer-complexes offers an attractive synthetic route to preparation of organometallic compounds due to three important features: (i) a strong terdentate ligand−metal interaction provides high stability and durability for the catalyst; (ii) coordination of the terdentate ligand restricts the number of the available coordination sites on palladium to a single one; and (iii) under ambient conditions the oxidation-state of palladium is restricted to +2. Because of these properties, palladium pincer-complexes have proven to be robust and effective as catalysts, which are reflected by their high functional group tolerance and broad synthetic scope.[1−13]

The above-mentioned favorable features of pincer-complexes inspired us to further extend the catalytic utility of these species in organoselenium chemistry.[14−19]

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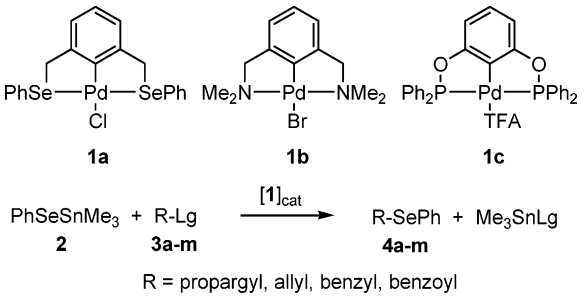
SCHEME 1. Palladium Pincer-Complex-Catalyzed Phenylselenylation

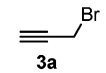
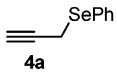
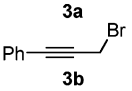
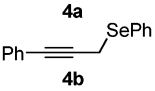
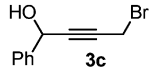
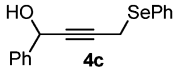
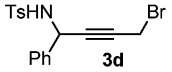
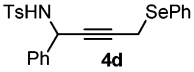
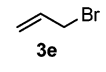
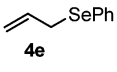
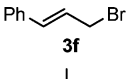
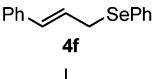
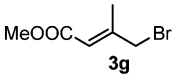
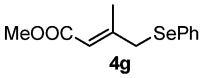
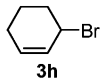
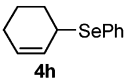
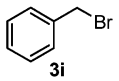
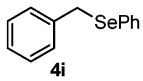
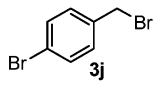
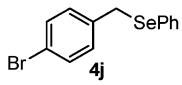
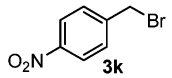
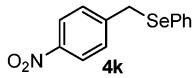
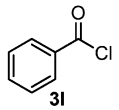
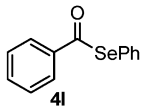
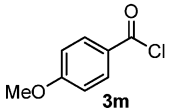
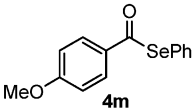


Because palladium pincer-complexes are known to catalyze the transfer of organostannyl and organosilyl groups to electrophiles from dimetallic trimethyltin reagents,[7,9] we have studied the possibility of employment of trimethylstannylphenylselenide[20] (**2**) as a source of phenylselenyl group in related reactions (Scheme 1).[20−26] Thus, in this paper we report our results on palladium pincer-complex-catalyzed transfer of phenylselenyl group from **2** to propargyl-, allyl-, benzyl-, and benzoyl halides. The mechanism of the phenylselenyl transfer has been investigated by stoichiometric reactions and DFT modeling studies. We have also compared the mechanism of the organoselenium and -stannane[8] transfer reactions to propargylic substrates. The DFT results obtained for the corresponding TS structures of these processes indicate some very interesting mechanistic differences between the two metal transfer processes.

2. Results and Discussion

Considering the fact that SeCSe complex **1a** displayed the highest activity in trimethyltin transfer processes,[8] we employed this readily available[27] catalyst in the selenylation reactions. Indeed, various organic substrates, involving propargyl-, allyl-, benzyl-, and benzoyl halides (**3a**−**m**), readily undergo (Scheme 1) halogen−selenium exchange in the presence of **2** and catalytic amounts (2 mol %) of **1a** affording organoselenides **4a**−**m** in good to excellent yield (Table 1). Analysis of the crude reaction mixtures indicated that the catalytic transformations proceeded very cleanly providing the selenated products almost quantitatively, which led to high isolated yields. The only exception appears to be **4b** (entry 2, 66% yield), which probably underwent partial decomposition under the isolation process. The reactions were conducted under mild and neutral conditions without employment of inert gas atmosphere. In the absence of catalyst **1a**, only traces of the selenylated products were formed.[25]

TABLE 1. Palladium Pincer-Complex-Catalyzed Phenylselenylation of Organohalides[a]

Entry	Electrophile	T (°C) / Time (h)	Product	Yield[b]
1	 **3a**	20 / 15	 **4a**	90%
2	 **3b**	20 / 5	 **4b**	66%
3	 **3c**	20 / 17	 **4c**	95%
4	 **3d**	20 / 17	 **4d**	91%
5	 **3e**	20 / 15	 **4e**	80%
6	 **3f**	20 / 2	 **4f**	89%
7	 **3g**	20 / 3	 **4g**	85%
8	 **3h**	60 / 24	 **4h**	87%
9	 **3i**	20 / 17	 **4i**	89%
10	 **3j**	20 / 17	 **4j**	90%
11	 **3k**	20 / 17	 **4k**	89%
12	 **3l**	20 / 3	 **4l**	95%
13	 **3m**	20 / 3	 **4m**	95%

[a] All reactions were conducted in THF using 2 mol % of **1a**. [b] Isolated yield.

In the presented reactions, we did not observe formation of organostannanes indicating that exclusively the phenylselenyl group of **2** was transferred to the electrophile. The reaction also displays a remarkable high functional group tolerance as carbmethoxy, tosylamino, nitro, aryl bromide, and unprotected hydroxy groups are tolerated. The regioselectivity of the substitution involving allylic and propargylic substrates is excellent as only products resulting from the direct substitution of the halogenated carbon are formed. Thus, employment of propargyl bromides **3a**−**d** afforded propargyl selenides **4a**−**d** (entries 1−4) in good to excellent yields. When unsubstituted propargyl bromide **3a** was used as electrophile, traces (about 2%) of allenyl selenide product were also observed in the crude reaction mixture. Predominant formation of propargyl selenides from propargyl bromides **3a**, **3c**, and **3d** (entries 1, 3, and 4) is in

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(18) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435.
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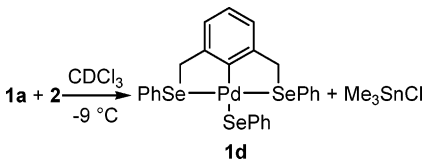
(27) Yao, Q.; Kinney, E. P.; Zheng, C. *Org. Lett.* **2004**, *6*, 2997.

SCHEME 2. Stoichiometric Reaction of 2 with 1a



sharp contrast to the corresponding palladium pincer-complex-catalyzed stannylation and silylation reaction of propargyl chlorides, which gave the corresponding allenyl stannane and silane products.[7,8]

Allyl bromides **3e**−**g** reacted also with high regioselectivity affording primary allyl selenides **4e**−**g** as the sole product in high yields (entries 5−7). Secondary allyl bromide **3h** could also be employed as electrophile (entry 8); however, this substitution reaction was sluggish even at 60 °C, and therefore an elongated reaction time was required. Benzyl bromides (**3i**−**k**) were also effective as electrophiles affording benzyl selenides (**4i**−**k**) in high yields (entries 9−11); however, **3i**−**k** reacted somewhat slower than propargyl and allyl bromides **3a**−**g**. Benzoyl chlorides (**3l**,**m**), on the other hand, reacted rapidly and afforded carboselenoates (**4l**,**m**) in excellent yields in 3 h (entries 12 and 13). It was found that elongated reaction times (over 8 h) often resulted in a partial disproportionation[25] of **2** to give Ph_2Se, decreasing the yield of the corresponding selenylation reactions. We have also attempted to use allyl-, propargyl-, and benzyl-chlorides instead of the corresponding bromides as electrophiles; however, under mild conditions these reactions proceed with a low conversion of the chloride substrates to the corresponding phenylselenides.

3. Mechanistic Considerations

Stoichiometric Reactions. Our previous studies have shown that pincer-complexes such as **1b** do not react with propargyl or allyl halogenides at ambient temperature.[8] On the other hand, dimetallic organostannanes, such as $(Me_3Sn)_2$ or $Me_3SnSiMe_2Ph$, undergo transmetalation with **1b** to give the corresponding organometal (tin or silicon) coordinated pincer-complex, which could be observed by ^{119}Sn and ^{29}Si NMR spectroscopy.[7,8] Thus, to elucidate the mechanism of the organoselenium transfer reaction, we have conducted a series of stoichiometric experiments for the reaction of SeCSe complex **1a** and selenium-stannane **2** monitored by ^1H NMR and ^{77}Se NMR at −9 °C (Scheme 2). When the pale-yellow solution of **1a** was treated with 1.1 equiv of **2** in $CDCl_3$, the color of the reaction mixture immediately turned to dark orange. The ^1H NMR spectrum of **1a** also underwent substantial changes upon addition of **2**, as the characteristic signals from the methylene groups of **1a** (4.73, 4.72, 4.32, and 4.27 ppm) were considerably broadened. Unfortunately, the extensive line-broadening of 50 Hz encumbered the identification of the product of the stoichiometric reaction. We have also analyzed the reaction mixture of the stoichiometric reaction of **1a** and **2** using ^{77}Se NMR spectroscopy. The ^{77}Se NMR spectrum of pure **1a** displays two signals at 427.1 and 424.9 ppm, indicating the presence of two diastereomeric forms,[27] while the selenium atom of pure **2** resonates at 0.5 ppm. When **2** was added to **1a**, the ^{77}Se NMR signal of **2** (0.5 ppm) was vanished, and at the same time the two signals of **1a** (427.1 and 424.9 ppm) were broadened and shifted downfield to 432.9 and 425.7 ppm, respectively, and a new peak appeared at 83.8 ppm. Once again, the extensive line-broadening of the ^{77}Se NMR signals did not allow clear identification of the product. Our further efforts to isolate and purify the product of the stoichiometric reactions were fruitless, because of its low stability.

Although the NMR studies clearly indicated that in the above stoichiometric process **2** was consumed and that the NMR spectrum of **1a** underwent substantial changes, conclusive results for the identity of the reaction product could not be obtained from these experiments. On the other hand, our previous studies with $(Me_3Sn)_2$ or $Me_3SnSiMe_2Ph$ clearly indicated[7,8] transmetalation of these dimetallic reagents with pincer-complex **1b**, and therefore we assume that the stoichiometric reaction of **1a** and **2** results in formation of a phenyl-selenide coordinated complex **1d** (Scheme 2). Formation of **1d** is also indicated by the fact that addition of benzoyl chloride derivative **3m** to the reaction mixture of **1b** and **2** subjected to the above ^{77}Se NMR studies results in immediate formation of **4m** and recovery of **1a**.

DFT Modeling of the Phenylselenyl Transfer Reaction. Based on the assumption that the initial step of the pincer-complex-catalyzed reaction is formation of **1d**, we performed DFT modeling studies to explore the mechanism of the organoselenium group transfer from the palladium atom to the organic substrate. In these studies, we investigated the potential energy surface of the organoselenium transfer to a propargylic substrate (cf., entries 1−4), to compare the mechanism of this process and the previously reported[8] reactions involving organotin species.

Computational Methods. All geometries were fully optimized employing a Becke-type[28] three-parameter density functional model B3PW91 using a double-ζ-(DZ)+P basis constructed from the LANL2DZ[29−31] basis by adding one set of d-polarization functions to the heavy atoms (exponents: C, 0.630; Cl, 0.514; Se, 0.338; Sn, 0.183) and one set of diffuse d-functions on palladium (exponent: 0.0628). Harmonic frequencies have been calculated at the level of optimization for all structures to characterize the calculated stationary points and to determine the zero-point energies. Fully optimized transition state structures **5a**, **5b**, and **8** have been characterized by a single imaginary frequency, while the rest of the optimized structures possess only real frequencies. All calculations were carried out by employing the Gaussian 03 program package.[32]

Reaction Profile for the Selenium Transfer Process. The scope of the DFT studies involved exploration of the role of the palladium catalyst as well as investigation of the regioselectivity of the catalytic selenylation reaction. Because of computational limitations, we employed slightly simplified model systems to describe the mechanism of the experimentally studied reaction of **3a** with **2**. Accordingly, we have approximated (Scheme 3)

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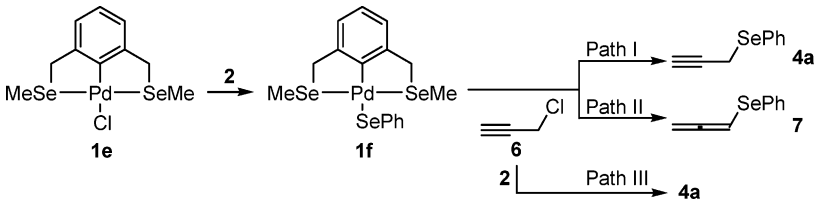
SCHEME 3. Reactions Studied by DFT Modeling; Paths I and II Describe the Pincer-Complex-Catalyzed Reaction, While Path III Is the Uncatalyzed Reaction



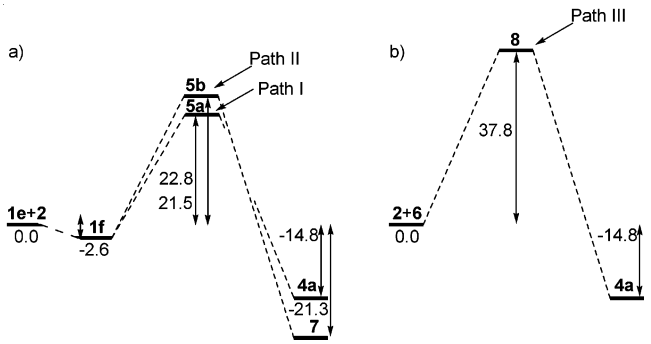
the phenylselenyl groups in palladium pincer-complex **1a** and **1d** with methylselenyl groups (**1e** and **1f**), and the bromine atom of **3a** was approximated with a chlorine atom (**6**). The mechanistic discussions (vide infra) are restricted to the analysis of the TS geometries and the relative activation energies of the different reaction pathways, which are probably not affected by these approximations. Furthermore, employment of **6** as substrate in the DFT studies simplifies the comparison of the mechanistic features of the present selenium transfer and the previously published[8] tin transfer reactions.

Using the above-described model systems, we have investigated three different pathways (Scheme 3) for the phenylselenylation of propargyl chloride **6**. The first pathway (Path I) involves transfer of the phenylselenyl group from pincer-complex **1f** to give propargyl selenide **4a**, while the second pathway (Path II) is the corresponding reaction affording allenyl selenide **7**. To clarify the role of the palladium catalyst in this reaction, we have investigated the mechanism of the uncatalyzed reaction (Path III) involving direct transfer of the phenylselenyl group from **2** to the propargylic substrate to give **4a**.

According to the DFT results, the reaction between **1e** and **2** is exothermic by 2.6 kcal mol^{-1} affording **1f** (Schemes 3 and 4), which is the active selenylating agent in the selenium transfer process. The fact that **1f** is such a stable species also supports our assumptions that stoichiometric reaction (Scheme 2) of **1a** and **2** results in selenium coordinated complex **1d**.

The reaction of **1f** and **6** affording propargyl selenide **4a** (Path I) proceeds through TS **5a** requiring an activation energy of 21.5 kcal mol^{-1}. The subsequent formation of propargyl selenide **4a** is strongly exothermic by 14.8 kcal mol^{-1} (Scheme 4a). The second pathway (Path II) leads to formation of allenyl selenide **7** via TS structure **5b** and requires somewhat higher activation energy (22.8 kcal mol^{-1}) than Path I resulting in **4a**. Interestingly, although the activation barrier of Path II is higher than that of Path I, formation of allenyl selenide **7** is more

SCHEME 4. PES of the Phenylselenylation Reaction: a) Paths I and II, b) Path III[a]



[a] Energies in kcal mol^{-1}.

exothermic (−21.3 kcal mol^{-1}) than formation of propargyl product **4a** (−14.8 kcal mol^{-1}). The activation energy of the uncatalyzed reaction of **2** with **6** (Path III) is considerably higher (37.8 kcal mol^{-1}) than the corresponding reactions (Path I and II) involving pincer-complex **1f**. These results are in agreement with our experimental findings that the palladium-catalyzed reaction of **2** with **3a** leads predominantly to propargyl product **4a** (entry 1) and that the selenylation reaction requires palladium catalysis.

Inspection of the calculated structures of complexes **1e** and **1f**, as well as TS structures **5a**,**b** and **8**, reveals some interesting mechanistic details (Figure 1). Complex **1e** has C_2 symmetry with a tightly coordinated pincer ligand. The palladium−carbon bond is relatively short (2.004 Å), while the palladium−selenium bond lengths (2.432 Å) are similar to the Pd−Se bond lengths (2.42−2.44 Å) obtained from X-ray data for a related complex.[27] The phenylselenide coordinated structure **1f** is characterized by a similar, strong metal−ligand bonding (Pd−C; 2.039 Å, Pd−Se; 2.433 and 2.435 Å, respectively); however, the newly formed Pd−Se bond is relatively long, 2.540 Å (Figure 1). In TS **5a**, the characteristic five-member ring topology of the sidearms of the pincer-complex is preserved, while the bond length to the phenylselenide group is elongated (Pd−Se = 2.574 Å). The distance of the propargylic carbon (C_α) to the selenium atom (2.482 Å) and the C_α−Cl bond (2.504 Å) are very long, indicating that the formation of the carbon−selenium bond and the cleavage of the carbon−chloride bond is a concerted process. Furthermore, the Se−C_α−Cl bond angle is 151.9°, which is close to the characteristic displacement angle of the S_N2-reactions (180°). These geometrical features indicate that in TS structure **5a** the selenium atom is involved in an S_N2-type of displacement of the leaving group (Cl) without direct involvement of the palladium atom (Pd−C_α = 3.313 Å). This hypothesis is

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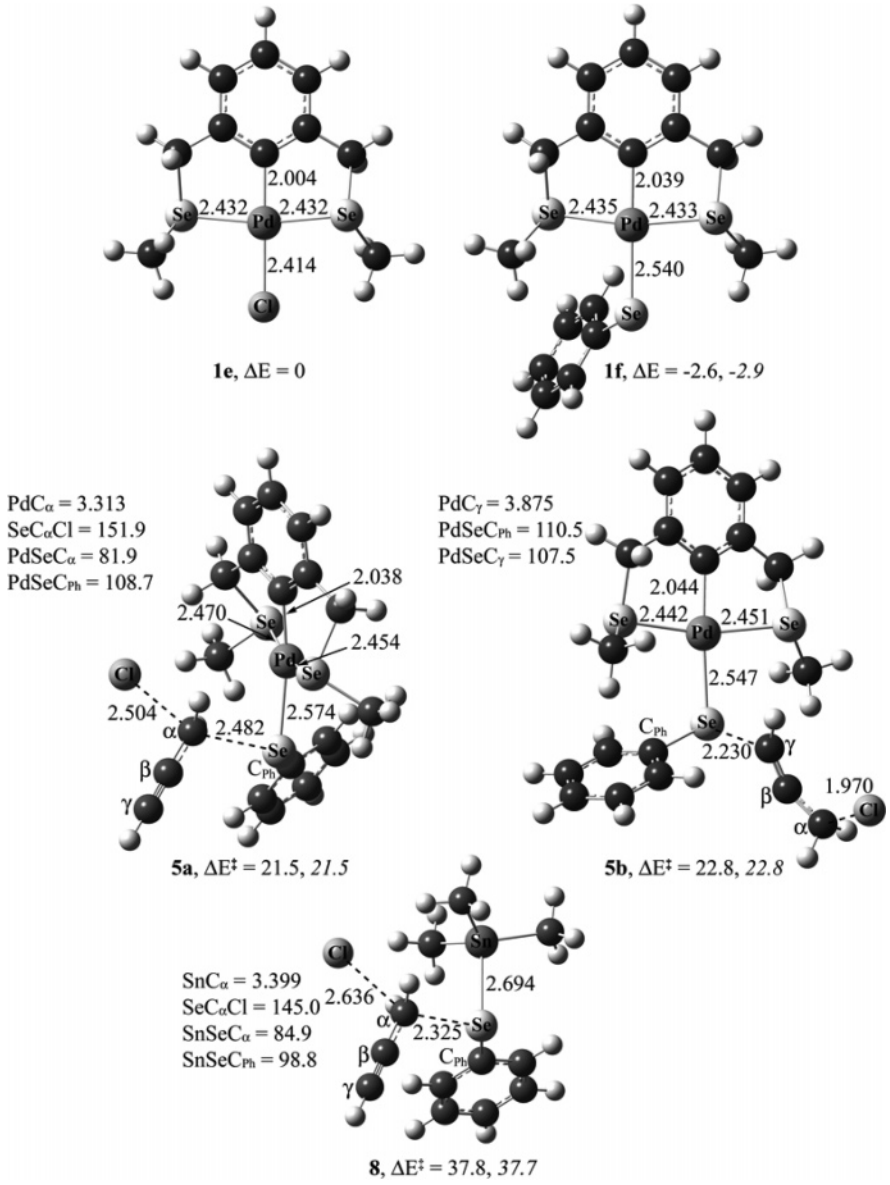


FIGURE 1. Calculated geometries of **1e** and **1f** and the TS's of the selenylation reactions (**5a**,**b** and **8**). Bond lengths are given in angstroms, angles in degrees, energies in kcal mol^{-1}, and the ZPV-corrected energies in italics.

supported by other geometrical features; the Pd−Se−C_α angle is 81.9° and the Pd−Se−C_{Ph} angle is 108.7°, clearly indicating that the nucleophilic attack is initiated by the lone-pair electrons of the selenium atom. The TS structure of Path II (**5b**) leading to allenyl product **7** is characterized by features similar to those of **5a**. The Se−C_γ distance (2.230 Å) and the C_α−Cl distance (1.970 Å) indicate nucleophilic displacement in an S_N2' fashion. The long Pd−C_γ distance (3.857 Å) indicates that the palladium atom is not directly involved in the substitution reaction. Similarly to **5a**, TS structure **8** of the uncatalyzed reaction (Path III) also displays the attributes of an S_N2 process: long Se−C_α (2.325 Å) and C_α−Cl (2.636 Å) distances as well as a wide Se−C_α−Cl angle (145.0°). The long Sn−C_α distance (3.399 Å) shows that the tin atom is not directly involved in the substitution process. These geometrical features indicate a similar mechanism (S_N2/ S_N2') for the palladium-catalyzed (Paths I and II) and the uncatalyzed (Path III) reactions. However, these modeling results raise the question on the catalytic role of palladium in the substitution process.

The above analysis clearly indicates that the nucleophilic substitution of the chloride atom in **6** is initiated by the lone-pair orbital of the selenium atom. Inspection of the HOMO orbital of **1f** and **2** clearly shows that in both species the main component of this MO is the n_π lone-pair of selenium (Figure 2). This explains the similar geometry of the TS structures of the catalyzed (**5a**,**b**) and uncatalyzed (**8**) processes. However, the orbital energy of the n_π lone-pair in palladium complex **1f** (−4.67 eV) is much higher than the corresponding orbital energy (−6.00 eV) in **2**, indicating that the lone-pair electrons of **1f** are much easier accessible by electrophiles (such as **6**) than the lone-pairs of **2**. Accordingly, formation of **1f** from **2** leads to an increase of the lone-pair energy of selenium, increasing the nucleophilicity of the selenium atom. The high energy of the lone-pair electrons of selenium in **1f** can probably be explained by a four-

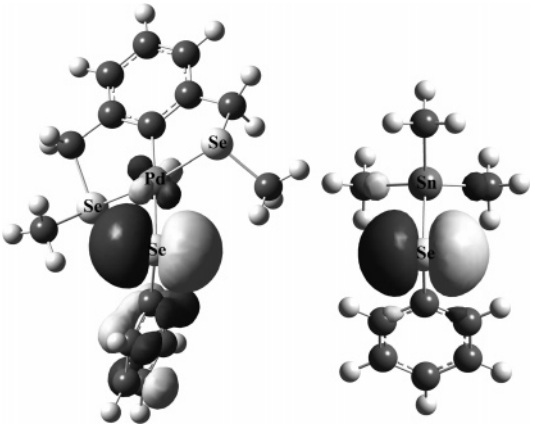
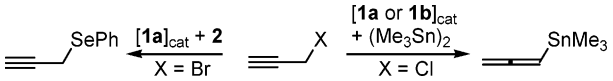


FIGURE 2. HOMO orbital of complex **1f** ($\epsilon_{HOMO} = -4.67$ eV) and **2** ($\epsilon_{HOMO} = -6.00$ eV).

SCHEME 5. Differences in the Regioselectivity of the Selenylation and the Stannylation Reactions Catalyzed by Palladium Pincer-Complexes



electron interaction between the n_π/n_σ orbitals of selenium and the high-lying nonbonding d-orbitals of palladium. These types of interactions do not occur in **8** because of the lack of d-valence orbitals in tin.

In summary, the catalytic effect of palladium can be explained by the presence of high energy lone-pair electrons in **1f**, which leads to an increase of the nucleophilicity of the selenium atom in **1f** compared to **2**. This higher nucleophilicity is reflected by the fact that palladium-catalyzed nucleophilic selenylation requires lower activation barrier (21−22 kcal mol^{-1}) than the uncatalyzed process (37.8 kcal mol^{-1}).

Comparison of the Mechanism of the Organoselenium and -tin Transfer Reactions. As shown above, the phenylselenylation of propargyl chloride (**6**) affords the propargylic product **4a** via displacement of the chloride by the lone-pair electrons of the selenium atom. This regioselectivity is in sharp contrast to the reaction of $(Me_3Sn)_2$ with **6**, which exclusively affords the allenyl product[8] (Scheme 5), indicating mechanistic differences between the palladium-catalyzed selenylation and stannylation process of propargylic substrates.

The differences in the TS structures of the selenylation and stannylation[8] reactions are highlighted in Figure 3. As mentioned above, the selenylation reaction is based on nucleophilic displacement of the leaving group by the high-lying lone-pair electrons of the selenium atom. On the other hand, the stannylation reaction (**9a**,**b**) is initiated by the nucleophilic attack of the palladium−tin σ-orbital.[8] This is indicated by the relatively short Pd−C_α and Pd−C_γ distances in the TS structures of the stannylation reaction[8] (Pd−C_α = 2.961 in **9a** and Pd−C_γ = 2.638 Å in **9b**), which is shorter by 0.35−1.23 Å than the corresponding distances in **5a** and **5b**. Furthermore, the Sn−C_α−Cl angle in **9a** (132°) is more acute by almost 20° than the Se−C_α−Cl angle (150.9°) in **5a**. According to the DFT calculations,[8] formation of allenyl stannane via TS structure **9b** requires lower activation energy (by 13 kcal mol^{-1}) than formation of the propargyl product

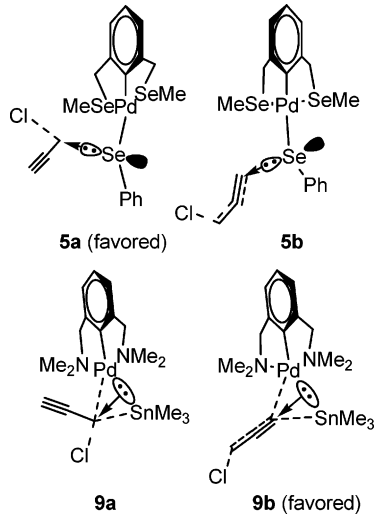
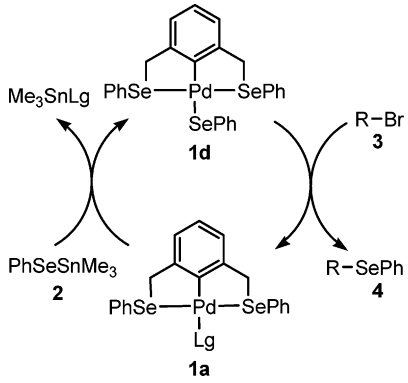


FIGURE 3. TS structures of selenylation (**5a** and **5b**) and stannylation[8] (**9a** and **9b**) of propargyl chloride determined at the B3PW91/LANL2DZ+P level of theory.

SCHEME 6. The Catalytic Cycle of the Phenylselenylation Reaction



through TS structure **9a**. Because of the different mechanism in the selenylation process, formation of the propargyl product (**4a**) via **5a** is favored over the formation of the allenyl derivative (**7**) by 1.3 kcal mol^{-1}. A possible explanation is that the TS structure of the direct stannylation process (**9a**) is sterically more congested than the corresponding TS of the selenylation process (**5a**), in which the palladium atom does not participate in the displacement of the leaving group.

The Catalytic Cycle of the Phenylselenyl Transfer Reaction. On the basis of the above presented results, we propose a catalytic cycle for the palladium pincer-complex-catalyzed phenylselenyl transfer from **2** to the organic substrates (Scheme 6). Thus, the catalytic cycle of the substitution reaction is initiated by formation of intermediate **1d** by transmetalation of **2** with **1a**. In the transmetalation process, the phenylselenyl group is transferred to palladium. Formation of **1d** is then followed by an S_N2-type of displacement of the bromide leaving group by the high-lying lone-pair electrons of selenium regenerating catalyst **1a**. It is interesting to point out that the mechanistic features of the above-described S_N2-type of selenation process show an interesting analogy to the fluoride ion-catalyzed selenyl transfer reaction developed by Beletskaya and co-workers.[22,23] An important feature of the presented catalytic

cycle (Scheme 6) is that the catalytic process occurs in a single free coordination site of palladium, as well as the oxidation state of palladium is restricted to +2.

Several publications have appeared in the literature for coupling of selenium−tin reagents with organohalides for preparation of organoselenides.[21−26] Beletskaya, Nishiyama, and their co-workers[21,24−26] have shown that $Pd(PPh_3)_4$ efficiently catalyzes the coupling of tributylstannylphenylselenide with organohalides. The presented palladium pincer-complex-catalyzed phenylselenylation of organohalides represents an interesting synthetic alternative to the palladium(0) catalyzed and other transformations. The catalytic process with **1a** proceeds via a redox-free reaction mechanism extending the functional group tolerance (e.g., unprotected hydroxy group and aryl bromide) of the palladium-catalyzed selenylation reactions. In addition, the catalytic reactions can be performed in the absence of phosphines under so-called ligand-free conditions without employment of inert-gas atmosphere or use of manifold technique.

4. Conclusions

Palladium pincer-complexes can be employed as catalysts in the coupling of a phenylselenyl group with organohalides extending the synthetic scope of the phenylselenylation reactions. These reactions proceed under mild and neutral conditions, and therefore many functionalities, including COOMe, OH, NHTs, NO_2, and even aryl Br, are tolerated. The selenylation of functionalized allylic and propargylic substrates proceeds with excellent regioselectivity as only the linear products are formed. Mechanistic studies for selenylation of propargyl chloride (**6**) indicate that the lowest energy path provides propargyl selenide product via a phenylselenyl-coordinated palladium pincer-complex. In this reaction, the lone-pair electrons of the selenium atom initiate the nucleophilic displacement of the leaving group in an S_N2-type of process. This mechanism is significantly different from the previously reported[8] mechanism of the palladium pincer-complex-catalyzed stannylation process, in which the palladium−tin σ-bond initiates the nucleophilic displacement of the leaving group. The different mechanisms in the selenylation and stannylation reactions lead to different regioselectivity for the substitution of propargylic substrates.

5. Experimental Section

General Procedure for the Palladium Pincer-Complex-Catalyzed Phenylselenylation. Trimethylstannylphenylselenide[20] **2** (88 mg, 0.275 mmol) and the corresponding electrophile (0.25 mmol) in THF (1.0 mL) were added to catalyst **1a** (2.8 mg, 0.005 mmol) at room temperature. This reaction mixture was then stirred for the allotted temperatures and times given in Table 1. Thereafter, the solvent was removed and the product was purified by silica gel chromatography.

Phenyl-(2-propynyl)-selenide (4a). This product was prepared by the above general procedure. For purification, silica gel chromatography was employed using pentane as eluent. The obtained ^{1}H NMR data are in agreement with the published literature values.[33] ^{1}H NMR: δ 2.25 (t, ^3J = 2.7 Hz, 1H), 3.49 (d, ^3J = 2.7 Hz, ^2J (Se, H) = 13.0 Hz, 2H), 7.30 (m, 3H), 7.61 (m, 2H). ^{13}C NMR: δ 12.7, 72.1, 81.2, 128.1, 129.5, 129.8, 133.6.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council (VR). The computer time granted by the Swedish National Allocation Committee (SNAC) is greatly appreciated. We acknowledge the financial support by the Knut and Alice Wallenberg Foundation (KAW).

Supporting Information Available: Detailed experimental section, computational details of the DFT studies, and ^{13}C NMR spectra of compounds **4a**−**m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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