

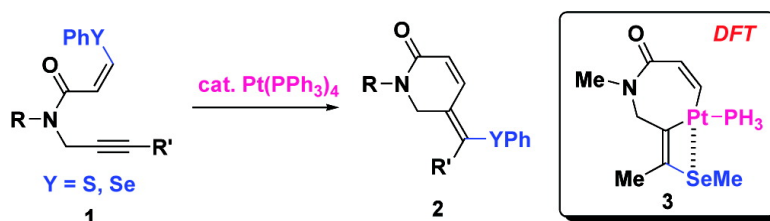
Communication

**Platinum-Catalyzed Intramolecular Vinylchalcogenation
 of Alkynes with #-Phenylchalcogeno Conjugated Amides**

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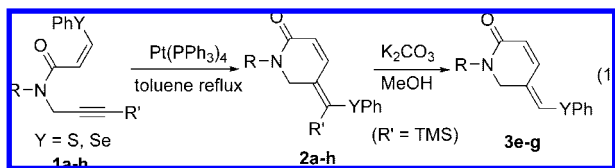
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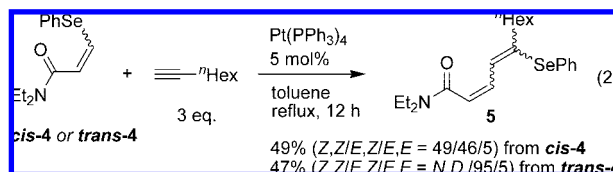
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Simultaneous addition of carbon and heteroatom units (represented as “C” and “E”, respectively) to alkynes with the cleavage of “C–E” bond by transition metal complexes has attracted great interest in recent organic and organometallic chemistry.^{1–5} This reaction proceeds with *cis*-selective stereochemistry to give multifunctionalized alkenyl heteroatom compounds. Introduction of allyl,¹ alkynyl,² acyl,³ and cyano⁴ groups as carbon units has been well studied. However the corresponding introduction of vinyl group (addition of the “vinyl-E” molecule across the triple bond) leading to 1,3-dienes remains as a challenging theme.^{6–9} When the new “vinyl-E” unit exhibits the reactivity similar to that of starting vinyl heteroatom compounds, further reaction or oligomerization could be a serious problem.^{5c} To the best of our knowledge, successful examples reported so far have been limited to the ring-expansion reaction via addition of three- or four-membered heterocyclic compounds such as silacyclopropenes,^{5a} methylenesiliranes,^{5b} allene episulfides,^{5c} and silacyclobutenes^{5d} to alkynes. In these systems, ring strain of starting compounds may promote the initial cleavage of the “vinyl-E” bond by the metal catalyst.

Recently, we found that an anion stabilizing group on the β -position of acyclic vinyl sulfides and selenides enhanced oxidative addition to Pt(0) complex.¹⁰ This finding led us to develop a new type of catalytic reaction using vinyl sulfides and selenides.¹¹ Here we disclose Pt(0) catalyzes intramolecular *cis*-vinylthiolation and -selenation of alkynes leading to effective construction of six-membered lactam framework **2** or **3** having a high degree of unsaturation (eq 1).



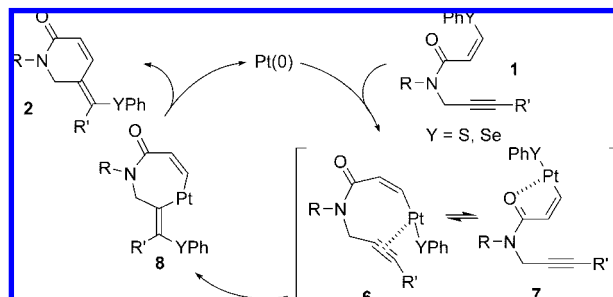
At first, the reaction of vinyl selenides **4** (*cis* and *trans*) having a carbamoyl group on β -position of vinyl moiety with 1-octyne was examined to check the possibility of vinylchalcogenation of alkynes, since this electron withdrawing group may accelerate oxidative addition of the vinyl–SePh bond to Pt(0).^{10b,12} When toluene (0.4 mL) containing *cis*-**4** or *trans*-**4** (0.3 mmol), 1-octyne (3 equiv), and Pt(PPh₃)₄ (5 mol%) was heated at reflux for 12 h, 1,3-dienes **5** were obtained in moderate yields (eq 2). The stereochemistry of **4** did not affect the yield of **5**. Then, we undertook intramolecular vinylchalcogenation and the working hypothesis is shown in Scheme 1. The first step in this process is oxidative addition of vinyl–YPh (Y = S, Se) bond to Pt(0) giving



rise to alkyne-coordinated complex **6** and/or carbonyl-coordinated complex **7**. Subsequent insertion of alkyne into the Pt–Y bond occurs on **6** affording the platinumacycle **8**. Reductive elimination leads to the cyclized products **2** and regenerates the Pt(0) species.

When toluene (0.5 mL) containing a vinyl sulfide **1a** (0.2 mmol) and Pt(PPh₃)₄ (5 mol%) was heated at reflux for 2.5 h, intramolecular vinylthiolation product **2a** was obtained in 90% yield with excellent stereoselectivity (Table 1, run 1).¹³ In contrast with an intermolecular reaction (eq 2), the stereochemistry of the substrates was essential in this cyclization. While intramolecular vinylselenation of **1b** took place efficiently to form lactam **2b** (run 2), the reaction of the *trans*-isomer of **1b** gave no detectable product under similar reaction conditions. In the oxidative addition adduct of *trans*-isomer, intramolecular alkyne coordination affording the intermediate like **6** might be conformationally impossible. Bulkier alkyl substituents on nitrogen, for example, 1-phenylethyl, did not retard the reaction (run 3). The reaction of vinyl sulfide **1d** and selenide **1e** having a TMS group at the terminus gave the corresponding lactam **2d** and **2e** in high yields (runs 4 and 5). This catalytic system was not able to apply to terminal alkynes (R' = H, eq 1) probably due to further reaction or oligomerization.¹⁴ However, **2e** easily underwent desilylation with K₂CO₃ in MeOH to afford **3e** in 90% total yield from **1e** (run 6). Longer alkyl substituents on nitrogen of **1f**, for example, 2-phenylethyl, affected the reaction rate and stereoselectivity (run 7). Interestingly, a crude *E/Z* mixture of **2f** was treated with K₂CO₃ in MeOH to form desilylated lactam **3f** with high *E*-selectivity in high yield (run 8).¹⁵ Similarly, **1g** having unprotected indole ring gave desilylated *E*-lactam **3g** in 86% yield (run 9). Vinyl sulfide **1h** having aryl group at the terminus also

Scheme 1. A Possible Pathway Leading to Six-Membered Lactams



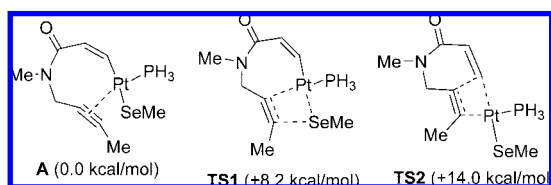
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Table 1. Pt(0)-Catalyzed Intramolecular Vinylchalcogenation of Alkynes to Form Six-Membered Lactams (eq 1)^a

run	1	Y	R	R'	Product, % ^b	E/Z ^c
1	1a	S	CH ₂ Ph	Et	2a , 90	>99/1 ^d
2	1b	Se	CH ₂ Ph	Et	2b , 92 (99)	>99/1 ^d
3	1c	S	CH(Me)Ph	Et	2c , 88	>99/1 ^d
4	1d	S	CH ₂ Ph	TMS	2d , 92	96/4
5	1e	Se	CH ₂ Ph	TMS	2e , 95	96/4
6 ^e	1e	Se	CH ₂ Ph	TMS	3e , 90	>99/1 ^d
7 ^f	1f	Se	(CH ₂) ₂ Ph	TMS	2f , (94)	71/29
8 ^{e,f}	1f	Se	(CH ₂) ₂ Ph	TMS	3f , 78 (85)	95/5
9 ^{e,f}	1g	Se	(CH ₂) ₂ (3-Indolenyl)	TMS	3g , 86	>99/1 ^d
10	1h	S	CH ₂ Ph	<i>p</i> -ClC ₆ H ₄	2h , (82)	96/4

^a Conditions: **1** (0.2 or 0.3 mmol), Pt(PPh₃)₄ (5 mol %), toluene (0.5 or 0.8 mL), reflux, 2.0–3.5 h. ^b Isolated yields. Numbers in parentheses are NMR yields. ^c Determined by ¹H NMR. ^d Z-isomer was not detected in crude ¹H NMR analysis. ^e Sequential treatment of crude **2** with K₂CO₃ (5 equiv) in MeOH (2–3 mL) at room temp for 12–14 h. ^f Reaction run for 12 h.

Scheme 2. Computational Models for Alkyne Insertion Processes

underwent intramolecular vinylthiolation to afford the desired lactam **2h** (run 10).¹⁶

Next, density functional theory (DFT) calculations were performed to get information on the mechanism. In Scheme 2, **A** is the model compound for alkyne-coordinated complex **6**. **TS1** and **TS2** are transition state models for the reaction proceeding from **A** and calculated energies of optimized **TS1** and **TS2** relative to **A** are shown in parentheses.¹⁷ **TS1** is 5.8 kcal/mol more stable than **TS2** and this result indicates that *selenoplatination* leading to platinacycle-like **8** is kinetically the more favored pathway than *carboplatination*.¹⁸ In the case of Pd, the transition state for *selenopalladation* (+9.1 kcal) is less stable than **TS1** (+8.2 kcal). In fact, Pd(PPh₃)₄ worked as catalyst in this system but the efficiency was lower than Pt(PPh₃)₄.¹⁹

In summary, Pt(PPh₃)₄ catalyzes intramolecular vinylthiolation and -selenation of internal alkynes with vinyl chalcogenides having a carbamoyl group on the *cis*- β -position of the vinyl moiety giving rise to the highly conjugated δ -lactam frameworks.²⁰ DFT calculations for alkyne insertion processes suggest the formation of seven-membered platinacycle is kinetically favored. Introduction of electron withdrawing groups to β -position on vinyl moiety may be a key to develop a new type of catalytic reaction using vinyl heteroatom compounds.

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Supporting Information Available: Experimental and calculation details and characterization data of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) In a stoichiometric reaction of *cis*-**4** with Pt(PPh₃)₄ in C₆D₆, formation of the oxidative adduct was confirmed by ³¹P NMR analysis. See Supporting Information for the details.
- (13) Radical mechanism can be denied since radical scavengers such as TEMPO and galvinoxyl did not retard the reaction of **1a**.
- (14) The reaction of vinyl selenide **1i** (Y = Se, R = CH₂Ph, R' = H, eq 1) gave a complex mixture and neither Z-**3e** nor E-**3e** was detected.
- (15) Similar thermodynamic resolution of E/Z mixture was also observed in **2e**. See Supporting Information for the details.
- (16) **2h** was easily hydrolyzed during purification by PTLC or HPLC. Formation of **2h** was confirmed by crude ¹H NMR, ¹³C NMR, and HRMS analysis. In addition, the hydrolyzed product was isolated and characterized. See Supporting Information for the details.
- (17) For the details about calculations, see Supporting Information.
- (18) For insertion of alkynes into Pt-SAR bond: Kuniyasu, H.; Yamashita, F.; Terao, J.; Kambe, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5929.
- (19) Although Pd(PPh₃)₄ worked as catalyst for cyclization of **1a**, the reaction was slower and **2a** was obtained in 37% NMR yield after 2.5 h.
- (20) Attempts to lactone synthesis using a vinyl selenide **9** (Z)-PhSe—CH=CH—C(O)OCH₂—CMe failed. This result as well as substituent effect on nitrogen described in the text may indicate that accessibility of alkyne unit to Pt is important for the present vinylchalcogenation to take place.

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