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Transition-metal-catalyzed cleavage of carbon–selenium bond and addition to alkynes and allenes*

Shin-ichi Fujiwara[1], Masashi Toyofuku[2], Hitoshi Kuniyasu[2], and Nobuaki Kambe[2,‡]

[1]Department of Chemistry, Osaka Dental University, Kuzuha-hanazonocho 8-1, Hirakata Osaka 573-1121, Japan; [2]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871, Japan

Abstract: This account summarizes our recent results on transition-metal-catalyzed cleavage of C–Se bond and addition to unsaturated hydrocarbons such as alkynes and allenes. Pd(0)-catalyzed intramolecular carbamoselenation of alkynes forms four- to eight-membered α-alkylidenelactams. Interestingly, four-membered ring formation is faster than five- and six-membered ring formation. Intramolecular vinylselenation of suitably structured alkynes offers pathways to conjugated δ-lactam frameworks. Electron-withdrawing groups on the vinyl moiety are essential to promote this reaction. Intermolecular 1,2-addition of selenol esters onto allenes proceeds with excellent regioselectivity and high stereoselectivity in the presence of a Pd(0) catalyst, producing functionalized allyl selenides. In addition, Pd(0)-catalyzed intramolecular selenocarbamoylation of allenes gives α,β-unsaturated γ- and δ-lactams with perfect regioselectivity. The scope and limitations, as well as reaction pathways, are discussed.

Keywords: alkynes; allenes; carbamoselenation; carbon–selenium bond; carboselenation; lactam; vinylselenation.

INTRODUCTION

Transition-metal-catalyzed addition of heteroatom-containing compounds to unsaturated hydrocarbons has been well exploited as one of the most straightforward methods for the introduction of heteroatom functionality to organic molecules. In the presence of transition-metal catalysts, hydrogen–heteroatom or heteroatom–heteroatom bonds such as H–SiR_3 and R_2B–BR_2 are cleaved and added smoothly to unsaturated hydrocarbons [1]. Recently, addition involving cleavage of carbon–heteroatom bonds has attracted great interest [2]. This reaction forms new carbon–heteroatom bonds concomitantly with construction of C–C skeletons. As the precedent examples of this transformations, our group has already reported Pt(0)-catalyzed intermolecular decarbonylative addition of thiol or selenol esters to alkynes giving rise to functionalized vinylchalcogenides [3,4], which is triggered by oxidative addition of carbon–chalcogen (sulfur or selenium) bonds of thiol or selenol esters to Pt(0). Transition-metal-cat-

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‡Corresponding author

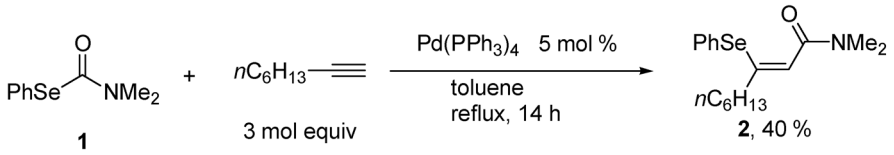
alyzed reaction initiated by oxidative addition of carbon–chalcogen bonds has been less explored than the ones using carbon–halogen bonds [5]. However, since the oxidative addition of carbon–chalcogen bonds is faster than the corresponding carbon–halogen bonds [6], organochalcogenides should have great potential as substrates for various catalytic reactions.

This account summarizes our recent work on group 10 metal-catalyzed transformations via the cleavage of C–Se bond and addition to alkynes and allenes.

PALLADIUM(0)-CATALYZED INTRAMOLECULAR CYCLIZATION OF CARBAMOSELENOATES HAVING AN ALKYNE MOIETY

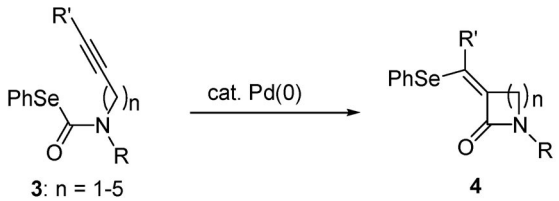
Transition-metal-catalyzed addition of organochalcogen compounds to alkynes with cleavage of heteroatom–heteroatom bonds such as RS-SR', RS-BR'_2, RSe-$P(O)(OR')_2$, etc. is a promising synthetic route to functionalized alkenes [7]. Although another attractive and challenging theme of interest would be the insertion of C–C unsaturated units across chalcogen–carbon bonds that can construct new chalcogen–carbon and C–C bonds in one step, this transformation remains much less explored [3,4a,b,8,9].

We first examined the possibility of selenocarbamoylation by reacting a carbamoselenoate, PhSe-$C(O)NMe_2$ (**1**), with an alkyne [10]. When toluene (0.3 ml) containing **1** (0.5 mmol), oct-1-yne (3 equiv) and $Pd(PPh_3)_4$ (5 mol %) was heated at reflux for 14 h, the selenocarbamoylation product, β-seleno acrylamide **2**, was obtained in 40 % yield with high regio- and stereoselectivities (eq. 1).



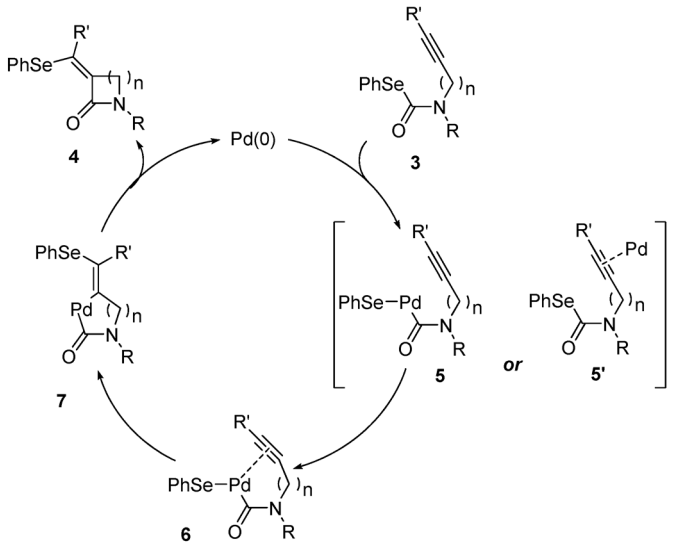
(1)

This finding led us to examine the construction of the α-alkylidene-β-lactam framework, a core-structure of antibiotics and various synthetic intermediates, by applying an intramolecular cyclization strategy to this reaction [11–13]. We could develop Pd-catalyzed intramolecular selenocarbamoylation of alkynes to give α-alkylidenelactams (eq. 2) [14].



(2)

This reaction proceeds as shown in Scheme 1. The first step in this process is oxidative addition of the Se–C(=O)N bond of **3** to Pd(0) giving **6** via **5** or **5'**. Subsequent insertion of alkyne into the Se–Pd bond affords the palladacyle **7**. Reductive elimination leads to the cyclized products **4** and regenerates the Pd(0) species.



Scheme 1 A proposed pathway leading to α-alkylidenelactam **4**.

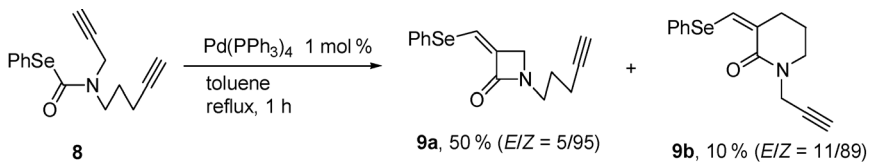
When *Se*-phenyl *N*-methyl-*N*-prop-2-ynyl carbamoselenoate **3a** (0.4 mmol) was treated with $Pd(PPh_3)_4$ (5 mol %) in refluxing toluene (0.5 ml), the corresponding α-alkylidene-β-lactam **4a** was formed in 74 % yield within 1 h with excellent regio- and stereoselectivities (Table 1, run 1). The results obtained using different carbamoselenoates are also summarized in Table 1. This reaction proceeds efficiently even when the amount of $Pd(PPh_3)_4$ is reduced to 1 mol % (run 2). Bulkier alkyl substituents on nitrogen, e.g., butyl or benzyl, did not affect the reaction (runs 3 and 4). In contrast to the fact that internal alkynes are sluggish in thioesterification reactions [4b], carbamoselenoates **3d** and **3e** having an internal alkyne moiety readily undergo intramolecular selenocarbamoylation to afford the desired lactams **4d** and **4e** in high yields (runs 5 and 6, respectively). The developed strategy was applied successfully to the synthesis of larger α-alkylidenelactams. When a carbamoselenoate **3f** having a but-3-ynyl group on the N atom was treated under similar conditions, α-alkylidene-γ-lactam **4f** was obtained in 70 % isolated yield with perfect regio- and stereoselectivities (run 7). γ-Lactam **4g** and δ-lactams **4h** and **4i** were also readily formed from corresponding carbamoselenoates **3g–i** (runs 8–10). Although the reaction of carbamoselenoate **3j** having a hex-5-ynyl group was slower, seven-membered lactam **4j** was obtained in 74 % yield after 12 h (run 11). In the case of **3k** having a hept-6-ynyl group, eight-membered lactam **4k** was also prepared albeit in a low yield (run 12).

Very interestingly, when carbamoselenoate **8** having both prop-2-ynyl and pent-4-ynyl groups on N atom was employed, the more strained four-membered lactam **9a** was obtained preferentially (50 %) over the more thermodynamically stable six-membered lactam **9b** (10 %) (eq. 3). This result indicates that formation of the four-membered ring is kinetically favored.

Table 1 Intramolecular cyclization of **3** to form **4**.

run	3	n	R	R'	product, %[a]	*E*/*Z*
1	**3a**	1	Me	H	**4a**, 74	0/100
2[b]	**3a**	1	Me	H	**4a**, 81	0/100
3[c]	**3b**	1	^{n}Bu	H	**4b**, 60	2/98
4	**3c**	1	Bn	H	**4c**, 59	3/97
5[c]	**3d**	1	Bn	Et	**4d**, 88	3/97
6[d]	**3e**	1	Me	4-ClC$_6$H$_4$	**4e**, 76	11/89
7	**3f**	2	Bn	H	**4f**, 70	0/100
8	**3g**	2	^{n}Bu	^{n}Hex	**4g**, 90	0/100
9	**3h**	3	^{n}Bu	H	**4h**, 75	0/100
10	**3i**	3	^{n}Bu	^{n}Pen	**4i**, 90	0/100
11[e]	**3j**	4	^{n}Bu	H	**4j**, 74	0/100
12[f]	**3k**	5	^{n}Bu	H	**4k**, 30	0/100

Conditions: **3** (0.4 mmol), $Pd(PPh_3)_4$ (5 mol %), toluene (2 mL), reflux, 1-2 h.
[a] Isolated yield. [b] $Pd(PPh_3)_4$ (1 mol %). [c] Toluene (0.5 mL). [d] Toluene (4 mL), 20 h.
[e] Toluene (2 mL), 12 h. [f] Xylene (2 mL), reflux, 12 h.

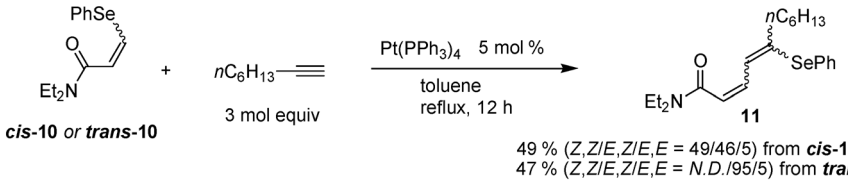


8 **9a**, 50 % (*E*/*Z* = 5/95) **9b**, 10 % (*E*/*Z* = 11/89) (3)

PLATINUM(0)-CATALYZED INTRAMOLECULAR CYCLIZATION OF VINYL SELENIDES HAVING AN ALKYNE MOIETY

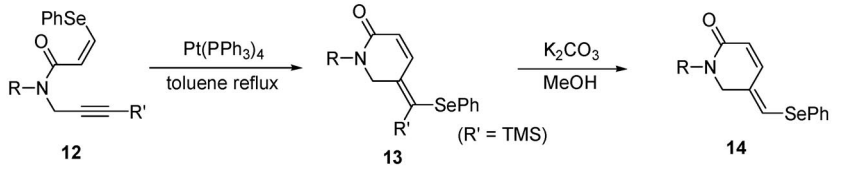
In the presence of transition-metal catalysts, allyl, alkynyl, acyl, and cyano groups can be introduced as carbon units into alkynes concomitantly with heteroatom groups. However, the corresponding introduction of vinyl group still remains as a challenging theme [15–18], because newly formed vinyl-heteroatom bond in products, like that in the substrates employed, can also undergo addition to alkynes leading to oligomerization and/or undesired further reactions. To the best of our knowledge, successful examples of insertion of alkynes to vinyl-heteroatom bonds reported so far are the reactions of strained three- or four-membered heterocyclic compounds such as silacyclopropenes [19a], methylidenesiliranes [19b], allene episulfides [4a], and silacyclobutenes [19c] to alkynes.

We have revealed that an anion-stabilizing group on the β-position of acyclic vinyl sulfides and selenides facilitated oxidative addition to Pt(0) complex [20]. As the synthetic application, cross-coupling reaction has been developed using vinyl selenides [21]. We studied intermolecular reaction of vinyl selenides **10** (*cis* and *trans*) having a carbamoyl group on the β-position of vinyl moiety with 1-octyne to prove the possibility of vinylchalcogenation of alkynes. When toluene (0.4 ml) containing ***cis*-10** or ***trans*-10** (0.3 mmol), 1-octyne (3 equiv), and $Pt(PPh_3)_4$ (5 mol %) was heated at reflux for 12 h, 1,3-dienes **11** were obtained in moderate yields (eq. 4). The stereochemistry of **10** did not affect the yield of **11**.



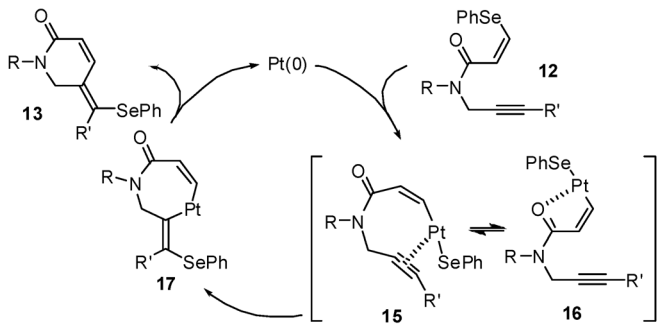
(4)

Then, we examined intramolecular reaction and found that Pt(0) catalyzed *cis*-vinylselenation of alkynes leading to effective construction of six-membered conjugated lactam framework **13** or **14** (eq. 5) [22].



(5)

The first step in this process is oxidative addition of vinyl-SePh bond to Pt(0), giving rise to alkyne-coordinated complex **15** and/or carbonyl-coordinated complex **16** (Scheme 2). Subsequent insertion of alkyne into the Pt–Se bond occurs on **16** affording the platinacycle **17**. Reductive elimination leads to the cyclized products **13** and regenerates the Pt(0) species.



Scheme 2 A possible pathway leading to six-membered lactams.

When toluene (0.5 ml) containing a vinyl selenide **12a** (0.2 mmol) and $Pt(PPh_3)_4$ (5 mol %) was heated at reflux for 2.5 h, intramolecular vinylselenation product **13a** was obtained in 92 % yield with excellent stereoselectivity (Table 2, run 1). In contrast with intermolecular reaction (eq. 4), stereochemistry of the substrates exerts crucial effect in this cyclization. While intramolecular vinylselenation of **12a** took place efficiently to form lactam **13a**, the reaction of the *trans*-isomer of **12a** gave no detectable product under similar reaction conditions. This may be because intramolecular alkyne coordination of an oxidative addition intermediate from *trans*-isomer, like that in **15**, might be conformationally difficult. The reaction of vinyl selenide **12b** having a trimethylsilyl (TMS) group at the terminus gave the corresponding lactam **13b** in high yield (run 2). This catalytic system was not able to apply to terminal alkynes (R' = H, eq. 5) probably due to further reaction or oligomerization. However, **13b** easily underwent desilylation with K_2CO_3 in MeOH to afford **14b** in 90 % total yield from **12b** (run 3). Longer alkyl substituents on nitrogen of **12c**, e.g., 2-phenylethyl, affected the reaction rate and stereoselectivity (run 4). When a crude *E*/*Z* mixture of **13c** was treated with K_2CO_3 in MeOH, desired desilylated lactam **14c** was obtained with high *E*-selectively in high yield (run 5). Similarly, **12d** having unprotected indole ring gave desilylated *E*-lactam **14d** in 86 % yield (run 6).

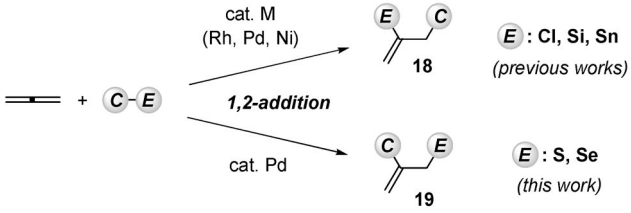
Table 2 Pt(0)-catalyzed intramolecular vinylselenation of alkynes to form six-membered lactams (eq. 5).

run	12	R	R'	product, %[a]	*E*/*Z*[b]
1	**12a**	CH_2Ph	Et	**13a**, 92 (99)	>99/1[c]
2	**12b**	CH_2Ph	TMS	**13b**, 95	96/4
3[d]	**12b**	CH_2Ph	TMS	**14b**, 90	>99/1[c]
4[e]	**12c**	$(CH_2)_2Ph$	TMS	**13c**, (94)	71/29
5[d,e]	**12c**	$(CH_2)_2Ph$	TMS	**14c**, 78 (85)	95/5
6[d,e]	**12d**	$(CH_2)_2$(3-Indolenyl)	TMS	**14d**, 86	>99/1[c]

Conditions: **12** (0.2 or 0.3 mmol), $Pt(PPh_3)_4$ (5 mol %), toluene (0.5 or 0.8 mL), reflux, 2.0-3.5 h. [a] Isolated yields. Numbers in parentheses are NMR yields. [b] Determined by ^{1}H NMR. [c] Z-isomer was not detected in crude ^{1}H NMR analysis. [d] 12 h. [e] Sequential treatment of crude **13** with K_2CO_3 (5 mol equiv) in MeOH (2-3 mL) at rt for 12-14 h.

PALLADIUM(0)-CATALYZED ADDITION OF SELENOL ESTERS TO ALLENES LEADING TO REGIOSELECTIVE FORMATION OF ALLYL SELENIDES

During the past 20 years, allenes have been shown to be versatile building blocks in organic synthesis [23]. It is known that a variety of heteroatom compounds such as organotin, -borane, -selenium species add to allenes in the presence of transition-metal catalysts, where an allene double bond inserts into R_3Sn–H, R_3Si–BR'_2, RSe–SeR' bonds [24]. There are only fewer known examples, however, of allene insertion into carbon–heteroatom bonds [25], and in these cases, vinylic heteroatom products like **18** were obtained as the major products rather than allylic compounds **19** (eq. 6). We disclosed the first example of carbothiolation and carboselenation of allenes that proceeds with reverse regioselectivity leading to **19** (eq. 7).



(6)

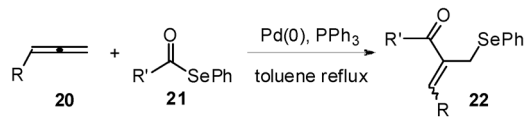
(7)

When a toluene solution (0.3 ml) containing cyclohexylallene **20a** (R = ^{c}Hex, 1.2 equiv), selenol ester **21a** (R' = ^{n}Hex, 0.4 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol %) and PPh_3 (10 mol %) was heated at reflux for 12 h, selenoacylation product, allyl selenide **22a** [26] (corresponds to **19** in eq. 7), was obtained in 70 % yield (Table 3, run 1) with excellent regio- and stereoselectivity [27]. In this reaction, the selenol ester adds to the terminal C–C double bond of the allene exclusively with the acyl moiety at the inner carbon and the SePh group at the terminal carbon to form an allyl selenide. Regioisomers such as vinyl selenide **18** or its stereoisomers were not detected by ^{1}H NMR analysis of the crude mixture of products.

Table 3 summarizes the results obtained using several selenol esters and allenes. Although the reaction of phenylallene **20b** with **21a** gave allyl selenide **22b** in 90 % yield in 5 h (run 2), a small amount of *E*-isomer was also detected. When allene **20c** having a benzyloxy group was subjected to selenoacylation using **21a**, allyl selenide **22c** was obtained in 87 % yield (run 3). However, ethyl 2,3-butadienoate (R = CO_2Et) did not afford the expected allyl selenide, probably due to oligomerization of the allene, with recovery of **21a**. Selenol ester **21b** bearing a cyclohexyl group also underwent selenoacylation with **20b** to give **22d** but with a lower stereoselectivity (run 4). In all cases, no decarbonylative product was formed. Next, selenoesterification and selenocarbamoylation of allenes were examined. When the reaction of selenocarbonate **21c** with phenylallene **20b** was carried out under

similar conditions, the expected allyl selenide **22e** was obtained in high yield with perfect regio- and stereoselectivities (run 5) [3d]. In contrast, although reaction of **20b** with carbamoselenoate **21d** proceeded to give **22f** in high yield, the *E*-isomer was formed predominantly (run 6).

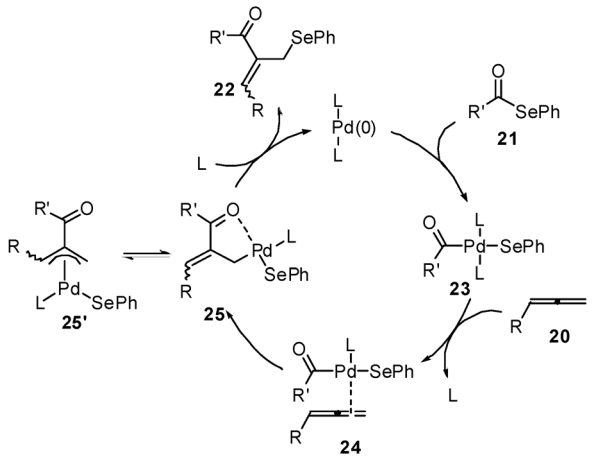
Table 3 Pd(0)-catalyzed selenoacylation of allenes.



run	allene **20**	selenide **21**	time, h	product, %[a]	*Z*/*E*[b]
1	**20a:** R = ^{c}Hex	**21a:** R' = ^{n}Hex	12	**22a**, 70	>98/2
2	**20b:** R = Ph	**21a**	5	**22b,** 90	98/2
3	**20c:** R = OBn	**21a**	12	**22c**, 87	98/2
4	**20b**	**21b:** R' = ^{c}Hex	5	**22d**, 69	91/9
5	**20b**	**21c:** R' = O^{n}Bu	5	**22e**, 70	>98/2
6[c]	**20b**	**21d:** R' = NMe_2	3	**22f**, 83	21/79

Conditions: **20** (0.4 mmol), **21** (0.48 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol %), PPh_3 (10 mol %), toluene (0.3 mL), reflux. [a] Isolated yields. [b] Determined by ^{1}H NMR. "a *Z*/*E* ratio >98/2" means no minor isomer was detected by NMR. [c] 5 mol % of $Pd(PPh_3)_4$ was used as catalyst.

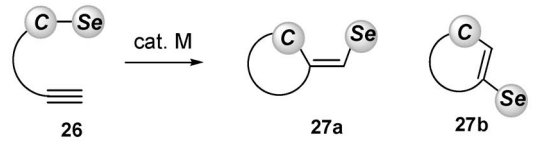
A plausible reaction pathway for allyl selenide formation involving a π-allylpalladium intermediate is shown in Scheme 3, which explains the regioselectivity of the products. This catalytic process is initiated by oxidative addition of the *acyl-Se* bond of selenol ester **21** to Pd(0) affording the *acyl-Pd-Se* complex **23**. Insertion of the coordinated allene into the *acyl-Pd* bond generates σ-allylpalladium **25** (in equilibrium with π-allylpalladium **25'**) having an acyl group at the central carbon of the allene unit prior to reductive elimination forming allyl selenide **22** [28].



Scheme 3 A proposed pathway leading to allyl selenide **22**.

PALLADIUM(0)-CATALYZED INTRAMOLECULAR CYCLIZATION OF CARBAMOSELENOATES HAVING AN ALLENE MOIETY

As mentioned above, we have developed transition-metal-catalyzed intramolecular cyclization of **26** via cleavage of C–Se bond. In this system, insertion of alkyne to C–Se bond would proceed regioselectively to give cyclic products like **27a** having an *exo*-methylene moiety without the formation of its regioisomer **27b** (eq. 8).



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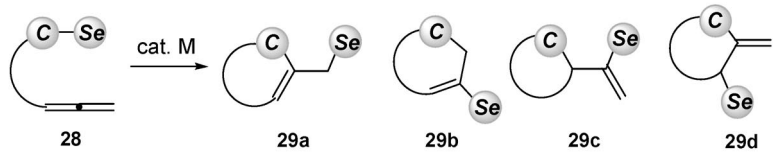
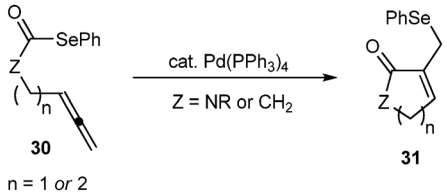


(9)

When this catalytic system is applied to allenes **28**, four possible regioisomeric products **29a–d** can be formed (eq. 9). As shown above, selenol esters and their analogs add intermolecularly to the distal double bond of terminal allenes regioselectively in the presence of Pd(0) catalyst giving rise to conjugated allyl selenides, we undertook intramolecular cyclization using allenic substrates **30** aiming at efficient construction of α,β-unsaturated lactam frameworks (eq. 10). Although intramolecular addition of a C–H bond to the allene unit is well known and employed for cyclization of allenes [29], intramolecular insertion of allenes to carbon–heteroatom bonds has not been studied extensively [30].



(10)

At first we carried out the reaction of carbamoselenoate **30a** (Z = NCH_2Ph, n = 1) possessing a terminal allene unit on the nitrogen atom under typical reaction conditions employed for the corresponding intermolecular system [27]. When toluene (0.5 ml) containing carbamoselenoate **30a** (0.4 mmol) and $Pd(PPh_3)_4$ (5 mol %) was heated at 110 °C for 5 h, an α,β-unsaturated five-membered lactam **31a** was obtained in 50 % yield along with 24 % of an unexpected six-membered lactam **32** (without a SePh group) as a by-product [31].

By changing the solvent, five-membered lactams were found to be formed selectively and efficiently. For example, the reaction of carbamoselenoate **30a** in DMF at 80 °C for 5 h afforded lactam **31a** in 90 % yield without formation of unexpected lactam **32** (Table 4, run 1). Results obtained using several substrates are summarized in Table 4. Similar γ-lactams **31b** and **31c** were formed readily in high yields, indicating that the substituent on the N-atom does not affect the reaction (runs 1–3). The six-membered lactam **31d** was also obtained in good yield under similar reaction conditions with perfect regioselectivity when carbamoselenoate **30d** was employed. In contrast to the reaction of **30a**, **30d** afforded **31d** selectively even in refluxing toluene, and the by-product like **32** was not detected (run 4). Similarly, the cyclopentenone ring could be constructed selectively in toluene (run 5). For all runs listed in Table 4, no regioisomer of **31**, which may arise by the addition to the inner double bond of the allene unit, was detected.

Table 4 Intramolecular cyclization of **30** to form products **31** (eq. 10).

run	**30**	product, %[a]
1	**30a:** Z = NCH_2Ph, n = 1	**31a**, 90[b]
2	**30b:** Z = N^{n}Bu, n = 1	**31b,** 76
3	**30c:** Z = NCH_2CH_2Ph, n = 1	**31c**, 85
4	**30d:** Z = NCH_2Ph, n =2	**31d**, 75[c]
5	**30e:** Z = CH_2, n =1	**31e**, 88[c]

Conditions: **30** (0.4 mmol), $Pd(PPh_3)_4$ (5 mol %), DMF (0.5 mL), 80 °C, 5 h. [a] Isolated yield. [b] Reaction run for 1 h. [c] Reaction run in toluene reflux for 5 h (run 4) or 0.5 h (run 5).

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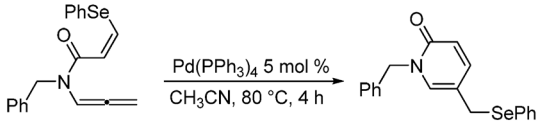
Vinylselenation of allene was also examined. When allenic substrate **33** was treated with $Pd(PPh_3)_4$ in CH_3CN at 80 °C for 4 h, lactam **34** was obtained in 68 % yield as a sole product (eq. 11). In contrast with vinylselenation of alkynes (eq. 5), $Pt(PPh_3)_4$ was not effective in this transformation.



33 **34**, 68 % (11)

In conclusion, Pd and Pt were found to catalyze intermolecular and intramolecular addition of organoselenium compounds to alkyne or allene units via C–Se bond cleavage. This reaction provides useful tools for synthesis of and synthetic manipulation of new organochalcogen compounds, especially those having four-membered to medium size cyclic carbon skeletons.

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