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Palladium-Catalyzed Decarbonylative Rearrangement of *N*-Allenyl Seleno- and Tellurocarbamates

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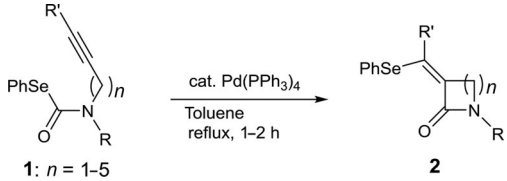
ABSTRACT: *Decarbonylative rearrangement of seleno- and tellurocarbamates carrying an allenyl group on the nitrogen was found to proceed in the presence of a palladium catalyst to afford 3-chalcogeno-1-azadienes. This transformation may involve oxidative addition of Pd to a carbon–chalcogen bond, decarbonylation from a carbamoylpalladium unit (R_2N-C(O)-PdChPh: Ch = Se or Te), Pd shift, and reductive elimination.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:518–524, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21217

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 functionalities to organic molecules [1]. This transformation becomes more attractive and useful if carbon–carbon bonds can be created concomitantly with carbon–heteroatom bond formation. A promising approach to achieve this transformation is the insertion of an unsaturated carbon unit over a carbon–heteroatom bond. This type of transformation has been extensively explored using transition metal catalysts [2]. For example, we have reported that carbamoselenoates **1** having a terminal alkynyl moiety on the nitrogen atom underwent selenocarbamoylation of alkynes intramolecularly with high regio- and stereoselectivities to afford four- to eight-membered lactams **2** having an exocyclic double bond in high yields by the use of $Pd(PPh_3)_4$ as a catalyst (Eq. (1)) [3]. The treatment of vinylselenides **3** having a alkynylmethyl group on the nitrogen atom with $Pt(PPh_3)_4$ afforded six-membered lactam frameworks **4** or **5** having a dienone unit by *cis*-vinylselenation of alkynes (Eq. (2)) [4]. We also demonstrated Pd(0)-catalyzed selenocarbamoylation of allene, where carbamoselenoates **6** with a terminal allenyl group on the nitrogen atom afforded the corresponding α,β-unsaturated lactams **7** bearing an allylselenide moiety with perfect regioselectivity (Eq. (3)) [5].



1: *n* = 1–5 **2** (1)

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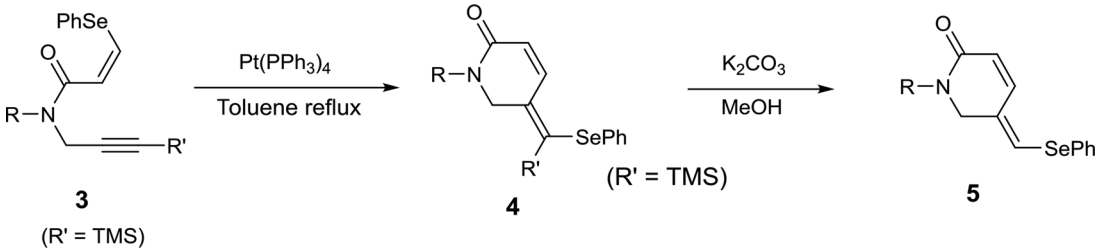
Dedicated to 77th birthday of Professor Renji Okazaki.



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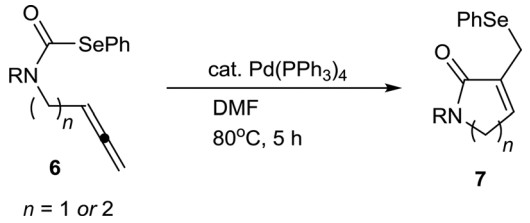

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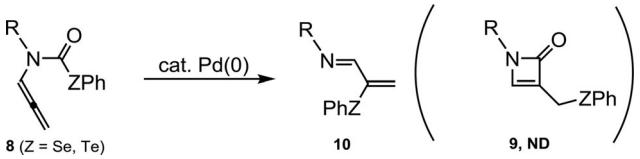
In this paper, we examined the reaction of seleno- and tellurocarbamate **8** possessing an allenyl group on the nitrogen atom and unexpectedly found that the decarbonylative rearrangement occurred, giving rise to 1-azadienes **10** without the formation of a four-membered lactam **9** (Eq. (4)).



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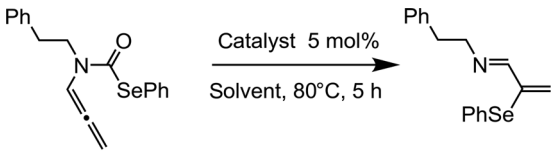
RESULTS AND DISCUSSION

At first, we conducted the reaction of **8** under similar conditions as employed in Eq. (3). Thus, when a toluene solution containing selenocarbamate **8a** and $Pd(PPh_3)_4$ (5 mol%) was heated at 80°C for 5 h, 1-azadiene **10a** was obtained in 36% yield (Table 1, entry 1). $Ni(cod)_2$ and $Pt(PPh_3)_4$ were also effective as a catalyst albeit in lower yields (entries 2 and 3). The use of aprotic and polar solvents such as CH_3CN, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) afforded the product in better yields. Among them, DMF gave the best yield of 58% (entries 4–8). In all entries, diphenyl diselenide and several unidentified compounds were detected as by-products.

In Table 2, results obtained using monodentate and bidentate phosphine ligands were summarized. Triarylphosphines-bearing electron-donating or -withdrawing groups afforded similar results (entries 1–3). Monodentate alkyl phosphines and phosphites were not effective for the synthesis of 1-azadiene **10a** (entries 4–8). Interestingly, a four-membered lactam **11**, not incorporating selenium, was obtained as the major product when $PPhMe_2$ was employed (entry 5). To suppress decarbonylation, the reaction was performed under pressurized carbon monoxide (20 atm); however, the yield of lactam **11** was not improved (entry 6). The use of electron-rich and sterically less hindered phosphine ligands tends to favor the lactam formation. However, PCy_3 gave nearly 1:1 mixture of **10a** and **11**, indicating that product selectivities cannot be simply explained (entry 7). Bidentate ligands such as 1,4-Bis(diphenylphosphino)butane (dppb) and 1,2-Bis(diphenylphosphino)ethane (dppe) afforded only azadiene **10a** like PPh_3 (entry 1) in a similar manner with a lower yields, respectively (entries 1, 9, 10). Both 1,5-Bis(diphenylphosphino)pentane (dppen) and 1,6-Bis(diphenylphosphino)hexane (dpphex) gave a mixture of **10a** and **11** with nearly 3:1 and 2:1 ratio, respectively, as in the case of PPh_2Me probably due to the flexible tether chains (entries 4, 11, 12). On the contrary, when 2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene (BINAP) was employed, 3-seleno-1-azadiene **10a** was obtained in 88% yield (entry 13). Although it is unclear yet why BINAP can promote this reaction efficiently, the formation of by-products was largely suppressed. From the results in entries 9–14, the yields of azadiene **10a** do not

TABLE 1 Reaction of **8a** with Group 10 Metal Complexes in Various Solvents

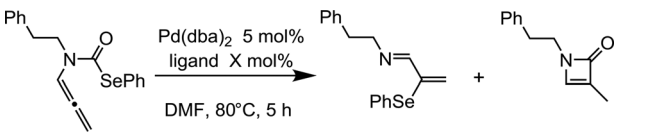


8a **10a**

Entry	*Catalyst*	*Solvent*	*Conversion (%)*[a]	*Yield (%)*[a]
1	$Pd(PPh_3)_4$	Toluene	77	36
2	$Ni(cod)_2$	Toluene	>95	28
3	$Pt(PPh_3)_4$	Toluene	17	<5
4	$Pd(PPh_3)_4$	CH_3CN	>95	53
5	$Pd(PPh_3)_4$	DMF	>95	58
6	$Pd(PPh_3)_4$	DMSO	92	52
7	$Pd(PPh_3)_4$	Dioxane	63	33
8	$Pd(PPh_3)_4$	EtOH	77	20

[a] ^1H NMR yield.

TABLE 2 Pd-Catalyzed Rearrangement of **8a** Using Various Ligands



8a **10a** **11**

Entry	*Ligand*	*X*	***10a*** *(%)*[a]	***11*** *(%)*[a]	*Angle*[b]
1	PPh_3	10	47	–	145
2	$P(C_6H_4$-*p*-$MeO)_3$	10	53	5	145
3	$P(C_6H_4$-*p*-$CF_3)_3$	10	51	–	145
4	PPh_2Me	10	23	12	136
5	$PPhMe_2$	10	<5	30	122
6[c]	$PPhMe_2$	10	6	36	122
7	PCy_3	10	17	15	170
8	$P(OEt)_3$	10	48	–	109
9	dppe[d]	5	26	–	86
10	dppb[e]	5	45	–	94
11	dpppen[f]	5	51	18	
12	dpphex[g]	5	19	12	
13	*rac*–BINAP[h]	5	88 (79)	–	93
14	DPEphos	5	61	–	104

[a] ^{1}H NMR yield (isolated yield).
[b] Cone angles (entry 1–8) and bite angles (entry 9–14).
[c] The reaction was carried out under 20 atm CO.
[d] 1,2-Bis(diphenylphosphino)ethane.
[e] 1,4-Bis(diphenylphosphino)butane.
[f] 1,5-Bis(diphenylphosphino)pentane.
[g] 1,6-Bis(diphenylphosphino)hexane.
[h] 2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene.

seem to have simple correlation with bite angles of bidentate phosphines [6].

Plausible reaction pathways for the formation of 1-azadiene **10** and lactam **11** are depicted in Scheme 1. In the formation of 1-azadiene **10a** (right-hand side), the first step would be oxidative addition of the carbamoyl carbon–selenium bond of selenocarbamate **8a** to palladium to generate a NC(O)—Pd—Se unit affording intermediate **A**. Since no methylene chain exists between the nitrogen atom and the allenyl group in **A**, coordination of the terminal double bond of the allenyl group to palladium is sterically difficult. Thus decarbonylation may occur to give intermediate **B**. Azadien **10a** may be obtained by reductive elimination of **D**, generated from **B** via aza-π-allylpalladium intermediate **C**. The formation of aza-π-allylpalladium is suggested in the literature [7].

As for the formation of the lactam **11** (left-hand side), the SePh group of oxidative adduct **A** would be replaced with the hydrogen atom leading to **E**. The Allen part of **E** then undergoes carbo- or hydropalladation giving **F** or **G**, and the following reductive elimination would afford lactam **11**. Although the formation of diphenyl diselenide was confirmed, all our attempts to identify the hydrogen source failed

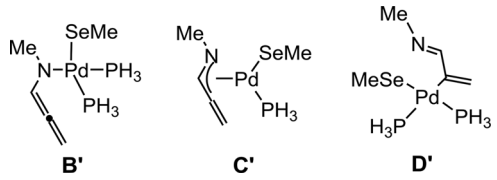
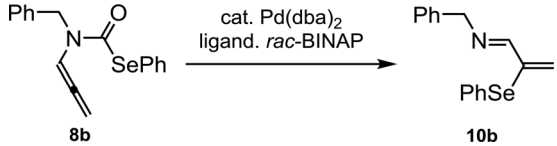


FIGURE 1 DFT Calculations.

unfortunately. Another possible pathway via intermediate **9** formed by intramolecular cyclization of **A** may not likely because deselenation did not proceed when the similar α,β-unsaturated lactams **7** bearing an allylselenide moiety were treated with Pd(PPh3)4 [[5]a]. The formation of π-allylpalladium intermediate **F**′ from **A** leading to **F** via reductive deselenation cannot be ruled out.

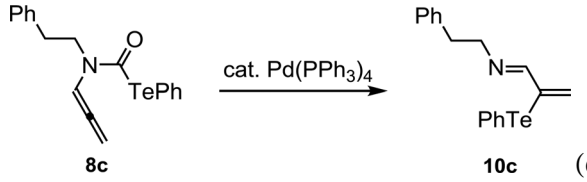
DFT calculations [8] were performed to get information on the rearrangement pathways. These calculations were carried out using the Gaussian 09W set of programs with the B3LYP functional, the 6-31+G(d) basis set for all nonmetallic atoms (H, C, O, N, P), and the LANL2DZ basis set for Pd and Se. In Fig. 1, **B′**, **C′**, and **D′** are the model compounds for possible intermediates **B**, **C**, and **D** in Scheme 1. Although aza-π-allylpalladium complex **C′** was not optimized as a stable structure, complex **D′** was found to be 19.2 kcal/mol more stable than complex **B′**. This result may reflect the difference of bond dissociation energies between C—Pd and N—Pd bonds [9]. Although the bond dissociation energy of the N—Pd bond is unknown, the C—Pt bond is about 49 kcal/mol more stable than the N—Pt bond. From these results, we propose that the relative stability of **D′** over **B′** would be the driving force of decarbonylation and rearrangement, and the rearrangement from **B′** to **D′** may proceed through an aza-π-allylpalladium complex **C′**.

Next, carbamoselenoate **8b** bearing a benzyl group on the nitrogen was employed as a substrate. When **8b** was treated under similar reaction conditions, a decarbonylative rearrangement also proceeded giving rise to 3-seleno-1-azadiene **10b** in 47% yield (Eq. (5)). ^{1}H NMR of the crude mixture of the reaction using a selenocarbamate having a phenyl group on the nitrogen suggested that the corresponding 1-azadiene was formed in 37%; however, isolation of this product was not successful because it was hydrolyzed during purification.



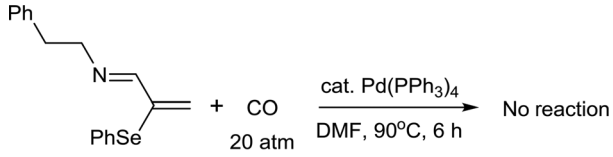
8b **10b** (5)

In addition, this transformation also proceeded when a tellurium analogue was used (Eq. (6)). The corresponding 1-azadiene **10c** was obtained in 49% yield from tellurocarbamate **8C**.



8c **10c** (6)

When 1-azadiene **10a** was allowed to react with CO (20 atm) in the presence of $Pd(PPh_3)_4$**, 10a** was remained unchanged (Eq. (7)). This result indicates that the reverse process does not exist in this transformation.



10a (7)

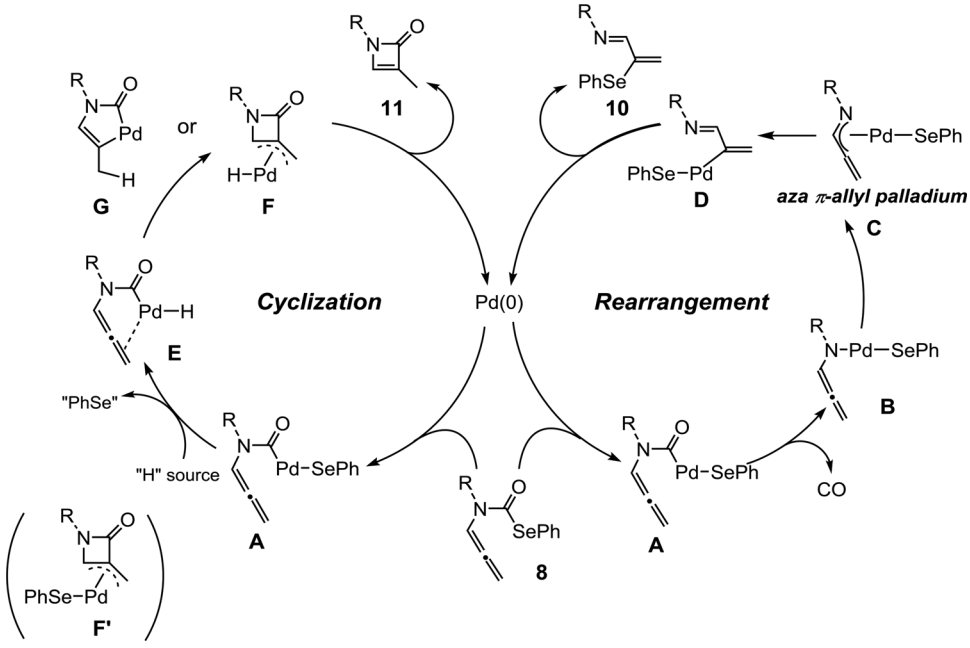
Decarbonylation is frequently encountered in transition metal mediated reactions of carbonyl compounds. This decarbonylation usually occurs from intermediates having a structure of R—C(O)—M, generated by oxidative addition of acid halides, aldehydes, etc. [10]. Transition metal catalyzed decarbonylation of esters, thioesters, acylstannanes, and phthalimides has also reported been and is considered to proceed through oxidative adducts having the R—C(O)—M structure [11]. To the best of our knowledge, decarbonylation from the carbamoyl–metal unit (R_2N—C(O)—M) has never been reported.

In summary, we found that the decarbonylative rearrangement proceeded by the treatment of an *N*-allenyl seleno- and tellurocarbamates **8** with the palladium catalyst to give a 3-seleno or 3-telluro-1-azadiene **10**, in which the use of *rac*-BINAP as a ligand afforded the highest yield. This transformation involves unusual decarbonylation from carbamoyl-Pd units. In addition, a four-membered lactam **11** incorporating no chalcogen atom was obtained as a major product in moderate yields by using $PPhMe_2$ as the ligand.

EXPERIMENTAL

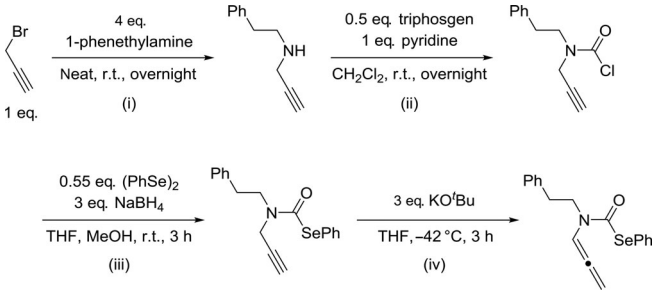
General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 and 100 MHz, respectively) spectrometer using $CDCl_3$ as solvents and using Me_4Si as an internal standard. Chemical shifts were reported in parts per million (δ) downfield from internal tetramethylsilane. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, br = broad singlet, m = multiplet, c = complex), coupling constant (Hz), integration. Infrared spectra (IR) were obtained on a JASCO Corporation FT/IR-4200 instrument equipped with ATR



SCHEME 1 A plausible reaction pathway.

PRO450-S. Infrared spectra were recorded with a JASCO Corporation FT/IR-4200 instrument. Both conventional and high-resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer (EI) or JEOL JMS-T100TD (DART). HPLC separations were performed on a recycling preparative HPLC (Japan Analytical; Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. 1-Phenethylamine, diphenyl diselenide (Sigma-Aldrich, Tokyo, Japan), diphenyl ditelluride, propargyl bromide, triphosgen (Tokyo Chemical, Tokyo, Japan), pyridine, sodium borohydride (Kishida Chemical, Osaka, Japan), potassium *tert*-butoxide (Nacalai Tesque, Kyoto, Japan), and dehydrated solvents (Wako Pure Chemical, Osaka, Japan) were purchased and used as received.



Synthesis of Selenocarbamate **8a**.

i. A-30 mL three-necked flask with a magnetic stirrer and a 100-mL dropping funnel were dried with a heat gun at 120°C and then purged with N_2. After cooling to room temperature, 1-phenethylamine (120 mmol) was placed in the flask, 1-propargyl bromide (30 mmol) was added in the dropping funnel, and the flask was cooled in an ice bath. The solution in the funnel was added into the flask dropwise, and the reaction mixture was stirred overnight at room temperature. After the mixture was poured into NaOH (1 M) and extracted with Et_2O (30 mL × 2), the combined organic phase was dried with $MgSO_4$. The solvents were removed in vacuo, and the residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 4/3, $R_f = 0.3$) to afford *N*-phenethyl-*N*-propa-2-ynylamine (82%).

ii. A-200 mL three-necked flask with a magnetic stirrer and a 100-mL dropping funnel were dried with the heat gun at 120°C and then purged with N_2. Into a flask, triphosgen (12.3 mmol) and CH_2Cl_2 (60 mL) were placed under N_2. After cooling in an ice bath, pyridine (24.6 mmol) was added carefully. To the solution, *N*-phenethyl-*N*-prop-2-ynylamine (24.6 mmol) was then added dropwise in CH_2Cl_2 (60 mL) from the funnel. After the mixture was warmed up to room temperature, the stirring was continued overnight. After the mixture was poured into HCl (1 M) and extracted with CH_2Cl_2 (50 mL × 2), the combined organic phase was dried with $MgSO_4$. The solvents were removed in vacuo, and the black product was used in the next process without purification. *Caution*: Triphosgen decomposes slightly to generate highly poisonous phosgene in air. All operation should be carried out in a well-ventilated hood.

iii. A-300 mL three-necked flask with a magnetic stirrer and a 50-mL dropping funnel were dried with the heat gun at 120°C and then purged with N_2. Into a 300-mL flask, diphenyl diselenide (5.5 mmol), sodium borohydride (30 mmol), and THF (50 mL) were placed under N_2 and the suspension was cooled to 0°C. After methanol (4 mL) was added slowly, vigorous bubbling was occurred. After the color changed from pale yellow to white (about 30 min), *N*-phenethyl-*N*-prop-2-ynylcarbamoyl chloride (10 mmol) in THF (60 mL) was added at the room temperature, and the mixture was stirred for 3 h. After the mixture was poured into brine (50 mL) and extracted with Et_2O (50 mL × 2), the combined organic phase was dried with $MgSO_4$. The solvents were removed in vacuo, and the residue was purified by silica gel column chromatography (*n*-hexane/Et_2O = 2/1, $R_f = 0.5$) to afford *Se*-phenyl *N*-phenethyl-*N*-propa-2-ynylcarbamoselenoate (83%).

iv. A-50 mL two-necked flask with a magnetic stirrer was dried with the heat gun at 120°C and then purged with N_2. Into a 50-mL flask, *Se*-phenyl *N*-phenethyl-*N*-propa-2-ynyl carbamoselenoate (8.29 mmol) and THF (50 mL) were placed and the suspension was cooled to –42°C (CH_3CN/dry ice bath). Into the flask, potassium *tert*-butoxide (1.66 mmol) was added at the same temperature and the mixture was stirred for 3 h. After the potassium *tert*-butoxide was filtered with celite and Et_2O, the mixture was poured into brine (30 mL) and extracted with Et_2O (30 mL × 2), the combined organic phase was dried with $MgSO_4$. The solvents were removed in vacuo, and the residue was purified by GPC to afford *Se*-phenyl *N*-phenethyl-*N*-propa-1,2-dien-1-ylcarbamoselenoate **8a** (60%): ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 2.94$ (td, $J = 7.5$ Hz, $J = 26.8$ Hz, 2H), 3.68 (td, $J = 7.8$ Hz, $J = 14.4$ Hz, 2H), 5.47 (dd, $J = 6.0$ Hz, $J = 12.9$ Hz, 2H), 6.65

(s, 1H), 7.19–7.59 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.7, 34.5, 48.8, 87.0, 87.9, 98.9, 99.7, 125.9, 128.4, 128.6, 128.8, 129.1, 136.6 ($J_{Se\text{-}C}$ = 5.8 Hz), 137.9, 138.4, 163.1, 202.0 ppm. IR (NaCl) 3037, 2968, 2939, 2359, 1955, 1713, 1670 (C=O), 1441, 1382, 1257, 1245, 1139, 1001, 874, 732, 694, 687, 672, 607, 561 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 343 (M^+, 5), 315 (8), 234 (34), 224 (9), 186 (6), 157 (14), 130 (7), 105 (100); Anal. Calcd for $C_{18}H_{17}NOSe$: C, 63.16; H, 5.01; N, 4.09, Found C, 62.98; H, 4.83; N, 4.15.

Pd(dba)$_2$/rac-BINAP-Catalyzed Decarbonylative Isomerization of **8a**. A 5-mL reaction flask equipped with a reflux condenser was dried with the heat gun at 120°C and then purged with N_2. After cooling to room temperature, $Pd(dba)_2$ (0.02 mmol), *rac*-BINAP (0.02 mmol), DMF (1.0 mL), and **8a** (0.4 mmol) were placed in the flask and added to the resulting black solution. The reaction mixture was heated in an oil bath at 80°C for 5 h. After cooling to room temperature, the volatiles were removed in vacuo. After the yield of 1-azadiene **10a** was determined by ^{1}H NMR spectroscopy with 3-pentanone as an internal standard, **10a** was purified with GPC (79%).

(E)-N-Phenetyhyl-2-(phenylselanyl)prop-2-en-1-imine **10a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.98 (t, *J*= 7.6 Hz, 2H), 3.80 (t, *J* = 7.6 Hz, 2H), 5.21 (s, 1H), 5.89 (s, 1H), 7.18–7.69 (m, 10H), 7.85 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.3, 62.2, 121.8, 128.3, 128.4, 128.8, 129.0, 129.0, 129.5, 130.5, 137.2 ($J_{Se\text{-}C}$ = 5.3 Hz), 139.7, 143.3, 161.1 ppm. IR (NaCl) 3055, 3027, 2921, 1649, 1624 (C=N), 1592, 1574, 1495, 1448, 1338, 1189, 1092, 981, 885, 757, 694, 629, 556 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 315 (M^+, 15), 234 (100), 224 (22), 210 (11), 195 (14), 157 (33); Anal. HRMS (EI) calcd for $C_{17}H_{17}NSe$: 315.0526, Found 315.0528.

3-Methyl-1-phenethylazet-2(1H)-one **11**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 3H), 2.85 (t, *J* = 8.0 Hz, 2H), 3.68 (dd, *J* = 2.7, 5.0 Hz, 2H), 6.06 (s, 1H), 7.15–7.65 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 34.1, 51.0, 126.1, 126.4, 126.5, 127.1, 127.6, 128.6, 128.6, 128.7, 128.7, 128.7, 128.8, 128.9, 128.9, 129.0, 129.1, 129.2, 129.5, 135.2, 136.3, 136.3, 136.7, 138.3, 139.7, 165.0 ppm.

Se-Phenyl N-benzyl-N-propa-1,2-dien-1-ylcarbamoselenoate **8b**. The corresponding analogue **8b** was prepared in a similar procedure as described for **8a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.73 (s, 2H), 5.33 (d, *J* = 17.2 Hz, 2H), 6.64 (s, 1H), 7.25–7.45 (m, 8H), 7.57–7.65 (m, 2H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.2, 50.4, 87.2, 88.3, 99.5, 99.7, 126.7, 127.5, 128.1, 128.4, 128.6, 128.8, 129.2, 129.5, 129.9, 135.6, 136.0, 136.7 ($J_{Se\text{-}C}$ = 5.3 Hz), 136.7, 163.9, 164.2, 202.3, 202.9 ppm. IR (NaCl) 3059, 2373, 2323, 1955, 1667 (C=O), 1578, 1496, 1475, 1439, 1378, 1295, 1251, 1173, 1098, 1073, 1022, 960, 878, 737, 688 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 329 (M^+, 2), 301 (5), 238 (2), 220 (14), 172 (4), 157 (5), 91 (100). Anal. HRMS (EI) calcd for $C_{17}H_{15}NOSe$: 329.0319, Found . 329.0320.

(E)-N-benzyl-2-(phenylselanyl)prop-2-en-1-imine **10b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.80 (s, 2H), 5.27 (s, 1H), 5.97 (s, 1H), 7.24–7.44 (m, 8H), 7.60–7.69 (m, 2H), 8.05 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.6, 122.2, 126.7, 127.0, 127.9, 128.5, 128.6, 128.8, 129.5, 137.2 ($J_{Se\text{-}C}$ = 5.3 Hz), 138.7, 143.8, 161.5 ppm. IR (NaCl) 3059, 3028, 2848, 1953, 1632 (C=N), 1584, 1494, 1475, 1452, 1437, 1346, 1301, 1230, 1156, 1065, 1022, 999, 960, 889, 845, 819, 736, 692 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 301 (M^+, 21), 220 (92), 183 (4), 157 (6), 144 (14), 130 (23), 104 (18), 91 (100); Anal. HRMS (EI) calcd for $C_{16}H_{15}NSe$: 301.0370, Found. 301.0371.

Te-Phenyl phenethyl(propa-1,2-dien-1-yl)carbamotelluroate **8c**. The corresponding tellurium analogue **8c** was prepared in a similar procedure as described for **8a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (t, *J* = 7.8 Hz, 2H), 2.99 (t, *J* = 7.8 Hz, 2H), 3.49 (t, *J* = 7.8 Hz, 2H), 3.74 (t, *J* = 7.8 Hz, 2H), 5.38–5.40 (m, 2H), 5.51–5.53 (m, 2H), 6.24–6.27 (m, 2H), 7.17–7.41 (m, 16H), 7.72–7.90 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1, 35.0, 48.9, 50.4, 86.5, 87.6, 98.0, 100.2, 114.2, 114.9, 126.4, 126.9, 128.5, 128.8, 128.9, 129.0, 129.1, 129.4, 137.8, 138.4, 140.4, 140.5, 155.6, 156.3, 202.2, 203.4 ppm. IR (NaCl) 3055, 3026, 2938, 1656 (C=O), 1435, 1376, 1246, 1141, 999, 733, 699 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 393 (M^+, 4), 365 (13), 234 (14), 207 (15), 186 (22), 144 (27), 105 (100); Anal. Calcd for $C_{18}H_{17}NOTe$: C, 55.30; H, 4.38; N, 3.58, Found C, 55.02; H, 4.16; N, 3.54.

(E)-N-phenethyl-2-(phenyltellanyl)prop-2-en-1-imine **10c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (t, *J* = 7.3 Hz, 2H), 3.78 (t, *J* = 6.8 Hz, 2H), 5.46 (s, 1H), 6.38 (s, 1H), 7.18–7.41 (m, 8H), 7.73 (s, 1H), 7.88–7.90 (m, 2H) ppm. Nuclear Overhauser effect experiment; irradiation at δ 7.73 (H_a) resulted in 7.6% enhancement of signal at δ 3.78 (H_b) and 6.2%

enhancement of signal at δ 6.38 (H_c); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2, 61.4, 112.9, 126.1, 127.9, 128.3, 128.6, 129.1, 129.5, 133.4, 139.8, 141.7, 162.9 ppm. IR (NaCl) 3026, 2925, 2840, 1629 (C=N), 1585, 1433, 901, 735, 696 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 365 (M^+, 31), 274 (15), 234 (44), 207 (44), 144 (100); Anal. HRMS (EI) calcd for $C_{17}H_{17}NTe$: 365.0423, Found 365.0419.

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