

Ni-catalyzed addition reaction of allylic selenides to alkynes

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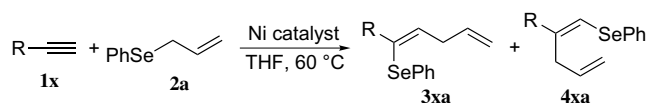
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Abstract—Nickel complex catalysts, Ni(cod)₂-2PPh₃ and Ni(cod)₂-dppb systems in particular, catalyze the addition reactions of phenyl allyl selenide to terminal alkynes to regioselectively afford 2-phenylseleno-1-allyl-1-alkenes in good to excellent yields. A mechanism that involves a η³-allyl–nickel complex is proposed on the basis of isolation, crystal structure determination and reactivity study of the complex.

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One of us has reported that chalcogen element–carbon bonds, Se–C and Te–C bonds in particular, undergo oxidative addition readily with low valent Ni triad metal complexes.¹ Oxidative addition of allylic selenides was also reported by two groups.² Despite easy synthesis³ and versatile reactivity⁴ of allylic selenides, transition metal-mediated or -catalyzed synthetic reactions triggered by the oxidative addition of Se–C bonds are still very limited.⁵ We have already reported that allyl phenyl sulfides add across alkynes to furnish 2-phenylthio-1-allyl-1-alkenes in high yields.⁶ Since Se–C bonds are more reactive than S–C bonds in most of the organic synthetic transformations, the synthesis of 2-phenylseleno-1-allyl-1-alkenes is envisioned to be useful in synthetic applications.^{7,8} Since the pioneering work on the metal-catalyzed manipulation of Se–Se bonds reported by Sonoda and coworkers,⁹ addition reactions of Se–H,¹⁰ Se–P,¹¹ Se–Si,¹² and Se–Ge¹² bonds to alkynes have been documented. The Se–C bond in selenoesters also adds to alkynes, but the major products are those formed through decarbonylative addition.¹³ In the present Letter, we disclose straightforward addition reactions of allylic selenides to alkynes catalyzed by nickel complexes (Scheme 1).



Scheme 1.

In a representative experiment (Table 1, entry 6), allyl phenyl selenide (2a, 197.1 mg, 1.0 mmol) and 1-octyne (1a, 220.4 mg, 2.0 mmol) were added to a mixture of Ni(cod)₂ (11.0 mg, 0.04 mmol) and dppb (17.1 mg, 0.04 mmol) in toluene (2.0 mL) under nitrogen. The mixture, which became deep red immediately, was heated in an oil bath at 60 °C for 6 h. Analysis of the resulting mixture by GC revealed that 5-phenylseleno-1,4-(Z)-undecadiene (3aa) and its regioisomer (4aa) were formed in a total yield of 96%, the regioselectivity for the former being 89%. Evaporation of volatiles and silica gel column chromatography (hexane/ether = 100:1) furnished a mixture of 3aa and 4aa, which was further purified by distillation (Kugelrohr, 55 °C/0.2 mmHg) to give a yellow oil in 93% yield. Preparative TLC (silica gel, 10:1 hexane/ether mixture) provided an analytically pure sample of 3aa. (Z)-Configuration of the internal double bond in 3aa and 4aa, indicative of *cis*-addition having taken place, was confirmed by NOE experiments.

Catalyst screening summarized in Table 1 shows that, besides the combination of Ni(cod)₂ and dppb, a Ni(cod)₂ + 2PPh₃ catalyst system works as well under the standard conditions (entry 2). Ni(cod)₂ alone also

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Table 1. Trial reactions of allyl phenyl sulfide with 1-octyne^a

Entry	Catalyst	Solvent	Time (h)	Conv. ^b (%)		Yield ^c (%)	Regioselect. ^d (%)
				1a	2a		
1	Ni(cod) ₂	Toluene	6	55	72	68	89
2	Ni(cod) ₂ + 2PPh ₃	Toluene	6	100	100	96	87
3	Ni(cod) ₂ + 2PEt ₃	Toluene	6	98	56	22	91
4	Ni(cod) ₂ + dppe	Toluene	6	23	45	32	85
5	Ni(cod) ₂ + dppp	Toluene	6	93	89	58	90
6	Ni(cod) ₂ + dppb	Toluene	6	100	100	96 (93)	89
7	Pd(PPh ₃) ₄	Toluene	6	20	10	4	—
8	Pt(PPh ₃) ₄	Toluene	6	0	0	0	—
9 ^e	Ni(cod) ₂ + dppb	Toluene	6	100	60	52	89
10	Ni(cod) ₂ + dppb	<i>n</i> -Octane	6	90	96	95	88
11	Ni(cod) ₂ + dppb	THF	6	94	88	84	89
12	Ni(cod) ₂ + dppb	Dioxane	3	47	100	78	85
13	Ni(cod) ₂ + dppb	DME	3	75	73	64	87
14	Ni(cod) ₂ + dppb	DMF	6	60	28	27	85
15	Ni(cod) ₂ + dppb	CH ₃ CN	6	55	76	31	83
16	Ni(cod) ₂ + dppb	CH ₃ CN	27	81	77	31	83

^a Reaction conditions: **1a** (2.0 mmol), **2a** (1.0 mmol), solvent (2 mL), catalyst (4 mol %), 60 °C, 6 h.

^b Determined by GC.

^c Total yield of **3aa** and **4aa** determined by GC. The figure in parentheses is isolated yield.

^d 100 × **3aa**/(**3aa** + **4aa**).

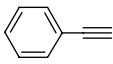
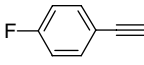
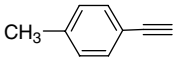
^e The quantity of **1a** was reduced to 1.0 mmol.

catalyzes the reaction, albeit somewhat slowly due presumably to partial decomposition of active species as visualized by a black material formation (vide infra), to furnish an acceptable yield of **3aa** with high regioselectivity (entry 1). However, other Ni–phosphine systems, such as those with more electron-donating PEt₃ and more strongly chelating dppe and dppp, are inferior (entries 3–5). Although palladium complexes catalyze addition reactions of selenium–E bonds (E = Se, H, P, Si, Ge, acyl),^{10–13} Pd(PPh₃)₄ displays only a low activity in the present reaction and Pt(PPh₃)₄ is totally inactive under the same conditions (entries 7 and 8).

The ratio of **1a/2a**, which was 2 in the foregoing representative reaction, is an important factor to achieve high yields of **3aa**. When the reaction was run using a ratio of 1 (entry 9), the yield decreased to 52%. The large gap between the conversion of **1a** and the yield observed in this reaction and the complete conversion of **1a** in the representative reaction run using a ratio of 2 suggest oligomerization of **1a** having taken place to form dimers and trimers, which were indeed detected.¹⁴ As compared with the Ni(cod)₂-dppb system, plain Ni(cod)₂ appears beneficial to decrease the extent of oligomerization. Brief screening of solvents revealed that the use of dioxane (entry 12) was also beneficial against the oligomerization, which may be associated with the coordinative nature of the solvent.

Applicability of the new reaction to various alkynes is summarized in Table 2. By using the same procedure as in the representative reaction, aliphatic terminal alkynes, inclusive of those substituted by cyano (**1b**), hydroxy (**1c**), chloro (**1d**), methoxy (**1e**) groups, reacted similarly without deterioration of the functional group. However, sterically congested alkynes, such as 3,3-dimethylbutyne (**1g**) and 4-octyne (**1h**), are much less reac-

Table 2. Nickel-catalyzed allylselenation of alkynes^a

Entry	Alkyne	Major product	Time (h)	Yield ^b (%)	Select. ^c
1	<i>n</i> -C ₆ H ₁₃ -C≡C- 1a	3aa	6	96 (93)	89
2	NC(CH ₂) ₃ -C≡C- 1b	3ba	6	99 (86)	88
3	HO(CH ₂) ₃ -C≡C- 1c	3ca	6	82 (74)	91
4	Cl(CH ₂) ₃ -C≡C- 1d	3da	6	95 (76)	85
5	CH ₃ OCH ₂ -C≡C- 1e	3ea	6	70 (50)	74
6	PhCH ₂ -C≡C- 1f	3fa	9	74 (66)	86
7	^t Bu-C≡C- 1g	3ga	9	10 (9)	100
8	C ₃ H ₇ -C≡C-C ₃ H ₇ - 1h	3ha	20	18 (13)	—
9		3ia	6	97 (84)	98
10		3ja	6	97 (89)	100
11		3ka	6	99 (81)	100

^a Reaction conditions: **1** (2.0 mmol), **2a** (1.0 mmol), toluene (2.0 mmol), Ni(cod)₂ (0.04 mmol), dppb (0.04 mmol), toluene (2 mL) at 60 °C.

^b Total yield of **3xa** and **4xa** determined by GC. Figures in parentheses are isolated yields.

^c 100 × **3a**/(**3a** + **4a**) determined by GC.

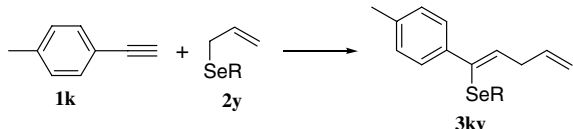
tive under the same conditions. Benzylic and aromatic alkynes conform to the addition reaction smoothly. Note that aromatic alkynes display nearly 100% regioselectivity, irrespective of the nature of the substituents.

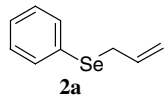
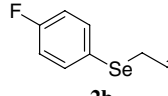
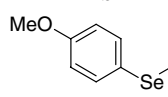
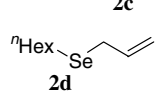
The organic group bound to selenium affects the reactivity, as seen in the reaction of *p*-ethynyltoluene reaction (Table 3). Although parent phenyl selenide and *p*-fluorophenyl selenide displayed similar reactivity, electron-donating *p*-methoxyphenyl selenide reacted somewhat slowly. In agreement with this trend, more electron-donating *n*-hexyl selenide was much less reactive than aromatic selenides. All these reactions with *p*-ethynyltoluene were highly regioselective; products with internal attachment of selenium (3ka–kd) were formed almost exclusively.

On the basis of the following experiments, the catalysis is envisioned to involve the oxidative addition of the allyl–Se bond, insertion of alkyne to the Se–Ni bond and reductive elimination (Scheme 2, which illustrates only actively reacting ligands).

The oxidative addition of 2a generating η^3 -allyl nickel species was confirmed by the reaction with Ni(cod)₂ in the absence or presence of a phosphine ligand (Scheme 3). When Ni(cod)₂ was treated with 2a (1.1 equiv) in toluene at room temperature, the colour of the mixture changed instantaneously from yellow to deep red. Stirring for 2 h at room temperature,¹⁵ evaporation and crystallization at a low temperature in the presence of free 2a in solution,¹⁶ gave bis(η^3 -allyl)bis(μ^2 -phenylseleno)dinickel(II) (5) as deep red needles (39% yield).^{17–20}

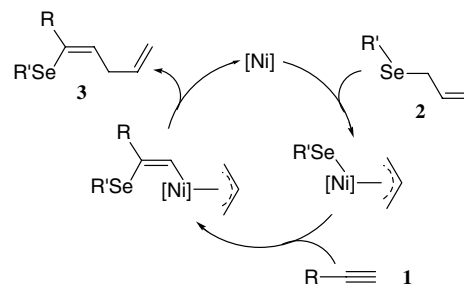
Table 3. Allylselenation of *p*-ethynyltoluene with other allyl selenide derivatives^a



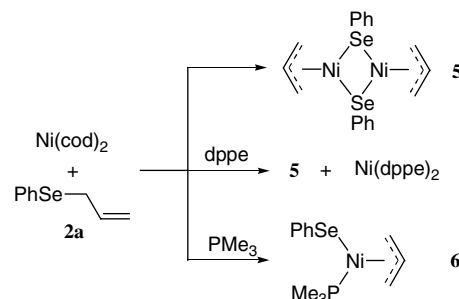
Entry	RSe-CH ₂ -CH=CH ₂	Product	Time (h)	Yield ^b (%)
1		3ka	6	99
2		3kb	6	98 (81)
3		3kc	6	70 (54)
4		3kd	30	31 (29)

^a Reaction conditions: 1k (2.0 mmol), 2y (1.0 mmol), toluene (2.0 mL), Ni(cod)₂ (0.04 mmol), dppb (0.04 mmol).

^b Determined by GC. Figures in parentheses are isolated yields.



Scheme 2.



Scheme 3.

The structure of 5 was unequivocally verified by X-ray diffraction analysis as illustrated in Figure 1,²¹ although it displays a disorder at the central carbon (C17 and C19), showing the presence of two isomers of *syn*- and *anti*-configurations with respect to the two allyl ligands (*syn/anti* = 35:65). Although we were able to obtain satisfactory ¹H NMR data, all signals were broad due presumably to possible *syn–anti* isomerization²² and to thermal instability of complex 5.²³ In practice, a few minutes after complex 5 had been dissolved in CDCl₃ or toluene-*d*₈, decomposition was already evident, as visualized by a black precipitate formation and after 30 min, complex 5 disappeared nearly completely, leading to a generation of pale yellow solution and a larger quantity of the black precipitate. GC–MS analysis of the pale yellow solution indicated that 2a was nearly the sole decomposition product. The observation indicates the reversibility of the oxidative addition of 2a with Ni(0)

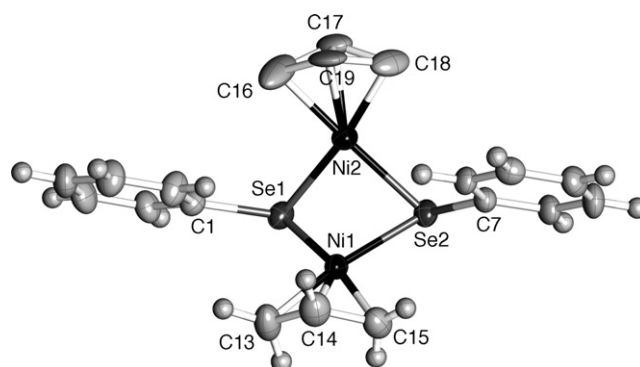
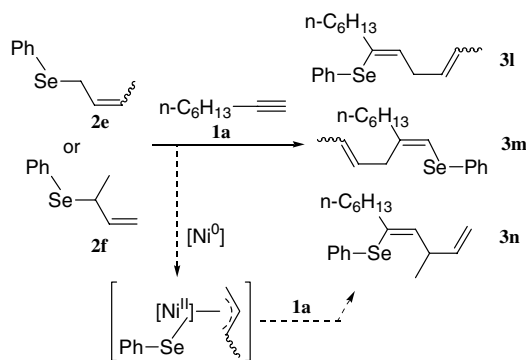


Figure 1. Molecular structure of complex 5 (50% probability level for C, Ni and Se atoms).

Table 4. The reaction of **1a** with **2e** or **2f** in the presence of Ni(cod)₂ and dppb^a

Entry	Selenides	Conversion ^b (%)		Yield ^{b,c} (%)	Distribution ^b		
		2e	2f		3l	3m	3n
1	2e ^d	57	(100) ^e	49 (40)	63	31	6
2	2f ^f	(<1) ^g	99	88	65	26	9

^a Reaction conditions: **1a** (2.0 mmol), **2e** or **2f** (1.0 mmol), toluene (2.0 mL), Ni(cod)₂ (0.04 mmol), dppb (0.04 mmol), 60 °C, 8 h.

^b Determined by GC.

^c The figure in parentheses is isolated yield.

^d Starting **2e** was contaminated slightly with **2f** (2%).

^e Conversion of **2f** present as a contaminant in starting **2e**, based on the quantity of **2f** in starting **2e**.

^f Starting **2f** was contaminated with **2e** (11%).

^g Conversion of **2e** present as a contaminant in starting **2f**, based on the quantity of **2e** in starting **2f**.

species. In the presence of free **2a**, complex **5** in solution could be more easily handled in the isolation process and ¹H NMR signals became somewhat sharp.²⁴

The reaction of Ni(cod)₂ with **2a** (1.0 equiv) in the presence of dppe (1.0 equiv) also resulted in the isolation of complex **5** in 15% yield together with Ni(dppe)₂. Another similar reaction using dppb appeared to proceed, but the product was thermally unstable and could not be characterized. However, the reaction with **2a** (1 equiv) in the presence of PMe₃ (2.2 equiv) at –60 °C–room temperature for 1 h afforded η³-allyl–nickel complex **6** in 35% isolated yield as a brown powder. This complex also showed unresolved broad ¹H NMR signals at room temperature.

Upon the treatment of complex **5** with 1-octyne at 60 °C for 3 h, a black material precipitated and a mixture of **3aa** and **4aa** was obtained in 49% total yield with 89% regioselectivity for **3aa**. Likewise, complex **6** also reacted with 1-octyne at 60 °C for 1 h to furnish a mixture of **3aa** and **4aa** (10% total yield, 89% regioselectivity).

The mechanistic proposal involving η³-allyl–nickel species as intermediate is reinforced by the following catalytic reactions of γ- (**2e**) or α-methylated allylic selenide (**2f**), illustrated in Table 4.²⁵ The reaction of **2e** under the standard conditions for 8 h formed a mixture of **3l**, **3m** and **3n** in a 49% total yield, the distribution of these three products being 63:31:6. The reaction starting with **2f** displayed basically the same distribution (65:26:9), which agrees with the involvement of η³-allyl–nickel species. Given these two reactions involve the common η³-allyl–nickel species, the reactivity difference between **2e** and **2f** should reflect the ease of oxidative addition. The results clearly show

that **2f** is more reactive and suggest that the oxidative addition proceeds through an S_N2'-type mechanism.²⁶

In summary, this Letter has disclosed the first examples of straightforward addition reactions of sp³-carbon-to-selenium bond to alkynes. The products will allow further synthetic applications by the elaboration of the terminal olefinic bond and the organoseleno group introduced.

Acknowledgements

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Supplementary data

Text giving experimental details, spectroscopic data for new compounds and crystallographic data in CIF format. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.07.112.

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14. Two isomers of dimers (**d1** and **d2**) and trimers (**t1** and **t2**) appear to have been formed on the basis of GC–MS measurement. For MS data, see [Supplementary data](#).
15. While the reaction was in progress, a black material precipitated gradually, indicative of partial decomposition of the product.
16. The necessity of free **2a** is associated with the reversibility of the oxidative addition (vide infra).
17. A Pd analogue of **5** has been documented. See: Singhai, A.; Jain, V. K. *J. Organomet. Chem.* **1995**, *494*, 75.
18. Five-coordinate (η^3 -allyl)NiBr(dppe) is known. See: Churchill, M. R.; O’Brien, T. A. *J. Chem. Soc., Chem. Commun.* **1968**, 246.
19. (a) Oxygen analogue of **6** has been documented. See: Bönemann, H. Dissertation, RWTH Aachen, 1967; (b) Bönemann, H.; Jentsch, J. D. *Appl. Organomet. Chem.* **1993**, *7*, 553.
20. In view of no need of phosphine ligand for oxidative addition to proceed, one of the roles of the phosphine ligand in the present catalysis may be associated with the stabilization of the η^3 -allyl–nickel intermediate (vide infra).
21. Crystal data for **5**: red needles, $C_{18}H_{20}Ni_2Se_2$, fw = 511.68, monoclinic, space group $P2_1/c$, $a = 11.1388(10)$ Å, $b = 14.4945(13)$ Å, $c = 11.3664(12)$ Å, $\beta = 98.514(8)$, $V = 1814.9(3)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.873$ g/cm³, $\mu = 6.078$ mm⁻¹, $T = 193(2)$, $R_1 = 0.0303$, $wR_2 = 0.0631$, GOF = 1.090. See [Supplementary data](#) for details.
22. Bis(η^3 -allyl)bis(μ^2 -organothio)dipalladium(II) complexes also exist as a mixture of *syn*- and *anti*-isomers and exhibit isomerization, depending on the structures of the allylic moiety and/or the organic group bound to sulfur. See Ref. 17.
23. Complex **5** is extremely air-sensitive. Upon exposure of a CDCl₃ solution of complex **5** to air, the deep red colour changed instantaneously to pale yellow and white insoluble material precipitated. GC–MS analysis of the resulting solution suggested the formation of **2a** (m/z 198, M⁺), PhSeSePh (m/z 314, M⁺) and 1,5-hexadiene (m/z 82, M⁺).
24. ¹H NMR (400 MHz, CDCl₃) of complex **5** in the presence of 4 equiv of **2a**: δ 7.05–7.55 (br m, 10H, Ph, overlapped with the signals arising from free allyl phenyl sulfide), 5.35 (br m, 2H, CH₂CHCH₂), 2.99 (br s, 4H, allyl-*syn*), 2.16 (d, $J = 12.8$ Hz, 4H, allyl-*anti*).
25. Starting **2e** was contaminated slightly with **2f** (2%), and **2f** was contaminated with **2e** (11%).
26. Osakada, K.; Matsumoto, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 857.