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Exclusive Selectivity in the One-Pot Formation of C–C and C–Se Bonds Involving Ni-Catalyzed Alkyne Hydroselenation: Optimization of the Synthetic Procedure and a Mechanistic Study

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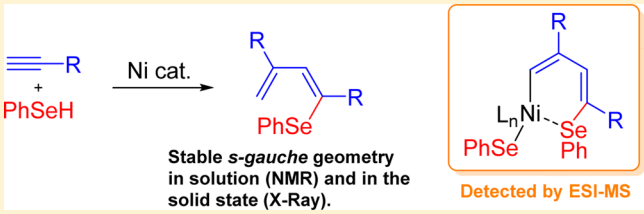
Supporting Information

ABSTRACT: A unique Ni-catalyzed transformation is reported for the one-pot highly selective synthesis of previously unknown monoseleno-substituted 1,3-dienes starting from easily available terminal alkynes and benzeneselenol. The combination of a readily available catalyst precursor, $Ni(acac)_2$, and an appropriately tuned phosphine ligand, PPh_2Cy, resulted in the exclusive assembly of the *s-gauche* diene skeleton via the selective formation of C–C and C–Se bonds. The unusual diene products were stable under regular experimental conditions, and the products maintained the *s-gauche* geometry both in the solid state and in solution, as confirmed by X-ray analysis and NMR spectroscopy. Thorough mechanistic studies using ESI-MS revealed the key Ni-containing species involved in the reaction.



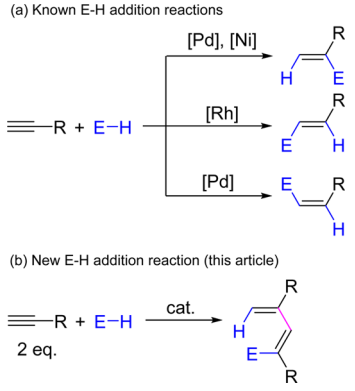
1. INTRODUCTION

The increasing complexity of molecular architectures, as demanded in organic synthesis and materials science, has led to the development of powerful tools to create new C–C and C–heteroatom (C–E) bonds with high selectivity in the specific framework of a polyfunctional molecule. Transition-metal-catalyzed transformations have significantly changed this area of selective organic synthesis, offering a number of outstanding synthetic approaches.[1−3] Great practical importance has been demonstrated in the large number of total syntheses of pharmaceuticals, biologically active compounds, and a new generation of functional materials that are hardly accessible by other methods.[1−3]

A highly efficient catalytic approach for the synthesis of functionalized alkenes involves the addition reactions of various heteroatom–hydrogen (E–H) bonds to alkynes (Scheme 1). The transformation is atom-economical by intrinsic design, and it can be coupled with transition-metal catalysis to achieve thorough selectivity control. Within this approach, various highly efficient catalytic systems leading to the formation of new C–E bonds have been developed. The incorporation of C–N,[4,5] C–O,[4] C–P,[4,6,7] C–S,[4,8,9] C–Se,[4,8,9] C–I,[10] and other C–E bonds[11] into organic molecules using transition-metal catalysis is now a common practice.

It is important to note that even sulfur and selenium compounds, which have long been considered catalyst poisons, are now routinely involved in metal-catalyzed transformations to access various organic chalcogenides.[4,8,9,12] The regio- and stereoselectivity of the addition process can be tuned by selection of the transition-metal catalyst (Scheme 1).[13,14] Many catalytic systems have been developed for the preparation of Markovnikov-type (branched) products[8,9,15] as well as anti-Markovnikov (linear) products with *cis*[8,9,16] or *trans* geometry.[8,9,17]

Scheme 1. Atom-Economical Procedures via the Catalytic Addition of E–H Bonds to Alkynes: (a) Synthesis of Alkenes; (b) One-Pot Formation of C–C and C–E Bonds in the Synthesis of Dienes



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One-pot transformations involving two molecules of an alkyne in the addition reaction remain a more challenging goal in the synthesis of organochalcogen derivatives. In such a case, the one-pot formation of C−C and C−E bonds leads to the construction of a diene skeleton with a predefined position of the functional group. As a related process, a few examples of such catalytic transformations were demonstrated for E−E (E = S, Se) additions starting from diaryl dichalcogenides and terminal alkynes and furnishing bisfunctionalized dienes in one step.[18−20] However, the synthesis of dienes via the addition of E−H bonds has remained unexplored.

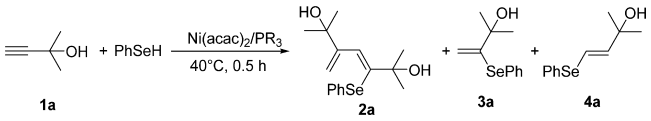
Here we report such a new reaction to access selenium-functionalized diene products involving an E−H bond addition reaction (Scheme 1b; E = Se). The Ni-catalyzed transformation constitutes the development of a highly stereo- and regioselective catalytic system to obtain previously unknown Se-substituted 1,3-dienes. This three-component reaction involving two molecules of the alkyne and one molecule of benzeneselenol is a unique transformation that combines the advantages of atom-economical additions and one-pot transformations. The synthesis of substituted functionalized dienes with a predetermined configuration is of great demand because of their importance as building blocks in organic synthesis, Diels−Alder reactions, and polymer chemistry.[21,22]

In the present article, we describe a practical procedure for the one-pot preparation of monofunctionalized dienes via the addition reaction of benzeneselenol to alkynes. A mechanistic study carried out with ESI-MS, NMR, and X-ray methods revealed the structure of the product and intermediate metal complexes involved in the catalytic transformation.

2. RESULTS AND DISCUSSION

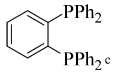
2.1. Rendering a Highly Selective Transformation toward the 1-PhSe-1,3-diene Framework. We chose the Ni-catalyzed reaction between 2-methylbut-3-yn-2-ol (**1a**) and benzeneselenol as a model system to optimize the reaction conditions (Scheme 2). Both components of the reaction (the alkyne and PhSeH) gave clearly resolved signals in the NMR spectrum and allowed the reaction progress to be efficiently monitored. The readily available $Ni(acac)_2$ salt was chosen as a catalyst precursor to develop a cost-efficient practical procedure. We avoided the use of $Ni(COD)_2$ since it is much more expensive and highly air- and moisture-sensitive.

Scheme 2. Ni-Catalyzed Model Reaction of PhSeH with Alkyne 1a



After 30 min of stirring at 40 °C, 87% of the PhSeH was consumed, leading to the formation of alkene **3a** as the major product, diene **2a** as the minor product, and alkene **4a** as a trace component (Table 1, entry 1). It should be noted that the formation of diene **2** is a specific feature of the Ni-catalyzed transformation, taking into account the fact that a similar reaction involving other transition metals (Pt, Pd, and Rh) led only to the formation of alkenes. To utilize the unique opportunity provided by the Ni system, we improved the performance of the catalytic reaction to promote formation of the diene as the major product. The roles of the following factors were investigated: (i) ligand effect; (ii) catalyst loading effect; (iii) influence of the PhSeH:alkyne ratio; (iv) influence of the metal:ligand ratio; (v) solvent effect; and (vi) acid and base effect. Rigorous optimization of the reaction conditions was required in order to tune the transformation toward diene **2a** as the major product. Below we briefly consider the major findings required to create an efficient catalytic system.

Table 1. Ligand Effect in the Ni-Catalyzed Reaction of PhSeH and Alkyne 1a[a]

Entry	Ligand (PR_3)	Conversion of the PhSeH, %[b]	2a : 3a : 4a products ratio[b]
1	-	87	23:73:4
2	$P(i\text{-PrO})_3$	97	17:28:55
3	$CH_2{=}C(PPh_2)_2$[c]	3	27:73:0
4	$PPhCy_2$	97	29:67:4
5	PPh_3	93	30:58:12
6	$P(p\text{-}ClC_6H_4)_3$	87	30:39:31
7	PCy_3	99	32:64:4
8	$P(p\text{-}MeOC_6H_4)_3$	98	37:53:10
9		10	43:41:16
10	$CH_2(PPh_2)_2$[c]	61	44:43:13
11	PPh_2Bn	97	47:32:21
12	PPh_2Et	98	49:33:18
13	$PPh_2(CH_2)_4PPh_2$[c]	92	53:37:10
14	PPh_2Cy	95	53:38:9
15	PPh_2Me	98	56:30:14
16	$PPhMe_2$	12	73:27:0

[a]Conditions: 2 mol % $Ni(acac)_2$, PhSeH:alkyne = 1:4, $Ni(acac)_2$:PR_3 = 1:10, solvent-free, 40 °C, 0.5 h. [b]Determined by ^1H NMR spectroscopy of the crude reaction mixtures. [c]10 mol % ligand was used.

In the first stage, various phosphine ligands were evaluated in the catalytic reaction (Table 1). Most of the ligands resulted in good PhSeH conversion (61−99%); however, the selectivity of the reaction differed significantly depending on the structure of the ligand. The catalytic system with $P(i\text{-PrO})_3$ as the ligand demonstrated high activity, but relatively poor selectivity for the formation of diene **2a** was found (entry 2). Phosphine ligands with bulky aryl and alkyl substituents showed better performance (entries 3−8), increasing the selectivity for **2a** formation to 37% in the case of an arylphosphine with an electron-donating *p*-methoxy substituent (entry 8). The selectivity for diene **2a** formation was further improved to 53% using bidentate phosphines (entries 9, 10, and 13) and to 56% using alkyldiphenylphosphines (entries 11, 12, 14, and 15). The presence of one alkyl substituent in the arylphosphine ligand seems to be crucial for reaction selectivity (cf. entries 4, 5, and 14). Because substituents such as Me and Cy showed comparable results (cf. entries 14 and 15), we may suppose that the electronic factors of the ligands prevail over the steric factors with respect to achieving a highly selective catalytic system for the formation of diene **2a**. This is in agreement with the fact that $PPhMe_2$ was the most selective ligand, giving diene **2a** with 73% selectivity (entry 16).

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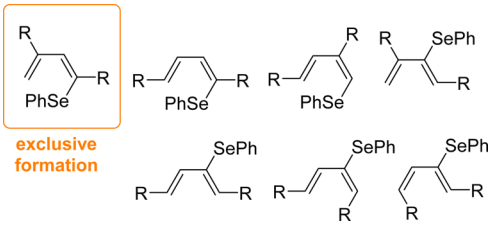
A practical evaluation of the scope of this catalytic reaction indicated that PPh_xMe_y ligands were disadvantaged because of quick oxidation during the reaction leading to degradation of the active catalytic species. As a result of this evaluation, PPh_2Cy was chosen as the ligand for further optimization of the catalytic system.

It should be emphasized that in the developed reaction, only one type of diene was formed upon the several structural frameworks potentially accessible through the addition reaction (Scheme 3). Such exclusive selectivity in the assembly of the

Scheme 3. Possible 1,3-Diene Frameworks Accessible via the Reaction of Two Molecules of an Alkyne with PhSeH



diene skeleton is an important feature of the developed catalytic system. This result is in sharp contrast with previously reported findings on Ni-catalyzed reactions, where mixtures of dienes or higher oligomers were observed in significant amounts.[18,20]

In the next stage, the catalyst loading in the studied catalytic system was varied. The amount of $Ni(acac)_2$ was changed in the range of 0.5, 2.0, and 5.0 mol %, while the $Ni(acac)_2$:PPh_2Cy ratio was kept constant. As little as 0.5 mol % catalyst precursor provided quantitative conversion of the PhSeH and a diene:alkenes ratio of **2a**:(**3a** + **4a**) = 50:50. When 2 mol % $Ni(acac)_2$ was used, the selectivity was slightly improved to 53:47, and further increasing the catalyst loading to 5 mol % resulted in a significant drop in the selectivity to 33:67. Thus, a 2 mol % loading of the catalyst precursor was found to be optimal.

Next, the influence of the PhSeH:alkyne ratio on the selectivity for diene formation was investigated. In all cases, high values of PhSeH conversion were observed (Table 2).

Table 2. Influence of the PhSeH:Alkyne Ratio on the Yield and Selectivity of the Ni-Catalyzed Reaction of PhSeH with Alkyne 1a[a]

		% conversion (**2a**:**3a**:**4a**)[b]	
entry	PhSeH:alkyne	method A[c]	method B[c]
1	1:2	91 (41:52:7)	95 (58:34:8)
2	1:3	91 (48:46:6)	96 (69:24:7)
3	1:4	95 (53:38:9)	93 (82:11:7)
4	1:5	90 (58:35:7)	89 (84:12:4)

[a]Conditions: 2 mol % $Ni(acac)_2$, 20 mol % PPh_2Cy, 40 °C, 0.5 h. [b]Determined by ^1H NMR spectroscopy of the crude reaction mixtures. [c]Method A: single-portion addition of PhSeH. Method B: dropwise addition of PhSeH during the reaction.

However, the measured diene:alkenes ratio was strongly dependent on the quantity of the alkyne. Increasing the excess of the alkyne led to higher yields of diene **2a** over the alkenes (Table 2, method A). Further improvement in the reaction selectivity was achieved by dropwise addition of PhSeH to the reaction mixture (method B). Indeed, dropwise addition of PhSeH yielded significant quantities of an excess of alkyne during the reaction and improved the selectivity. The observed selectivity of diene **2a** formation reached the value **2a**:(**3a** + **4a**) = 82:18 (method B, entry 3). To render a selective transformation, a PhSeH:alkyne ratio of 1:4 was chosen as the optimal value since further increasing the amount of alkyne only slightly influenced the selectivity but decreased the conversion (cf. method B, entries 3 and 4).

To avoid catalyst deactivation during the reaction, which involves precipitation of metal−chalcogen species, it was critical to determine a reliable $Ni(acac)_2$:PPh_2Cy ratio. Previous studies of Pd- and Ni-catalyzed C−Se bond formation via addition reactions noted that larger amounts of phosphine ligand may be required.[8] In the studied reaction, a $Ni(acac)_2$:PPh_2Cy ratio of 1:2 was sufficient to achieve full conversion of PhSeH, and diene **2a** was formed with 76% selectivity under dropwise addition conditions. Increasing the $Ni(acac)_2$:ligand ratio to 1:5 and 1:10 did not affect the conversion, but the selectivity for the formation of diene **2a** improved to 80 and 82%, respectively. Thus, for practical reasons, the $Ni(acac)_2$:PPh_2Cy ratio of 1:2 should be sufficient to carry out the reaction with good selectivity. It is interesting to note that even significant excess quantities of the phosphine ligand did not block the catalytic reaction and slightly increased the selectivity.

The solvent noticeably influenced the outcome of the studied reaction (Table 3). When the reaction was performed in THF,

Table 3. Effect of the Solvent in the Ni-Catalyzed Reaction of PhSeH with Alkyne 1a[a]

entry	solvent	% conversion (**2a**:**3a**:**4a**)[b]
1	none	95 (53:38:9)
2	THF	91 (55:41:4)
3	DMF	92 (37:56:7)
4	MeOH	90 (40:55:5)
5	MeCN	94 (44:47:9)
6	CH_2Cl_2	91 (70:26:4)
7	toluene	92 (70:27:3)
8	toluene	98 (80:17:3)[c]
9	toluene	98 (94:3:3)[c,d]

[a]Conditions: PhSeH:alkyne = 1:4, single-portion addition of PhSeH, 2 mol % $Ni(acac)_2$, 20 mol % PPh_2Cy, 40 °C, 0.5 h, 0.2 mL of solvent. [b]Determined by ^1H NMR spectroscopy of the crude reaction mixtures. [c]With dropwise addition of PhSeH. [d]In the presence of 10 mol % Et_3N.

slightly better selectivity was observed compared with solvent-free conditions (cf. entries 1 and 2). DMF, MeOH, and MeCN showed lower selectivities for diene formation (entries 3−5). Methylene chloride and toluene significantly improved the selectivity for the formation of diene **2a** (entries 6 and 7). In both cases, the selectivity for diene formation reached the value **2a**:(**3a** + **4a**) = 70:30. Toluene was chosen to develop the synthetic procedures in order to avoid Cl-containing solvents for environmental protection reasons. Carrying out the reaction in toluene with the dropwise addition of PhSeH led to the formation of diene **2a** with 80% selectivity and quantitative conversion of PhSeH (entry 8).

Previously, it was reported that the addition of a catalytic amount of acid or base can significantly influence the activity and selectivity of the catalytic system.[8,9] In the present study, we found that the addition of 10 mol % Et_3N to the catalytic system increased the diene:alkenes selectivity to 94:6 (Table 3,

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entry 9). When the amount of the additive was increased to 1 equiv, significantly lower conversion was observed without an improvement in the overall selectivity.

In terms of the overall progress of the optimization procedure, starting with a conversion of 87% and a selectivity of 23:77 (Table 1, entry 1), we were able to render a highly selective synthesis of the desired 1-PhSe-1,3-diene framework with 98% conversion and 94:6 selectivity (Table 3, entry 9). It should be emphasized that the direction of the addition reaction was changed to form the diene as the major product (94:6) instead of the alkenes (23:77).

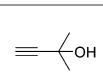
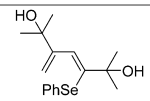
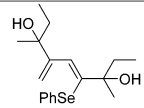
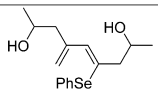
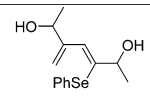
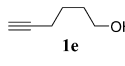
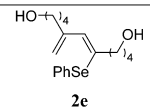
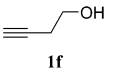
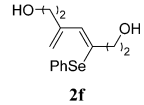
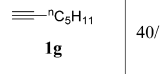
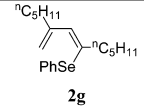
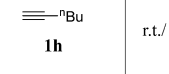
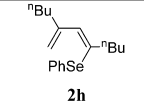
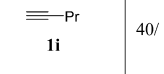
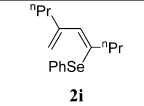
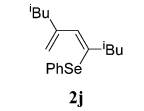
2.2. Scope of the Catalytic Reaction Using the Optimized Synthetic Procedure. Using the optimized synthetic procedure, we studied the scope of the catalytic reaction for various terminal alkynes (Table 4). The highest selectivity was observed for alkynes **1a** and **1b** bearing an OH group without an allylic hydrogen atom, which afforded yields of 86% and 80%, respectively (entries 1 and 3). In most of the studied cases, good to moderate product yields were found (entries 4−11). Phenylacetylene, as an alkyne bearing an aromatic substituent, was successfully involved in the catalytic reaction, but the corresponding vinyl selenides **3** and **4** were the major products [**2**:(**3** + **4**) = 36:64, 89% yield]. Amazingly, we found that the reaction can be performed under phosphine-free conditions in the presence of Et_3N only. In a few cases, the selectivity and yield of the phosphine-free system were close to that of the system with the phosphine ligand (cf. entries 1 and 2) or gave even higher values (entry 5).

For the purpose of a synthetic method, we addressed the possibility of scaling up the catalytic procedure. When 5 mmol of PhSeH was used under the optimized reaction conditions, dienes **2a** and **2h** were obtained in the yields of 78% (1.49 g) and 62% (0.94 g), respectively. It should be mentioned that the yield in a gram-scaled experiment in the case of 1-hexyne was 13% larger than the yield obtained on a 0.5 mmol scale (Table 4, entry 9). The products were purified by column chromatography, and the structures were confirmed by ^1H, ^{13}C, ^{77}Se, 2D COSY, and 2D NOESY NMR experiments.

The *s-gauche* conformation of diene **2a** in solution was evident from the 2D NOESY experiment (Figure S1 in the Supporting Information). The structure of the synthesized diene in a crystal was unambiguously confirmed by the X-ray analysis of **2a** (Figure S3 in the Supporting Information). X-ray analysis revealed the unique geometry of the synthesized diene, which preserved the *s-gauche* conformation with a C(1)−C(2)−C(3)−C(4) dihedral angle of 24.66°. In contrast, 1,3-dienes are typically expected to hold the *s-trans* conformation. To clarify the possibility of the existence of an *s-trans* conformer, DFT calculations at the ωB97X-D/6-311G(d) level were performed for diene **2a**. The obtained results demonstrated that formation of the *s-trans* conformer is unfavorable for such dienes (no energy minimum was localized), and thus, the *s-gauche* form is the only stable conformer, which is in excellent agreement with the experimental results.

2.3. Mechanistic Study of the Catalytic Reaction. The high selectivity of the transformation toward only one type of diene framework (Scheme 3) and the formation of the unusual *s-gauche* diene geometry are interesting features of the developed catalytic transformation. A detailed mechanistic investigation of the developed catalytic reaction was performed using a combination of ESI-MS/MS and ESI-MS methods. Electrospray ionization (ESI) has several well-known advantages for liquid-phase mechanistic studies.[23−25] This method deals with solutions and allows the solutions to be easily and quickly monitored (both offline and online) with minimal or no sample pretreatment. It is important to note that ionization occurs under gentle conditions at atmospheric pressure and

Table 4. Scope of the Developed Catalytic System and Yields of Dienes 2[a]

Entry	Alkyne	T, °C/ time, h	Diene	Conversion of 2, % (yield, %)[b]
1	 **1a**	40/ 0.5	 **2a**	92 (86) 90 (78)[e]
2				76 (69)[c]
3	 **1b**	40/ 1.5	 **2b**	84 (80)[d]
4	 **1c**	30/ 1.5	 **2c**	77 (58)[d]
5	 **1d**	r.t./ 1.5	 **2d**	67 (51)[c,d]
6	 **1e**	r.t./ 1.5	 **2e**	54 (46)
7	 **1f**	r.t./ 2	 **2f**	52 (42)
8	 **1g**	40/ 1.5	 **2g**	56 (50)
9	 **1h**	r.t./ 2	 **2h**	64 (49) 76 (62)[e]
10	 **1i**	40/ 1.5	 **2i**	57 (44)
11	 **1j**	r.t./ 1.5	 **2j**	57 (52)[f]

[a]Toluene, PhSeH:alkyne = 1:4, dropwise addition of PhSeH, 2 mol % $Ni(acac)_2$, 20 mol % PPh_2Cy, 10 mol % Et_3N. [b]Conversions were determined by ^1H NMR spectroscopy of the crude reaction mixtures; the yields of the isolated products after column chromatography are given in parentheses. [c]Reaction was performed without PPh_2Cy in the catalytic system containing $Ni(acac)_2/Et_3N$ (see the Experimental Section). [d]An equimolar mixture of diastereomeric dienes was formed in the case of alkynes possessing chiral centers. [e]Gram-scaled experiments with 5 mmol of benzeneselenol (see the text). [f]The product contained alkene **3j** (20%) as a contaminant.

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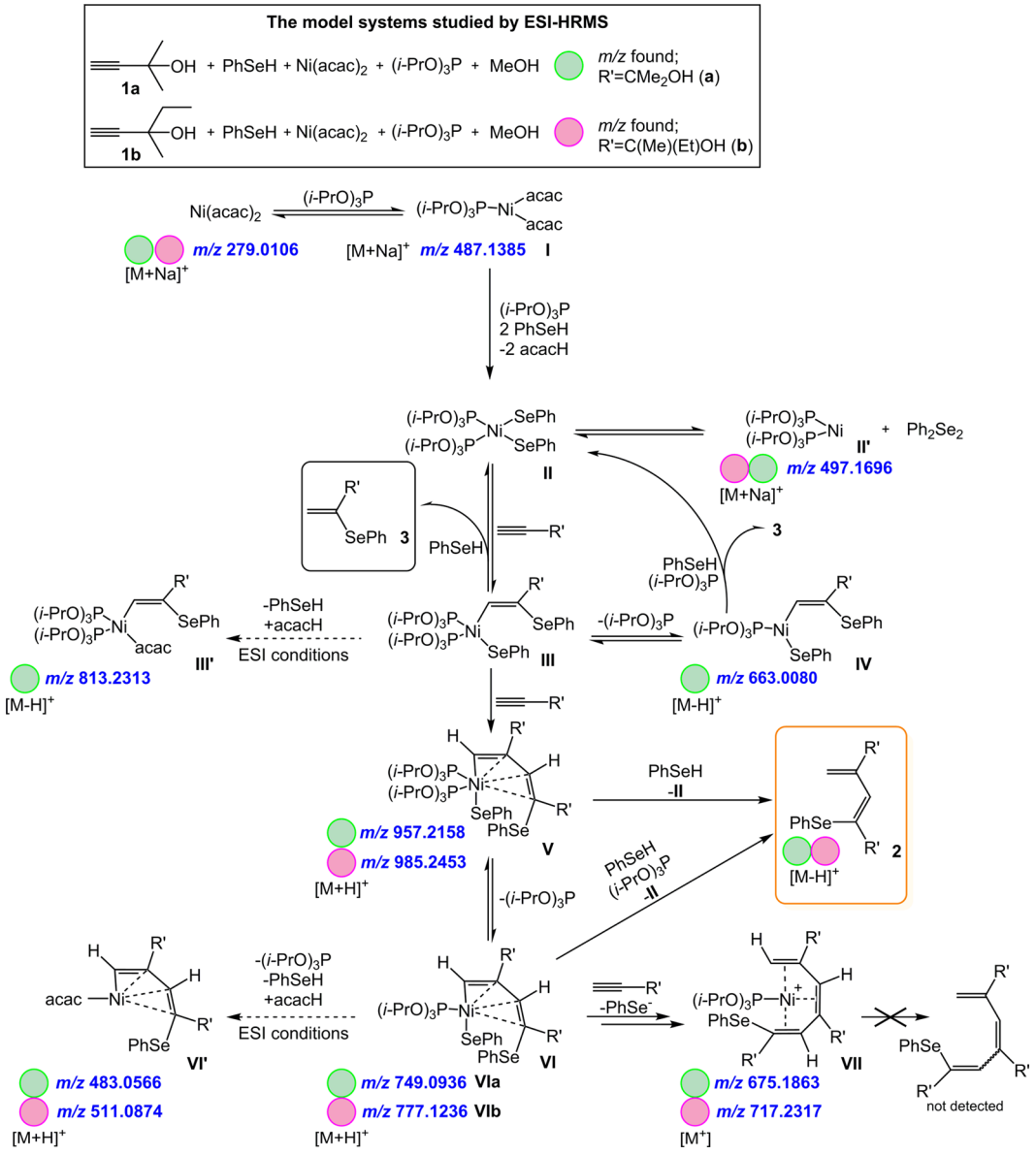
Scheme 4. ESI-(+MS) Study of the Mechanism of the Ni-Catalyzed Reaction of PhSeH with 1a and 1b (Green and Pink Dots Denote Compounds Detected in the Reactions with 1a and 1b, Respectively)



leads to the formation of singly and/or multiply charged gas-phase ions from primarily intact neutral species (reagents, intermediates, products). In the case of dissolved species that are initially charged (charged metal complexes, etc.), ESI may simply serve as a "bridge" for transferring the compounds from the liquid reaction medium to the mass analyzer and detector without additional perturbation. The "soft" electrospray ionization, together with accurate mass measurements, provides valuable insight into the intermediates and mechanisms of catalytic reactions.[23−25] The tandem version of this technique, ESI-MS/MS, is an important tool for obtaining information about the structure of the analyzed compounds by means of collision-induced dissociation (CID).[26] Furthermore, it should be noted that the fragmentation pathways of selected ions at various collision energies address questions about possible transformations and the strength of bonding within molecular fragments.

The reaction between **1a** (R′ = CMe_2OH) and PhSeH (added dropwise) in methanol using the $Ni(acac)_2$/P(*i*-PrO)$_3$ catalytic system was chosen for study by ESI-(+MS). The P(*i*-PrO)$_3$ ligand was selected for two reasons: (i) the ligand is preferable for the mechanistic study because it delivers signals with higher intensity in the mass spectrum[27] and (ii) high conversion and formation of both types of products were observed (Table 1, entry 2). The reaction was conducted for 10 min to reach partial conversion (as confirmed by ^{1}H NMR spectroscopy). Aliquots were taken directly from the reaction mixture and immediately injected into the ESI ion source (see the Experimental Section for details).

For unambiguous MS data interpretation, an independent catalytic reaction involving the homologous alkyne 3-methyl-pent-1-yn-3-ol (**1b**) was studied by ESI-(+MS) in exactly the same manner as described above for **1a**. The difference between alkynes **1a** and **1b** is equivalent to a single CH_2 group, and this exact molecular mass difference simplified the analysis of the spectral data.

The mass spectra were registered and analyzed for both model systems, composed of the two independent reactions of

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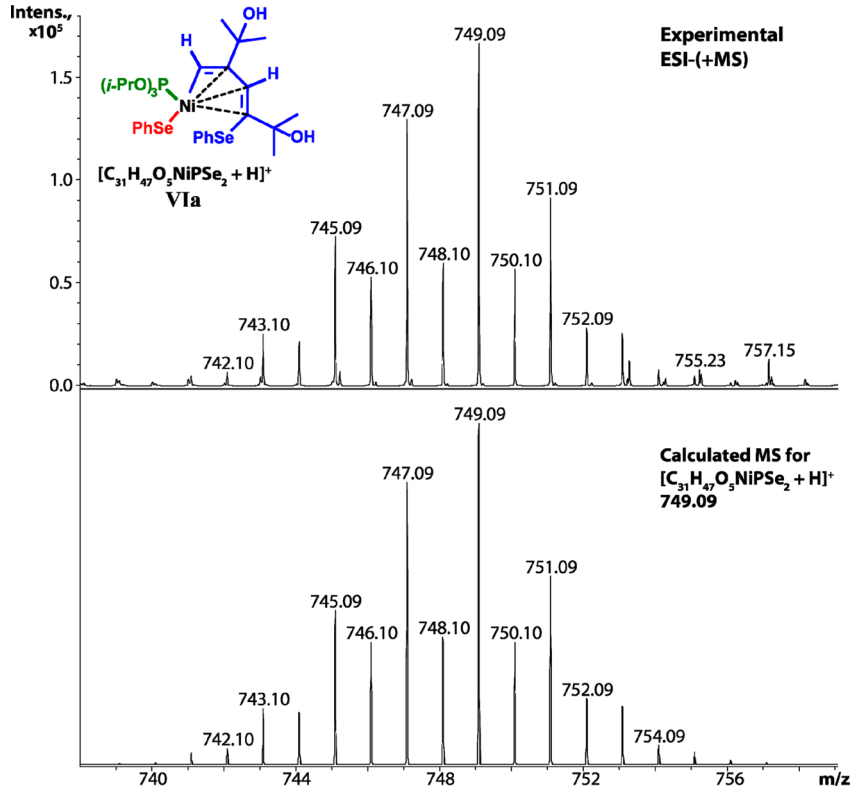

Figure 1. (top) Experimentally measured and (bottom) calculated ESI-(+MS) spectra of Ni complex **VIa** showing the specific isotopic patterns (here and later the intensities of the signals are given in arbitrary units).

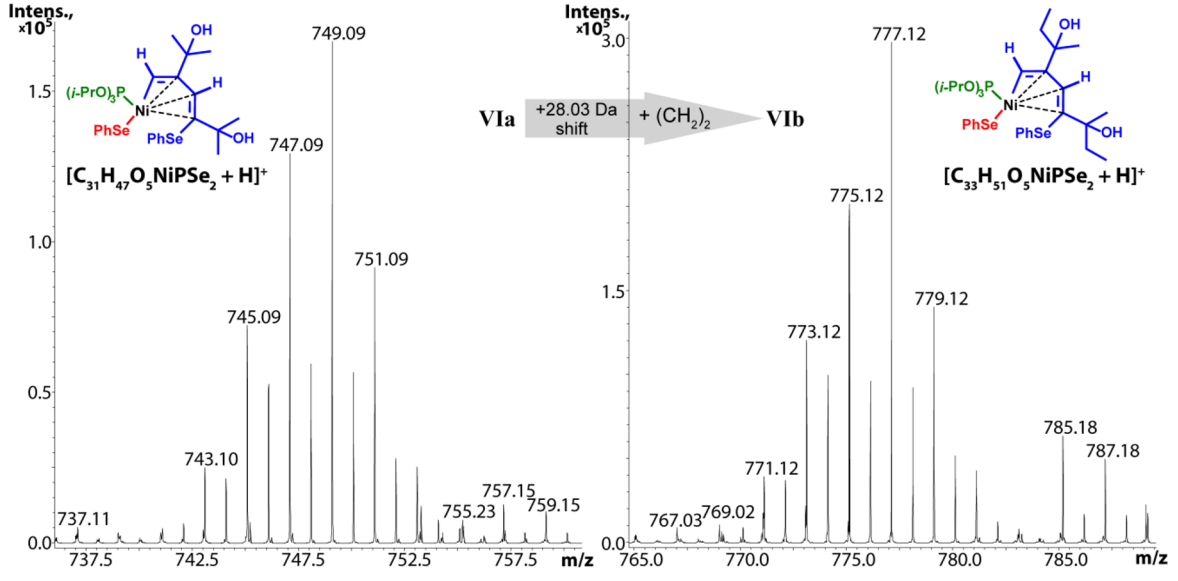

Figure 2. ESI-(+MS) experiments on the homologous alkynes 2-methylbut-3-yn-2-ol (**1a**) and 3-methylpent-1-yn-3-ol (**1b**) showing a shift of 28 Da for complex **VI**.

PhSeH with the alkynes **1a** (R′ = CMe_2OH) and **1b** [R′ = C(Me)(Et)OH]. Unexpectedly, no signals of complex **II** were detected in the mass spectra of the catalytic reactions studied. Instead, the signals of the preceding complex with one coordinated P(*i*-PrO)$_3$ ligand (**I**) were observed in the mass spectra for the simplified model system consisting of Ni(acac)$_2$ and P(*i*-PrO)$_3$ only (Scheme 4). Surprisingly, the Ni(acac)$_2$ signal was clearly observed in all of the studied systems with good intensity.[28] A number of species corresponding to the reaction of interest (**II**′ and **III**′−**VI**) were successfully detected by ESI-(+MS). This ESI-MS study enabled us to propose a plausible mechanism of the catalytic reaction (Scheme 4). Within the studied mechanism, we can suppose that the protonolysis of complexes **III** and **IV** with PhSeH results in the formation of undesired alkene **3**.

The representative experimental and calculated mass spectra of the key intermediate **VIa** are shown in Figure 1. Unequivocal identification of the Ni complex was facilitated by the unique isotopic distributions of selenium and nickel. Similar data were

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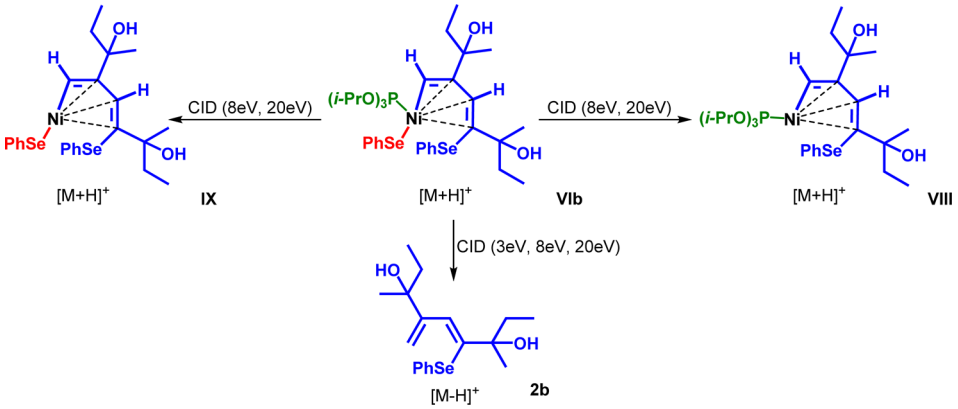
Scheme 5. Fragmentation Pathways of Complex VIb in ESI-(+MS/MS) Experiments with Different Values of the Laboratory-Frame Collision Energy (E_{Lab})



obtained for the other Ni complexes discussed in the present study.

The formation of the diene skeleton deserves a special note. Because of the presence of a Ni−C bond, complex **III** undergoes insertion of the second alkyne molecule, giving complex **V**. Dissociation of the $P(i\text{-}PrO)_3$ ligand was observed to mediate the formation of complex **VI** (see Figure 1 for the fragment of the spectrum containing **VIa**). Protonolysis of both complexes **V** and **VI** leads to the desired monoseleno-substituted diene **2** with the regeneration of **II** (Scheme 4).

Upon analysis of the spectral data, the nickel complex **VII** containing three alkyne moieties and one PhSe group was also observed in the ESI-(+MS) spectra (Scheme 4). Most likely, complex **VII** is a result of insertion of a third alkyne molecule into the Ni−C bond of **VI** accompanied by elimination of the PhSe fragment (presumably during electrospraying). Although protonolysis of **VII** may lead to a monoseleno-substituted triene, we did not detect such a species in either the ESI-(+MS) or ^{1}H NMR spectrum. Nickel complexes are known to catalyze oligomerization of alkynes,[29] but no feasible contribution of this side reaction to the formation of soluble products was observed experimentally in the developed catalytic system. Oligomerization may still be involved as a side reaction leading to the formation of insoluble species.

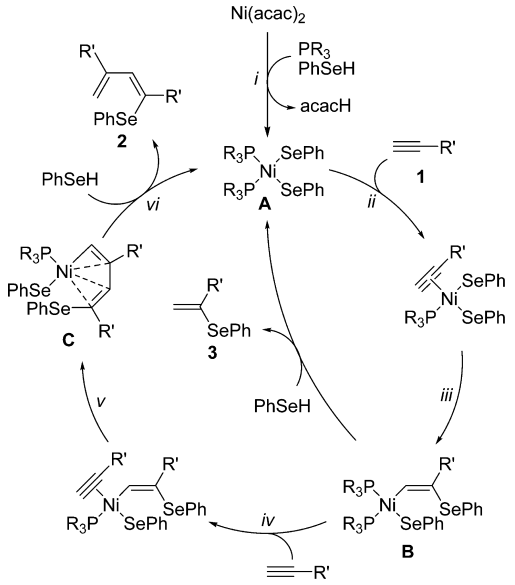
Complexes **III′** and **VI′** containing the acac moiety were also observed in the mass spectra. As shown above, $Ni(acac)_2$ was formed directly inside the ESI ion source from a Ni^{2+} cation and acacH.[28] We suggest that **III′** and **VI′** were formed from acacH and complexes **III** and **VI**, respectively, in similar way under ESI conditions (Scheme 4).

It is important to note that in the case of the ESI-(+MS) experiment for the reaction of PhSeH with **1b** [R′ = C(Me)(Et)OH], the signals of all of the intermediates resulting from the insertion of a second alkyne molecule (complexes **V** and **VI**) were shifted to higher mass by exactly 28.03 Da (two CH_2 moieties) compared with those for **1a** (R′ = CMe_2OH). Representative mass spectra exhibiting shifts of 28 Da for **VI** are shown in Figure 2. The signal of complex **VII** resulted from insertion of a third alkyne molecule, causing a shift to higher mass by 42.05 Da (three CH_2 moieties). It should be noted that complexes **V** and **VI** led to the desired formation of diene **2** after protonolysis with PhSeH (Scheme 4), with their presence being independently confirmed by ESI-(+MS) for both alkynes.

The nickel complex **VIb** was selected for ESI-(+MS/MS) experiments via CID at different values of the laboratory-frame collision energy (E_{Lab}) (Scheme 5). When E_{Lab} values as low as 3 eV were applied to the $[M + H]^+$ ion of **VIb**, the appearance of a signal from diene **2b** was clearly observed in the ESI-(+MS/MS) spectrum. This fact confirmed product formation from **VIb** and indicated relatively easy dissociation of a monoseleno-substituted diene fragment from the Ni center. Increasing E_{Lab} to 8 eV caused the independent cleavage of Ni−Se and Ni−P bonds in **VIb** and the respective formation of the complexes **VIII** and **IX** (Scheme 5). The corresponding mass spectrum of **VIII** obtained via CID of **VIb** was registered for the studied system (Figure S2 in the Supporting Information).

In summary, on the basis of the ESI-MS and ESI-MS/MS studies, a plausible overall mechanism for the formation of monoseleno-substituted dienes **2** can be proposed (Scheme 6).

Scheme 6. Proposed Mechanism of the Catalytic Cycle



At the starting point (*i*), the catalytically active nickel complex **A** is formed from the $Ni(acac)_2$ catalyst precursor. Then coordination of the alkyne to nickel takes place (*ii*), followed by alkyne insertion into the Ni−Se bond to generate complex **B** (*iii*). Protonolysis of this complex by PhSeH leads to alkene **3**. The competitive process of coordination (*iv*) and insertion (*v*) of the second alkyne molecule results in the formation of a diene moiety.[30] Finally, protonolysis of complex **C** by PhSeH

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leads to product formation and regeneration of complex **A** (*vi*). The alternative possibility of C−Se reductive elimination can be excluded because formation of the bis-seleno-substituted diene was not observed in the experiment (Scheme S2 in the Supporting Information). The involvement of protonolysis in the studied system was independently confirmed by a separate experiment in the presence of an acid (Scheme S3 in the Supporting Information). Most likely protonolysis of complex **IV** is favored over reductive elimination since the reaction results in the formation of monoseleno-substituted dienes rather than bis-seleno-substituted ones.

Within the proposed mechanism, we can rationalize the formation of only one type of diene framework. The insertion of alkyne **1** into the Ni−Se bond followed by insertion of the second alkyne into the Ni−C bond mediates the formation of a specific 1-PhSe-1,3-diene moiety. In both alkyne insertion steps, the metal center is bound to the least-substituted carbon atom of the alkyne, thus directing the radical (R) out of the metal center. As a result, only one type of diene skeleton is accessible during the catalytic cycle. The preferential *s-gauche* geometry is maintained in complex **C** through coordination to the metal center and released in the structure of product **2**. Within the catalytic cycle we can also rationalize the role of the phosphine ligand: fine-tuning is required in order to facilitate coordination and insertion of the second alkyne molecule (steps *iv* and *v*). Another important feature of the catalytic system is the need to avoid protonolysis at the earlier stage (in complex **B**) and C−Se reductive elimination in both complexes **B** and **C**.

3. CONCLUSIONS

We have developed an efficient Ni-based catalytic system that allows the selective synthesis of previously unknown monoseleno-substituted 1,3-dienes starting from easily available terminal alkynes and PhSeH. The unique properties of the catalytic system enable the exclusive formation of one type of diene. The developed synthetic procedure affords yields of up to 86% under mild reaction conditions (rt to 40 °C). The synthetic protocol developed here is tolerant of various alkynes and can easily be scaled up to prepare gram quantities of Se-functionalized dienes.

The mechanism of the catalytic reaction was studied using a combination of ESI-MS and ESI-MS/MS methods, and the key Ni-containing species involved in the reaction were successfully detected in the mass spectra. The proposed catalytic cycle rationalizes the exclusive formation of (*Z*)-1-PhSe-1,3-dienes via a sequence of regioselective alkyne insertions into the Ni−Se and Ni−C bonds.

4. EXPERIMENTAL SECTION

4.1. General. Unless otherwise noted, the synthetic work was carried out under an argon atmosphere. The reagents were obtained from commercial sources and were used as supplied (checked by NMR before use). $Ni(acac)_2$ was dried under vacuum (0.005−0.02 Torr, 60 °C, 30 min) before use. The solvents were purified according to published methods.

All of the NMR measurements were performed using a three-channel 600 MHz spectrometer operating at 600.1, 242.9, 150.9, and 114.5 MHz for ^{1}H, ^{31}P, ^{13}C, and ^{77}Se nuclei, respectively. The spectra were processed on a Linux workstation using the TopSpin 2.1 software package. All of the 2D spectra were recorded using an inverse triple resonance probehead with an active shielded *Z*-gradient coil. ^{1}H and ^{13}C chemical shifts are reported relative to the corresponding solvent signals used as internal references, whereas external $Ph_2Se_2/CDCl_3$ (δ = 463.0 ppm) was used for ^{77}Se. The yields given below were calculated on the basis of the initial amount of PhSeH.

The high-resolution mass spectra were recorded on a Q-TOF instrument equipped with an ESI ion source. The measurements were performed in positive-ion mode (+MS; +MS/MS) using a high-voltage (HV) capillary set at 4500 V and an HV end plate offset of −500 V with a scan range of m/z 50−3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). Direct syringe injection (a flow rate of 3 μL/min) was used for all of the analyzed samples (solutions in MeOH). Nitrogen was used as the nebulizer gas (0.4 bar), dry gas (4.0 L/min), and collision gas for all of the MS/MS experiments; the dry temperature was set at 180 °C.

4.2. General Synthetic Procedure for 2a−c and 2e−j. $Ni(acac)_2$ (1×10^{-5} mol) and PPh_2Cy (1×10^{-4} mol) were placed in a screw-capped test tube, and argon-flushed toluene (0.2 mL), alkyne (2×10^{-3} mol), and Et_3N (5×10^{-5} mol) were added. A light-green solution was formed within 1−2 min upon stirring at room temperature. The reaction mixture was heated to the appropriate temperature (Table 4), and PhSeH (5×10^{-4} mol) was added dropwise using a syringe pump over the time period indicated in Table 4. After PhSeH was added, the reaction was allowed to continue for an additional 5 min, and then the reaction mixture was cooled to room temperature.

After completion of the reaction, the products were purified by column chromatography on silica with hexane/ethyl acetate gradient elution. After drying in vacuum, pure products were obtained. In all cases, the structures of the products were confirmed by ^{1}H, ^{13}C{^{1}H}, and ^{77}Se{^{1}H} NMR spectroscopy. The stereochemistry was determined using 2D NOESY and ^{1}H−^{77}Se HMQC NMR experiments.

4.3. Procedure for the Scaled Synthesis of 2a and 2i. $Ni(acac)_2$ (1×10^{-4} mol) and PPh_2Cy (1×10^{-3} mol) were placed in a screw-capped test tube, and argon-flushed toluene (2 mL), alkyne (2×10^{-2} mol), and Et_3N (5×10^{-4} mol) were added. A light-green solution was formed in 1−2 min upon stirring at room temperature. The reaction mixture was heated to the appropriate temperature (Table 4), and PhSeH (5×10^{-3} mol) was added dropwise using a syringe pump over the time period indicated in Table 4. After PhSeH was added, the reaction was allowed to continue for an additional 5 min, and then the reaction mixture was cooled to room temperature.

After completion of the reaction, the products were purified by column chromatography on silica with hexane/ethyl acetate gradient elution. After drying in vacuum, pure products were obtained. In all cases, the structures of the products were confirmed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. The stereochemistry was determined using 2D NOESY and ^{1}H−^{77}Se HMQC NMR experiments.

4.4. General Synthetic Procedure for the Phosphine-Free Synthesis of 2a and 2d. $Ni(acac)_2$ (1×10^{-5} mol) was placed in a screw-capped test tube, and argon-flushed toluene (0.2 mL), alkyne (2×10^{-3} mol), and Et_3N (5×10^{-5} mol) were added. A light-green solution was formed in 1−2 min upon stirring at room temperature. The reaction mixture was heated to the appropriate temperature (Table 4), and PhSeH (5×10^{-4} mol) was added dropwise using a syringe pump over the time period indicated in Table 4. After PhSeH was added, the reaction was allowed to continue for an additional 5 min, and then the reaction mixture was cooled to room temperature.

After completion of the reaction, the products were purified by column chromatography on silica with hexane/ethyl acetate gradient elution. After drying in vacuum, pure products were obtained. The structures of the products were confirmed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy.

4.5. ESI-MS Mechanistic Study of the Catalytic Reaction. $Ni(acac)_2$ (1×10^{-5} mol) and $P(Oi\text{-}Pr)_3$ (1×10^{-4} mol) were placed in a screw-capped test tube, and HPLC-grade methanol (0.5 mL) and the corresponding alkyne (2×10^{-3} mol) were added. A light-green solution was formed in 1−2 min upon stirring at room temperature. The reaction mixture was heated to 40 °C, and PhSeH (2×10^{-4} mol) was added dropwise over 10 min using a syringe pump. After this time, the tube was centrifuged (5 min, 4000 rpm). A 7 μL aliquot of the

crude reaction mixture was diluted with MeOH (0.5 mL) and immediately injected into the ion source of the mass spectrometer. A 30 μL aliquot of the crude reaction mixture was taken independently for NMR analysis. The systems without alkyne, $Ni(acac)_2/P(i\text{-}PrO)_3$/MeOH, and PhSeH/$Ni(acac)_2/P(i\text{-}PrO)_3$/MeOH were analyzed in exactly the same manner.

4.6. Compound Characterization Data. *(Z)-2,6-Dimethyl-5-methylene-3-(phenylselanyl)hept-3-ene-2,6-diol (**2a**).* Yellow oil, 86% (0.1364 g), 78% (1.49 g) for the scaled reaction. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, J = 7.4 Hz, 2H, Ar), 7.20 (t, J = 7.5 Hz, 2H, Ar), 7.16 (t, J = 7.5 Hz, 1H, Ar), 6.94 (s, 1H, CH═), 5.19 (s, 1H, CH═), 5.18 (s, 1H, CH═), 2.87 (s, 1H, OH), 1.74 (s, 1H, OH), 1.49 (s, 6H, $2CH_3$), 1.23 (s, 6H, $2CH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 151.37, 142.95, 133.20, 133.08, 131.12, 129.10, 126.48, 112.90, 75.45, 72.91, 29.88, 29.19. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 287.36. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{16}H_{21}O_2Se$ 325.0702, found 325.0709. Anal. Calcd for $C_{16}H_{22}O_2Se$: C, 59.07; H, 6.82; Se, 24.27. Found: C, 59.44; H, 7.18; Se, 23.92.

*(Z)-3,7-Dimethyl-6-methylene-4-(phenylselanyl)non-4-ene-3,7-diol (**2b**) (Mixture of Diastereomers).* Yellow oil, 80% (0.1418 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, J = 7.4 Hz, 2H, Ar), 7.22 (t, J = 7.5 Hz, 2H, Ar), 7.17 (t, J = 7.5 Hz, 1H, Ar), 6.81 (s, 1H, CH═), 5.23 (s, 1H, CH═), 5.22 (s, 1H, CH═, second diastereomer), 5.18 (s, 1H, CH═), 2.50 (br s, 1H, OH), 1.83−1.69 (m, 2H, CH_2), 1.61−1.49 (m, 3H, CH_2, OH), 1.44 (s, 3H, C−CH_3), 1.20 (s, 3H, C−CH_3), 1.18 (s, 3H, C−CH_3, second diastereomer), 0.88 (t, J = 7.5 Hz, 3H, CH_2−CH_3), 0.81 (t, J = 7.4 Hz, 3H, CH_2−CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 150.37, 150.32, 141.60, 141.51, 134.80, 134.74, 133.17, 131.23, 131.20, 129.15, 126.56, 114.12, 77.80, 77.75, 75.35, 75.34, 34.81, 34.74, 33.70, 27.27, 27.09, 26.98, 26.94, 8.57, 8.22. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 287.89, 286.88. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{18}H_{25}O_2Se$ 353.1015, found 353.1008.

*(Z)-6-Methylene-4-(phenylselanyl)non-4-ene-2,8-diol (**2c**) (Mixture of Diastereomers).* Brown oil, 58% (0.0979 g). ^{1}H NMR (600 MHz, $CDCl_3$, first eluted diastereomer): δ 7.54−7.48 (m, 2H, Ar), 7.34−7.26 (m, 3H, Ar), 6.32 (s, 1H, CH═), 5.28 (s, 1H, CH═), 5.04 (s, 1H, CH═), 3.99−3.89 (m, 2H, CH_2), 2.39 (dt, J = 13.3 Hz, 3.6 Hz, 1H, C*H*H), 2.30−2.17 (m, 3H, CH_2, C*H*H), 2.10 (br s, 2H, 2OH), 1.24 (d, J = 6.1 Hz, 3H, CH_3), 1.05 (d, J = 6.4 Hz, 3H, CH_3). ^{1}H NMR (600 MHz, $CDCl_3$, second eluted diastereomer): δ 7.54−7.48 (m, 2H, Ar), 7.34−7.26 (m, 3H, Ar), 6.31 (s, 1H, CH═), 5.29 (s, 1H, CH═), 5.04 (s, 1H, CH═), 3.99−3.89 (m, 2H, CH_2), 2.39 (dt, J = 13.3 Hz, 3.6 Hz, 1H, C*H*H), 2.30−2.17 (m, 3H, CH_2, C*H*H), 2.10 (br s, 2H, 2OH), 1.24 (d, J = 6.1 Hz, 3H, CH_3), 1.03 (d, J = 6.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, first eluted diastereomer): δ 142.99, 135.15, 133.93, 133.84, 129.35, 128.28, 119.27, 66.66, 66.51, 47.66, 46.89, 22.75, 22.41. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, second eluted diastereomer): δ 143.14, 135.25, 133.93, 133.34, 129.35, 128.33, 119.46, 66.41, 66.21, 47.62, 47.07, 22.75, 22.48. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$, first eluted diastereomer): δ 381.65. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$, second eluted diastereomer): δ 377.47. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{16}H_{21}O_2Se$ 325.0702, found 325.0706.

*(Z)-5-Methylene-3-(phenylselanyl)hept-3-ene-2,6-diol (**2d**) (Mixture of Diastereomers).* Yellow oil, 51% (0.0821 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50−7.45 (m, 2H, Ar), 7.28−7.22 (m, 3H, Ar), 6.82 (s, 1H, CH═), 5.34 (s, 1H, CH═), 5.09 (s, 1H, CH═), 5.06 (s, 1H, CH═, second diastereomer), 4.44−4.36 (m, 1H, CH), 4.29−4.21 (m, 1H, CH), 2.09 (br s, 2H, 2OH), 1.36 (d, J = 6.3 Hz, 3H, CH_3), 1.32 (d, J = 6.5 Hz, 3H, CH_3, second diastereomer), 1.30 (d, J = 6.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 148.54, 148.52, 141.30, 140.93, 133.33, 133.21, 129.74, 129.60, 129.37, 129.19, 128.31, 127.58, 127.54, 115.05, 115.03, 71.34, 71.26, 71.10, 70.96, 23.40, 23.26, 22.33, 22.18. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 332.03, 328.35. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{14}H_{17}O_2Se$ 297.0389, found 297.0394.

*(Z)-7-Methylene-5-(phenylselanyl)undec-5-ene-1,11-diol (**2e**).* Brown oil, 46% (0.0925 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52−7.49 (m, 2H, Ar), 7.30−7.23 (m, 3H, Ar), 6.24 (s, 1H, CH═), 5.13 (s, 1H, CH═), 4.91 (s, 1H, CH═), 3.65 (t, J = 6.3 Hz, 2H, CH_2), 3.51 (t, J = 6.5 Hz, 2H, CH_2), 2.22 (t, J = 7.3 Hz, 2H, CH_2), 2.18 (t, J = 7.3 Hz, 2H, CH_2), 1.65−1.46 (m, 10H, $4CH_2$, 2OH). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 145.72, 135.72, 134.63, 134.08, 131.80, 128.95, 127.61, 115.44, 62.76, 62.60, 38.21, 36.59, 32.31, 31.71, 25.39, 24.39. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 375.43. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{18}H_{25}O_2Se$ 353.1002, found 353.1015.

*(Z)-5-Methylene-3-(phenylselanyl)hept-3-ene-1,7-diol (**2f**).* Yellow oil, 42% (0.1320 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 (d, J = 7.1 Hz, 2H, Ar), 7.32−7.26 (m, 3H, Ar), 6.34 (s, 1H, CH═), 5.27 (s, 1H, CH═), 5.05 (s, 1H, CH═), 3.73 (t, J = 6.1 Hz, 2H, CH_2), 3.64 (t, J = 6.2 Hz, 2H, CH_2), 2.45 (t, J = 6.0 Hz, 2H, CH_2), 2.40 (t, J = 6.1 Hz, 2H, CH_2), 2.00 (br s, 2H, 2OH). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 142.79, 136.56, 134.87, 133.68, 132.51, 129.36, 128.16, 118.94, 61.34, 61.09, 41.32, 40.10. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 370.99. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{14}H_{17}O_2Se$ 297.0389, found 297.0392.

*(Z)-(8-Methylenetridec-6-en-6-yl)(phenyl)selane (**2g**).* Yellow oil, 50% (0.0888 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53−7.48 (m, 2H, Ar), 7.28−7.19 (m, 3H, Ar), 6.23 (s, 1H, CH═), 5.11 (s, 1H, CH═), 4.88 (s, 1H, CH═), 2.21−2.11 (m, 4H, $2CH_2$), 1.52−1.40 (m, 4H, $2CH_2$), 1.35−1.29 (m, 4H, $2CH_2$), 1.21−1.16 (m, 2H, CH_2), 1.15−1.08 (m, 2H, CH_2), 0.90 (t, J = 6.9 Hz, 3H, CH_3), 0.82 (t, J = 7.3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 146.52, 136.12, 134.78, 131.90, 131.50, 128.99, 127.56, 114.94, 38.79, 37.12, 31.67, 31.11, 29.23, 28.16, 22.73, 22.51, 14.22, 14.12. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 375.94. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{20}H_{29}Se$ 349.1430, found 349.1437.

*(Z)-(7-Methyleneundec-5-en-5-yl)(phenyl)selane (**2h**).* Yellow oil, 49% (0.1599 g), 62% (0.94 g) for the scaled reaction. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52−7.49 (m, 2H, Ar), 7.28−7.22 (m, 3H, Ar), 6.23 (s, 1H, CH═), 5.11 (s, 1H, CH═), 4.88 (s, 1H, CH═), 2.18 (t, J = 7.5 Hz, 2H, CH_2), 2.14 (t, J = 7.5 Hz, 2H, CH_2), 1.54−1.28 (m, 6H, $3CH_2$), 1.20−1.13 (m, 2H, CH_2), 0.93 (t, J = 7.2 Hz, 3H, CH_3), 0.78 (t, J = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 146.38, 136.04, 134.74, 131.83, 131.42, 128.93, 127.52, 114.90, 38.40, 36.77, 31.66, 30.57, 22.45, 21.91, 14.07, 13.88. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 377.69. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{18}H_{25}Se$ 321.1117, found 321.1120. Anal. Calcd for $C_{18}H_{26}Se$: C, 67.27; H, 8.16; Se, 24.57. Found: C, 67.50; H, 8.32; Se, 24.18.

*(Z)-(6-Methylenenon-4-en-4-yl)(phenyl)selane (**2i**).* Yellow oil, 44% (0.0635 g). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52−7.49 (m, 2H, Ar), 7.29−7.22 (m, 3H, Ar), 6.23 (s, 1H, CH═), 5.12 (s, 1H, CH═), 4.89 (s, 1H, CH═), 2.16 (t, J = 7.5 Hz, 2H, CH_2), 2.12 (t, J = 7.3 Hz, 2H, CH_2), 1.55−1.40 (m, 4H, $2CH_2$), 0.94 (t, J = 7.3 Hz, 3H, CH_3), 0.77 (t, J = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 146.22, 135.77, 134.74, 132.06, 131.48, 129.00, 127.57, 115.16, 40.72, 39.22, 22.60, 21.61, 13.95, 13.33. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 375.01. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{16}H_{21}Se$ 293.0803, found 293.0797.

*(Z)-(2,8-Dimethyl-6-methylenenon-4-en-4-yl)(phenyl)selane (**2j**).* Yellow oil, 52% (0.0931 g). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52−7.49 (m, 2H, Ar), 7.27−7.22 (m, 3H, Ar), 6.16 (s, 1H, CH═), 5.11 (s, 1H, CH═), 4.90 (s, 1H, CH═), 2.07 (d, J = 7.2 Hz, 2H, CH_2), 1.97 (d, J = 6.9 Hz, 2H, CH_2), 1.90−1.82 (m, 1H, CH), 1.81−1.73 (m, 1H, CH), 0.93 (d, J = 6.6 Hz, 6H, $2CH_3$), 0.75 (d, J = 6.6 Hz, 6H, $2CH_3$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 145.35, 135.70, 135.01, 132.81, 132.35, 128.96, 127.65, 116.32, 47.83, 46.95, 27.52, 27.38, 22.67, 22.05. $^{77}Se\{^1H\}$ NMR (114 MHz, $CDCl_3$): δ 377.90. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{18}H_{25}Se$ 321.1117, found 321.1109.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra of new compounds **2a**−**i**; X-ray structure determination of compound **2a** (CIF); mechanistic schemes; and 2D NOESY NMR and ESI-MS/MS spectra are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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DEDICATION

This article is dedicated to the memory of Dr. Z. A. Starikova.

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(28) The fact that Ni(acac)$_2$ was detected in the presence of excess PhSeH looks somewhat unusual, since substitution of an acac ligand with a PhSe group is known to proceed rapidly (see ref 15). We checked this three-component mixture with ^{1}H NMR spectroscopy, and release of acacH was proven to be fast and complete at room temperature. We suggest that formation of Ni(acac)$_2$ takes place directly upon electrospraying in the charged droplets. To obtain experimental proof, we performed the independent control ESI-MS analysis of a Ni(CH$_3$COO)$_2$/acacH (1:2.5 molar ratio) mixture dissolved in methanol. Indeed, the signals of Ni(acac)$_2$ (both protonated and sodium adduct) together with the [Ni$_2$(acac)$_3$]$^+$ cation were detected as the most abundant ions.

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(30) Indeed, two pathways for insertion of the second alkyne molecule are possible: into either the Ni−C or Ni−Se bond (Scheme S1 in the Supporting Information). On the basis of the experimental results, we can rule out the latter case because a bis-seleno-subsituted diene would be formed after reductive elimination, and it was not observed in the experiment. Therefore, the catalytic cycle involves the insertion of the second alkyne molecule into the Ni−C bond and the formation of a diene skeleton in the coordination sphere of the metal (Scheme 6).