Efficient and Convenient Synthesis of β-Vinyl Sulfides in Nickel-Catalyzed Regioselective Addition of Thiols to Terminal Alkynes under Solvent-Free Conditions

Valentine P. Ananikov,*[,†] Nikolay V. Orlov,[†] and Irina P. Beletskaya*[,‡]

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 119991, Russia, and Chemistry Department, Lomonosov Moscow State University, Vorob'evy gory, Moscow, 119899, Russia

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A new nanosized catalytic system has been developed for convenient preparation of β-vinyl sulfides $H_2C{=}C(SAr)R$ with high yields (79−98%) and excellent selectivity (>98:2). Inexpensive and easily available $Ni(acac)_2$ was used as catalyst precursor. Solvent-free conditions were combined with high atom efficiency of the ArSH addition reaction to terminal alkynes ($HC{\equiv}C-R$) in order to create an environmentally friendly synthetic procedure. The mechanistic study has indicated that catalytic reaction takes place under heterogeneous conditions with alkyne insertion into the Ni−S bond as a key step.

1. Introduction

The application of vinyl sulfides in organic synthesis has increased tremendously in recent years.[1] The arylthio group (ArS) can stabilize both negative and positive charges on neighboring carbon atoms, therefore increasing the reactivity of vinyl sulfides toward electrophilic and nucleophilic reagents. Not surprisingly, vinyl sulfides became attractive reagents and have been widely utilized in various synthetic reactions.[1,2] Another very useful feature of vinyl sulfides concerns unique selectivity-controlling properties of the sulfur atom in the cyclization reactions.[3] It was already shown that arylvinyl sulfides are attractive reagents in [1+2], [2+2], [3+2], and [4+2] cycloaddition reactions.[3,4]

A very useful practical method for the preparation of vinyl sulfides involves addition of the S−H bond of thiols to alkynes (Scheme 1). The method is of particular importance since the addition reaction proceeds in an atom-efficient manner without waste. Under nucleophilic or free radical conditions anti-Markovnikov products **3** and **4** were obtained.[5] These conditions are especially useful for the activated alkynes (R = Ph, COOR′, COR′, etc.), which smoothly react with thiols in high yields. Regular unactiveted alkynes require longer reaction time or heating.[5]

Markovnikov-type addition leading to β-vinyl sulfides **2** can be achieved under transition metal-catalyzed conditions.[6] Palladium-catalyzed ArSH addition to terminal alkynes was shown to proceed with high regioselectivity and yields,[7] although the overall yield of **2** may not be high in some cases due to a noncatalytic side reaction leading to **3** and **4** or isomerization of **2** to internal alkenes **5** and **6** (Scheme 2). Very good yields of **2** (70−85%) were achieved in $Pd(OAc)_2$-catalyzed reactions carried out for 16 h at 40 °C.[7] Attempts to decrease reaction time by increasing the temperature were unsuccessful, since the amount of byproducts (**3**−**6**) dramatically increases at elevated temperature.

* To whom correspondence should be addressed. (V.P.A.) E-mail: val@ioc.ac.ru. Fax: +007 (495) 1355328. (I.P.B.) E-mail: beletska@org.chem.msu.ru. Fax: +007 (495) 9393618.

† Zelinsky Institute of Organic Chemistry.

‡ Lomonosov Moscow State University.

(1) (a) McReynolds, M. D.; Dougherty, J. M.; Hanson, P. R. *Chem. Rev.* **2004**, *104*, 2239. (b) Zyk, N. V.; Beloglazkina, E. K.; Belova, M. A.; Dubinina, N. S. *Russ. Chem. Rev.* **2003**, *72*, 769. (c) Sizov, A. Yu.; Kovregin, A. N.; Ermolov, A. F. *Russ. Chem. Rev.* **2003**, *72*, 394. (d) Mangini, A. *Sulfur Rep.* **1987**, *7*, 313. (e) *Organic Sulfur Chemistry. Theoretical and Experimental Advances;* Studies in Organic Chemistry. V.19; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985. (f) Ager, D. J. *Chem. Soc. Rev.* **1982**, *11*, 493. (g) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978.

(2) See, for example: (a) Muraoka, N.; Mineno, M.; Itami, K.; Yoshida, J.-I. *J. Org. Chem.* **2005**, *70*, 6933. (b) Aucagne, V.; Lorin, C.; Tatibouet, A.; Rollin, P. *Tetrahedron Lett.* **2005**, *46*, 4349. (c) Woodland, C. A.; Crawley, G. C.; Hartley, R. C. *Tetrahedron Lett.* **2004**, *45*, 1227. (d) Farhat, S.; Marek, I. *Angew. Chem., Int. Ed.* **2002**, *41*, 1410. (e) Marciniec, B.; Chadyniak, D.; Krompiec, S. *J. Mol. Catal. A* **2004**, *224*, 111. (f) Su, M.; Yu, W.; Jin, Z. *Tetrahedron Lett.* **2001**, *42*, 3771. (g) Lee, Y. R.; Kim, N. S.; Kim, B. S. *Tetrahedron Lett.* **1997**, *38*, 5671. (h) Andres, D. F.; Dietrich, U.; Laurent, E. G.; Marquet, B. S. *Tetrahedron* **1997**, *53*, 647. (i) Krief, A.; Kenda, B.; Remacle, B. *Tetrahedron Lett.* **1995**, *36*, 7917. (j) Andres, D. F.; Laurent, E. G.; Marquet, B. S.; Benotmane, H.; Bensadat, A. *Tetrahedron* **1995**, *51*, 2605. (k) Backvall, J.-E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850. (l) Magnus, P.; Quagliato, D. *J. Org. Chem.* **1985**, *50*, 1621. (m) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075. (n) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 840. (o) Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.

(3) Yamazaki, S. *J. Synth. Org. Chem.* **2000**, *58*, 50.

(4) For representative examples see (and references therein): (a) Bruckner, R.; Huisgen, R. *Tetrahedron Lett.* **1990**, *31*, 2561. (b) Singleton, D. A.; Church, K. M. *J. Org. Chem.* **1990**, *55*, 4780. (c) Sugimura, H.; Osumi, K. *Tetrahedron Lett.* **1989**, *30*, 1571. (d) Gupta, R. B.; Franck, R. W.; Onan, K. D.; Soll, C. E. *J. Org. Chem.* **1989**, *54*, 1097. (e) Weber, A.; Sabbioni, G.; Galli, R.; Stampfli, U.; Neuenshwander, M. *Helv. Chim. Acta* **1988**, *71*, 2026. (f) Tsuge, O.; Kanemasa, S.; Sakamoto, K.; Takenaka, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2513. (g) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730.

(5) (a) Kondoh, A. K.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468. (b) Trofimov, B. A. *Curr. Org. Chem.* **2002**, *6*, 1121. (c) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans.* **1995**, 1035. (d) Back, T. G.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 2533. (e) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J.-L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647. (f) Trofimov, B. A. *Russ. Chem. Rev.* **1981**, *50*, 138. (g) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391. (h) Truce, W. E.; Heine, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 5311.

(6) (a) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew Chem., Int. Ed.* **2004**, *43*, 3368. (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (c) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205. (d) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463. (e) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080.

(7) (a) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108. (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902.

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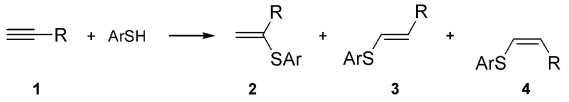
Scheme 1



Scheme 2

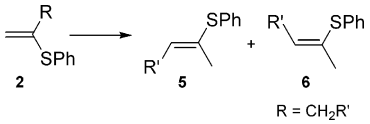


Table 1. PhSH Addition to 1-Heptyne Catalyzed by Various Metal Complexes[a]

entry	catalyst	conditions[b]	alkyne conversion,[c] %	yields,[c] % **2**:**5**+**6**:**3**+**4**
1	$Pd(OAc)_2$	THF, 40 °C, 16 h	99	80:19:0
2	$Pd(OAc)_2$	THF, 40 °C, 30 min	24	24:0:0
3	$Pd(OAc)_2$	40 °C, 30 min[d]	35	29:6:0
4	$Ni(OAc)_2$	40 °C, 30 min[d]	28	2:0:26
5	$Ni(Cp)_2$	40 °C, 30 min[d]	65	55:8:2
6	$Ni(acac)_2$	40 °C, 30 min[d]	99	89:5:5

[a] See Schemes 1 and 2 for the reactions (R = C_5H_{11}). [b] Using 2 mmol of PhSH, 1 mmol of 1-heptyne, and 2 mol % of the catalyst in a sealed tube with stirring. [c] Determined by NMR. [d] Solvent-free.

An excellent study of the catalytic S−H bond addition to alkynes made by A. Ogawa, N. Sonoda, et al. has proven the great potential of transition metal catalysis in the synthesis of β-vinyl sulfides.[6,7] The synthetic procedures reported so far were designed for small-scale synthesis resulting in ∼0.2−0.3 g of product **2** and required chromatography at the purification stage. The increasing cost of palladium-based catalysts imposes significant limits to synthetic utilization of β-vinyl sulfides prepared in that way. Recently we have suggested $NiCl_2$ as a catalyst precursor for alkyne hydrothiolation.[8] However, this methodology again was proven to be useful only for the reactions on a 1 mmol scale (<0.3 g of product). Therefore, there is an obvious lack of practical method for the preparation of β-vinyl sulfides on a synthetic scale. On the other hand, β-vinyl sulfides are of particular importance for metathesis and cyclization reactions, the synthesis of biologically active compounds, and the development of new materials.[1−4]

In the present study we report a new method for a convenient and efficient synthesis of β-vinyl sulfides, which meets the following criteria: (1) easily scalable procedure suitable for the preparation of 0.5−50 g of product; (2) inexpensive and easily available Ni catalyst; (3) avoidance of chromatography at the purification stage; (4) high efficiency of catalysis and short reaction time; (5) high selectivity with minimal amount of byproducts; (6) solvent-free conditions.

2. Results and Discussion

At first we tested whether solvent-free conditions provide an advantage for the studied addition reaction. For this purpose we have selected a known procedure with $Pd(OAc)_2$ catalyst developed for THF solution.[7] In the model reaction of PhSH addition to 1-heptyne 99% conversion of the alkyne was observed after 16 h at 40 °C (Table 1, entry 1). This result is in good agreement with literature data.[7] For a proper comparison the experiments with shorter reaction time (30 min) have been carried out. In THF solution 24% conversion of the alkyne was observed after 30 min (Table 1, entry 2). Under solvent-free conditions 35% conversion was found within the same time period (Table 1, entry 3), which corresponds to a 1.5-fold reaction rate enhancement. Most likely, the rate enhancement originates from the concentration effect.[9] In both cases, in THF solution and under solvent-free conditions, Markovnikov-type product **2** was formed (Table 1, entries 2 and 3). The complete conversion of the alkyne under solvent-free conditions was observed after ca. 12 h (cf. ca. 16 h in THF; Table 1, entry 1). Therefore, excluding solvent provides not only ecological and economical benefits but also an additional advantage of shortening the reaction time.

Table 2. $Ni(acac)_2$-Catalyzed PhSH Addition to 1-Heptyne at Different Temperatures[a]

entry	conditions[b]	yield,[c] % **2**:**5**+**6**:**3**+**4**
1	80 °C, 10 min	28:61:10
2	40 °C, 10 min	81:4:4
3	25 °C, 10 min	72:3:3
4	10 °C, 10 min	34:3:0
5	10 °C, 20 min	67:9:0
6	10 °C, 90 min	84:15:0

[a] See Schemes 1 and 2 for the reactions (R = C_5H_{11}). [b] Using 2 mmol of PhSH, 1 mmol of 1-heptyne, and 2 mol % of $Ni(acac)_2$ in a sealed tube with stirring (solvent-free). [c] Determined by NMR.

At the next stage we searched for a replacement of the palladium catalyst. Surprisingly, nickel complexes have shown desired catalytic activity under the studied mild conditions. The rather poor catalytic activity of $Ni(OAc)_2$ (2% of **2**) was significantly improved (55% of **2**) by using $NiCp_2$ as a catalyst (Table 1, entries 4 and 5, respectively). Utilizing $Ni(acac)_2$ leads to 99% alkyne conversion after 30 min at 40 °C (Table 1, entry 6). It is important to point out that $Ni(acac)_2$ provides better overall selectivity than $Pd(OAc)_2$. The yield of Markovnikov product **2** was 89% and 80% for $Ni(acac)_2$ and $Pd(OAc)_2$, respectively (Table 1, entries 6 and 1). The other acetylacetonate compounds, $Cu(acac)_2$, $Co(acac)_2$, and $VO(acac)_2$, did not show significant catalytic activity (<1% yield of **2**). Interesting to note, using $Pd(acac)_2$ as a catalyst did not lead to a noticeable improvement over the $Pd(OAc)_2$; similar yields and selectivity were observed. Therefore, nickel acetylacetonate is the catalyst of choice for the studied reaction due to its remarkable efficiency and selectivity.

In addition to the catalytic Markovnikov-type reaction, two side reactions could take place in the studied system: (1) noncatalytic addition leading to compounds **3** and **4** (Scheme 1) and (2) isomerization of product **2** to compounds **5** and **6** (Scheme 2). This is a common problem of transition metal-catalyzed H−E bond addition to alkynes.[6,7,10] Our study of the Ni-catalyzed reaction has shown that reaction temperature and amount of catalyst are the key factors that need to be optimized to reduce the contribution of the side reactions.

To find optimal conditions, we varied the reaction temperature in the range 10−80 °C (Table 2) and the amount of catalyst in the range 0.5−5 mol % (Table 3). The noncatalytic addition leading to **3** and **4** was facilitated at elevated temperature (Table 2, entries 1−3). The selectivity of the catalytic reaction decreased from 25.0 at 25 °C to 8.9 at 80 °C.[11] More

(8) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *Adv. Synth. Catal.* **2005**, *347*, 1993.

(9) For a related discussion of rate enhancement in the catalytic C−E (E = S, Se) bond formation reaction under solvent-free conditions see: Ananikov, V. P.; Beletskaya, I. P. *Org. Biomol. Chem.* **2004**, *2*, 284.

(10) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *679*, 162.

(11) The selectivity of the addition reactions is reflected by the ratio of catalytic and noncatalytic products (**2**+**5**+**6**)/(**3**+**4**).

Table 3. $Ni(acac)_2$-Catalyzed PhSH Addition to 1-Heptyne with Different Amounts of Catalyst[a]

entry	$Ni(acac)_2$, mol %	conditions[b]	alkyne conversion,[c] %	yields,[c] % **2**:**5**+**6**:**3**+**4**
1	5.0	25 °C, 30 min	99	75:19:4
2	2.0	25 °C, 30 min	89	80:5:4
3	1.0	25 °C, 30 min	74	60:7:7
4	0.5	25 °C, 30 min	26	23:7:3

[a] See Schemes 1 and 2 for the reactions (R = C_5H_{11}). [b] Using 2 mmol of PhSH, 1 mmol of 1-heptyne, and $Ni(acac)_2$ in a sealed tube with stirring (solvent-free). [c] Determined by NMR.

complicated behavior was observed for the isomerization reaction. The minimum amount of byproducts **5** and **6** within the reasonable conversion of the alkyne was detected approximately in the middle of the studied temperature range. The higher the reaction temperature, the greater the yield of isomerization products (cf. entries 1−3, Table 2). At 80 °C internal alkenes **5** and **6** are the major reaction products with 61% yield (Table 2, entry 1). On the other hand, longer reaction time at lower temperature also increases the contribution of the isomerization process (cf. entries 4−6, Table 2).[12] Finally, the temperature range 25−40 °C seems to be the most favorable for the studied model reaction in order to minimize the yield of the byproducts.

Using 2 mol % of the catalyst seems to be the most appropriate for the addition reaction (Table 3, entry 2). Decreasing the amount of catalyst slows the rate of the reaction (Table 3, entries 2−4). As has been discussed already, the contribution of the isomerization reaction may significantly increase at longer reaction time. On the other hand, increasing the amount of catalyst facilitates the isomerization reaction (entry 1, Table 3) due to contribution of the metal-catalyzed pathway.[12] Therefore, 2 mol % of the Ni catalyst can be accepted as a reasonable estimation (entry 2, Table 3).

Despite the common side reactions (noncatalyzed addition and isomerization, see discussion above), a specific feature of the nickel complexes is high activity in oligo- and polymerization. The key step of the oligo- and polymerization reactions is alkyne insertion into the metal−carbon bond, which proceeds easily for nickel compounds.[13] If a 1.0:1.0 ratio of the alkyne and PhSH was used in the reaction, about 10−12% of the alkyne was converted to oligomers, as evidenced by ^{1}H NMR, and with a 1.0:0.5 ratio of the alkyne and PhSH, an even larger amount of the oligomers was detected (15−25%). However, we have found that this side reaction can be suppressed by an excess of PhSH. With a 1.0:2.0 ratio of the alkyne and PhSH the amount of oligomers was below detectable limit of ^{1}H NMR. Unreacted benzenethiol can be easily recovered in the product purification stage and reused in the reaction. Unless otherwise noted, the 1.0:2.0 ratio of alkyne:ArSH was employed throughout this article.

Under the optimized conditions (2 mol % of $Ni(acac)_2$, 40 °C, 2:1 ratio of PhSH:alkyne, solvent-free) the addition reaction proceeded with high selectivity and yields for various alkynes and arylthiols (Table 4). Functional group-substituted alkynes react slower compared to hexyne-1 (entry 1, Table 4). In some cases heating at 60 °C is required to achieve high product yields (entries 4, 5, 7, 9, 10; Table 4). It is important to point out that the catalyst can tolerate typical organic functional groups such as OH, OMe, and MeCOO (entries 2−10; Table 4). In the developed catalytic system even the activated alkyne **1i** (phenylacetylene) reacts with benzenethiol in a Markovnikov manner, producing vinyl sulfides in 82% yield and 73:27 selectivity. This result is superior to the $NiCl_2$ catalyst (yield 27%, selectivity 3:10)[8] reported earlier. Except for phenylacetylene, in all other cases the catalytic reactions lead to β-vinyl sulfides with excellent regioselectivity (Table 4). Compounds **2c**−**2h**, without allylic hydrogen, did not isomerize under the studied conditions (see Scheme 2).

The developed synthetic procedure can be very easily scaled for the synthesis of various amounts of products (Table 5). The same yields and selectivity were obtained in the catalytic reactions performed with 5, 10, 100, and 300 mmol of the initial alkyne, which corresponds to 0.8−49.0 g of the isolated product (Table 5, entries 1−4).

We have found that the rate of the catalytic reaction was greatly decreased by traces of water. To verify this observation, we have undertaken a comparative study of $Ni(acac)_2$-catalyzed PhSH addition to **1a** in the presence and in the absence of added water. Particularly, 15 mol % of water significantly suppressed the catalytic reaction: 41% yield was observed after 10 min of reaction time, compared to 81% yield (entry 2, Table 2) observed after the same time without water addition. To eliminate the reproducibility problem, freshly dried $Ni(acac)_2$ should be used and the alkynes should be stored under molecular sieves.

In addition to the synthetic part it was very interesting to reveal the mechanism of the chemical reactions in the developed catalytic system. The plausible mechanism of the hydrogen−element (H−E) bond addition to alkynes may involve either an external nucleophile attack to the coordinated triple bond or an insertion reaction into the metal−element bond (Scheme 3).[6] If a terminal alkyne is involved in the reaction (R′ = H, Scheme 3), exactly the same β-substituted vinylic compounds may be formed as final products for both mechanisms. Therefore, on the basis of the product structure it is impossible to distinguish the mechanisms of the addition reaction. However, if an internal alkyne is involved, nuleophilic attack leads to *trans*-isomer **7**, while *cis*-isomer **8** is formed as a result of an insertion reaction (Scheme 3).[15]

To reveal the mechanism of the reaction, we have performed catalytic PhSH addition to 3-pentyn-1-ol (Scheme 4). In this case four products could be expected: compounds **9** and **10** if insertion reaction takes place and compounds **11** and **12** if nucleophilic attack is involved. After 8 h of reaction 86% conversion of the alkyne has been observed. Compounds **9** and **10** were formed with 1:1 ratio and 42% yield each; only trace amounts of **11** and **12** were detected (<2%). This experiment clearly indicates that insertion reaction is the key step of the C−S bond formation in the studied catalytic cycle.[16]

Another question concerns the nature of the catalyst in the studied system. It has been shown that H−E and E−E bond (E = S, Se) activation by transition metal complexes may produce mononuclear, dinuclear, or polymeric species.[10,17,18] In all

(12) It was shown that the isomerization reaction may proceed under transition metal-catalyzed, radical or photochemical conditions (refs 7 and 9). Therefore, different isomerization mechanisms may play the dominant role depending on reaction conditions and amount of catalyst.

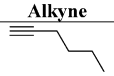
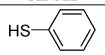
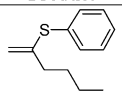
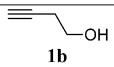
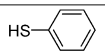
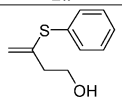
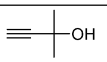
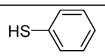
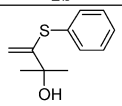
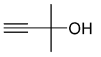
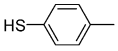
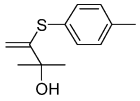
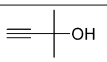
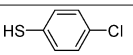
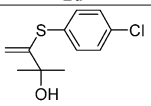
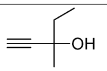
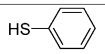
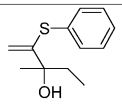
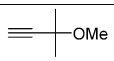
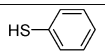
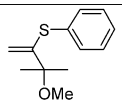
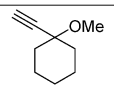
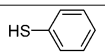
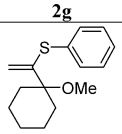
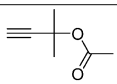
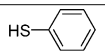
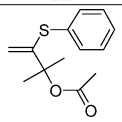
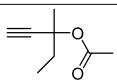
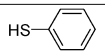
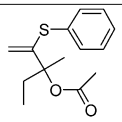
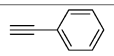
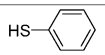
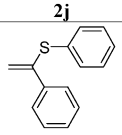
(13) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974.

(14) The *E*/*Z* ratio of anti-Markovnikov isomers was in the range 2:1−1:1. This suggests a radical nature of the side reaction.

(15) In Scheme 3 "E" means element (not electrophile) as usually accepted in the literature concerning E−H and E−E bond addition to unsaturated molecules (see reviews[6a−d]). *Trans* and *cis* notations indicate the position of the R and R′ groups.

(16) Longer heating at 40 °C resulted in isomerization of initially formed compounds **9** and **10** to **11** and **12**. Decrease in intensity of ^{1}H NMR signals of **9** and **10** was accompanied with simultaneous increase in intensity of corresponding signals of **11** and **12**. Therefore, **9** and **10** are the kinetic products of the *syn*-addition reaction.

Table 4. Ni-Catalyzed ArSH Addition to Various Alkynes[a]

Entry	Alkyne	ArSH	Product	Conditions	Yield, [b] %
1	 **1a**		 **2a**	40°C, 15 min	79 (94:5)[c]
2	 **1b**		 **2b**	40°C, 75 min	93 (>98:2)[c]
3	 **1c**		 **2c**	40°C, 30 min	80 (>98:2)[c]
4	 **1c**		 **2d**	60°C, 60 min	90 (>98:2)[c]
5	 **1c**		 **2e**	60°C, 70 min	81 (>98:2)[c]
6	 **1d**		 **2f**	40°C, 30 min	96 (>98:2)[c]
7	 **1e**		 **2g**	60°C, 3.5 h	84 (>98:2)[c]
8	 **1f**		 **2h**	40°C, 3 h	85 (>98:2)[c]
9	 **1g**		 **2i**	60°C, 3.5 h	96 (>98:2)[c]
10	 **1h**		 **2j**	60°C, 3.5 h	98 (>98:2)[c]
11	 **1i**		 **2k**	40°C, 8 min	82 (73:27)[c]

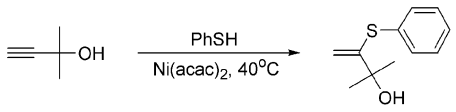
[a] Using 20 mmol of PhSH, 10 mmol of alkyne and 2 mol % of the catalyst under solvent free conditions (see experimental part for details). [b] After washing and filtering of crude mixture (see experimental part for details). [c] The regioselectivity of the addition reaction (the ratio of Markovnikov: anti-Markovnikov products).[14]

catalytic reactions discussed in the present study (Table 4) an insoluble dark brown polymer $[Ni(SAr)_2]_n$ was formed, as confirmed by elemental analysis. The important point is whether this polymer is an active catalyst or the major contribution to the product formation makes the remaining metal complex soluble in the liquid phase. To reveal the nature of the catalyst, we have performed a comparative study of two model reactions. The first reaction was performed using a 2:1 ratio of PhSH:**1a**

(17) (a) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Yu. *Organometallics* **2005**, *24*, 1275. (b) Ananikov, V. P.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *Organometallics* **2003**, *22*, 1414. (c) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *687*, 451.

(18) (a) Hannu-Kuure, M. S.; Wagner, A.; Bajorek, T.; Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *Main Group Chem.* **2005**, *4*, 49. (b) Hannu-Kuure, M. S.; Paldan, K.; Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *J. Organomet. Chem.* **2003**, *687*, 538. (c) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *J. Organomet. Chem.* **2001**, *623*, 168. (d) Dey, S.; Jain, V. K.; Varghese, B. *J. Organomet. Chem.* **2001**, *623*, 48. (e) Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *J. Organomet. Chem.* **1999**, *587*, 200. (f) Nakanishi, I.; Tanaka, S.; Matsumoto, K.; Ooi, S. *Acta Crystallogr., Sect. C* **1994**, *C50*, 58. (g) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736.

Table 5. Catalytic Benzenethiol Addition to 1c at Different Scales[a]

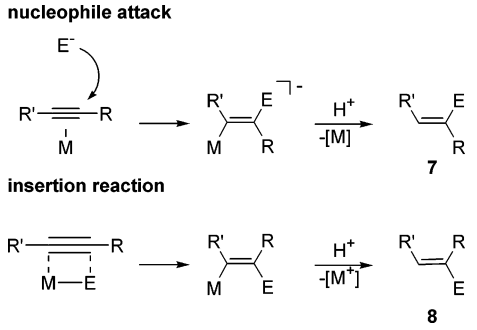


1c **2c**

entry	alkyne,[b] mmol	yield,[c] %	amount of product,[c] g
1	5	82	0.8
2	10	81	1.6
3	100	82	15.9
4	300	84	49.0

[a] A detailed description of the experiments is given in the Experimental Section. [b] Initial amount of alkyne. [c] After washing and filtering of the crude mixture (see Experimental Section for details).

Scheme 3



Scheme 4

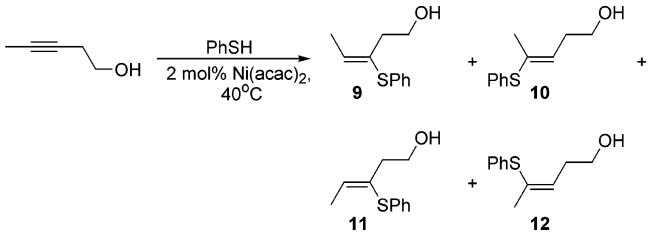
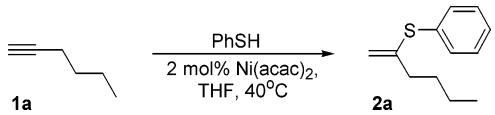


Table 6. Catalytic PhSH Addition to 1a in the Presence and in the Absence of the Solid Phase



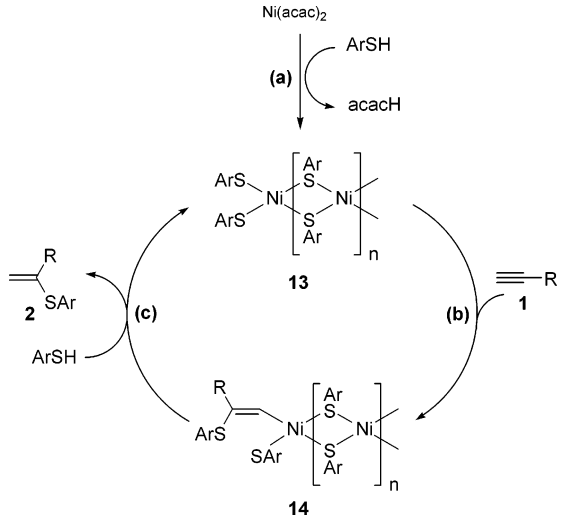
1a **2a**

		relative yield of **2a**,[a] %	
entry	time, min	heterogeneous reaction	without solid phase[b]
1	60	36	0
2	180	58	0
3	300	70	0

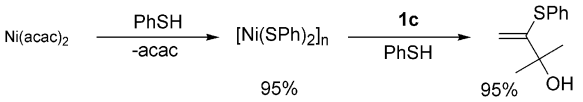
[a] Reaction mixtures stirred for 30 min were used as a reference point (see Experimental Section for details). [b] The precipitate was removed by centrifugation.

with 2 mol % $Ni(acac)_2$ in THF solution. The heterogeneous mixture was stirred at 40 °C for 30 min and used in NMR monitoring without further treatment. This experiment was designed as a model of the typical catalytic procedure employed in the present study. The second reaction was performed with the same amounts of reagents and catalyst, but the solid phase was removed by centrifugation. Both reactions were investigated with ^1H NMR monitoring (Table 6). Under heterogeneous conditions (the first reaction) the yield of the product was

Scheme 5



Scheme 6



smoothly increased, while no product formation was observed in the second reaction (Table 6). The results clearly indicate that polymeric metal species represent an active form of the catalyst in the studied system. The contribution of the remaining metal complex available in the liquid phase is negligible.

The plausible catalytic reaction mechanism is shown in Scheme 5. It involves alkyne insertion as a key C−S bond formation step and polymeric nickel species as an active form of the catalyst. The mechanism also explains the observed dependence of the product yield on the alkyne:PhSH ratio. Trapping intermediate complex **14** with PhSH leads to product formation and suppresses alkyne insertion into the Ni−C bond of **14**.

To confirm the proposed mechanism, we have performed a series of stoichiometric reactions (Scheme 6). The polymeric compound $[Ni(SPh)_2]_n$ has been isolated in 95% yield after the reaction of $Ni(acac)_2$ with PhSH. According to the elemental analysis, both acac ligands were substituted with PhS groups (see Experimental Section for details). This reaction corresponds to stage (**a**) of the catalytic cycle (Scheme 5). Isolated polymeric compound $[Ni(SPh)_2]_n$ reacted with alkyne in the presence of PhSH, leading to the expected Markovnikov-type product in 95% yield (Scheme 6).[19] The reaction corresponds to stages (**b**) and (**c**) of the catalytic cycle (Scheme 5).

In addition to the stoichiometric reactions, the isolated polymeric compound was successfully utilized in the catalytic reaction. Using the isolated Ni compound as a catalyst (2 mol %) in the PhSH addition reaction to **1c** the complete conversion of the alkyne and 98:2 selectivity were observed after 30 min at 40 °C (see Experimental Section for details). The same results were observed using $Ni(acac)_2$ as the initial form of the catalyst (entry 3, Table 4).

It was impossible to characterize polymeric compound $[Ni(SPh)_2]_n$ by NMR, since it was insoluble in common organic solvents. To investigate the structure and morphology of the Ni species, we have carried out light microscopy and scanning

(19) In agreement with proposed mechanism, no reaction took place in the absence of PhSH.

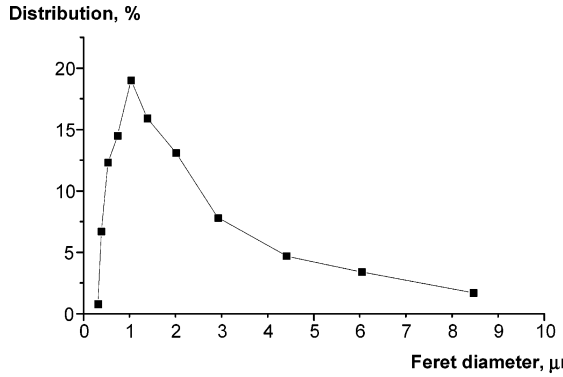


Figure 1. Size distribution of $[Ni(SPh)_2]_n$ particles determined by light microscopy.

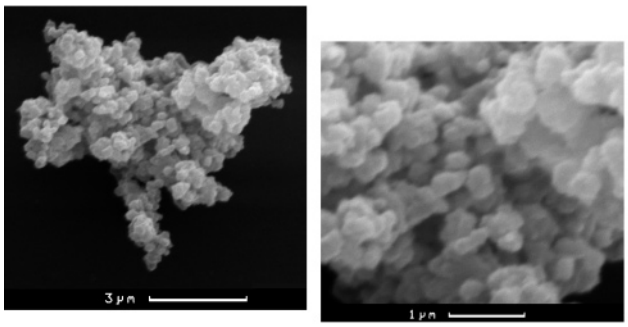


Figure 2. SEM images of catalyst particle (A) and magnified central region of this particle (B). Particle size is 6.5 × 8.2 μm (largest dimensions), particle area is 30.7 μm^2, and Feret diameter is 6.2 μm.

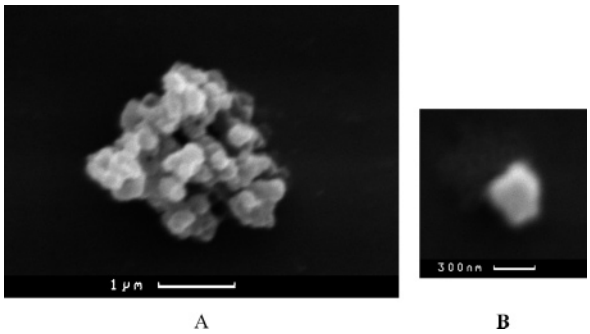


Figure 3. SEM images of two different catalyst particles: (A) particle size 2.4 × 2.4 μm (largest dimensions), particle area 3.6 μm^2, Feret diameter 2.1 μm; (B) Feret diameter 380 nm.

electron microscopy (SEM) studies. The distribution of particle sizes determined by light microscopy in solution is shown in Figure 1. About 75% of observed particles were 0.5−2.0 μm in size. The unsymmetrical form of the distribution curve indicates the tendency for particle adhesion and a noticeable amount of larger particles of 4.5−8.5 μm size were also detected (∼10%). The SEM study has indicated that both larger and smaller particles have the same structure and consist of nanosized building units. Examples of 6.2 and 2.1 μm particles are shown in Figure 2 and Figure 3A, respectively. Analysis of the SEM images gave the typical size of the unit of 300 ± 90 nm. An example of the individual nanosized unit is shown in Figure 3B. Therefore, the size of the building unit is close to the upper range observed in nanocatalytic systems.[20] We believe that the nanosized structure of the catalyst is a key factor responsible for high activity of the Ni complexes.

3. Conclusions

In the present article we describe a new catalytic system for highly regioselective arylthiol addition to terminal alkynes resulting in selective formation of β-vinyl sulfides. The catalytic reaction is based on the inexpensive and easily available compound nickel acetylacetonate as a catalyst precursor.

In the developed system atom economy of the addition reaction is combined with ecological and economical benefits of the solvent-free methodology in agreement with green chemistry requirements. To minimize solvent waste, chromatography was avoided in the product purification stage. The developed synthetic procedure can be easily scaled-up to prepare up to 50 g of products with high selectivity.

It is very important to note that nickel provides useful replacement for palladium catalysts. Moreover, the nickel-based catalyst is more efficient and selective. The mechanistic investigations revealed that alkyne insertion into the Ni−S bond is a key step of the catalytic cycle. The $[Ni(SAr)_2]_n$ species represent an active form of the catalyst, which is built from nanosized structural units.

Further studies concerning the application of nickel-catalyzed reactions in carbon−element bond formation as well as structural studies of the catalyst are in progress.

3. Experimental Section

3.1. General Procedures. Unless otherwise noted, the synthetic work was carried out under an argon atmosphere. The alkynes **1e**,[21] **1f**,[22] **1g**,[23] and **1h**[23] were prepared according to published procedures. Other reagents were obtained from Acros and Lancaster and 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. Solvents were purified according to published methods.

All NMR measurements were performed using a three-channel Bruker DRX-500 spectrometer operating at 500.1 and 125.8 MHz for ^1H and ^{13}C nuclei, respectively. The spectra were processed on a Silicon Graphics workstation using the XWINMR software package. All 2D spectra were recorded using an inverse triple resonance probehead with an active shielded Z-gradient coil. ^1H and ^{13}C chemical shifts are reported relative to the corresponding solvent signals used as internal reference. Estimated errors in the yield determination by ^1H NMR are <2% (Tables 1−3, 6).

3.2. General Synthetic Procedure for 2a−2k. The alkyne (1.0×10^{-2} mol) was added to $Ni(acac)_2$ (2.0×10^{-4} mol) and stirred at room temperature until a uniform green suspension was formed (ca. 5−10 min). PhSH (2.0×10^{-2} mol) was added to the stirred mixture at ∼5 °C (water/ice bath). The stirring was continued for an additional 10 min, and the color of the suspension changed from green to dark. The reaction was carried out at 40−60 °C under stirring until complete conversion of the alkyne (small aliquots were taken from the mixture and checked by ^1H NMR). See Table 4 for details about reaction time and temperature.[24]

The reaction mixture was filtered through Celite using CH_2Cl_2 as an eluent (40 mL). Then 20 mL of hexane was added to the

(20) Typically accepted range of particles sizes for the nanocatalytic systems is 1−100 nm; see reviews: (a) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103. (b) Buchachenko, A. L. *Russ. Chem. Rev.* **2003**, *72*, 375. (c) Bukhtiyarov, V. I.; Slin'ko, M. G. *Russ. Chem. Rev.* **2001**, *70*, 147.

(21) Wagner, C. E.; Shea, K. J. *Org. Lett.* **2004**, 313.

(22) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546.

(23) Chakraborti, A. K.; Sharma, L.; Gulhane, R.; Shivani. *Tetrahedron* **2003**, *59*, 7661.

(24) Catalyst activity depends on the amount of water in the reaction mixture. NMR monitoring (or GC) is the easiest way to determine appropriate reaction time.

mixture after filtration, and remaining PhSH was removed by extraction with 25 mL of aqueous NaOH (5 M).[25] The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The products were obtained as light brown oils (92−95% purity as confirmed by NMR). Highly pure, colorless products were obtained after distillation in a vacuum (98+% as confirmed by NMR).

The products $H_2C{=}C(SPh){-}(CH_2)_3{-}CH_3$ (**2a**),[26] $H_2C{=}C(SPh){-}C(CH_3)_2OH$ (**2c**),[7b] and $H_2C{=}C(SPh){-}Ph$ (**2k**),[27] were identified according to the published data. The data for the other compounds are given below.

2-(Phenylthio)hexene, $H_2C{=}C(SPh)$-$CH_2{-}CH_2{-}CH_2{-}CH_3$ (2a): light brown oil, 79% (1.52 g); yield after distillation 58% (1.12 g), bp 39−42 °C, 1.5×10^{-2} Torr, colorless oil.

2-(Phenylthio)-4-hydroxy-1-butene, $H_2C{=}C(SPh){-}CH_2{-}CH_2{-}OH$ (2b): light brown oil, 93% (1.68 g); yield after distillation 70% (1.26 g), bp 75−77 °C, 1.0×10^{-2} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 1.97 (s, 1H), 2.48 (dt, J = 7.3, J = 0.8, 2H), 3.77 (t, J = 7.3, 2H), 5.00 (s, 1H), 5.24 (d, J = 0.8, 1H), 7.25−7.35 (m, 3H), 7.43 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 39.56, 60.74, 115.07, 127.97, 129.16, 132.41, 133.13, 142.16. Anal. Calcd for $C_{10}H_{12}OS$: C 66.63; H 6.71; S 17.79. Found: C 66.56; H 6.86; S 17.73. Mass spectrum (EI): m/e 180 (M^+ 37%).

2-(Phenylthio)-3-hydroxy-3-methyl-1-butene, $H_2C{=}C(SPh){-}C(CH_3)_2OH$ (2c): light brown liquid, 80% (1.55 g); yield after distillation 55% (1.07 g), bp 65−66 °C, 7.0×10^{-3} Torr, colorless oil.

2-[(*p*-Methylphenyl)thio]-3-hydroxy-3-methyl-1-butene, $H_2C{=}C(p\text{-}MeC_6H_4S)$-$C(CH_3)_2OH$ (2d): brown liquid, 90% (1.87 g); yield after distillation 56% (1.17 g), bp 75−80 °C, 9.0×10^{-3} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 1.51 (s, 6H), 2.29 (br s, 1H), 2.34 (s, 3H), 4.60 (s, 1H), 5.37 (s, 1H), 7.14 (m, 2H), 7.36 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 21.08, 29.63, 73.80, 108.79, 129.50, 130.01, 134.09, 138.22, 155.55. Anal. Calcd for $C_{12}H_{16}OS$: C 69.19; H 7.74; S 15.39. Found: C 69.20; H 7.79; S 15.03. Mass spectrum (EI): m/e 208 (M^+ 60%).

2-[(*p*-Chlorophenyl)thio]-3-hydroxy-3-methyl-1-butene, $H_2C{=}C(p\text{-}ClC_6H_4S){-}C(CH_3)_2OH$ (2e): light brown liquid, 81% (1.85 g); yield after distillation 61% (1.40 g), bp 96−100 °C, 1.0×10^{-3} Torr, colorless oil. ^{1}H NMR (500 MHz; DMSO-d_6; δ, ppm; J, Hz): 1.35 (s, 6H), 4.55 (s, 1H), 5.45 (s, 1H), 7.41−7.46 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz; DMSO-d_6; δ, ppm): 29.16, 71.91, 109.48, 128.94, 132.28, 132.49, 134.27, 154.83. Anal. Calcd for $C_{11}H_{13}ClOS$: C 57.76; H 5.73; S 14.02; Cl 15.50. Found: C 57.71; H 5.68; S 13.92; Cl 15.40. Mass spectrum (EI): m/e 228 (M^+ 92%).

2-(Phenylthio)-3-hydroxy-3-methyl-1-pentene, $H_2C{=}C(SPh){-}C(OH)(CH_3){-}CH_2{-}CH_3$ (2f): light brown liquid, 96% (2.0 g); yield after distillation 76% (1.58 g), bp 73−75 °C, 1.0×10^{-2} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 0.90 (t, J = 7.3, 3H), 1.46 (s, 3H), 1.72−1.87 (m, 2H), 2.03 (br s, 1H), 4.70 (s, 1H), 5.38 (s, 1H), 7.28−7.37 (m, 3H), 7.50 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 8.13, 27.50, 33.95, 76.41, 110.41, 128.12, 129.23, 133.22, 134.05, 153.50. Anal. Calcd for $C_{12}H_{16}OS$: C 69.19; H 7.74; S 15.39. Found: C 68.91; H 7.87; S 15.45. Mass spectrum (EI): m/e 208 (M^+ 20%).

2-(Phenylthio)-3-methoxy-3-methyl-1-butene, $H_2C{=}C(SPh){-}C(OCH_3)(CH_3)_2$ (2g): yellow liquid, 84% (1.75 g); yield after distillation 76% (1.58 g), bp 65−68 °C, 5.0×10^{-3} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 1.49 (s, 6H), 3.23 (s, 3H), 4.58 (s, 1H), 5.20 (s, 1H), 7.31−7.39 (m, 3H), 7.50 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 26.41, 50.69, 77.94, 109.48, 128.33, 129.24, 132.89, 135.08, 153.66. Anal. Calcd for $C_{12}H_{16}OS$: C 69.19; H 7.74; S 15.39. Found: C 68.89; H 7.75; S 15.10. Mass spectrum (EI): m/e 208 (M^+ 9%).

2-(Phenylthio)-2-(1-methoxycyclohexyl)-1-ethene, $H_2C{=}C(SPh){-}C_6H_{11}(OCH_3)$ (2h): light brown liquid, 85% (2.11 g); yield after distillation 65% (1.61 g), bp 71−73 °C, 5.0×10^{-3} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 1.24 (m, 2H), 1.50−1.69 (m, 8H), 3.18 (s, 3H), 4.62 (s, 1H), 5.21 (s, 1H), 7.20−7.38 (m, 3H), 7.50 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 21.78, 25.78, 34.08, 49.63, 78.55, 110.07, 127.11, 129.24, 135.17, 133.08, 153.68, 128.08. Anal. Calcd for $C_{15}H_{20}OS$: C 72.53; H 8.12; S 12.91. Found: C 72.21; H 7.82; S 13.15. Mass spectrum (EI): m/e 248 (M^+ 3%).

2-(Phenylthio)-3-acetoxy-3-methyl-1-butene, $H_2C{=}C(SPh){-}C(OOC{-}CH_3)(CH_3)_2$ (2i): light brown liquid, 96% (2.27 g); yield after distillation 79% (1.87 g), bp 91 °C, 3.0×10^{-2} Torr, colorless oil. ^{1}H NMR (500 MHz; DMSO-d_6; δ, ppm; J, Hz): 1.60 (s, 6H), 1.97 (s, 3H), 4.59 (s, 1H), 5.37 (s, 1H), 7.38−7.45 (m, 5H). $^{13}C\{^1H\}$ NMR (126 MHz; DMSO-d_6; δ, ppm): 21.18, 26.54, 80.99, 110.36, 128.03, 129.09, 131.66, 133.27, 150.53, 168.39. Anal. Calcd for $C_{13}H_{16}O_2S$: C 66.07; H 6.82; S 13.57. Found: C 66.30; H 7.10; S 13.24. Mass spectrum (EI): m/e 236 (M^+ 39%).

2-(Phenylthio)-3-acetoxy-3-methyl-1-pentene, $H_2C{=}C(SPh){-}C(OOC{-}CH_3)(CH_3){-}CH_2{-}CH_3$ (2j): light yellow liquid, 98% (2.45 g); yield after distillation 87% (2.18 g), bp 93−97 °C, 3.0×10^{-2} Torr, colorless oil. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 0.90 (t, 3H, J = 7.5), 1.70 (s, 3H), 1.94 (m, 1H), 2.03 (m, 1H), 2.05 (s, 3H), 4.67 (s, 1H), 5.26 (s, 1H), 7.31−7.36 (m, 3H), 7.49 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm): 7.98, 21.97, 23.04, 32.34, 85.04, 110.54, 128.34, 129.24, 132.51, 134.72, 150.56, 169.58. Anal. Calcd for $C_{14}H_{18}O_2S$: C 67.16; H 7.25; S 12.81. Found: C 67.07; H 7.27; S 12.74. Mass spectrum (EI): m/e 250 (M^+ 59%).

2-(Phenylthio)-2-phenyl-1-ethene, $H_2C{=}C(SPh){-}Ph$ (2k): light brown liquid, 82% (1.74 g); yield after distillation 50% (1.06 g), bp 87−89 °C, 3.0×10^{-2} Torr, colorless oil.

3.3. Synthetic Procedure at Different Scales. The same general synthetic procedure has been used (see 3.2) with the following amounts of reagents: alkyne (5.0×10^{-3} mol), $Ni(acac)_2$ (1.0×10^{-4} mol), and PhSH (1.0×10^{-2} mol) for 5 mmol scale reaction (Table 5, entry 1); alkyne (0.1 mol), $Ni(acac)_2$ (2.0×10^{-2} mol), and PhSH (0.2 mol) for 100 mmol scale reaction (Table 5, entry 3); alkyne (0.3 mol), $Ni(acac)_2$ (6.0×10^{-2} mol), and PhSH (0.6 mol) for 300 mmol scale reaction (Table 5, entry 4).

3.4. PhSH Addition to 3-Pentyn-1-ol (Scheme 4). The alkyne (2.0×10^{-3} mol) was added to $Ni(acac)_2$ (4.0×10^{-5} mol) and stirred at room temperature until a uniform green suspension was formed (ca. 5−10 min). PhSH (4.0×10^{-3} mol) was added to the stirred reaction mixture at ca. 5 °C (water/ice bath). The stirring was continued for an additional 10 min, and the color of the suspension changed from green to dark. The reaction was carried out at 40 °C under stirring. The structure of the products was determined with 2D COSY, NOESY, HMQC, and HMBC NMR experiments.

3.5. Catalytic PhSH Addition to 1a in the Presence and in the Absence of Solid Phase. Reaction in the Presence of the Solid Phase. The alkyne **1a** (0.082 g, 1.0×10^{-3} mol) and THF (0.5 mL) were added to $Ni(acac)_2$ (0.005 g, 2.0×10^{-5} mol) and stirred until a homogeneous green solution was formed (ca. 5−10 min). PhSH (0.220 g, 2.0×10^{-3} mol) was added to the stirred solution at ca. 5 °C (water/ice bath), and stirring was continued for an additional 10 min. The color of the solution changed from green to dark and an insoluble dark brown precipitate was formed. The reaction was carried out with stirring at 40 °C and monitored with ^{1}H NMR (Table 6).

(25) Unreacted PhSH can be easily recovered from the water phase by addition of aqueous HCl and extraction with hexane.

(26) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L. *Synthesis* **1987**, 1034.

(27) Labiad, B.; Villemin, D. *Synthesis* **1989**, 143.

Reaction in the Absence of the Solid Phase. The alkyne **1a** (0.082 g, 1.0×10^{-3} mol) and THF (0.5 mL) were added to Ni(acac)$_2$ (0.005 g, 2.0×10^{-5} mol) until a homogeneous green solution was formed (ca. 5−10 min). PhSH (0.220 g, 2.0×10^{-3} mol) was added to the stirred solution at ca. 5 °C (water/ice bath), and stirring was continued for an additional 10 min. The color of the solution changed from green to dark, and an insoluble dark brown precipitate was formed. The temperature was increased to 40 °C, and stirring was continued for 5 min. The precipitate was removed by centrifugation (6000 rpm, 15 min). The reaction was carried out with stirring at 40 °C and monitored with ^{1}H NMR (Table 6).

3.6. Preparation of [Ni(SPh)$_2$]$_n$ (Scheme 6). PhSH (7.7×10^{-3} mol) was added to Ni(acac)$_2$ (1.1×10^{-3} mol) at ca. 5 °C (water/ice bath), leading to the formation of dark brown suspension. The suspension was stirred for 10 min at ca. 5 °C (all manipulations were carried out in air). The precipitate was separated by centrifugation (6000 rpm, 15 min), washed with hexane (3 × 5 mL) and THF (3 × 5 mL), and dried in a vacuum. Yield: 95% (0.29 g) of a dark brown solid. Anal. Calcd for $C_{12}H_{10}NiS_2$: C 52.03; H 3.64; Ni 21.19; S 23.15. Found: C 52.22; H 3.79; Ni 21.07; S 22.90.

3.7. Reaction of [Ni(SPh)$_2$]$_n$ with Alkyne (Scheme 6). The alkyne **1c** (2.0×10^{-3} mol), PhSH (2.0×10^{-3} mol), and THF (0.5 mL) were added to [Ni(SPh)$_2$]$_n$ (1.0×10^{-3} mol) and stirred at 40 °C until complete conversion of the alkyne (∼45 min) as confirmed by NMR.

3.8. Catalytic Reaction Using [Ni(SPh)$_2$]$_n$ as a Catalyst. The alkyne **1c** (1.0×10^{-3} mol) was added to [Ni(SPh)$_2$]$_n$ (2.0×10^{-5} mol) and stirred at room temperature until a uniform dark brown suspension was formed (ca. 5−10 min). PhSH (2.0×10^{-3} mol) was added to the stirred reaction mixture at ca. 5 °C (water/ice bath), and stirring was continued for 10 min. The reaction was carried out with stirring at 40 °C and monitored with ^{1}H NMR until complete conversion of the alkyne (∼30 min).

3.9. SEM and Light Microscopy Studies.[28] **Sample Preparation.** The alkyne **1i** (1.84 g, 1.8×10^{-2} mol) was added to Ni(acac)$_2$ (0.093 g, 3.6×10^{-4} mol) and stirred until a homogeneous green solution was formed (ca. 5−10 min). PhSH (3.98 g, 3.6×10^{-2} mol) was added to the stirred solution at ca. 5 °C (water/ice bath), and stirring was continued for an additional 10 min. The color of the solution changed from green to dark and an insoluble dark brown precipitate was formed. The reaction mixture was heated at 40 °C for 30 min, followed by adding 10 mL of toluene and washing with 20 mL of aqueous NaOH (5 M) to remove unreacted PhSH. The suspension of the precipitate in toluene was used in the light microscopy study. For the SEM study the precipitate was dried in a vacuum.

General Comments. Image processing, object analysis, size determination, and statistical analysis were performed using the UTHSCSA ImageTool 3.0 program.

Light Microscopy. The analysis was performed in a 10 μm × 10 μm sample area containing 358 particles. The particles were classified into 11 groups according to the occupied area. The distribution of the particles in each group (mean Feret diameter[29] in μm and percentage): 0.32, 0.8%; 0.39, 6.7%; 0.53, 12.3%; 0.74, 14.5%; 1.03, 19.0%; 1.39, 15.9%; 2.01, 13.1%; 2.92, 7.8%; 4.41, 4.7%; 6.04, 3.4%; 8.46, 1.7% (for graphical representation see Figure 1).

SEM Study. The sizes of 300 ± 90 nm were determined for 50 building units selected at random. Examples of SEM images are shown in Figures 2 and 3, and an example of an individual structural unit is represented in Figure 3B.

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(28) In the studied system particle size and distribution depend on the sample preparation conditions. Therefore, these values obtained should be used as an estimation only.

(29) Feret diameter is the diameter of a circle having the same area as the object. It was computed as $(4 \times area/PI)^{1/2}$, where *area* is the area of the object.