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Nickel(II) Chloride-Catalyzed Regioselective Hydrothiolation of Alkynes

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Abstract: Regioselective Markovnikov-type addition of PhSH to alkynes (HC≡C-R) has been performed using easily available nickel complexes. The non-catalytic side reaction leading to anti-Markovnikov products was suppressed by addition of γ-terpinene to the catalytic system. The other side reaction leading to the bis(phenylthio)alkene was avoided by excluding phosphine and phosphite ligands from the catalytic system. It was found that catalytic amounts of Et_3N significantly increased the yield and selectivity of the catalytic reaction. Under optimized conditions high product yields of 60–85% were obtained for various alkynes [R = *n*-C_5H_{11}, CH_2NMe_2, CH_2OMe, CH_2SPh, $C_6H_{11}(OH)$, $(CH_2)_3CN$]. The X-ray structure of one of the synthesized products is reported.

Keywords: alkynes; catalytic reaction; nickel; regioselectivity; γ-terpinene; vinyl sulphides

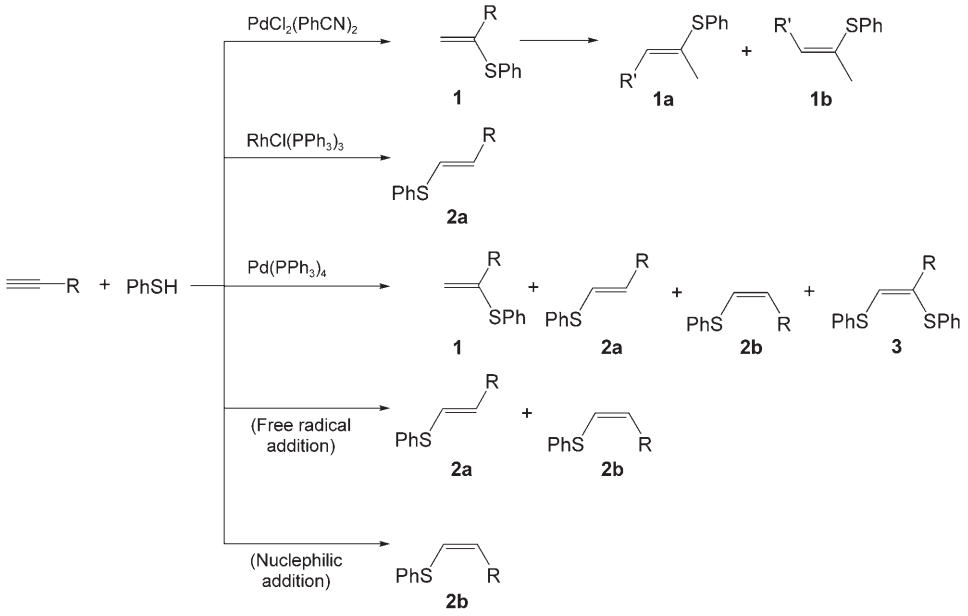
Introduction

Addition of the S–H bond to alkynes is an important method in the synthesis of vinyl sulphides.[1–3] It was shown that $Pd(OAc)_2$ catalyzes the selective synthesis of (phenylthio)alkenes **1**,[4] while the chloride complex of palladium $PdCl_2(PhCN)_2$ catalyzes Markovnikov-type addition of PhSH to the C≡C bond (Scheme 1) followed by isomerization of **1** to internal alkenes **1a** and **1b** (for R groups with α-H atom).[5,6] Wilkinson's complex $RhCl(PPh_3)_3$ catalyzes the regio- and stereoselective addition of benzenethiol to alkynes leading to the anti-Markovnikov product **2a** with *trans*-stereochemistry.[6] A mixture of compounds **1**, **2a**, **2b** and **3** was obtained when a phosphine complex of Pd(0) was used as the catalyst (Scheme 1).[6] The non-catalytic free radical addition of benzenethiol to alkynes gave a mixture of anti-Markovnikov isomers **2a** and **2b**.[7–9] Under nucleophilic conditions the reaction proceeds in a more selective manner leading to the *cis*- isomer **2b**.[10,11]

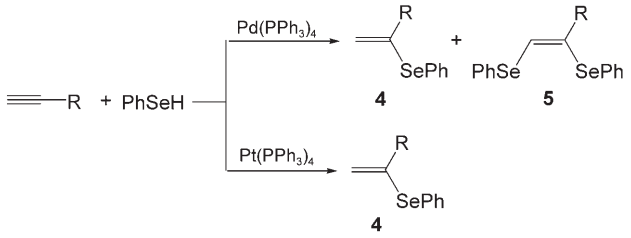
It is interesting to note that the $Pd(PPh_3)_4$-catalyzed reaction led to the formation of bis(phenylthio)alkene **3** as a by-product (Scheme 1).[6] A similar process involving PhSeH addition to alkynes gave the mixture of **4** and **5** (Scheme 2).[12] Selective addition of the Se–H bond was achieved using $Pt(PPh_3)_4$ as the catalyst (Scheme 2).[12]

A mechanistic study has shown that hydride complex **6**, formed after oxidative addition of the Se–H bond, can react with the second PhSeH molecule leading to the complex **7** (Scheme 3). The formation of complex **6** (M = Pt) and evolution of molecular hydrogen were detected by NMR.[12] The structure of complex **7** (M = Pd, Pt) was established by independent synthesis using the oxidative addition reaction of PhSe-SePh to $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$.[12] Alkyne insertion into the M–Se bond of **7** followed by C–Se reductive elimination gave the bis(phenylseleno)alkene **5**. Alkyne insertion into the M–Se bond of **6** followed by C–H reductive elimination led to the Markovnikov product **4** (Scheme 3). Another pathway leading to **4** involves protonolysis of the σ-vinyl complex (obtained after alkyne insertion to the M–E bond of **7**; E = S, Se) as proposed for the PhSeH[12] and PhSH[4–6] addition reactions.

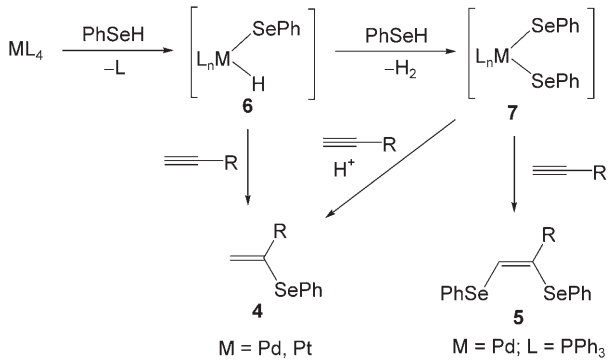
The aim of the present study was to develop a convenient practical method for synthesis of the Markovnikov product (**1**) by addition of benzenethiol to terminal



Scheme 1.



Scheme 2.



Scheme 3.

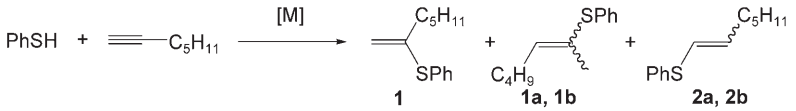
alkynes, as well as to study the effect of the phosphine ligand in this reaction.

Results and Discussion

At first we have studied the catalytic activity of $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ in the model reaction of PhSH addition to 1-heptyne. We have found that in the case of the palladium complex the mixture of **1**, **2a** + **2b** and **3** with the yields of 20, 25 and 30%, respectively, was formed. These results are in agreement with those of a previous study performed for another alkyne.[6] NMR monitoring of the reaction of PhSH with $Pd(PPh_3)_4$ detected the formation of molecular hydrogen (see Experimental Section for details). Therefore, the $Pd(PPh_3)_4$-catalyzed PhSH addition reaction proceeds in the same manner as the reaction involving PhSeH studied earlier (Scheme 3).[12] The platinum complex $Pt(PPh_3)_4$ was not an efficient catalyst of alkyne hydrothiolation. In the studied model reaction of PhSH addition to 1-heptyne the non-catalytic products **2a** + **2b** were mainly formed with 40% yield, and the yield of the Markovnikov product **1** was $<40\%$. These results are also in agreement with the literature data, where poor catalytic activity of $Pt(PPh_3)_2(CH_2{=}CH_2)$ has been reported.[6] Since complete separation of product **1** from compounds **2a**, **2b** and **3** is not possible with conventional purification techniques, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ can hardly be used for the selective synthesis of **1**.

Next, we have studied the catalytic activity of chloride complexes of different transition metals (Table 1). In the model reaction of addition of PhSH to 1-heptyne the yield of the Markovnikov product **1** was rather poor for all studied metal complexes. In the case of K_2PtCl_4 the catalytic product **1** was not formed at all (Table 1, entry 3). For $PdCl_2$ and $NiCl_2$ the non-catalytic pathway leading to **2a** and **2b** made the major contribution to the reaction (Table 1, entries 1, 4), the selectivity was 3/10 and 1/5, respectively (the ratio of **1** + **1a** + **1b** : **2a** + **2b** will be considered as selectivity throughout this article). Only for the $RuCl_3$ catalytic and non-catalytic products were formed with comparable yields of

Table 1. The addition of PhSH to 1-heptyne catalyzed by different transition metal chloride complexes.[a]



Entry	Complex	Yield [%][b]			
		Without Et_3N		With Et_3N[c]	
		1+**1a**+**1b**	**2a**+**2b**	**1**+**1a**+**1b**	**2a**+**2b**
1	$PdCl_2$	20	65	73	4
2	$RuCl_3$	29	41	83	10
3	K_2PtCl_4	0	90	75	12
4	$NiCl_2$	15	75	84	11

[a] 1.0 mmol of PhSH, 0.5 mmol of alkyne, 3 mol % of metal complex in 1 mL of toluene at 120 °C for 3 h in a sealed tube with stirring.
[b] Total yield of vinyl sulphides **1**–**2** determined by NMR and calculated based on alkyne.
[c] One equivalent of Et_3N was added for each chloride atom of the metal complex (6 mol % for $PdCl_2$ and $NiCl_2$, 9 mol % for $RuCl_3$, 12 mol % for K_2PtCl_4).

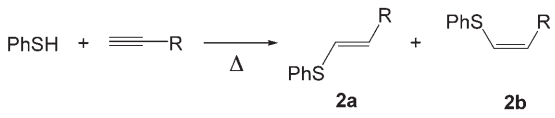
29% and 41%, which corresponds to a 7/10 selectivity (Table 1, entry 2). In spite of the poor yield and selectivity, there is an important advantage of the chloride complexes, namely the absence of the side reaction leading to bis(phenylthio)alkene **3** [*cf.* $Pd(PPh_3)_4$ and $PdCl_2$].

The direction of the addition reaction was dramatically changed upon addition of catalytic amounts of Et_3N. The Markovnikov product **1** was formed with high yields of 75–86%. The biggest effect was observed for $PdCl_2$ and the selectivity was changed from 3/10 to 18/1 (Table 1, entry 1). In the presence of catalytic amounts of triethylamine the Markovnikov product was the major one for all studied complexes (Table 1, entries 1–4). For the nickel-catalyzed reaction the selectivity changed from 1/5 to 8/1 (Table 1, entry 4).

Although the selectivity of the $NiCl_2$-catalyzed reaction was not the highest one we have decided to study it in detail for two reasons: 1) Ni complexes are cheap and easily available; and 2) the application of Ni complexes in the catalytic E–H bond addition to unsaturated compounds is scarcely studied.[13] Particularly, recent studies have proven a great potential of Ni complexes in selective addition of P–H[13c–e] and S–H[13b] to alkynes.

We made an attempt to suppress the non-catalytic side reaction (Scheme 1). For this reason we have studied the reaction between benzenethiol and alkynes without a catalyst (Table 2). Heating PhSH and alkyne in toluene at 120 °C for 3 h resulted in the mixture of **2a**+**2b** in 13% and 20% yields for 1-heptyne and methyl propargyl ether, respectively (Table 2, entries 1 and 2). Activated alkynes (phenylacetylene and methyl propiolate) reacted with PhSH with quantitative yields (Table 2, entries 3 and 4). However, the side-reaction can be suppressed by addition of a radical trap – γ-terpinene (1-isopropyl-4-methylcyclohexa-1,4-diene). In the cases of 1-heptyne and methyl propargyl ether only the traces of the anti-

Table 2. The influence of γ-terpinene on the non-catalytic addition of PhSH to alkynes.[a]



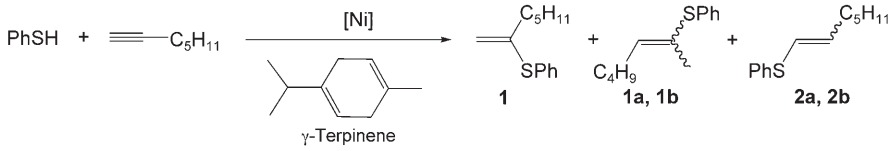
Entry	Alkyne	Yield of **2a**+**2b** [%][b]	
		Without γ-terpinene	With γ-terpinene[c]
1	HC≡C-*n*-C_5H_{11}	13	3
2	HC≡C-CH_2OMe	20	<2
3	HC≡C-Ph	99	56
4	HC≡C-COOMe	90	20

[a] 1 mmol of PhSH, 0.5 mmol of alkyne, in 1 mL of toluene at 120 °C for 3 h in a sealed tube.
[b] Determined by NMR and calculated based on initial amount of alkyne.
[c] 1 equivalent to alkyne.

Markovnikov products **2a** and **2b** (2–3%) were obtained (Table 2, entries 1 and 2). For the activated alkynes the yields of the radical reaction were significantly decreased from 99% and 90% to 56% and 20%, respectively (Table 2, entries 3 and 4). The remaining part of the anti-Markovnikov products may be connected with a Michael-type addition.

The radical side reaction was efficiently suppressed by γ-terpinene under the catalytic conditions as well. Even a small amount of the radical trap (0.05 equivalents to alkyne) increased the selectivity of the PhSH addition to 1-heptyne from 7.9/1 to 10.9/1 towards the Markovnikov product (Table 3, entries 1 and 2). Increasing the amount of γ-terpinene further improved the selectivity of the reaction (Table 3, entries 1–4). The highest value

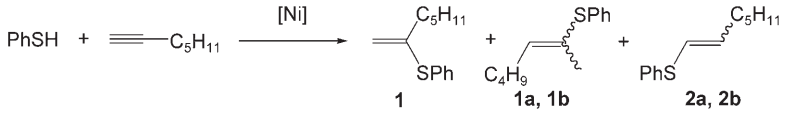
Table 3. The influence of the γ-terpinene on the selectivity of the catalytic PhSH addition to 1-heptyne.[a]



Entry	γ-Terpinene[b]	Yield [%][c]	Selectivity[d]
1	0.00	95	7.9:1.0
2	0.05	95	10.9:1.0
3	0.20	95	13.0:1.0
4	1.00	95	19.0:1.0

[a] 1 mmol of PhSH, 0.5 mmol of alkyne, 3 mol % $NiCl_2$, 6 mol % Et_3N in 1 mL of toluene at 120 °C for 3 h in a sealed tube with stirring.
[b] Equivalents to alkyne.
[c] Determined by NMR and calculated based on initial amount of alkyne.
[d] The ratio of Markovnikov/anti-Markovnikov products (**1**+**1a**+**1b**):(**2a**+**2b**).

Table 4. Effect of solvent on the catalytic addition of PhSH to 1-heptyne.[a]



Entry	Solvent	Yield [%][b]	Selectivity[d]
1	$CHCl_3$	99	19:1
2	Dioxane	95	18:1
3	Hexane	92	17:1
4	Toluene	90	17:1
5	Acetonitrile	81[c]	18:1
6	THF	79	15:1

[a] 1 mmol of PhSH, 0.5 mmol of alkyne, 0.5 mmol of γ-terpinene, 3 mol % of $NiCl_2$, 6 mol % of Et_3N and 1 mL of solvent at 95 °C for 10 h in a sealed tube with stirring.
[b] Determined by NMR and calculated based on initial amount of alkyne.
[c] Unknown products were formed with a yield of about 10–15%.
[d] The ratio of Markovnikov/anti-Markovnikov products (**1**+**1a**+**1b**):(**2a**+**2b**).

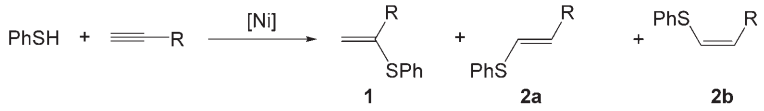
of 19/1 was achieved using 1 equivalent of the radical trap to alkyne (Table 3, entry 4). The further increase of the γ-terpinene decreased the yield of the Markovnikov product, since in that case it dilutes the toluene solution and acts like a co-solvent with unfavourable properties.

A significant drawback of most modern catalytic reactions is their high sensitivity to the purity of the solvent. Quite often even traces of water in organic solvents diminish the yield and selectivity of the reactions. In our case the catalytic reaction was not sensitive to water. Using $NiCl_2$, its hexahydrate $NiCl_2 \cdot 6\,H_2O$ or a mixture of $NiCl_2 + 6\,H_2O$ as a catalyst did not cause noticeable changes in the selectivity and yield of the PhSH addition to 1-heptyne. Moreover, utilizing a 90%:10% mixture of toluene and water as a solvent led to 90% yield and 7.7/1.0 selectivity. The same reaction in pure toluene gave 95% yield with 7.9/1.0 selectivity (Table 3, entry 1).

The Ni-catalyzed reaction was successfully performed in different solvents (Table 4). Excellent yields (90–95%) and selectivity (19/1–17/1) were achieved in chloroform, dioxane, hexane and toluene (Table 4, entries 1–4). Among the studied solvents toluene is a solvent of choice for reactions at high temperature, in other cases chloroform may be also used. Dioxane is less convenient due to more complicated product separation procedure. It is interesting to note that even solvents that are rarely used in catalytic reactions, such as hexane, gave good results in the studied reaction (Table 4, entry 3).

For developing an efficient synthetic procedure the optimal reagents ratio should be determined. With an equimolar ratio of the reagents incomplete conversion was observed, while increasing the amount of alkyne led to the formation of oligomerization products (Ni

Table 5. $NiCl_2$-catalyzed PhSH addition to alkynes.[a]



Entry	Alkyne	Conditions[b]	Yield [%][c]	Selectivity[d]
1	HC≡C-*n*-C_5H_{11} (**A**)	2.5 h., 80 °C, $CHCl_3$	95(80)	18.0 : 1.0
2	HC≡C-CH_2NMe_2 (**B**)	6 h, 95 °C, $CHCl_3$	93(85)	7.7 : 1.0
3	HC≡C-CH_2OMe (**C**)	4 h, 100 °C, toluene	85(75)	8.6 : 1.0
4	HC≡C-CH_2SPh (**D**)	4 h, 100 °C, toluene	93(60)	7.7 : 1.0
5	HC≡C-C_6H_{10}(OH) (**E**)	4 h, 100 °C, toluene	75(63)	7.0 : 1.0
6	HC≡C-$(CH_2)_3$ CN (**F**)	2.5 h, 80 °C, $CHCl_3$	95(84)	13.3 : 1.0
7	HC≡C-Ph (**G**)	5 h, 80 °C, $CHCl_3$	27(5)	0.3 : 1.0
8	HC≡C-COOMe (**H**)	5 h, 80 °C, $CHCl_3$	100(0)	0 : 1.0

[a] 1.0 mmol of PhSH, 0.5 mmol of alkyne, 0.5 mmol of γ-terpinene, 3 mol % of $NiCl_2$, 10 mol % of Et_3N and 1.0 mL of solvent in a sealed tube with stirring.
[b] The reactions were monitored with NMR to determine the optimal time.
[c] The yields determined by NMR and the isolated yields (in parenthesis) of **1**.
[d] The ratio of Markovnikov/anti-Markovnikov products **1**:(**2a**+**2b**).

complexes are known to catalyze alkyne polymerization, see ref.[14]). The best yields and selectivity were observed with the ratio of PhSH : alkyne = 2 : 1. The further increase of benzenethiol amount does not improve the yield of the reaction. Therefore, the PhSH : alkyne = 2 : 1 ratio was used throughout this study.

Another very interesting question concerns the isomerization of the Markovnikov product **1** to internal alkenes **1a** and **1b** (Scheme 1). It was shown that the isomerization of vinyl sulphides can be catalyzed by palladium complexes.[6] The isomerization may also proceed without transition metal complexes.[12] NMR monitoring of the catalytic reaction has shown that only compound **1** is formed at the beginning of the reaction (2–3 h at 80 °C). Heating at higher temperature (> 100 °C) facilitated formation of the isomers **1a** and **1b**. Decreases in the intensity of the NMR signals corresponding to **1** were accompanied with simultaneous increases in the intensities of the signals corresponding to **1a** and **1b**. This observation suggests that **1** is a kinetic product of the catalytic reaction, while **1a** and **1b** are the thermodynamic products. Therefore, to minimize the contribution of the double bond isomerization, the catalytic reaction should be carried out during a short period of time and avoiding overheating.

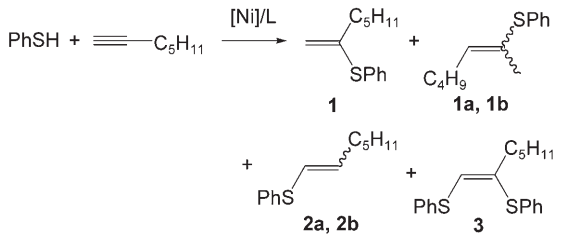
To estimate the optimal reaction time we have performed NMR monitoring of the catalytic reactions of PhSH with 1-heptyne and methyl propargyl ether. The time needed for 50% conversion of 1-heptyne at 80 °C was $t_{1/2}$ = 24 min and 90% conversion of the alkyne was achieved after ~3.5 h. Increasing the temperature to 95 °C decreased the $t_{1/2}$ value to 9 min and 90% conversion of the alkyne was achieved after ~1 h of reaction. Methyl propargyl ether was significantly less reactive, $t_{1/2}$ = 110 min at 80 °C. The optimal reaction conditions for this alkyne were ~4 h at 100 °C.

Under optimized conditions, the Ni-catalyzed reaction was performed with high selectivity and yields for different alkynes (Table 5, entries 1–6). For the alkynes **A**–**F** the isolated yields of the products (**1A**–**1F**) were 60–85% with the selectivity 18/1–7/1 (Table 5, entries 1–6). Obtaining good yields for the alkynes bearing heteroatoms (which could coordinate to the metal) required longer reaction time and higher temperature (Table 5, entries 2–5). Most likely competitive binding of heteroatom lone pair to the metal retards alkyne coordination and breaks the catalytic cycle. Due to the rather fast non-catalytic side-reaction for the activated alkynes (**G**–**H**) we were unable to achieve good yields of the Markovnikov products **1G** and **1H**.

The structures of the products were determined by ^1H and ^{13}C NMR spectroscopy and the stereochemistry was established by 2D NOESY and COSY-LR experiments. The molecular structure of one of the Markovnikov product was determined by an X-ray study (see below).

As we have already mentioned, the formation of bis-(phenylthio)alkene **3** was observed in the case of palladium complexes containing phosphine or phosphite ligands.[6,12,15,16] A similar behaviour was found for the nickel complexes as well (Table 6). Addition of $P(OPh)_3$, $P(OBu)_3$, $P(O\text{-}i\text{-}Pr)_3$ or DPPE to the catalytic system facilitated the formation of compound **3** (Table 6, entries 2–5). Moreover, the yield of **3** was increased upon increasing the amount of the added ligand (Table 6, entries 5, 6). Triphenylphosphine suppressed both catalytic reactions leading to the Markovnikov product **1** and compound **3** (Table 6, entry 1). Therefore, the best results in the Ni-catalyzed Markovnikov-type

Table 6. Effect of phosphine ligands on the $NiCl_2$-catalyzed PhSH addition to 1-heptyne.[a]



Entry	Ligand	Yield [%][b]		
		1+1a+1b	**2a+2b**	**3**
1	PPh_3[c]	0	15	0
2	DPPE	72	11	12
3	$P(OPh)_3$[c]	0	52	8
4	$P(OBu)_3$[c]	62	16	7
5	$P(O\text{-}i\text{-}Pr)_3$[c]	65	15	5
6	$P(O\text{-}i\text{-}Pr)_3$[c, d]	16	18	16

[a] 1.0 mmol of PhSH, 0.5 mmol of alkyne, 3 mol % of $NiCl_2$, 12 mol % of ligand and 1.0 mL of toluene at 120 °C for 3 h in a sealed tube with stirring.
[b] The yields were determined by NMR.
[c] Unidentified products were formed with approximate yields of 10–30%.
[d] 50 mol % of $P(O\text{-}i\text{-}Pr)_3$.

addition of PhSH to alkynes were obtained in the absence of phosphine or phosphite ligands.

Excluding PR_3 ligands also made the catalytic system insensitive to the Ph_2S_2 impurity in PhSH, which is formed due to easy oxidation of the latter by air. Indeed, in the nickel-catalyzed reaction, product **3** was not formed and Ph_2S_2 remained unreacted. In contrast to $NiCl_2$, phosphine complexes of palladium are efficient catalysts of the PhS-SPh addition to alkynes.[15,16]

It is interesting to understand the role of the amine in the studied reaction. The mechanism of the reaction may include generation of the nucleophilic anion PhS^- from PhSH, followed by substitution of chloride ligands in $NiCl_2$ by PhS^-. A similar reaction was observed in the case of chloride complexes of palladium.[17] It was shown that chloride ligand substitution in $PdCl_2(PPh_3)_2$ gave the same product as PhS-SPh oxidative addition to $Pd(PPh_3)_4$.[17] This suggests that $Ni(SPh)_2$ [or the oligomer $(Ni(SPh)_2)_n$] could be the active form of the catalyst in the studied reaction. Another possibility concerns coordination of the amine as a ligand. This explanation has been proposed for the amine effect in palladium-catalyzed hydroselenation reactions.[18] At the moment it is difficult to say which of the mechanisms (or both) takes place in the studied catalytic system. This question will be addressed in our future studies.

Recently we have reported the X-ray structure of $H_2C{=}C(SePh)CH_2N^+HMe_2\cdot HOOC{-}COO^-$, which was prepared by PhSeH addition to $HC{\equiv}CCH_2NMe_2$ and crystallized as the 1:1 oxalic acid salt.[12] In the present study we have successfully applied this methodology for preparing X-ray quality single crystals of the $H_2C{=}C(SPh)CH_2N^+HMe_2\cdot HOOC{-}COO^-$ (**1-B**·HOOC–COOH). The molecular structure of the compound is shown in Figure 1 (main geometric parameters are listed in the Supporting Information). Similar to the selenium analogue, two slightly different conformations were found in the crystal.[12] The alkene unit possesses the typical geometry expected for the Markovnikov product, with C=C distances of 1.261(13) and 1.330(8) Å; C=C–S bond angles of 127.6(10)° and 125.7(3)° close to expected value of 120°. Two sulphur atoms are located at the 1.782(11) and 1.755(8) Å distances from the C2 and C13 vinyl atoms, respectively. The hydrogen bonds involving the carboxylic oxygen atoms and N–H hydrogen were found in the studied molecules. In addition, the non-covalent S...O interactions were found in the crystal: S1–O2 = 3.323, S1–O4 = 3.636, S2–O6 = 3.346, S2–O8 = 3.667 Å. A similar conformation has been found for the selenium analogue suggesting that this could be a general property of the Markovnikov-type products.

Conclusions

The present study describes the first example of regioselective S–H bond addition to alkynes catalyzed by nickel complexes. The usage of easily available and cheap $NiCl_2$ is an important advantage compared to traditional methods based on expensive palladium, platinum or rhodium catalysts.

We have found that a catalytic amount of Et_3N facilitated Markovnikov-type addition and significantly increased the yield of the product. Triethylamine may be used as an activating agent for a broad range of transition metal chlorides MCl_n.

The non-catalytic pathway leading to the anti-Markovnikov products was suppressed for non-activated alkynes using a radical trap. The formation of bis(phenylthio)alkenes was avoided by excluding phosphine and phosphite ligands from the catalytic system. Suppressing these side-reactions greatly improved the yield and selectivity. An important practical advantage of the developed catalytic system is the tolerance to common impurities like Ph_2S_2 in PhSH and water in solvents and reagents.

Further studies on the scope of Ni-catalyzed reactions in carbon-element bond formation are in progress in our group.

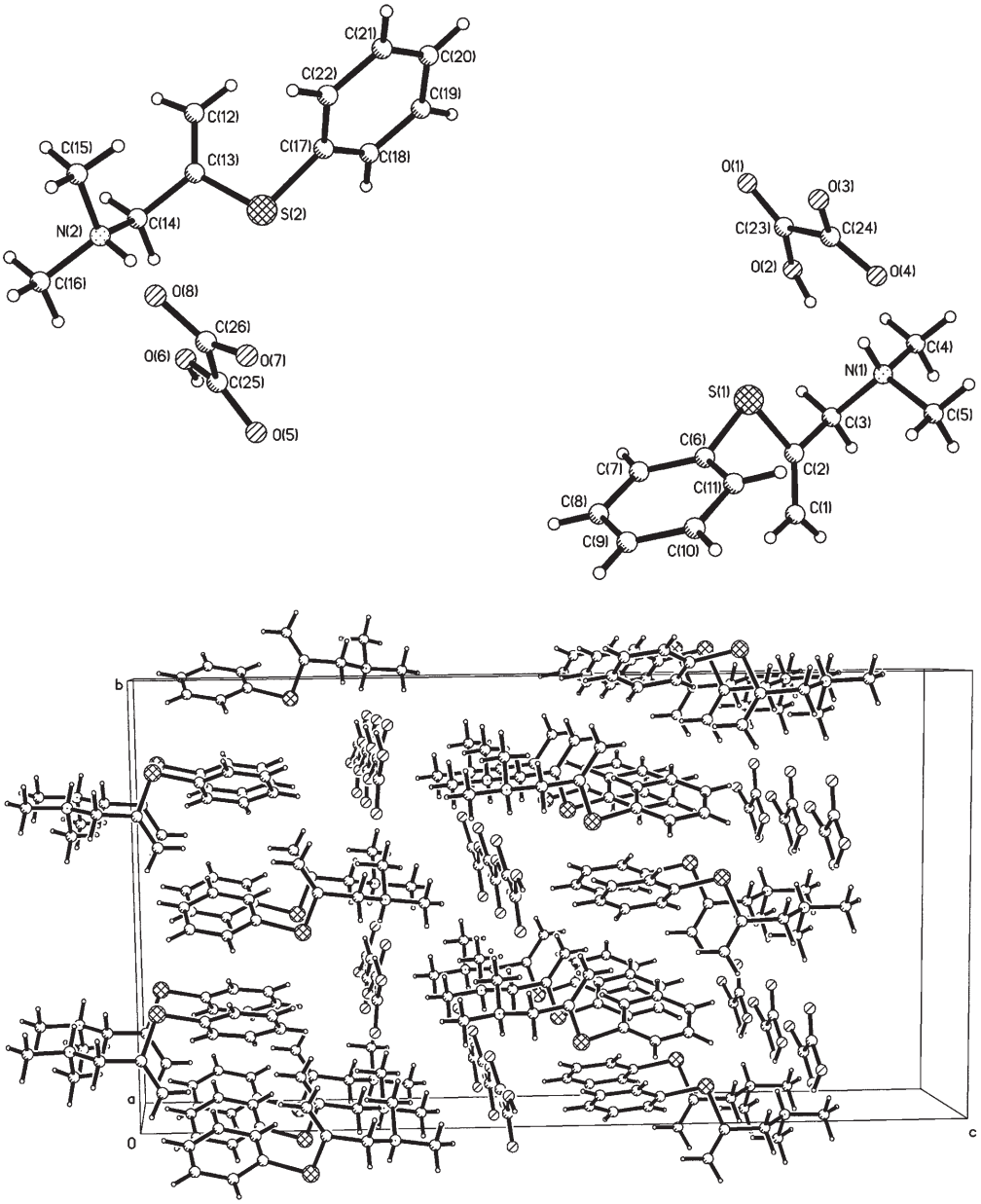


Figure 1. Molecular structure (*top*) and crystal packing (*bottom*) for the $H_2C{=}C(SPh)CH_2N^+HMe_2 \cdot HOOC{-}COO^-$ (**1-B**·HOOC–COOH).

Experimental Section

General

Unless otherwise stated, the synthetic work was carried out under an argon atmosphere. The reagents were obtained from commercial sources (Aldrich, Acros) and checked by NMR before usage. The alkyne $HC{\equiv}C\text{-}CH_2\text{-}SPh$ was prepared according the literature method.[19] All NMR measurements were performed using a three-channel Bruker DRX500 spectrometer operating at 500.1, and 125.8 MHz for ^1H and ^{13}C nuclei, respectively. ^1H and ^{13}C chemical shifts are reported relative to the corresponding solvent signals used as internal reference. The structure and stereochemistry of the products were proven with 2D COSY-LR and NOESY spectra as described earlier.[20] All 2D spectra were recorded using inverse triple resonance probehead with active shielded Z-gradient coil.

General Synthetic Procedure for 1-A–1-E

$NiCl_2 \cdot 6\,H_2O$ (3 mol %, 3.6 mg, 1.5×10^{-5} mol), PhSH (110.2 mg, 1.0×10^{-3} mol), γ-terpinene (68.1 mg, 5.0×10^{-4} mol), triethylamine (6 mol %, 3.0 mg, 3.0×10^{-5} mol), alkyne (5.0×10^{-4} mol) and solvent (1 mL) were added into the reaction tube and purged with argon. The tube was sealed in an ar-

gon atmosphere and reaction mixture was heated (other reaction conditions are given in Table 5). The colour of the solution changed to dark brown upon addition of Et_3N. After completion of the reaction the precipitate was filtered off, the solvent was removed on a rotary evaporator and the crude product extracted with 2.0 mL of $CHCl_3$. The products (except **1-B**) were purified by rapid flash chromatography[21] on silica L5/40 with hexane/ethyl acetate gradient elution. Compared to a regular column chromatography this gives a slightly smaller isolated yield, however it is very economical in respect of solvents and silica. After drying under vacuum the pure products were obtained as light oils. The isolated yields are given in Table 5. The products $H_2C{=}C(SPh)\text{-}C_6H_{10}(OH)$ (**1-E**),[22] $H_2C{=}C(SPh)\text{-}(CH_2)_4\text{-}CH_3$ (**1-A**),[23] $H_2C{=}C(SPh)\text{-}(CH_2)_3\text{-}CN$ (**1-F**),[24] were identified according to the published data. The data for the other compounds is given below.

$H_2C{=}C(SPh)\text{-}CH_2\text{-}NMe_2\cdot HOOC{-}COOH$ (1-B·HOOC–COOH): White solid. After completing the reaction and removing the solvent on a rotary evaporator a THF solution of HOOC-COOH (0.065 g in 1 mL of THF) was added to the residue resulting in immediate white precipitate formation. The solid was washed with THF (3×3 mL) extracted with 5 mL of methanol and dried in vacuum. ^{1}H NMR (500 MHz; CD_3OD); $\delta=7.50$ (d, $J=7.5$, 2H, *o*-Ph), 7.43 (m, 3H, *m*- and *p*-Ph), 5.71 (s, 1H, HC=), 5.28 (s, 1H, HC=), 3.90 (s, 2H, -CH_2-), 2.90 (s, 6H, -CH_3); $^{13}C\{^1H\}$ NMR (126 MHz; CD_3OD); $\delta=166.5$ (C=O), 137.4 [=C(SPh)-], 131.6 (*i*-Ph), 134.8, 131.0 (*o*- and *m*-Ph), 130.4 (*p*-Ph), 123.2 (CH_2=), 61.8 (-CH_2-), 43.4 (-CH_3); anal. calcd for $C_{13}H_{17}NO_4S$: %: C 55.11, H 6.05, N 4.94; found: 54.79; H 6.12; N 4.65; mass spectrum (EI): $m/e=193$ ($M^+-HOOC{-}COOH$, 3), 109 (SPh^+, 50), 84 ($CH_2{=}C\text{-}CH_2\text{-}NMe_2^+$, 65); 58 ($CH_2\text{-}NMe_2^+$, 100).

$H_2C{=}C(SPh)\text{-}CH_2\text{-}OCH_3$ (1-C): Colourless oil. ^{1}H NMR (500 MHz; $CDCl_3$) $\delta=7.44$ (d, $J=7.5$ Hz, 2H, *o*-Ph), 7.31 (t, $J=7.5$ Hz, 2H, *m*-Ph), 7.28 (d, $J=7.5$ Hz, 1H, *p*-Ph), 5.48 (s, 1H, HC=), 5.12 (s, 1H, HC=), 3.97 (s, 2H, $-CH_2$-), 3.33 (s, 3H, -CH_3); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=141.8$ [$CH_2{=}C$(SPh)-], 132.5 (*i*-Ph), 132.8, 129.1 (*o*- and *m*-Ph), 127.8 (*p*-Ph), 115.1 (CH_2=), 74.3 ($-CH_2$-), 58.0 ($-CH_3$); anal. calcd. for $C_{10}H_{12}OS$, %: C 66.63, H 6.71; found: C 66.30, H 6.91; mass spectrum (EI): $m/e=180$ (M^+, 50).

$H_2C{=}C(SPh)\text{-}CH_2\text{-}SPh$ (1-D): Colourless oil. ^{1}H NMR (500 MHz; $CDCl_3$): $\delta=7.20$–7.40 (m, 10H, Ph), 5.38 (s, 1H, HC=), 5.09 (s, 1H, HC=), 3.67 (s, 2H, $-CH_2-$); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=141.0$ [$CH_2{=}C$(SPh)-], 135.6, 132.6 (*i*-Ph), 133.0, 130.3, 129.2, 128.8 (*o*- and *m*-Ph), 128.0, 126.6 (*p*-Ph), 116.9 (CH_2=), 40.2 ($-CH_2-$); anal. calcd. for $C_{15}H_{14}S_2$, %: C 69.72, H 5.46, S 24.82; found: C 69.66, H 5.43, S 24.96; mass spectrum (EI): $m/e=258$ (M^+, 60); 149 [$CH_2{=}C(SPh){-}CH_2^+$, 100], 109 (SPh^+, 50).

NMR Monitoring of the Catalytic Reaction

PhSH (110.2 mg, 1.0×10^{-3} mol), $NiCl_2\cdot6\,H_2O$ (3.6 mg, 1.5×10^{-5} mol), triethylamine (3.0 mg, 3.0×10^{-5} mol), alkyne (5.0×10^{-4} mol) and 0.5 mL of $CDCl_3$ were placed into the NMR tube and purged with argon. The reactions were monitored at different temperatures using ^{1}H NMR.

NMR Monitoring of the PhSH Reaction with $Pd(PPh_3)_4$ and Hydrogen Evolution

At room temperature PhSH (22.0 mg, 2.0×10^{-4} mol) was dissolved in 0.5 mL of C_6D_6 and placed in an NMR tube under an argon atmosphere. $Pd(PPh_3)_4$ (46.2 mg, 4.0×10^{-5} mol) was added to the solution, immediately changing from a colourless solution to dark. Gas evolution occurred for the time period over 10–15 min. ^{1}H NMR spectra indicated the appearance of the H_2 peak at 4.5 ppm, which vanishes after purging the solution with argon. An authentic H_2 sample was prepared by purging hydrogen from a balloon through the C_6D_6 and $\delta=$ 4.5 ppm was the only new peak seen.[12] Literature data: $\delta\approx$ 4.5 ppm for H_2 dissolved in toluene-d_8.[25]

Supporting Information

Crystal structure determination, selected bond lengths and bond angles and data collection and processing parameters. Crystallographic data for the structure **1-B**·HOOC–COOH have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-269630. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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References

[1] M. Beller, J. Seayad, A. Tillack, H. Jiao, *Angew. Chem. Int. Ed.* **2004**, *43*, 3368.
[2] F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079.
[3] T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205.
[4] a) H. Kuniyasu, A. Ogawa, K. Sato, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1992**, *114*, 5902; b) J.-E. Backvall, A. Ericsson, *J. Org. Chem.* **1994**, *59*, 5850.
[5] A. Ogawa, *J. Organomet. Chem.* **2000**, *611*, 463.
[6] A. Ogawa, T. Ikeda, K. Kimura, T. Hirao, *J. Am. Chem. Soc.* **1999**, *121*, 5108.
[7] T. G. Back, M. V. Krishna, *J. Org. Chem.* **1988**, *53*, 2533.
[8] L. Benati, L. Capella, P. C. Montevecchi, P. Spagnolo, *J. Chem. Soc. Perkin Trans.* **1995**, 1035.
[9] Y. Ichinose, K. Wakamatsu, K. Nozaki, J.-L. Birbaum, K. Oshima, K. Utimoto, *Chem. Lett.* **1987**, 1647.
[10] W. E. Truce, R. F. Heine, *J. Am. Chem. Soc.* **1957**, *79*, 5311.
[11] B. A. Trofimov, *Russ. Chem. Rev.* **1981**, *50*, 138.

[12] V. P. Ananikov, D. A. Malyshev, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, *J. Organomet. Chem.* **2003**, *679*, 162.
[13] a) S. Kanemasa, Y. Oderaotoshi, E. Wada, *J. Am. Chem. Soc.* **1999**, *121*, 8675; b) L.-B. Han, C. Zhang, H. Yazawa, S. Shimada, *J. Am. Chem. Soc.* **2004**, *126*, 5080;c) M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, *Org. Lett.,* **2002**, *4*, 761; d) M. A. Kazankova, M. O. Shulyupin, I. P. Beletskaya, *Synlett,* **2003**, *14*, 2155; e) P. Ribiere, K. Bravo-Altamirano, M. I. Antczak, J. D. Hawkins, J.-L. Montchamp, *J. Org. Chem.* **2005**, *70*, 4064.
[14] P. W. Jolly, G. Wilke, *The Organic Chemistry of Nickel,* Academic Press, New York, **1974**.
[15] H. Kuniyasu, A. Ogawa, S.-I. Miyazaki, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1991**, *113*, 9796.
[16] V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, V. N. Khrustalev, M. Yu. Antipin, *Organometallics* **2005**, *24*, 1275.
[17] V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, G. G. Aleksandrov, I. L.Eremenko, *J. Organomet. Chem.* **2003**, *687*, 451.
[18] I. Kamiya, E. Nishinaka, A. Ogawa, *J. Org. Chem.* **2005**, *70*, 696.
[19] G. Pourcelot, P. Cadiot, *Bull.Chem.Soc.Fr.* **1966**, 3016.
[20] V. P. Ananikov, I. P. Beletskaya, G. G. Aleksandrov, I. L. Eremenko, *Organometallics* **2003**, *22*, 1414.
[21] a) D. S. Pedersen, C. Rosenbohm, *Synthesis* **2001**, 2431; b) L. M. Harwood, *Aldrichimica Acta* **1985**, *18*, 25.
[22] M. Yus, F. A. Gutierrez, F. Foubelo, *Tetrahedron* **2001**, *57,* 4411.
[23] A. Ogawa, J. Kawakami, N. Sonoda, T. Hirao *J. Org. Chem.* **1996**, *61*, 4161.
[24] T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 7219–7225.
[25] M. Jang, S. B. Duckett, R. Eisenberg, *Organometallics* **1996**, *15*, 2863.

