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Two Distinct Mechanisms of Alkyne Insertion into the Metal–Sulfur Bond: Combined Experimental and Theoretical Study and Application in Catalysis

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Abstract: The present study reports the evidence for the multiple carbon–carbon bond insertion into the metal–heteroatom bond via a five-coordinate metal complex. Detailed analysis of the model catalytic reaction of the carbon–sulfur (C–S) bond formation unveiled the mechanism of metal-mediated alkyne insertion: a new pathway of C–S bond formation without preliminary ligand dissociation was revealed based on experimental and theoretical investigations. According to this pathway alkyne insertion into the metal–sulfur bond led to the formation of intermediate metal complex capable of direct C–S reductive elimination. In contrast, an intermediate metal complex formed through alkyne insertion through the traditional pathway involving preliminary ligand dissociation suffered from "improper" geometry configuration, which may block the whole catalytic cycle. A new catalytic system was developed to solve the problem of stereoselective S–S bond addition to internal alkynes and a cost-efficient Ni-catalyzed synthetic procedure is reported to furnish formation of target vinyl sulfides with high yields (up to 99%) and excellent *Z*/*E* selectivity (>99:1).

Keywords: heterogeneous catalysis · homogeneous catalysis · insertion · nickel · stereoselectivity · vinyl sulfides

Introduction

Insertion of the carbon–carbon (CC) multiple bonds into a metal–heteroatom bond is a key-step of transition-metal-catalyzed heterofunctionalization of alkynes, alkenes, allenes, and dienes.[1] It is generally accepted that the insertion step involves a preliminary ligand dissociation and coordination of the CC multiple bond to the metal ("activation of the multiple bond"). The necessity of preliminary activation of the unsaturated substrate introduces some prerequisites into catalyst design and excludes several classes of metal complexes from consideration as possible catalysts.[1] Of course, a catalytic system without these limitations would be a fascinating and novel opportunity for constructing carbon–heteroatom (C–E) bonds.

An excellent model for the study of catalytic C–E bond formation is alkyne insertion into the metal–sulfur bond. The field remains less studied, since sulfur species are well-known catalyst poisons,[2] but a solution to this problem was rationalized not long ago through the utilization of an excess of the phosphine ligand to suppress catalyst deactivation.[3] Nowadays transition-metal-catalyzed S–S and S–H bond addition to alkynes is a versatile approach to vinyl sulfides, which combines 100% atom efficiency with excellent stereoselectivity and high yields. Convenient synthetic methods were developed to carry out stereoselective addition of S–S bond to terminal alkynes (**3**) and regio- and stereoselective addition of S–H bond to terminal and internal alkynes (**5** and **4**, respectively; Scheme 1).[3] However, none of the known catalytic systems were succeeded to carry out S–S bond addition to internal alkynes leading to **2** (Scheme 1).

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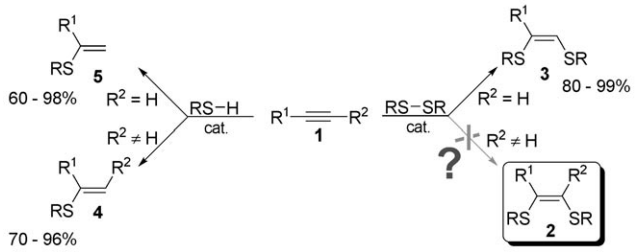
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902928. It contains: 1) the structures optimized at the PBE/TZP level; 2) molecular structures of **2d** and **2e** and details of X-ray crystal structure determination; and 3) tables with geometry parameters of **2d** and **2e**.

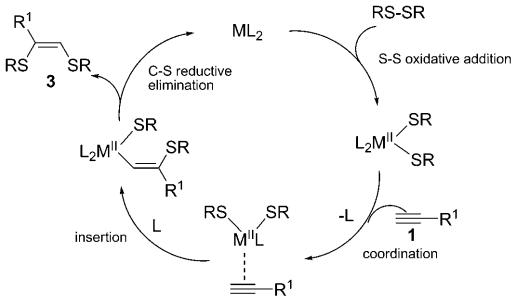


Scheme 1. Transition-metal-catalyzed S-S and S–H bonds addition to alkynes.

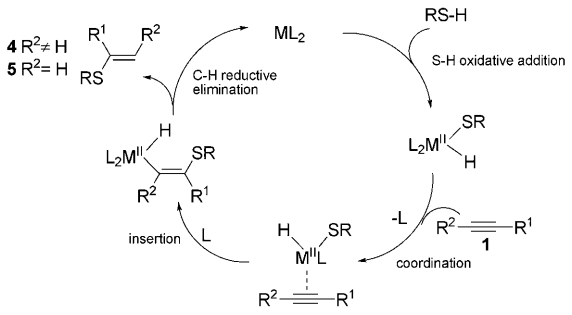
At first sight the question may seem very special and less important. However, the lack of success in carrying out the reaction for several years and the failure to identify a clear reason in spite of continuous efforts, highlighted a stumbling block in our understanding of mechanistic picture of this field.

To understand the nature of this problem first we should consider briefly the scope and mechanism of both catalytic reactions, that is, S–S and S–H bond addition. The first study reported for the arylthiol addition to alkynes utilized a Pd catalyst and was successfully carried out for terminal and internal alkynes.[4] Catalytic activities of Pt,[5] Rh and Ir,[4,6] and Ni[5] complexes in this reaction aimed at the formation of **4** and **5** are now established. A high-performance catalytic system for gram-scale preparation of vinyl sulfides from terminal and internal alkynes has been developed by using nano-structured Ni complexes as the catalytic species.[7] A self-organized nano-sized catalytic system based on Pd complexes solved the problem of stereoselective alkanethiol addition to the triple bond of alkynes.[8] The mechanism of S–H bond addition to alkynes involving phosphine complexes of transition metals as a catalyst was shown to include the following steps: 1) oxidative addition, 2) dissociation of the ligand L and alkyne coordination, 3) alkyne insertion into the M–S bond, and 4) C–H reductive elimination (Scheme 2).[9] No differences in the mechanism of the catalytic cycle have been reported for terminal and internal alkynes, and similar synthetic procedures have been used for the preparation of both types of vinyl sulfides **4** and **5**.[3–8] Thus, preparation of vinyl sulfides through the thiol addition to alkynes is now recognized as a well-established synthetic method.

The first study of $[Pd(PPh_3)_4]$-catalyzed diaryldichalcogenide addition to terminal alkynes leading to formation of product **3** with high selectivity and yields was reported by Ogawa, Sonoda et al.[11] A further mechanistic study revealed the di- and polynuclear nature of intermediate transition-metal complexes in the catalytic reaction and the importance of the excess of phosphine ligands to achieve high performance of the catalytic system.[12] An important step of the catalytic reaction—alkyne insertion into the ArS–M bond—was studied by Kuniyasu, Kambe et al.[13] Catalytic activity of Rh complexes in this reaction was established by Yamaguchi et al.;[14] however, Pt complexes were found inactive and the difference between Pd and Pt was rationalized.[15] For synthetic purposes microwave-assisted synthesis,[16] solvent-free reactions,[17] and polymer-supported catalysts[18] were developed for the addition reactions involving terminal alkynes. Recently this fascinating synthetic methodology was extended to include dialkyldichalcogenides by utilizing an Ni catalyst,[19] cyanothiolation of terminal alkynes on Pd,[20] and preparation of dienes from terminal alkynes on Pt and Ni.[21,22] The mechanism of the catalytic reaction of S–S bond addition to terminal alkynes was shown to include the following steps: 1) oxidative addition of the S–S bond, 2) dissociation of the ligand L and alkyne coordination, 3) alkyne insertion into the M–S bond, and 4) C–S reductive elimination from the metal center (Scheme 3).



Scheme 3. The mechanism of the catalytic S–S bond addition to terminal alkynes.[10]



Scheme 2. The mechanism of the catalytic S–H bond addition to terminal and internal alkynes.[9,10]

In spite of intrinsic similarity between these reactions (cf. Schemes 2 and 3), only terminal alkynes gave the final product in the S–S bond addition reaction (Scheme 1). To summarize, the origins of such dramatic difference in reactivity between the terminal and internal alkynes in the catalytic S–S bond addition remains unclear and the results published in the literature give no hints to overcome the problem.

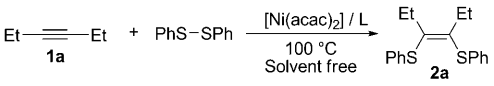
The fact not only breaks consistency of an overall mechanistic picture of this field, but also limits synthetic application of this catalytic methodology. Vinyl sulfides **2** are in demand in organic synthesis, catalysis, and material science;[23] thus the development of a cost-efficient and eco-

friendly synthetic procedures to access them would be useful.

In the present study, we have solved this intriguing problem and revealed the mechanistic reasons of different activity between terminal and internal alkynes in the catalytic S–S bond addition reaction. A novel catalytic system was developed to carry out stereoselective addition of diaryldisulfides to terminal alkynes with good yields and excellent selectivity.

Results and Discussion

The performance of the catalytic system was investigated using diphenyl disulfide addition to 3-hexyne (**1a**) as a model reaction (Scheme 4). The reaction was carried out



Scheme 4. The model catalytic reaction.

under solvent-free conditions. Since Pd and Pt catalytic systems have already been studied and showed poor performance in the reaction of interest, we investigated Ni complexes as possible catalysts.

First, we studied the catalytic system with triphenylphosphine ligand, since PPh_3 was most frequently used as a ligand in catalytic reactions of S–S bond addition to terminal alkynes.[3] Carrying out the model reaction at 100 °C for 8 h failed to produce the desired product **2a** (entry 1, Table 1). Next, we utilized various phosphine and phosphite ligands with alkyl and aryl groups and found them inactive in the formation of **2a** (entries 2–9, Table 1). Surprisingly, using the $PMePh_2$ ligand resulted in 99% yield of product **2a** and excellent stereoselectivity, $Z/E > 99{:}1$ (entry 10, Table 1).

It is evident that such dramatic difference cannot be explained by simple consideration of the ligand effect. Pronounced variation in the reaction yield with the PPh_3 (0%), $PMePh_2$ (99%) and PMe_2Ph (0%) ligands highlight the extraordinary nature of the catalytic system studied (Table 1).

Table 1. Ligand effect on the yield of **2a** in Ni-catalyzed reaction of Ph_2S_2 and 3-hexyne (**1a**).[a]

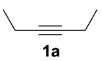
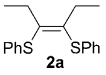
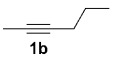
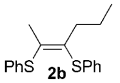
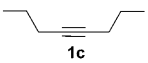
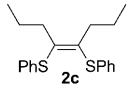
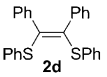
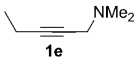
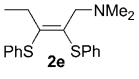
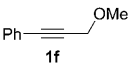
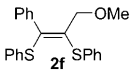
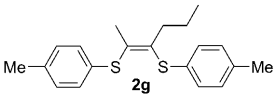
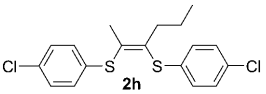
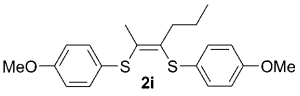
Entry	Ligand (L)	Yield [%]	Entry	Ligand (L)	Yield [%]
1	PPh_3	0	6	$PCyPh_2$	0
2	PCy_3	0	7	PCy_2Ph	0
3	PBu_3	0	8	PMe_2Ph	0
4	$P(PhO)_3$	0	9	PTh_3[b]	0
5	$P(iPrO)_3$	0	10	$PMePh_2$	99

[a] 1 mmol of Ph_2S_2, 1.5 mmol of 3-hexyne, 3 mol% of $[Ni(acac)_2]$, 30 mol% of the ligand, 100 °C, 8 h, solvent free. [b] PTh_3 = tris(2-thienyl)-phosphine.

Optimization of the reaction conditions has shown that the addition reaction can also be carried out in the presence of solvent (toluene, 0.5 mL, 8 h), but resulted in a lower yield—80% (cf. 99% solvent free; entry 10, Table 1). The temperature of 100 °C was found optimal, since the reaction was not complete after 8 h at 80 °C. A further increase of reaction temperature was impractical, since it diminished stereoselectivity of the reaction due to *Z/E* isomerization (observed with ^1H NMR spectroscopy).

The scope of the developed catalytic system was investigated for a variety of internal alkynes and diaryldisulfides with different substituents (Table 2). The excellent stereoselectivity was observed in all studied cases ($Z/E > 99{:}1$).

Table 2. The scope of the Ni-catalyzed addition of diaryldisulfides to internal alkynes.[a]

Entry	Alkyne	RS–SR	Product[b]	Yield[c] [%]
1	 **1a**	Ph_2S_2	 **2a**	99 (85)
2	 **1b**	Ph_2S_2	 **2b**	93 (82)
3	 **1c**	Ph_2S_2	 **2c**	99 (91)
4	 **1d**	Ph_2S_2	 **2d**	99 (89)
5	 **1e**	Ph_2S_2	 **2e**	91 (80)
6	 **1f**	Ph_2S_2	 **2f**	60 (55)
7	**1b**	$(p\text{-}MeC_6H_4)_2S_2$	 **2g**	75 (67)
8	**1b**	$(p\text{-}ClC_6H_4)_2S_2$	 **2h**	95 (82)
9	**1b**	$(p\text{-}MeOC_6H_4)_2S_2$	 **2i**	99 (85)

[a] See Experimental Section for complete description of synthesis and isolation details. [b] Stereoselectivity > 99:1. [c] NMR yield after completing the reaction and isolated yield after separation and purification (in parenthesis).

High product yields (82–91 % isolated) were found in the catalytic Ph_2S_2 addition to 3-hexyne, 2-hexyne, and 4-octyne (entries 1–3, Table 2). High yields and selectivity were also obtained in the case of activated alkyne **1d** (entry 4, Table 2), in contrast to the previous studies of Ph_2S_2 addition to terminal alkynes, in which the presence of the Ph groups decreased the observed selectivity.[3] The catalytic system was tolerant to functional groups in alkynes leading to good yields for **1e**, **1f** (entries 5, 6, Table 2); somewhat lower yields compared to **1a**–**1d** were caused by by-product formation due to alkyne polymerization. Although polymerization of alkynes on Ni is a facile and well-known reaction,[24] in the developed catalytic system we observed it only with some selected alkynes to a limited extent. Electron donor and acceptor substituents in the phenyl ring of Ar_2S_2 did not affect the scope of the developed catalytic system and resulted in good yields of products (entries 7–9, Table 2).

After exploring the synthetic potential of the developed catalytic system, it is of interest to understand the mechanism of this reaction and to reveal the origins of the crucial difference in reactivity of internal alkynes depending on the ligand L. Considering a commonly accepted mechanism of S–S bond addition, we may assume that failure of internal alkynes to proceed in the catalytic reaction with PPh_3 and PMe_2Ph ligands may originate either due to inability to undergo coordination and insertion steps or due to loss of reactivity on the C–S reductive elimination step (Scheme 3).

To distinguish between these two possibilities we have determined catalytic activity of particular metal/ligand combinations in the S–H bond addition reaction (this catalytic cycle involves alkyne insertion, but does not involve C–S reductive elimination; see Scheme 2). We have found very low activity in the Ni/PMe_2Ph catalytic system: addition of PhSH to 3-hexyne (100 °C, 8 h) resulted only in 30 % yield of **4a**. This result has shown that for the PMe_2Ph ligand alkyne coordination and insertion into the Ni–S bond can be a limiting factor. Carrying out this reaction with the Ni/$PMePh_2$ and Ni/PPh_3 systems led to 95 and 73 % yields of **4a**,[25] respectively. Therefore, for the both ligands L = $PMePh_2$ and PPh_3 alkyne coordination and insertion proceeded smoothly, since these stages are involved in the mechanism of catalytic formation of product **4a** (Scheme 2).

To confirm the proposed route of C≡C bond insertion in the case of catalytic systems with $PMePh_2$ and PPh_3 ligands, we carried out a structural study to determine configuration of the double bond of the addition product **2**.[26] In all cases in the present study only a single isomer was detected on the product formation step with excellent selectivity (Table 2). The *syn* fashion of the addition reaction and *Z* configuration of the final product were confirmed by X-ray structure analysis for **2d** and **2e**, the S-C-C-S dihedral angles are equal to 18.6(1) and −0.5(4), 2.3(5)° (for the two crystallographically independent cations), respectively (Figure 1).[27] The 2D NOESY spectroscopy was utilized to determine geometry of products **2b** and **2e**–**2i**; a *Z* configuration was found in all cases. The structure of the products

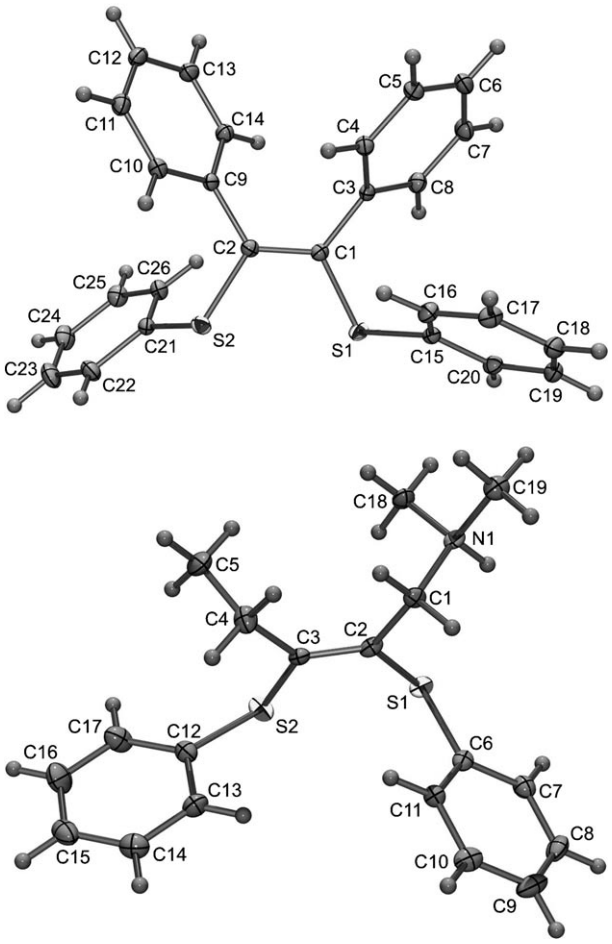
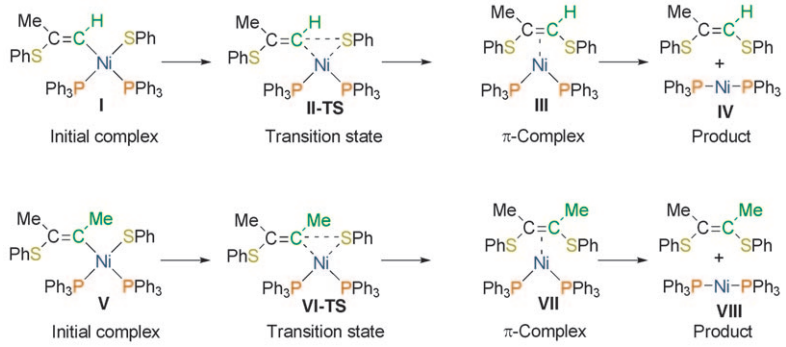


Figure 1. X-ray structures of **2d** (top) and **2e** (bottom; only one of the two crystallographically independent cations is shown).

was in total agreement with proposed mechanism confirming the involvement of an alkyne insertion step into the Ni–S bond in the catalytic cycle and ruling out the possibilities of other routes of C≡C bond activation.[26] Remarkably, that catalytic procedure provides access to thermodynamically less stable *Z* isomers that cannot be reached in high selectivity by other synthetic routes.

Our study has shown that alkyne insertion took place with both $PMePh_2$ and PPh_3 ligands. Therefore, it could be that the reductive elimination stage is responsible for the absence of catalytic activity with PPh_3 ligand. We decided to carry out a theoretical study to verify this assumption and to find out to what extent C–S reductive elimination is sensitive to the substitution of the carbon atom in α-position to the metal. The model system used in the study is shown on Scheme 5, the theoretical calculations were carried out at the PBE/TZP level. Full geometry optimization was carried for the PPh_3 ligands and SPh groups without any simplifying approximations (100 and 103 atoms in structures **I**–**IV** and **V**–**VIII**, respectively).

Theoretical study was carried out for the C–S reductive elimination stages modeling both reactions (Scheme 5): vinyl ligand resulted from the terminal (R^2 = H) and internal



Scheme 5. The model system for theoretical study of C–S reductive elimination reaction involving α-unsubstituted vinyl group (top) and α-Me-substituted vinyl group (bottom); C-H and C-Me groups in α-position are highlighted with green color.[28]

alkynes (R^2 = Me). Starting from initial complexes **I** and **V** both transition stages were successfully located (**II-TS** and **VI-TS**, respectively). Overcoming transition states led to intermediate formation of π-complexes **III** and **VII**, followed by dissociation of the organic products (**IV** and **VIII**).[29] Representative optimized structures of complex **V** and transition state **VI-TS** together with selected structural parameters are shown in Figure 2. Comparing both reductive elimination reactions **I**→**IV** and **V**→**VIII** we did not notice a significant difference in the key structure units.[28] This observation was in total agreement with calculated energetic parameters. The activation energies were $\Delta E^{\neq} = 10.0$ and 13.8 kcal mol^{-1} for the **I**→**II-TS** and **V**→**VI-TS** barriers, respectively. Indeed, enlarged steric strain due to the presence of the additional Me group increased the activation energy by 3.8 kcal mol^{-1}. This could make the latter reductive elimination reaction less favorable, but clearly this cannot account for observed dramatic difference in reactivity. Therefore, difficulties on the C–S reductive elimination step cannot be assumed as a reason for complete loss of catalytic activity in the Ni/PPh_3 system. The calculated reaction free energies were $\Delta G = -5.8$ and -7.9 kcal mol^{-1} for the **I**→**III** and **V**→**VII** reactions, respectively, thus, providing the necessary driving force for both transformations.

A more detailed inspection of the transition-state **VI-TS** and initial complex **V** has shown that C=C unit of the vinyl ligand should be out-of-plane with P-Ni-P unit in order to undergo C–S bond formation by reductive elimination (Figure 2).[30] For the considered pathway it means that complex **9** has to undergo ligand reorientation before the actual reductive elimination could take place (Scheme 6). However, this reorientation is retarded in case of internal alkyne ($R^2 \neq$ H) due to steric hindrance between the R^2 group and PR'_3 ligand. Thus, for the terminal alkynes (R^2 = H) complex **9** is an intermediate of the catalytic reaction, while for the internal alkynes ($R^2 \neq$ H) complex **9** is a resting state lying off the catalytic cycle. In this context it is worth mentioning that a recent study of C–C reductive elimination from Ir complexes has shown that ligand reorientation in the Ir–C(sp^2) system can contribute up to $\Delta G^{\neq} \approx 17$ kcal mol^{-1} to the activation barrier, therefore decreasing reaction rate by many orders of magnitude.[31]

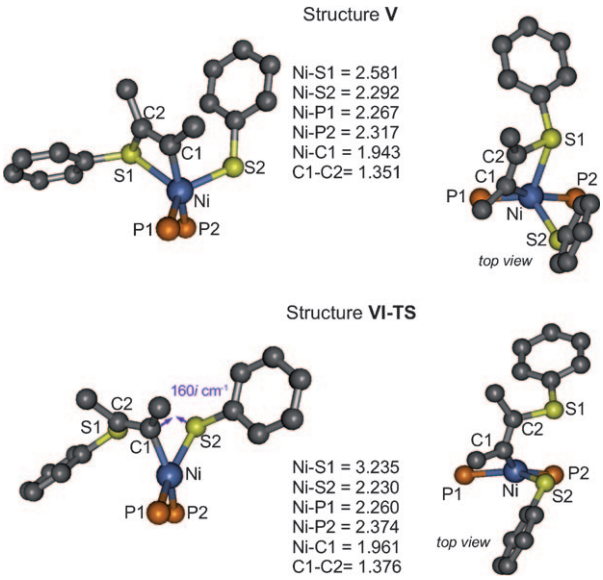
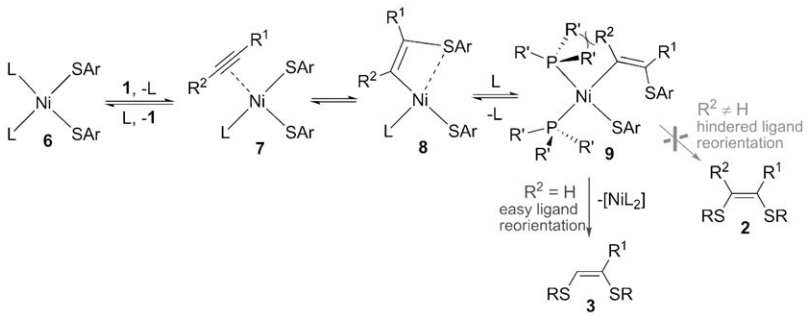
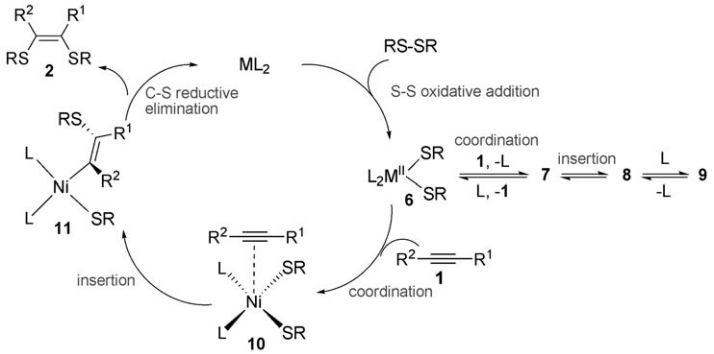


Figure 2. The structures of **V** and **VI-TS** optimized at PBE/TZP level (some atoms are omitted for clarity[28]); selected bond lengths are given in Å.

Based on our experimental and theoretical study we propose another mechanism of the catalytic reaction in the Ni/$PMePh_2$ system (Scheme 7). The more electron-donating $PMePh_2$ ligand does not dissociate easily in contrast to labile PPh_3 ligand; this retards formation of the π-complex **7**



Scheme 6. C–S reductive elimination by means of the ligand dissociative pathway (L = PPh_3).



Scheme 7. C–S reductive elimination through the apical site of the metal without ligand dissociation (L = $PMePh_2$).

and the resting state **9**. On the other hand, the $PMePh_2$ ligand is also less sterically crowded compared to PPh_3 and allows alkyne molecule to coordinate to the apical site of the metal complex **6** leading to complex **10**. Insertion of the alkyne into the Ni–S in such a case would provide complex **11** with the vinyl ligand in out-of-plane orientation to undergo reductive elimination. Therefore, vinyl ligand reorientation is not required and C–S bond formation may proceed directly from the complex **11**. It should be pointed out that complex **8** may also represent a resting state in case of high thermodynamic stability of vinyl ligand coordination in chelate fashion (taking into account that direct C–S reductive elimination from complex **8** is impossible due to geometry reasons).

To scrutinize the reliability of this mechanism we carried out two sets of experiments. First, within this mechanism not only internal, but also terminal alkynes should be successfully involved in the Ni/$PMePh_2$ catalytic system. To check this possibility we carried out Ph_2S_2 addition to 1-hexyne. Indeed, we observed almost quantitative conversion of the alkyne after 3 h at 70 °C in excellent agreement with proposed mechanism.[32]

Second, within the proposed mechanism an unusual dependence of the performance of the catalytic system should be expected upon changing ligand/metal ratio. An excess of the ligand would decrease the possibility of ligand dissociation pathway (leading to **7** and resting state **9**), therefore, increasing the contribution of the pathway involving the apical metal site (**10**) and enhancing the product formation. If phosphine ligand dissociation precedes alkyne coordination, the opposite dependence should be observed—an excess of the ligand would retard alkyne coordination and suppress the reaction. We have carried out the NMR monitoring of the catalytic reactions at different L/Ni ratios (Table 3). No reaction was observed with the 1:2 ratio (entry 1, Table 3) and only 12% of the product was formed with the 1:5 ratio (entry 2, Table 3). With the higher ligand/metal ratios, particularly 10:1, 15:1, and 20:1, complete conversion was observed after 8 h at 100 °C (entries 3–5, Table 3), while comparison of the yields at shorter reaction time has clearly indicated reaction rate enhancement. The

Table 3. The yields of **2a** in Ni-catalyzed reaction of Ph_2S_2 and 3-hexyne (**1a**) at different L/Ni ratios.[a]

Entry	MePh2P [mol%]	L/Ni ratio	Yield [%] after		
			1 h	3 h	8 h
1	6	2:1[b]	0	0	0
2	15	5:1[b]	5	8	12
3	30	10:1[c]	26	55	99
4	45	15:1[c]	43	79	99
5	60	20:1[c]	55	92	99

[a] Reaction conditions: [Ni(acac)$_2$] (3 mol%), Ph_2S_2 (1 mmol), 3-hexyne (1.5 mmol), 100 °C, solvent free. [b] Heterogeneous reaction mixture with metal species partially precipitated. [c] Homogeneous reaction mixture.

best result within the studied range of ratios was observed for the 20-fold excess of the ligand (entry 5, Table 3).[33] It is worth noting that such a large excess of the ligand did not block the catalytic activity.

For economic reasons we have chosen L/Ni = 10:1 for the synthetic procedure (Table 2), since it is a minimal excess of the phosphine ligand that ensures a homogeneous system (Table 3) and high performance of the catalytic reaction.

Conclusion

To summarize, the present experimental and theoretical study has not only solved a long standing problem of selective S–S bond addition to internal alkynes, but also resulted in development of a new look at the mechanistic picture of these reactions.

With a more labile ligand (PPh_3), the dissociative pathway of C–S bond formation is facilitated, which strongly depends on the ability of the vinyl ligand to undergo reorientation in order to adopt proper conformation required for reductive elimination. Hindered reorientation of the vinyl ligand caused by substitution of the α-carbon atom blocked the catalytic reaction with internal alkyne. With a more strongly bound ligand ($PMePh_2$), the alkyne insertion took place through another pathway and did not require preliminary ligand dissociation. This pathway led to intermediate metal complex, which may undergo direct reductive elimination without the need of ligand reorientation. Thus, we have found that two pathways of C–S reductive elimination are possible and the nature of the ligand is the key controlling factor. The first pathway selectively involves only the terminal alkynes, while the second pathway is suitable for both the terminal and internal alkynes.

Based on discovered catalytic system we have developed the first synthetic approach to accomplish stereoselective S–S bond addition to internal alkynes. The addition reaction was carried out with high yields and excellent selectivity for various alkynes and diaryldisulfides. The readily available nickel complex [Ni(acac)$_2$] (acac = acetylacetonate) was utilized as a catalyst precursor.

The evidence for the insertion step through a five-coordinate metal complex reported in the present study may be also useful in taking a new look at (and possibly reevaluate)

reaction mechanisms of some other catalytic cycles involving insertion of carbon–carbon multiple bonds, like alkynes and alkenes heterofunctionalization, Heck reaction, and so forth.

Experimental Section

General procedures: Unless otherwise noted, the synthetic work was carried out under argon atmosphere. $[Ni(acac)_2]$ was dried under vacuum (0.1–0.05 Torr, 60 °C, 30 min) before use. Other reagents were obtained from Acros and Lancaster and used as supplied (checked by NMR spectroscopy before use). Solvents were purified according to published methods. The reaction was carried out in PTFE screw capped tubes or flasks.

All NMR measurements were performed by using a three-channel Bruker AVANCE 500 spectrometer operating at 500.1, 202.5, and 125.8 MHz for ^1H, ^{31}P, and ^{13}C nuclei, respectively. The spectra were processed on a Linux workstation by using TOPSPIN software package. All 2D spectra were recorded using inverse triple resonance probehead with active shielded Z-gradient coil. The ^1H and ^{13}C chemical shifts are reported relative to the corresponding solvent signals used as internal reference. Estimated errors in the yields determined by ^1H NMR spectroscopy were $<2\%$.

Developed synthetic procedure: $[Ni(acac)_2]$ (3.0×10^{-5} mol, 7.8 mg), Ar_2S_2 (1.0×10^{-3} mol) and $PMePh_2$ (3.0×10^{-4} mol, 60.0 mg) were placed into reaction vessel and stirred at room temperature until homogeneous brown solution was formed (ca. 1–2 min). Alkyne (1.5×10^{-3} mol) was added to the solution and the reaction was carried out at 100 °C for 8 h under stirring. In case of the compound **2c** 13 h were required to achieve full conversion of Ph_2S_2.

Compound purification and characterization: After completion of the reaction the products were purified by dry column flash chromatography on silica.[34] Dry column flash chromatography has several practical advantages: 1) only a small amount of silica required, 2) quick elution, and 3) economy of solvents. However, slightly better isolated yields (by ≈5–10%) may be achieved using conventional column chromatography.

Hexanes/dichloromethane (**2f**, **2h**, **2i**), hexanes/benzene (**2a**, **2b**, **2c**, **2d**, **2g**) and hexanes/ethyl acetate (**2e**) gradient elution was applied. Silica was washed with a solution of Et_3N (5–6 drops) in hexanes (20 mL) prior to chromatography of product **2e**. After drying in vacuum the pure products were obtained. The isolated yields were calculated based on initial amount of Ar_2S_2.

{[(1*Z*)-1-Ethyl-2-(phenylsulfanyl)-1-butenyl]sulfanyl}benzene (2a): ^1H NMR (500 MHz; $CDCl_3$): $\delta=1.06$ (t, $J=7.39$ Hz, 6H), 2.34 (q, $J=7.39$ Hz, 4H), 7.21 (t, $J=7.20$ Hz, 2H), 7.28 (t, $J=7.67$ Hz, 4H), 7.35 ppm (d, $J=7.14$ Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=14.02$, 26.46, 126.60, 128.83, 130.76, 135.06, 139.13 ppm; MS (EI): *m/z* (%): 300 (52) [M^+]; elemental analysis calcd (%) for $C_{18}H_{20}S_2$: C 71.95, H 6.71, S 21.34; found: C 72.01, H 7.06, S 21.29.

{[(1*Z*)-2-(Phenylsulfanyl)-1-propyl-1-propenyl]sulfanyl}benzene (2b): ^1H NMR (500 MHz; $CDCl_3$): $\delta=0.84$ (t, $J=7.37$ Hz, 3H), 1.48–1.57 (m, 2H), 1.97 (s, 3H), 2.28 (t, $J=7.60$ Hz, 2H), 7.19 (t, $J=7.40$ Hz, 1H), 7.23 (t, $J=7.40$ Hz, 1H), 7.25–7.31 (m, 4H), 7.33 (d, $J=7.15$ Hz, 2H), 7.38 ppm (d, $J=7.01$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=$ 13.60, 20.39, 21.91, 35.69, 126.33, 127.12, 128.30, 128.83, 130.07, 132.03, 134.28, 134.42, 134.97, 135.28 ppm; MS (EI): *m/z* (%): 300 (90) [M^+]; elemental analysis calcd (%) for $C_{18}H_{20}S_2$: C 71.95, H 6.71, S 21.34; found: C 71.99, 6.80, S 21.23.

{[(1*Z*)-2-(Phenylsulfanyl)-1-propyl-1-pentenyl]sulfanyl}benzene (2c): ^1H NMR (500 MHz; $CDCl_3$): $\delta=0.82$ (t, $J=7.33$ Hz, 6H), 1.47–1.53 (m, 4H), 2.28 (t, $J=7.65$ Hz, 4H), 7.19 (t, $J=7.07$ Hz, 2H), 7.27 (t, $J=7.55$ Hz, 4H), 7.34 ppm (d, $J=7.14$ Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=13.71$, 22.44, 35.15, 126.53, 128.77, 130.71, 135.10, 138.09 ppm; MS (EI): *m/z* (%): 328 (40) [M^+]; elemental analysis calcd (%) for $C_{20}H_{24}S_2$: C 73.12, H 7.36, S 19.52; found: 72.94, 7.42, S 19.20.

[(*Z*)-2-Phenyl-1,2-bis(phenylsulfanyl)ethenyl]benzene (2d): ^1H NMR (500 MHz; $CDCl_3$): $\delta=6.80$–6.89 (m, 6H), 6.98 (t, $J=6.74$ Hz, 2H), 7.01–7.07 (m, 8H), 7.22 ppm (d, $J=8.20$ Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=126.57$, 126.68, 127.26, 128.37, 130.45, 131.36, 134.15, 138.02, 138.57 ppm; MS (EI): *m/z* (%): 396 (7) [M^+]; elemental analysis calcd (%) for $C_{26}H_{20}S_2$: C 78.75, H 5.08, S 16.17; found: C 78.68, H 5.37, S 16.09.

(2*Z*)-*N*,*N*-Dimethyl-2,3-bis(phenylsulfanyl)-2-penten-1-amine (2e): ^1H NMR (500 MHz; $CDCl_3$): $\delta=1.02$ (t, $J=7.33$ Hz, 3H), 2.19 (s, 6H), 2.41 (q, $J=7.33$ Hz, 2H), 3.07 (s, 2H), 7.17 (t, $J=7.33$ Hz, 1H), 7.22–7.31 (m, 5H), 7.34 (d, $J=7.33$ Hz, 2H), 7.40 ppm (d, $J=7.33$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=13.85$, 25.78, 45.02, 60.23, 126.05, 127.42, 128.69, 128.83, 129.57, 129.81, 132.61, 133.82, 135.48, 148.37 ppm; MS (EI): *m/z* (%): 329 (17) [M^+]; elemental analysis for the salt calcd (%) for $C_{21}H_{25}NO_4S_2$: C 60.12, H 6.01, N 3.34; found: C 59.89, H 6.09, N 3.20.

Methyl (2*Z*)-3-phenyl-2,3-bis(phenylsulfanyl)-2-propenyl ether (2f): ^1H NMR (500 MHz; $CDCl_3$): $\delta=3.01$ (s, 3H), 3.78 (s, 2H), 7.03-7.18 (m, 8H), 7.20 (d, $J=6.60$ Hz, 2H), 7.28 (t, $J=7.23$ Hz, 1H), 7.35 (t, $J=$ 7.60 Hz, 2H), 7.55 ppm (d, $J=7.16$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=57.57$, 71.14, 127.21, 127.55, 127.61, 128.26, 128.33, 128.82, 129.64, 131.61, 131.76, 132.94, 133.02, 133.88, 137.34, 144.48 ppm; MS (EI): *m/z* (%): 364 (7) [M^+]; elemental analysis calcd (%) for $C_{22}H_{20}OS_2$: C 72.49, H 5.53, S, 17.59; found: C 72.17, H 5.40, S 17.21.

1-Methyl-4-({(1*Z*)-2-[(4-methylphenyl)sulfanyl]-1-propyl-1-propenyl}sulfanyl)benzene (2g): ^1H NMR (500 MHz; $CDCl_3$): $\delta=0.83$ (t, $J=7.52$ Hz, 3H), 1.47–1.51 (m, 2H), 1.92 (s, 3H), 2.24 (t, $J=7.60$ Hz, 2H), 2.32 (s, 3H), 2.33 (s, 3H), 7.09–7.14 (m, 4H), 7.25 (d, $J=7.26$ Hz, 2H), 7.29 ppm (d, $J=7.26$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=13.62$, 20.23, 21.05, 21.10, 21.94, 35.53, 128.36, 129.63, 130.64, 130.87, 131.67, 132.58, 133.74, 134.51, 136.42, 137.30 ppm; MS (EI): *m/z* (%): 328 (42) [M^+]; elemental analysis calcd (%) for $C_{20}H_{24}S_2$: C 73.12, H 7.36, S 19.52; found: C 72.92, H 7.19, S 19.27.

1-Chloro-4-({(1*Z*)-2-[(4-chlorophenyl)sulfanyl]-1-propyl-1-propenyl}sulfanyl)benzene (2h): ^1H NMR (500 MHz; $CDCl_3$): $\delta=0.85$ (t, $J=7.42$ Hz, 3H), 1.46–1.52 (m, 2H), 1.96 (s, 3H), 2.26 (t, $J=7.53$ Hz, 2H), 7.24 (d, $J=8.78$ Hz, 2H), 7.27 (d, $J=8.78$ Hz, 2H), 7.28–7.30 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=13.61$, 20.42, 21.90, 35.72, 129.05, 129.10, 131.21, 132.46, 132.73, 133.34, 133.49, 133.70, 134.22, 135.28 ppm; MS (EI): *m/z* (%): 368 (32) [M^+]; elemental analysis calcd (%) for $C_{18}H_{18}Cl_2S_2$: C 58.53, H 4.91, S 17.36; found: C 58.74, H 5.01, S 17.19.

1-Methoxy-4-({(1*Z*)-2-[(4-methoxyphenyl)sulfanyl]-1-propyl-1-propenyl}sulfanyl) benzene (2i): ^1H NMR (500 MHz; $CDCl_3$): $\delta=0.81$ (t, $J=$ 7.35 Hz, 3H), 1.48–1.54 > (m, 2H), 1.86 (s, 3H), 2.17 (t, $J=7.52$ Hz, 2H), 3.80 (s, 3H), 3.81 (s, 3H), 6.85 (d, $J=3.07$ Hz, 2H), 6.87 (d, $J=3.07$ Hz, 2H), 7.34 (d, $J=8.82$ Hz, 2H), 7.37 ppm (d, $J=8.82$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$): $\delta=13.55$, 19.98, 21.89, 35.22, 55.30, 114.53, 114.55, 125.17, 125.82, 133.26, 133.51, 133.55, 133.86, 134.79, 159.13, 159.55 ppm; MS (EI): *m/z* (%): 360 (8) [M^+]; elemental analysis calcd (%) for $C_{20}H_{24}O_2S_2$: C 66.63, H 6.71, S 17.79; found: C 66.68, H 6.58, S 17.93.

PhSH addition to 3-hexyne catalyzed by Ni/PPh_3, Ni/$PMePh_2$ and Ni/PMe_2Ph systems: $[Ni(acac)_2]$ (1.5×10^{-5} mol, 3.9 mg), PhSH (5.0×10^{-4} mol, 55.1 mg), and PR_3 (1.5×10^{-4} mol) were placed into reaction vessel and stirred at room temperature for about 1–2 min. 3-Hexyne (5.0×10^{-4} mol, 41.1 mg) was added to the solution and the reaction was carried out at 100 °C for 8 h under stirring.

Catalytic reaction with various Ni/$PMePh_2$ ratios: $[Ni(acac)_2]$ (3.0×10^{-5} mol, 7.8 mg), Ph_2S_2 (1.0×10^{-3} mol, 218.4 mg) and appropriate amount of $PMePh_2$ were placed into reaction vessel and stirred at room temperature until homogeneous brown solution was formed (ca. 1–2 min). 3-Hexyne (1.5×10^{-3} mol, 123.2 mg) was added to the solution and the reaction was carried out at 100 °C for 1 or 3 h under stirring.

Theoretical calculations: The calculations were performed using the PBE exchange-correlation functional,[35] the scalar-relativistic Hamiltonian and large all-electron basis sets of triple-ζ quality with polarization functions as implemented in Priroda program.[36] Priroda makes use of the "resolution-of-identity" approach to solving the SCF equations and other effi-

ciency-enhancing techniques,[37] which make the performance of the code very efficient. Good accuracy in geometry optimization and energy calculations with Priroda program was confirmed for various systems involving transition metal compounds.[38] Our extensive testing over the known structures of metal chalcogenides confirmed the reliability of these calculations for the systems similar to those considered in the present study.

Full geometry optimization was performed without any symmetry constraints. Normal coordinate analysis was performed for all stationary points to verify the transition states (one imaginary frequency) and equilibrium structures (no imaginary frequencies) and to calculate zero point energy correction and Gibbs free energies. Utilizing intrinsic reaction coordinate calculations, reactants, transition states, and corresponding products were unambiguously proven to be connected by a single minimal-energy reaction path.

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[9] In the absence of the phosphine ligand another mechanism may take place involving protonolysis as a product formation step (Scheme 2). See reference [3] for discussion of various mechanistic details. In any case, alkyne coordination and insertion remain as the key steps in all reported reactions.

[10] Only mononuclear transition metal complexes are shown on the scheme for clarity reasons, see reference [3,12] for more details.

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[25] In case of PPh_3 ligand a slightly lower yield was observed due to by-products formation through the known mechanism involving benzenethiol conversion to diphenyl disulfide (see ref. [5]).

[26] The insertion step is known to proceed with high selectivity and leads to the formation of *syn*-addition products with *Z* configuration of the double bond.[1,3] This rules out an alternative route involving external attack of the sulfur group, which results in formation of *anti*-addition products with *E* configuration of the double bond.

[27] See the Supporting Information for detailed description of X-ray study and geometry parameters.

[28] See Figure S1 in the Supporting Information for the optimized structures **I**, **II-TS**, **IV**, **V**, **VI-TS**, and **VIII**.

[29] The calculated binding energies of the C=C double bond in the π complexes **III** and **VII** were 15.9 and 9.1 kcal mol^{-1} relative to **IV** and **VIII**, respectively.

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ductive elimination steps (see ref. [22] for the discussion of the mechanism of dienes formation).

[33] It should be noted that an additional role of the ligand excess is to suppress polymerization of Ni sulfide and formation of metal-containing precipitate as was reported earlier.[12,17,19] At the moment it is impossible to separate unambiguously these two types of the ligand effects and to estimate their contribution to the overall performance enhancement of the studied catalytic reaction. In any case, it is clear that the pathway involving alkyne coordination to the apical Ni site without the need of phosphine ligand dissociation better agrees with the results of the NMR monitoring.

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