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Switchable Ni-catalyzed bis-thiolation of acetylene with aryl disulfides as an access to functionalized alkenes and 1,3-dienes



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ABSTRACT

Keywords: Catalysis Nickel Acetylene Diene Sulfur derivatives Atom-economic addition Calcium carbide The article provides the first example of metal-catalyzed aryl disulfide addition to unsubstituted acetylene. The use of inexpensive Ni(acac)₂ precatalyst with phosphine ligands results in competitive formation of (*Z*)-1,2-bis (arylthio)ethenes and (*Z*,*Z*)-1,4-bis(arylthio)buta-1,3-dienes. The process with the PPhCy₂ as a ligand results in selective formation of diene molecular skeletons. Replacement of PPhCy₂ with the PPh₃ switches the reaction toward formation of alkenes. The use of substituted phenyl disulfides does not affect the selectivity and allows obtaining alkenes or dienes in good to high yields. Mechanistic investigations reveal major differences on the catalyst activation stage depending on the nature of phosphine ligand. Key novel point is to carry out videomonitoring of catalyst evolution with electron microscopy, which revealed the dynamic nature of the catalytic system and showed that the ligand played a prominent role in formation of the catalytically active phase. For PPh₃, the development of catalytically active species proceeds through nickel thiolate [Ni(SAr)₂]_n formation, which renders the system heterogeneous. In contrast to PPh₃, the PPhCy₂ ligand promotes direct activation of the catalyst in its molecular form without disturbing the homogeneous state of the system.

1. Introduction

Modern chemistry of catalytic reactions is like a vortex, which permanently swallows new starting materials to transform them into complicated substances. Increase of selectivity and yields always accompanies the development of new catalytic systems. Despite the variety of readily available building blocks for laboratory use, search for the reactions with the simplest and cheapest molecules are of utmost practical importance and represents a hot topic. Saturated and unsaturated hydrocarbons keep the first lines in rating of the cheap and easily available materials among the others bulk chemicals, as they are the main products of chemical industry.

Heterofunctionalization of hydrocarbons allows discovery of substances with completely new properties. In a major focus is the C–S bond construction [1-8] due to the great demand for organosulfur compounds, which find application in material, polymer, pharmaceutical, and chemical sciences and industries [7-13]. Conjugated sulfurcontaining substances are of special demand in bio-, opto-, and alternative energy electronics because of their enhanced mechanical and optical properties and the outstanding charge conductivity [12-17]. Acetylene is a simple and convenient building block for the synthesis of conjugated systems [18] and their optional modification with sulfur moieties.

In this work, we explore the possibility of S-functionalization of unsubstituted acetylene. Despite being the simplest alkyne, difficulties to handle and special precautions exclude C₂H₂ from the list of typical substrates. For comparison, in substituted alkynes the prevailing methods of C-S bond formation are metal-catalyzed syntheses with thiols, sulfides, and disulfides [19-22]. Wide substrate scopes along with high yields and high selectivities are typical for the transition metal complexes-catalyzed transformations. The chemistry of addition of thiols to alkynes is studied fairly well [1,23-31], while the reactions with disulfides are less studied [19,32]. Nevertheless, utilization of disulfides seems to have some advantages over thiols, as disulfides are nonvolatile, relatively odorless, and do not require storage under inert atmosphere. Several systems, based on Rh [33], Ni [34,35], Pd [36,37], Cu [38], or Ga [39] complexes, were reported to catalyze the addition of disulfides to various alkynes, but the issue of utilizing acetylene in this reaction was not considered.

 $Ni(acac)_2/PR_3$ catalytic systems, which have been previously developed in our laboratory, are efficient for construction of the C–S bond [34,35]. A fascinating feature of these systems is that, depending on the

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phosphine ligand, they selectively promote formation of either 1,2-bis (alkylthio)alkenes or 1,4-bis(arylthio)-1,3-dienes. However, the unique physical and chemical properties of C_2H_2 strongly distinguish it from other alkynes, thereby specific optimization of the catalytic system and reaction conditions is required for C_2H_2 involvement in the reaction.

In this study, we report an efficient catalytic system to obtain 1,2-bis (arylthio)ethenes or 1,4-bis(arylthio)-1,3-butadienes from acetylene in a highly selective manner. Controlled switching of the reaction toward one particular product is accomplished by specific choice of the ligand. As a result, two products can be obtained on demand in good to high yields and with high selectivity. Derivatives from acetylene are valuable for obtaining new materials and there is a particular practical demand for selective catalysts efficient in for synthesis of complex structures from small available molecules (acetylene).

2. Experimental

2.1. General procedures

Unless noted otherwise, the synthetic work was carried out under argon atmosphere. All synthetic procedures were designed for solvents presaturated with acetylene at 0 °C, which is mandatory to reach the best yields. The disulfides were prepared according to the previously published procedure [40]. The other reagents were obtained from Sigma Aldrich and used as supplied (checked by NMR before use). The solvents were purified according to the published methods. ¹H and ¹³C chemical shifts are reported relative to the corresponding solvent signals used as an internal reference.

2.1.1. General Synthetic Procedure for synthesis of (Z)-1,2-bis(arylthio) ethene (1)

Acetylene was bubbled through acetonitrile in a water-ice bath for 30 min. The solid reagents including disulfide (0.2 mmol), Ni(acac)₂ (6×10^{-3} mmol, 0.0015 g), and PPh₃ (6×10^{-2} mmol, 0.0157 g) were added into a screw-capped test tube. The test tube with the solid reagents was flushed with argon, and the presaturated MeCN (1 ml) was added. The tube was immediately closed with a screw cap. The reaction was carried out at 60 °C under stirring for 2 days. After completing the reaction, the solvent was evaporated on a rotary evaporator and the product was purified by flash chromatography on silica gel 60 (0.015-0.040 mm) with hexane/CH₂Cl₂ gradient elution. After drying under vacuum, the pure products were obtained.

2.1.2. General synthetic procedure for (Z,Z)-1,4-bis(arylthio)buta-1,3-diene (2)

Acetylene was bubbled through DMF in a water-ice bath for 30 min. The disulfide (0.2 mmol), Ni(acac)₂ (6×10^{-3} mmol, 0.0015 g), and PPhCy₂ (6×10^{-2} mmol, 0.0165 g) were added into a screw-capped test-tube. The test tube with the solid reagents was flushed with argon, and the presaturated DMF (3 ml) was added. The test tube was immediately closed with a screw cap connected to an acetylene balloon via an adapter. The reaction was carried out at 60 °C under stirring for 1 h. After completing the reaction, the solvent was evaporated on a rotary evaporator and the product was purified by flash chromatography on silica 60 (0.015-0.040 mm) with hexane/CH₂Cl₂ gradient elution. After drying under vacuum, the pure products were obtained as light yellow solids.

2.1.3. Synthesis of (Z,Z)-1,4-bis(phenylthio)-1,3-but adiene $(\mathbf{2a})$ using CaC_2

The reaction was carried out in a screw-capped H-type test-tube. One vessel was charged with Ph_2S_2 (0.2 mmol, 43.6 mg), Ni(acac)₂ (6 × 10⁻³ mmol, 1.5 mg), and PPhCy₂ (6 × 10⁻² mmol, 16.4 mg). Calcium carbide (2.5 mmol, 160.2 mg) and DMF (1 ml) were loaded into another vessel. Afterwards, DMF presaturated with C₂H₂ (3 ml) was quickly added to the first vessel, and distilled water (10 mmol,

0.18 ml) was added to the second one. Both vessels were closed immediately. The vessel with reagents was placed into a heating block (t = 60 °C). The reaction was carried out under stirring for 1 h.

2.2. Characterization data

The 1a [41] product was identified according to the published data.

2.2.1. (Z)-1,2-bis(4-tolylthio)ethene (1b)

White solid. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.32 (d, J = 8.2 Hz, 4 H), 7.21 (d, J = 8.1 Hz, 4 H), 6.58 (s, 2 H), 2.32 (s, 6 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 137.84, 132.48, 130.86, 130.26, 125.41, 20.97. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 378.9739, found 378.9758 ($\Delta = 5$ ppm).

2.2.2. (Z)-1,2-bis(3-tolylthio)ethene (1c)

Yellow oil. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.30 – 7.20 (m, 6 H), 7.15 – 7.07 (m, 2 H), 6.67 (s, 2 H), 2.34 (s, 6 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 140.06, 135.79, 130.32, 130.04, 128.57, 126.88, 125.32, 21.26. HRMS (ESI-TOF): m/z calcd for [M]⁺: 273.0766, found 273.0746 (Δ = 7.3 ppm).

2.2.3. (Z)-1,2-bis((4-bromophenyl)thio)ethene (1d)

White solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.45 (d, J = 8.6 Hz, 4 H), 7.26 (d, J = 8.5 Hz, 4 H), 6.49 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 134.31, 132.39, 131.12, 125.35, 121.21. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 506.7636, found 506.7637 ($\Delta = 0.2$ ppm).

2.2.4. (Z)-1,2-bis((3-bromophenyl)thio)ethene (1e)

White solid. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.60 (s, 2 H), 7.51 – 7.41 (m, 4 H), 7.35 (t, J = 7.9 Hz, 2 H), 6.84 (s, 2 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 138.37, 131.93, 131.74, 130.75, 128.42, 125.89, 123.53. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 506.7636, found 506.7629 ($\Delta = 1.4$ ppm).

2.2.5. (Z)-1,2-bis((2-bromophenyl)thio)ethene (1f)

Light oil. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.60 (dd, J = 8.0, 1.4 Hz, 2 H), 7.40 (dd, J = 7.9, 1.7 Hz, 2 H), 7.31 (td, J = 7.6, 1.4 Hz, 2 H), 7.15 – 7.05 (m, 2 H), 6.64 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 136.53, 133.37, 130.03, 128.12, 126.23, 124.03. HRMS (ESI-TOF): m/z calcd for $[M + Ag]^+$: 506.7636, found 506.7640 ($\Delta = 0.8$ ppm).

2.2.6. (Z)-1,2-bis((4-methoxyphenyl)thio)ethene (1g)

Yellow oil. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.38 (d, J = 8.9 Hz, 4 H), 6.96 (d, J = 8.9 Hz, 4 H), 6.43 (s, 2 H), 3.81 (s, 6 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 160.42, 132.81, 126.33, 125.63, 115.81, 55.74. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 410.9637, found 410.9648 ($\Delta = 2.7$ ppm). CCDC-1864715 contains the supplementary crystallographic data for this substance. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif

2.2.7. (Z)-1,2-bis((4-chlorophenyl)thio)ethene (1h)

White solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.38 – 7.28 (m, 8 H), 6.50 (s, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 133.64, 133.32, 130.94, 129.47, 125.38. HRMS (ESI-TOF): *m*/*z* calcd for [M + Ag]⁺: 418.8646, found 418.8648 (Δ = 0.5 ppm).

2.2.8. (1Z,3Z)-1,4-bis(phenylthio)buta-1,3-diene (2a)

White solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.43 – 7.37 (m, 4 H), 7.37 – 7.29 (m, 4 H), 7.30-7.19 (m, 2 H), 6.76 – 6.64 (m, 2 H), 6.45 – 6.33 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 135.69, 129.57, 129.27, 127.13, 126.97, 125.03. HRMS (ESI-TOF) *m/z* calcd for [M + Ag]⁺: 376.9582, found 376.9579 (Δ = 0.8 ppm).

2.2.9. (1Z,3Z)-1,4-bis(3-tolylthio)buta-1,3-diene (2b)

White solid. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.31 – 7.19 (m, 6 H), 7.16-7.07 (m, 2 H), 6.73 – 6.61 (m, 2 H), 6.56 – 6.48 (m, 2 H), 2.37 – 2.32 (m, 6 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 140.08, 135.85, 130.42, 130.04, 128.60, 127.80, 126.97, 124.97, 21.24. HRMS (ESI-TOF) m/z calcd for [M + Ag]⁺: 404.9895, found 404.9893 (Δ = 0,5 ppm).

2.2.10. (1Z,3Z)-1,4-bis(4-tolylthio)buta-1,3-diene (2c)

White solid. ¹H NMR (600 MHz, CDCl₃) δ , ppm: 7.29 (d, J = 8 Hz, 4 H), 7.14 (d, J = 8 Hz, 4 H), 6.66 – 6.60 (m, 2 H), 6.36 – 6.30 (m, 2 H), 2.34 (s, 6 H). ¹³C NMR (151 MHz, CDCl₃) δ , ppm: 137.12, 132.05, 130.03, 127.81, 124.28, 21.19. HRMS (ESI-TOF) m/z calcd for [M]⁺: 298.0844, found 298.0829 ($\Delta = 5$ ppm).

2.2.11. (1Z,3Z)-1,4-bis((3-bromophenyl)thio)buta-1,3-diene (2d)

Yellow solid. ¹H NMR (300 MHz, Acetone- d_6) δ , ppm: 7.58 (t, J = 1.8 Hz, 2 H), 7.51 – 7.40 (m, 4 H), 7.35 (t, J = 7.8 Hz, 2 H), 6.83 – 6.72 (m, 2 H), 6.68 – 6.56 (m, 2 H). ¹³C NMR (75 MHz, Acetone- d_6) δ , ppm: 138.71, 131.92, 131.72, 130.67, 128.38, 126.78, 126.44, 123.51. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 532.7793, found 532.7788 ($\Delta = 0.9$ ppm).

2.2.12. (1Z,3Z)-1,4-bis((4-bromophenyl)thio)buta-1,3-diene (2e)

Yellow solid. ¹H NMR (300 MHz, CD₂Cl₂) δ , ppm: 7.47 (d, J = 8.5 Hz, 4 H), 7.26 (d, J = 8.5 Hz, 4 H), 6.80 – 6.61 (m, 2 H), 6.44 – 6.28 (m, 2 H). ¹³C NMR (75 MHz, CD₂Cl₂) δ , ppm: 135.34, 132.75, 131.32, 126.98, 125.94, 121.23. HRMS (ESI-TOF): m/z calcd for [M + Ag]⁺: 532.7793, found 532.7679 ($\Delta = 21$ ppm).

2.2.13. (1Z,3Z)-1,4-bis((2-bromophenyl)thio)buta-1,3-diene (2f)

Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.57 (dd, J = 7.9, 1.0 Hz, 2 H), 7.37 – 7.27 (m, 4 H), 7.14 – 7.05 (m, 2 H), 7.00 – 6.89 (m, 2 H), 6.43 – 6.31 (m, 2 H). ¹³C NMR (126 MHz, CDCl₃) δ , ppm: 137.15, 133.21, 129.48, 128.15, 127.76, 127.69, 125.73, 123.41. HRMS (ESI-TOF): m/z calcd for $[M + Ag]^+$: 532.7793, found 532.7790 ($\Delta = 0.6$ ppm). CCDC-1864716 contains the supplementary crystallographic data for this substance. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif

2.2.14. (1Z,3Z)-1,4-bis((4-chlorophenyl)thio)buta-1,3-diene (2g)

White solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.30 (s, 8 H), 6.75 – 6.64 (m, 2 H), 6.39 – 6.27 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 134.12, 133.11, 130.79, 129.43, 126.87, 125.50. HRMS (ESI-TOF): *m/z* calcd for [M + Ag]⁺: 444.8803, found 446.8801 (Δ = 0.4 ppm).

2.2.15. (1Z,3Z)-1,4-bis((4-hydroxophenyl)thio)buta-1,3-diene (2h)

¹H NMR (300 MHz, Acetone-*d*₆) δ, ppm: 8.61 (s, 2 H), 7.33 – 7.27 (m, 4 H), 6.90 – 6.84 (m, 4 H), 6.54 – 6.42 (m, 2 H), 6.39 – 6.28 (m, 2 H). ¹³C NMR (75 MHz, Acetone-*d*₆) δ, ppm: 158.23, 133.37, 129.97, 124.77, 123.04, 117.24. HRMS (ESI-TOF): *m/z* calcd for $[M + Ag]^+$: 408.9481, found 408.9494 (Δ = 3,2 ppm).

2.2.16. (1Z,3Z)-1,4-bis((4-methoxyphenyl)thio)buta-1,3-diene (2i)

White solid. ¹H NMR (300 MHz, CDCl₃) δ , ppm: 7.35 (d, J = 8.5 Hz, 4 H), 6.88 (d, J = 8.5 Hz, 4 H), 6.62 – 6.49 (m, 2 H), 6.33 – 6.22 (m, 2 H), 3.81 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃) δ , ppm: 159.38, 132.48, 128.90, 126.04, 123.30, 114.92, 55.52. HRMS (ESI-TOF): m/z calcd for

 $[M + Ag]^+$: 436.9794, found 436.9779 ($\Delta = 3,4$ ppm).

3. Results and discussion

3.1. A model reaction with acetylene: the choice of the catalytic system and optimization of the reaction conditions

Selective catalytic addition of organic disulfides to unsubstituted acetylene is complicated by the fact that one of the reagents – acetylene – in its pure form at room temperature, is a gas. The easiest way of its addition to reaction is to involve the C_2H_2 presaturated solvent. It is a convenient method, which avoids application of complicated equipment (acetylene can be explosive under high pressure in the presence of metals). The main drawback is that the list of suitable solvents is limited to ones effectively dissolve acetylene [42]. Commonly disulfides addition to alkynes is carried out in MeCN [35], DMF [38,43], benzene or toluene [34,39,44], acetone [33,34] or without a solvent [34,37]. Concentration of dissolved acetylene in the solutions utilized in the reactions was measured at two representative temperatures at 22 °C and at 60 °C (Table S1). Under conditions studied here toluene dissolves only 0.02 mmol/ml of C_2H_2 , which makes it unsuitable for the synthesis; the other solvents dissolve about 0.1 mmol/ml of C_2H_2 at 60 °C.

Among the efficient catalysts for disulfides addition to alkynes our attention was caught by Ni-based catalytic systems. For the model reaction (Scheme 1) of acetylene with phenyl disulfide the Ni(acac)₂ was chosen as the catalytic precursor, nevertheless reaction cannot be carried out without a ligand (Table 1, entry 1). Evaluated efficiencies of the system for different phosphine ligands are given in Tables 1 and S2. The majority of the ligands were unable to promote catalytic process (Table 1, entry 2). Some interesting results were obtained for 1,1-bis (diphenylphosphino)methane (DPPM), with a good yield of the desired (Z)-1,2-bis(phenylthio)ethene (1a, 48%, Table 1, entry 3). However, the reaction was not selective and accompanied by formation of a mixture of poorly identifiable byproducts. Changing the solvent to acetone or DMF did not help to reduce the amount of byproducts (Table 1, entries 4 and 5). The competitive formation of 1a and (Z,Z)-1,4-bis(phenylthio)buta-1,3-diene 2a was observed for PPh₃ (Table 1, entries 6, 7 and 8), with the maximal ratio of 1a: 2a = 10: 1 obtained in MeCN (Table 1, entry 6). Attempts to carry out the reaction under slight acetylene overpressure led to reaction suppression (Table 2, entry 1). The product 1a yield was successfully increased to 76% by prolongation of the reaction time (Table 2, entries 2 and 3). The temperature effect was also tested; changing the temperature up to 80 °C and down to 40 °C led to decreased yield or selectivity of 1a formation (Table 2, entries 4 and 5). The amount of the PPh₃ was varied in the range from 12 mol% to 60 mol% (Table S3) and it was found that best selectivity and yield was obtained for 30 mol% of PPh3. The effect of basic additives was tested, and it was found that the introduction of inorganic bases such as Cs₂CO₃, K₂CO₃, or KOH affected the process selectivity, yielding a 3:2 mixture of 1a:2a. The utilization of organic bases (such as pyridine, Et₃N, DBU, or PhNMe₂) had no significant effect on the reactivity (Table S4).

The following conditions were finally accepted for (*Z*)-1,2-bis(arylthio)ethene **1** synthesis: Ni(acac)₂ with PPh₃ in MeCN at 60 °C. The reaction was set up in screw-capped test-tube by mixing all solid reagents, followed by addition of C_2H_2 -presaturated MeCN. To prevent the loss of C_2H_2 and, accordingly, to get better yields, the test-tube should be immediately closed. The developed reaction procedure was successfully scaled up to 1 mmol of Ph₂S₂, where the product **1a** was



Scheme 1. The model reaction of diphenyl disulfide addition to acetylene.

Table 1

Screening of ligands using a selection of solvents^a.

Entry	Ligand	Solvent	Ph_2S_2 conversion, %	Yield of $1a (\%)^b$	Yield of $2a (\%)^b$
1	-	MeCN	0	0	0
2	$P(n-C_8H_{17}),$	MeCN		< 5	< 5
	P(o-Tol) ₃ , [Ph ₂ PCH ₂ CH ₂] ₂ PPh, Cy ₂ PCH ₂ PCy ₂ , PPhMe ₂ , PPh ₂ Me, PCy ₂ (o-Tol), PCy ₃				
3	DPPM ^c	MeCN	100	48	0
4	DPPM ^c	Acetone	100	29	0
5	DPPM ^c	DMF	100	28	0
6	PPh ₃	MeCN	22	20	2
7	PPh ₃	Acetone	22	18	4
8	PPh ₃	DMF	62	39	23

^a Reaction conditions: Ph₂S₂ (0.2 mmol), Ni(acac)₂ (3 mol%), phosphine (30 mol%), C₂H₂-saturated solvent (1 ml), 3 h, 60 °C.

^b The yields were determined by ¹H NMR.

^c Full conversion to a complex mixture of unidentified products.

Table 2

Entry	Temperature (°C)	Time (h)	Yield of $1a (\%)^{b}$	Yield of $2a (\%)^{b}$
1	60 ^c	3	6	0
2	60	17	56	7
3	60	24	76	14
4	80	17	63	15
5	40	17	17	0

 a Reaction conditions: Ph_2S_2 (0.2 mmol), $Ni(acac)_2$ (3 mol%), PPh_3 (30 mol%), MeCN saturated with C_2H_2 (1 ml).

^b The yields were determined by ¹H NMR.

^c The reaction was carried under 0.045 \pm 0.005 atm C₂H₂ overpressure.

isolated in a 74% yield (82% as determined by ¹H NMR).

During the screening for optimal ligands, the competitive substrate transformation yielding 1,3-butadiene 2a was taken into consideration as an alternative route worth studying in more details. In earlier study carried out in our laboratory it was discovered that PPhCy₂ ligand specifically favors the formation of 1,3-dienes [35], thus all investigations of this transformation were carried out with this particular ligand. Utilization of the reaction conditions earlier optimized for the 1a synthesis resulted in formation of 10% product mixture (1a:2a = 3:7, Table 3, entry 1). Considering that formation of a diene requires 2 equiv. of acetylene, we increased the volume of the C₂H₂-saturated solvent and carried out the reaction under connection to a latex balloon filled with acetylene (see Section 3.6 for details). This modification raised the 2a yield to a remarkable 41% (Table 3, entry 2). Replacement of MeCN with acetone decreased the yield (Table 3, entry 3), but using DMF instead of MeCN increased the yield to 81% (Table 3, entry 4). Thus, the optimal reaction conditions for synthesis of 1,4-bis(phenylthio)-1,3-butadiene 2a are Ni(acac)₂ with PPhCy₂ in C₂H₂-presaturated DMF under C2H2 pressure at 60 °C. The procedure was successfully scaled up to 1 mmol of the disulfide, where the isolated yield of 2a was 64% (83% as determined by ¹H NMR).

Table 3	3
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Optimization of the 2a synthesis^a.

Entry	Solvent	Yield of $1a (\%)^b$	Yield of $2a (\%)^b$	Acetylene pressure
1	MeCN (1 ml)	3	7	NO
2	MeCN (3 ml)	7	41	Balloon
3	Acetone (3 ml)	2	15	Balloon
4	DMF (3 ml)	15	81	Balloon

 a Reaction conditions: Ph_2S_2 (0.2 mmol), Ni(acac)_2 (3 mol%), PPhCy_2 (30 mol%), C_2H_2 -saturated solvent, 1 h, 60 °C under C_2H_2 pressure 0.045 \pm 0.005 atm.

^b The yields were determined by ¹H NMR.

3.2. Notes on switching between bis(arylthio)ethene and bis(arylthio)-1,3butadiene products during the addition of disulfides to acetylene

During screening for the optimal reaction conditions for the Ni $(acac)_2$ -catalyzed addition of disulfides to acetylene, a competitive formation of two different products was observed: 1,2-bis(arylthio) ethene (1) and 1,4-bis(arylthio)-1,3-butadiene (2, Scheme 2). The developed systems for selective formation of a single product have much in common; their selectivities are defined by particular ligands and the acetylene pressure. When using PPh₃ in MeCN, the reaction switches to formation of 1. For successful synthesis of 2, it is required to replace PPh₃ with PPhCy₂ and to use the excess of acetylene, so the best yields of 2 are obtained in DMF. The use of solvents presaturated with C_2H_2 is essential for both syntheses. It is important to note that the synthesis of 2 can be completed in just 1 h.

With the optimized switchable procedures at hand, the scopes of both reactions were examined.

3.3. Synthesis of (Z)-1,2-bis(arylthio)ethenes (1)

Performances of various aromatic disulfides in the reaction of ethene 1 synthesis are shown in Scheme 3. The products were isolated in moderate to high yields (up to 85%). The directing effect of a substituent in the aromatic ring of disulfide is significant in the case of 1 synthesis, as the best yields of the products were invariably obtained with para-substituted disulfides. A shift of the substituent to ortho- or meta-position dramatically decreases the reactivity potential of disulfide. For example, despite the 85% yield of (Z)-1,2-bis(4-tolylthio) ethene 1b, the yield of (Z)-1,2-bis(3-tolylthio)ethene 1c was only 28%, even with the reaction time extension to 6 days. Moreover, no conversion was detected in the reaction with (2-TolS)₂. The same trend was observed in the case of electron-withdrawing bromine group, where the bromophenyl disulfide (products 1d > > 1e > 1f). The products with electron-donating groups in para-position (1b, 1g) were obtained in higher yields than the corresponding products with electron-withdrawing groups (1d, 1h). Interestingly, the utilization of the aliphatic disulfide (n-butyl disulfide) did not result in the product formation.

Molecular structure of 1g was determined by X-ray crystallography;







Scheme 3. The scope of 1,2-bis(arylthio)ethenes (1). Isolated yields (the yields determined by ¹H NMR are shown in parentheses). [a] The reaction proceeded for 6 days. [b] The reaction was carried out in acetone due to the low solubility of disulfide in MeCN.



Fig. 1. The structure of 1g, as determined by X-ray crystallography.

the analysis clearly indicated cis-configuration of the product (Fig. 1).

3.4. Synthesis of (Z,Z)-1,4-bis(arylthio)-1,3-dienes (2)

Performances of various aromatic disulfides in the reaction of butadiene **2** synthesis are shown in Scheme **4**. The products were isolated in moderate to high yields (28–85%). Effects of methyl, bromide, chloride, hydroxyl and methoxy substituents in various position of phenyl disulfide were studied. No considerable influence of the electronic properties of a substituent in the aromatic ring on the reactivity of disulfide was observed. The effect of substituent position in the synthesis of **2** was even stronger than in the synthesis of **1**. The best yields were obtained in reactions with *meta*-substituted phenyl disulfides. Relocation of a substituent from *meta*- to *para*- position generally resulted in lower yields. The presence of a substituent in *ortho*-position was fatal to the yields (*m*->*p*->*o*-, **2b**>**2c** and **2d**>**2e**>**2f**, Scheme 4); complete absence of the reactivity was observed for (*o*-TolS)₂. Interestingly, the pure **2h** product can be obtained from (*p*-HOC₆H₄S)₂ in a yield of 73%, while the counterpart synthesis of 1,2-bis(4-hydroxyphenylthio)ethene from the same disulfide did not



Scheme 4. The scope of afforded 1,4-bis(arylthio)-1,3-butadienes with corresponding isolated yields (the yields determined by ¹H NMR are shown in parentheses).



Fig. 2. The structure of 2e, as determined by X-ray crystallography.

proceed. At the same time, the usage of *para*-substituted bis(4-meth-oxyphenyl) disulfide allowed obtaining the products 1g and 2i in 85% and 66% yields, respectively. The reaction with *n*-butyl disulfide did not lead to the product formation.

Molecular structure of **2e** was determined by X-ray crystallography; the study clearly indicated *cis*, *cis*-configuration of butadiene skeleton (Fig. 2).

3.5. Mechanistic studies

Mechanistic features, which govern exclusive formation of products 1 or 2, were of much interest to investigate. Both reactions are nickeldriven and utilize the same starting materials, which is a great practical advantage. The main tool of switching among the products of disulfide addition to acetylene toward a particular product is the variation in phosphine ligand. Application of PPh₃ results in the slow formation of ethene 1, while PPhCy₂ promotes the fast conversion of the reactants into butadiene 2.

The mechanistic investigation was initially focused on the reaction of acetylene and phenyl disulfide catalyzed by Ni(acac)₂ with PPh₃ in MeCN (Scheme 2A). A ESI-MS monitoring of the model reaction was carried out and the obtained spectrum is shown on Figure S1. The dominant peaks correspond to the group of ions [PPh₃(SPh)]⁺ ion (m/z = 371.1027), [PPh₃(SPh)C₂H₂]⁺ (m/z = 397.1177), [PPh₃(SPh)(C₂H₂)₂]⁺ (m/z = 423.1331) and [PPh₃(SPh)(C₂H₂)₃]⁺ (m/z = 449.1484). Thus, none of the nickel-containing species were detected by the ESI-MS spectrum in positive ion mode. Using a number of different substrates and ligands more prone to ionization (*para*-methoxyphenyl disulfide, tris(*para*-methoxyphenyl) phosphine) led to similar results.

Since nickel-containing ions were not detected in solution by ESI-MS, we assumed that the catalyst might have heterogeneous contribution. The precipitate behavior in the liquid phase was studied by liquidphase scanning electron microscopy (SEM) (Fig. 3). All components of the reaction, except acetylene, were mixed and stirred at room

temperature for 10 min. An aliquot of the resulting suspension was placed into a microcapsule with an electron-beam permeable membrane [45]. The presence of spherical particles about 500 nm in diameter was observed in the sample. Electron beam irradiation of the sample area with particles produced the signals in energy dispersive X-Ray (EDX) spectrum corresponded to carbon, nickel, sulfur and minor amount of phosphorus (Fig. 3a). Comparison with the background spectrum of liquid sample area clearly demonstrated that the particles were enriched with nickel and sulfur, thus most likely they represent the nickel thiolate polymeric species. The uniform background areas of the sample formed by solution phase contained carbon, sulfur, phosphorous and traces of nickel (Fig. 3b). Obtained results allow to propose that before the catalysis nickel is accumulated in the solid phase in the form of [Ni(SPh)₂]_n coordination polymer. At the first stage of [Ni (SPh)₂]_n formation Ni(acac)₂ reacted with Ph₂S₂ with generation of Ni (SPh)₂ species in solution (Scheme 5a). Most likely Ni(II) precursor at first reduced to Ni(0) by PPh₃ (this is a known process, see [46] for example), followed by oxidative addition of S-S bond. The coordination between Ni(SPh)2 units led to the formation of particles with the polymeric structure [Ni(SPh)₂]_n (Scheme 5a).

Rapid dissolution of the $[Ni(SPh)_2]_n$ particles was observed under the electron beam irradiation at relatively high beam current densities. The complete disappearance of the particles was observed within 10 s of irradiation (Fig. 3c, Movie S1). Gradual and uniform decrease of the particles size without notable changes in their shape was observed during dissolution. Thus, the local heating of the nickel thiolate particles in the presence of phosphine and disulfide solution led to the transfer of Ni-containing species to the liquid phase which can be considered as a direct evidence of catalyst leaching (Scheme 5b). The dissolution of $[Ni(SPh)_2]_n$ did not proceed without PPh₃.

In order to demonstrate the correlation between the processes in a microcapsule in liquid-phase SEM and in a test-tube under the reaction conditions, we isolated the precipitate formed in the reaction mixture for the **1a** synthesis after 3 h at 60 °C. The morphology of the isolated solid phase was analyzed by SEM (Figure S2). It consisted of small spherical particles about 25 nm in diameter. EDX study confirmed the presence of nickel and sulfur in its composition and the absence of phosphorus. Therefore, the formation of $[Ni(SPh)_2]_n$ under the catalytic conditions was confirmed independently by liquid- and solid-phase SEM studies.



Fig. 3. SEM-EDX study of the nickel thiolate morphology in the liquid medium and its dissolution process. EDX spectra collected from the sample area with roundshaped particles (a) and from uniform sample area (b). Snapshots taken from the SEM video of particles dissolution under electron beam irradiation (c).



The comparison of two types of the precipitate showed a significant difference in the sizes of the particles. For the evaluation of the size effect, $[Ni(SPh)_2]_n$ was synthesized under the conditions identical to the liquid-phase SEM experiment. The analysis of its morphology and chemical composition by SEM/EDX showed the formation of spherical nickel thiophenolate particles with the size of 600–700 nm (Figure S3). Upon utilization of the obtained $[Ni(SPh)_2]_n$ as a catalyst in the model reaction, the yield of the desired product **1a** reached 20% after 3 h which was similar to the Ni(acac)₂ system (Table 1, entry 6). SEM analysis of the solid $[Ni(SPh)_2]_n$ after the reaction revealed a slight surface modification (Figure S3), what could be indicative of the only near-surface layer participation in catalysis. It should be noted that the PPh₃ addition was also required for the reaction of acetylene with phenyl disulfide catalyzed by $[Ni(SPh)_2]_n$.

To establish the role of leaching in the catalytic transformation, we carried out a hot centrifugation test of the reaction mixture (Fig. 4). The synthesis of **1a** from acetylene and phenyl disulfide catalyzed by the Ni $(acac)_2/PPh_3$ system in acetonitrile was chosen as a model reaction. After 3 h, the Ph₂S₂ conversion reached 18%, and the solution was separated from the precipitate. The catalytic activity of the solid was evaluated in the model reaction that shown high conversion of Ph₂S₂ into **1a** (78%).

The separated solution was bubbled with a new portion of acetylene and then was heated at 60 $^{\circ}$ C for 17 h. The yield of **1a** increased from

Scheme 5. Evolution of sulfur-containing nickel species: formation of coordination polymer from Ni(acac)₂ precursor (a) and leaching of mononuclear nickel species from [Ni(SPh)₂]_n in the presence of excess of phosphine ligand L = PPh₃ (b). The following steps are indicated: i – reduction of Ni(acac)₂ by phosphine ligand and reaction with Ph₂S₂ to form Ni(SPh)₂ species; ii - coordination of SPh groups in μ_2 -mode; iii - formation of polymeric species via coordination; iv – ligand-induced reversible leaching process.

18% to 55%. Notably, the formation of a thin layer of brown solid on the test-tube inner walls was observed. Therefore, the solution was removed and the test-tube was washed twice with acetonitrile (a solid layer remained on the walls after washing). Afterwards a new portion of the reagents and ligand were added. Subsequent heating of the reaction mixture resulted in formation of alkene **1a** (30%) and diene **2a** (3%).

The leaching test and liquid-phase SEM demonstrate that catalytically active species can be transferred from the solid phase to solution during the leaching process, which is probably initiated by phosphine ligands (Scheme 5b). According to the experiments, it can be proposed that the reaction proceeds in the solution (rather than on the surface of the precipitate) and transfer of metal-containing species between the solid precipitate and solution is an important feature of the studied system. It should be mentioned that leaching is most likely a reversible process and the ratio between solid polymer and soluble species may be affected by reaction conditions (excess of ligands, solvent, temperature, etc.).

To get a deeper understanding of the leaching process reversibility and of the role of thiolates in the catalytic transformation, we introduced two types of SAr groups into the reaction: Sp-BrC₆H₄ in the form of nickel thiolate and Sp-ClC₆H₄ in the form of disulfide. The transfer of groups with different halide substituent can be easily detected by EDX and SEM analysis of the solid. The freshly prepared complex [Ni(Sp-BrC₆H₄)₂]_n with a characteristic biconcave morphology



Fig. 4. Mechanistic study of the nature of the catalytic system by using the hot centrifugation leaching test.



Fig. 5. SEM-EDX study of the leaching-redeposition process in Ni-catalyzed disulfide addition to acetylene. Model reaction of *p*chlorophenyl disulfide addition to acetylene in the presence of $[Ni(Sp-BrC_6H_4)_2]_n$ thiolate precatalyst (a). SEM images of the initial nickel thiolate (b) and nickel thiolate isolated after the reaction (c) with corresponding EDX spectra (d and e, respectively).

(Fig. 5b) was utilized as a catalyst in $(p-\text{ClC}_6\text{H}_4\text{S})_2$ addition to acetylene (Fig. 5a). After 17 h the 54% conversion of $(p-\text{ClC}_6\text{H}_4\text{S})_2$ was reached, and the morphology and composition of the precipitate were investigated (Fig. 5). The experiment resulted in a complete transformation of the initial biconcave $[\text{Ni}(\text{Sp-BrC}_6\text{H}_4)_2]_n$ morphological patterns (Fig. 5b) into agglomerated nickel thiolate nanoparticles (Fig. 5c), with almost complete replacement of Br by Cl on the surface, what was proved with EDX analysis (compare spectra in Fig. 5d and e). This result supports the idea of leaching reversibility.

A plausible reaction mechanism was proposed taking into account the experimental data and catalytic cycles reported earlier [34,35,37,46–49]. Particularly, two possibilities of the interaction between the nickel precatalyst and substrates were considered: the reaction with disulfide resulting in the generation of a nickel thiolate complex **3** (Scheme 6) or the reaction with acetylene leading to the formation of a metallocycle (Scheme S1). On the basis of a set of experiments showing formation of nickel thiolate complexes the preference was given to the thiolate-based pathway (Scheme 6). This also agrees with the reported earlier studies of Ni-based systems [34,35,37,46–48].

The strength of Ni-P bond in the nickel-phosphine complex with the more electron-donating PPhCy₂ is higher than in the complex with PPh₃ [48,50]; thus, the formation of solid $[Ni(SAr)_2]_n$ is observed for PPh₃, but not for PPhCy₂. As we mentioned above (Scheme 5) nickel thiolate can form a coordination polymer with bridging SAr groups. Involvement in homogeneous catalysis may be achieved under the PPh₃ influence, resulting in the formation of soluble $Ni(SAr)_2L_2$ complex 4. This transformation from a heterogeneous form to a homogeneous one is reversible and depends on reaction conditions. The PPhCy₂ ligand apparently favor an alternative pathway of the direct catalyst activation (Scheme 6). The identity of the main product is therefore predetermined by the nature of the ligand.

The catalytic cycle starts after the precatalyst activation, which is followed by coordination of acetylene to nickel and its subsequent insertion into the Ni-S bond (Scheme 6). These events lead to intermediate 5. In the case of lower electron-donating $L = PPh_3$ the intermediate 5 is more prone to bis(arylthio)ethene 1 elimination. Whereas for $L = PPhCy_2$ the rate of elimination step is lower, thus the reaction

proceeds via the second alkyne insertion into Ni-C bond and results in formation of bis(arylthio)-1,3-butadiene **2** [51]. The way of insertion of the second acetylene molecule and the structure of intermediate **6** are deduced from computational studies [35]. An interesting consideration concerns life time of metal species in solution phase. In the case of $L = PPh_3$ ligand nickel intermediate may have a shorter life time, which may not be sufficient for reaction with the second acetylene molecule. While for nickel species stabilized with $L = PPhCy_2$ ligand sufficient life time in solution may provide better opportunities for reaction with more than one acetylene molecule.

3.6. Synthesis of 1,4-bis(arylthio)-1,3-butadienes using CaC₂

Storage and handling of acetylene under high pressure requires compliance with special safety precautions. Chemical synthesis with the direct involvement of gaseous C_2H_2 requires careful optimization of the reaction conditions and proper selection of a catalyst; for instance, Ag, Cu and some other contaminants should be avoided to exclude the formation of explosive acetylenides. Here we avoided usage of excess of gaseous acetylene and tried alternative experimental approach as well.

A method of synthesis of (*Z*,*Z*)-1,4-bis(arylthio)-1,3-butadienes, which is proposed in the current article, utilizes extra source of acetylene connected directly to a test tube (Fig. 6A). Alternative convenient way of handling acetylene in the laboratory, is to use solid acetylene source - CaC_2 , with direct release of C_2H_2 into reaction mixture.

The proof-of-principle for selective production of 2a with utilization of CaC₂ was studied here. It employs H-type test-tube with screw caps (Fig. 6B). One chamber of the H-type test-tube was loaded with the reaction mixture; another chamber contained CaC₂, water and DMF. It should be noted, that CaC₂ with water were used only to provide additional pressure of acetylene. The amount of CaC₂ was chosen to fit the same excess pressure range. The acetylene pressure is continuously maintained by slow release of acetylene from the carbide-and-water chamber. The reaction was carried out for 1 h at 60 °C and resulted in products **1a:2a** with 6%:69% yields.



Scheme 6. The plausible mechanism of switchable ethene/butadiene formation.



Fig. 6. Design of reactionware for the synthesis of 2a under acetylene pressure.

4. Conclusions

The proposed method of acetylene heterofunctionalization provides an access to bis(arylthio)-substituted ethenes 1 and butadienes 2 with moderate to high yields and with high selectivities. Specific choice of a phosphine ligand allows switching the process towards different products.

Certain technical difficulties of obtaining bis(arvlthio)butadienes can be solved by using a modified synthetic procedure, which involves an H-tube with calcium carbide as an acetylene source. Both procedures are scalable up to synthetically relevant 1 mmol quantities.

Mechanistically, both reactions have common points and proceed through the steps of catalyst activation, alkyne coordination, and product elimination. The difference is that the diene synthesis involves the direct formation of catalytically active species under homogeneous conditions, whereas the ethene synthesis has much more complex mechanism and involves the formation of insoluble [Ni(SAr)2]n and leaching of catalytically active species under the PPh₃ influence. This process was studied using an extended hot centrifugation test and was directly monitored by liquid-phase electron microscopy. Microscopy technique used in our studies goes far beyond the considered reaction and may provide a fascinating tool to investigate other catalytic systems at micro- and nano-scale in real time.

Although there are several experimental evidences of the homogeneous reaction pathway, it should be noted that typically all the leaching-driven processes are highly complex due to their dynamic nature and there are some limitations in the mechanistic knowledge that can be revealed at this stage. Further studies are needed to reveal

the phenomenon of dynamic transformations of catalytic centers in more details.

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Appendix A. Supplementary data

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