

## Transition Metal-Catalyzed Cross-Coupling of 1,4-Diiodobutadienes with Thiols—A Novel Route to 1,4-Bis(R-sulfanyl)buta-1,3-dienes

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**Abstract**—Cross-coupling of 1,4-diiodobuta-1,3-dienes with thiols in the presence of Pd, Ni, and Cu complexes gives 1,4-bis[aryl(alkyl)sulfanyl]buta-1,3-dienes in high yields.

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$\alpha,\omega$ -Bis(R-sulfanyl)alkadienes are poorly explored and difficultly accessible compounds. On the other hand, their use in the synthesis of functionally substituted carbo- [1, 2] and heterocyclic derivatives [3–5] has been reported. Buta-1,3-diene-1,4-dithiols are precursors of important analogs of naturally occurring compounds such as thiarubrines (1,2-dithiine derivatives) [6–8] that exhibit a broad spectrum of biological activity, including antiviral [9], antibacterial [10, 11], and antitumor action [12]; they also showed a considerable anti-HIV-1 effect [13].

1,4-Bis(sulfanyl)buta-1,3-dienes are usually synthesized by addition of thiols to diacetylene [14] and substituted diacetylenes [7, 8, 15] in the presence of a base or by reaction of 1,4-dilithiobuta-1,3-diene with disulfides or thiols [7, 16]. Nucleophilic replacement of halogen in polyhalobutadienes by thiols in alkaline medium was also reported [17–19]. However, the yields of 1,4-bis(sulfanyl)buta-1,3-dienes thus obtained were quite moderate, and the reactions were accompanied by formation of difficultly separable mixtures of mono- and disubstitution and addition products.

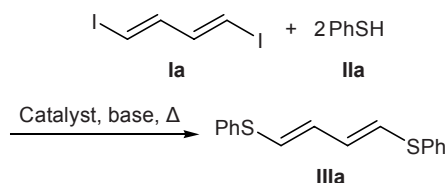
The use of transition metal complexes to catalyze addition of thiols to alkynes [20, 21] and cross-couplings of alkenyl halides with thiols, thiolates, or their synthetic equivalents ensures chemo- and stereoselective syntheses of alkenyl sulfides in high yields. Palladium [22–31], nickel [32, 33], and copper complexes [34–38] were used for this purpose.

We recently showed that (*E,E'*)-1,4-diiodobuta-1,3-diene is a synthetic equivalent of buta-1,3-diene-1,4-

diyl cation in Pd- or Ni-catalyzed cross-couplings with carbon- and heteroelement-centered nucleophiles [39]. Taking into account synthetic importance of bis(sulfanyl)dienes and our interest in developing new catalytic methods for building up *sp*<sup>2</sup>- and *sp*-carbon-heteroelement bonds [40–44], in the present work we examined cross-coupling reactions of (*E,E'*)-1,4-diiodobuta-1,3-diene and (*Z,Z'*)-1,4-diiodo-1,4-diphenylbuta-1,3-diene with benzene- and alkanethiols in the presence of transition metal complexes. We anticipated that this reaction will provide a simpler and general procedure for the synthesis of bis(sulfanyl)butadienes.

Using the reaction of (*E,E'*)-1,4-diiodobuta-1,3-diene (**Ia**) with benzenethiol (**IIa**) as an example (Scheme 1), we tried to select optimal catalytic system, base, and solvent. The results are collected in table. Cross-coupling of alkenyl halides with thiols is commonly carried out in the presence of a palladium catalyst and a base [24, 25]. We found that the nature of the base is very important for the reaction of diiodobutadiene **Ia** with thiol **IIa**, catalyzed by Pd complexes. No reaction occurred using 4 mol % of tetrakis(triphenylphosphine)palladium in the presence of triethylamine even on prolonged heating in boiling

Scheme 1.



Cross-coupling of (*E,E'*)-1,4-diiodobuta-1,3-diene with benzenethiol<sup>a</sup>

Run no.	Catalyst (mol %)	Base (solvent)	Temperature, °C (time, h)	Yield, %
1	No catalyst	<i>t</i> -BuOK ( <i>t</i> -BuOH)	83 (20)	30
2	Pd(PPh <sub>3</sub> ) <sub>4</sub> (4)	Et <sub>3</sub> N (toluene)	100 (10)	0
3	Pd(PPh <sub>3</sub> ) <sub>4</sub> (4)	<i>t</i> -BuOK (toluene)	110–120 (10)	80
4	Pd <sub>2</sub> dba <sub>3</sub> (2)/DPEphos (4) <sup>b</sup>	<i>t</i> -BuOK (toluene)	110 (2)	90
5	PdCl <sub>2</sub> (BDPB) (4) <sup>c</sup>	<i>t</i> -BuOK (toluene)	100–110 (2)	96
6	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (5)	<i>t</i> -BuOK (toluene)	110–115 (10)	84
7	Ni(cod) <sub>2</sub> (5)	K <sub>2</sub> CO <sub>3</sub> (DMF)	110–120 (23)	89
8	Ni[P(OEt) <sub>3</sub> ] <sub>4</sub> (5)	K <sub>2</sub> CO <sub>3</sub> (DMF)	110–120 (12)	78
9	NiBr <sub>2</sub> (5)	K <sub>2</sub> CO <sub>3</sub> (DMF)	120 (12)	95
10	Ni(acac) <sub>2</sub> (5)	K <sub>2</sub> CO <sub>3</sub> (DMF)	120 (4)	97
11	CuI (10)/ethylene glycol	K <sub>2</sub> CO <sub>3</sub> ( <i>i</i> -C <sub>5</sub> H <sub>11</sub> OH)	120 (9)	90

<sup>a</sup> 1,4-Diiodobuta-1,3-diene, 0.5 mmol; benzenethiol, 1 mmol; *t*-BuOK, 1.1 mmol, or K<sub>2</sub>CO<sub>3</sub>, 2 mmol; solvent, 2 ml.<sup>b</sup> DPEphos is 2,2'-bis(diphenyl-λ<sup>3</sup>-phosphanyl)diphenyl ether.<sup>c</sup> BDPB is (*Z,Z'*)-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene.

toluene (run no. 2). A stronger base, potassium *tert*-butoxide ensured successful cross-coupling of benzenethiol (**IIa**) with diiodobutadiene **Ia** in the presence of both Pd(0) complex (run no. 3) and bis(triphenylphosphine)palladium(II) dichloride (run no. 6). All Pd-catalyzed reactions with the use of potassium *tert*-butoxide as a base gave 1,4-bis(phenylsulfanyl)buta-1,3-diene (**IIIa**) in high yield, though they required fairly high temperature.

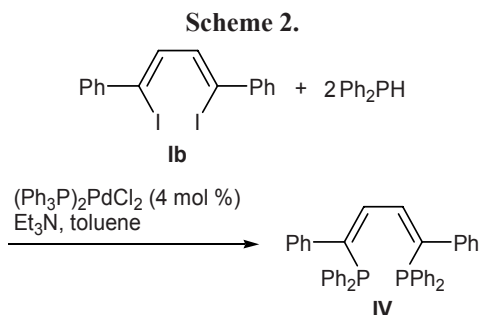
Mann et al. [45] previously studied reactions of vinyl halides with sodium thiolates and found that the use of Pd complexes with bidentate chelating phosphine ligands shortens the reaction time and increases the yield, presumably due to facilitation of the reductive elimination step. A positive effect of bidentate ligands was also observed in the cross-coupling of diiodobutadiene **Ia** with benzenethiol (**IIa**). In the presence of the catalytic system Pd<sub>2</sub>dba<sub>3</sub>–DPEphos the reaction time shortened from 10 to 2 h (run no. 4), and the yield of **IIIa** increased to 90%. Another bidentate ligand, (*Z,Z'*)-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-di-

phenylbuta-1,3-diene (**IV**) was synthesized by us for the first time by cross-coupling of (*Z,Z'*)-1,4-diiodo-1,4-diphenylbuta-1,3-diene (**Ib**) with diphenylphosphine in the presence of bis(diphenylphosphine)palladium(II) dichloride and triethylamine (Scheme 2).<sup>\*</sup> The complex derived from diphosphine **IV** and PdCl<sub>2</sub> successfully catalyzed the reaction of diiodobutadiene **Ia** with benzenethiol (run no. 5), and the yield of bis-sulfide **IIIa** was as high as 96%.

We recently showed [47–50] that nickel complexes and salts are efficient catalysts in reactions leading to formation of new C<sub>sp<sup>2</sup></sub>–P bonds. Catalytic systems on the basis of nickel complexes turned out to be efficient in the cross-coupling of (*E,E'*)-1,4-diiodobuta-1,3-diene with benzenethiol. Both Ni(0) (run nos. 7, 8) and Ni(II) complexes (run no. 10), as well as nickel salt containing no additional ligands (run no. 9), were tried. In these cases, the best results were obtained using dimethylformamide as solvent and potassium carbonate as base. The yields of 1,4-bis(phenylsulfanyl)buta-1,3-diene were comparable with those in Pd-catalyzed reactions, while NiBr<sub>2</sub> and Ni(acac)<sub>2</sub> as catalyst precursors ensured considerably higher yields than in the presence of Pd complexes with unidentate ligands.

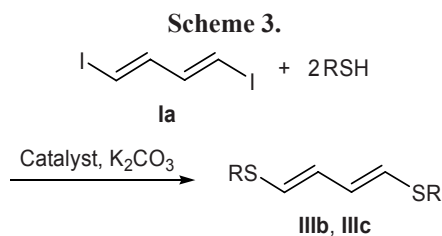
It is known that sulfanylation of alkenyl halides can be achieved using an equimolar amount of copper(I) salts [37, 38] or a catalytic amount of copper(I) complexes with nitrogen-containing ligands [36, 51, 52].

<sup>\*</sup> Tetrasubstituted (*Z,Z'*)-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)buta-1,3-dienes and their complexes with PdCl<sub>2</sub> and PtCl<sub>2</sub> were reported recently [46].

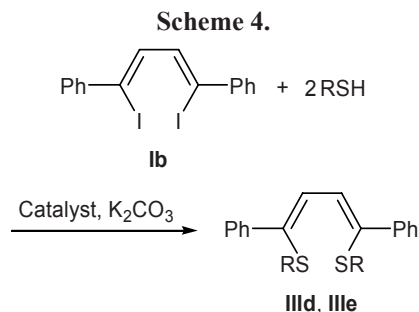


We examined the reactions of diiodobutadiene **Ia** with thiols in the presence of a copper-based catalyst. Copper(I) iodide in combination with 2 equiv of ethylene glycol in isopropyl alcohol is an active catalytic system for the amination [53] and sulfenylation [54] of aryl halides. Probably, ethylene glycol acts simultaneously as co-solvent and ligand. This simple catalytic system turned out to be efficient in the cross-coupling of 1,4-diiodobuta-1,3-diene with benzenethiol (run no. 12). Here, either potassium carbonate or potassium phosphate may be used as base, and high-boiling isopentyl alcohol, as solvent.

The optimal conditions found were applied to the synthesis of (*E,E'*)- and (*Z,Z'*)-1,4-bis[alkyl(aryl)sulfanyl]buta-1,3-dienes **IIIb–IIIe** via cross-coupling of **Ia** and **Ib** with alkanethiols and benzenethiol (Schemes 3, 4). The reactions occurred with conservation of the original double bond configuration. 1,4-Bis(benzylsulfanyl)-1,4-diphenylbuta-1,3-diene (**IIIe**) [8] was reported previously. Newly synthesized compounds **IIIa–IIIc** were isolated as colorless crystalline substances which can be stored in an inert atmosphere. Their structure was confirmed by elemental analysis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.



DMF, 5 mol % of Ni(acac)<sub>2</sub>; R = *n*-C<sub>6</sub>H<sub>13</sub> (**b**, 69%), PhCH<sub>2</sub> (**c**, 96%); *i*-C<sub>3</sub>H<sub>7</sub>OH, 10 mol % of CuI, 2 equiv of ethylene glycol; R = *n*-C<sub>6</sub>H<sub>13</sub> (**b**, 96%), PhCH<sub>2</sub> (**c**, 86%).



*i*-C<sub>3</sub>H<sub>7</sub>OH, 10 mol % of CuI, 2 equiv of ethylene glycol; R = Ph (**d**, 97%), PhCH<sub>2</sub> (**e**, 78%).

Thus we have developed a procedure for the synthesis of difficultly accessible 1,4-bis[aryl(alkyl)sulfanyl]buta-1,3-dienes via cross-coupling of 1,4-diiodo-

buta-1,3-dienes with thiols in the presence of both Pd complexes and very simple, accessible, and low-expensive catalytic systems such as nickel(II) acetylacetonate and copper(I) iodide–ethylene glycol.

## EXPERIMENTAL

The progress of reactions was monitored by thin-layer chromatography on Silufol plates using ethyl acetate–hexane as eluent. The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Varian VXR-400 instrument at 400, 100.6, and 162 MHz, respectively, using CDCl<sub>3</sub> as solvent and reference (<sup>1</sup>H, <sup>13</sup>C); the <sup>31</sup>P chemical shifts were measured relative to 85% H<sub>3</sub>PO<sub>4</sub>.

All operations with readily hydrolyzable and oxidizable compounds and transition metal complexes were carried out under dry argon (it was dried by passing through a column filled with phosphoric anhydride). The solvents used were purified and dehydrated according to standard procedures: benzene, toluene, THF, hexane, and petroleum ether were heated under reflux over metallic sodium in the presence of benzophenone; methylene chloride was distilled over phosphoric anhydride; DMF was preliminary held over anhydrous copper sulfate and distilled over calcium hydride; isopropyl and isopentyl alcohols and ethylene glycol were subjected to fractional distillation.

(*E,E'*)-1,4-Diiodobuta-1,3-diene [55], (*Z,Z'*)-1,4-diiodo-1,4-diphenylbuta-1,3-diene [56], diphenylphosphine [57], bis(triphenylphosphine)palladium(II) dichloride [58], tetrakis(triphenylphosphine)palladium(0) [59], bis(triphenylphosphine)nickel(II) dibromide [60], tetrakis(triethyl phosphite)nickel(0) [61], bis(cyclooctadienyl)nickel(0) [62], and (dibenzylideneacetone)-palladium(0) [63] were prepared by known methods. Benzenethiol, phenylmethanethiol, hexane-1-thiol, and 2,2'-bis(diphenylphosphino)diphenyl ether (DPEphos) were commercial reagents (Aldrich).

**(*E,E'*)-1,4-Bis(phenylsulfanyl)buta-1,3-diene (IIIa) (noncatalytic synthesis).** Benzenethiol (**IIa**), 0.743 g (6.75 mmol) and potassium *tert*-butoxide, 0.302 g (2.7 mmol), were added to a solution of 0.415 g (1.35 mmol) of (*E,E'*)-1,4-diiodobuta-1,3-diene (**Ia**) in 15 ml of *tert*-butyl alcohol. The mixture was heated to the boiling point, stirred for 20 h at that temperature, and cooled, and a saturated aqueous solution of sodium carbonate and 40 ml of ethyl acetate were added. The organic layer was separated, the solvent was removed under reduced pressure, and the solid residue was dried and recrystallized from petroleum ether. Yield 0.11 g (30%), mp 63–64°C.

**Catalytic system (Ph<sub>3</sub>P)<sub>4</sub>Pd.** *a. In the presence of triethylamine.* An ampule was flushed with argon and charged with 0.07 g (0.23 mmol) of compound **Ia**, 0.05 g (0.46 mmol) of benzenethiol, 0.051 g (0.5 mmol) of triethylamine, and 0.011 g (4 mol %) of tetrakis(triphenylphosphine)palladium(0) in 2 ml of toluene. The ampule was flushed again with argon, sealed, and heated for 10 h at 100°C. According to the TLC data (hexane–diethyl ether, 3:1), the mixture contained only 1,4-diiodobuta-1,3-diene (**Ia**) and benzenethiol.

*b. In the presence of potassium tert-butoxide.* An ampule was flushed with argon and charged with 0.153 g (0.5 mmol) of compound **Ia**, 0.11 g (1.0 mmol) of benzenethiol, 0.123 g (1.1 mmol) of potassium *tert*-butoxide, and 0.023 g (4 mol %) of tetrakis(triphenylphosphine)palladium(0) in 5 ml of toluene. The ampule was flushed again with argon, sealed, and heated for 10 h at 110–120°C. When the reaction was complete (TLC, hexane–ethyl acetate, 3:1), the mixture was filtered, the precipitate was washed with hexane (2 × 15 ml), the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield 0.108 g (80%), mp 63.8–64.5°C (from hexane). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 6.31 m (2H, =CHS), 6.34 m (2H, =CHCH=), 7.28 m (10H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 125.73 (=CC=), 130.44 (=CS), 126.98, 129.10, 129.88, 134.78 (C<sub>6</sub>H<sub>5</sub>). Found, %: C 71.09; H 5.47. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>. Calculated, %: C 70.95; H 5.19.

**Catalytic system Pd<sub>2</sub>dba<sub>3</sub>–DPEphos.** A Schlenk vessel was charged with 0.020 g (2 mol %) of Pd<sub>2</sub>dba<sub>3</sub>, 0.026 g (4 mol %) of DPEphos in 5 ml of toluene was added, the mixture was stirred for 5 min, and 0.306 g (1 mmol) of compound **Ia**, 0.220 g (2 mmol) of benzenethiol, and 0.246 g (2.2 mmol) of potassium *tert*-butoxide in 11 ml of toluene were added to the resulting solution. The mixture was heated for 2 h at 110°C (TLC, hexane–ethyl acetate, 3:1) and filtered, the precipitate was washed with hexane (2 × 15 ml), the solvent was distilled off under reduced pressure, and the solid residue was recrystallized from hexane. Yield 0.243 g (90%), mp 63–64°C.

**Catalytic system [(Z,Z')-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene]palladium(II) dichloride.** An ampule was charged with a solution of 0.230 g (0.5 mmol) of (Z,Z')-1,4-diiodo-1,4-diphenylbuta-1,3-diene, 0.101 g (1 mmol) of triethylamine, and 0.014 g (4 mol %) of bis(triphenylphosphine)palladium(II) dichloride in 5 ml of benzene, 0.186 g (1 mmol) of diphenylphosphine was added, and the ampule was

sealed and heated for 2 h at 85°C. When the reaction was complete (<sup>31</sup>P NMR), the precipitate was filtered off and washed with 5 ml of benzene–petroleum ether (1:1), the solvent was removed under reduced pressure, and the residue was recrystallized from methanol. Yield of (Z,Z')-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene (**IV**) 0.250 g (87%), colorless crystals, mp 115.8–116.5°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 7.19 m (C<sub>6</sub>H<sub>5</sub>), 7.31 d.d (2H, =CHCH=, <sup>3</sup>J<sub>PH</sub> = 20, <sup>3</sup>J<sub>HH</sub> = 8 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 127.28, 127.99, 128.22, 134.96 (C<sub>6</sub>H<sub>5</sub>), 129.67 d (<sup>4</sup>J<sub>PC</sub> = 8 Hz), 133.09 d (<sup>3</sup>J<sub>PC</sub> = 19.0 Hz), 134.30 d (<sup>2</sup>J<sub>PC</sub> = 20.0 Hz), 136.20 d (<sup>1</sup>J<sub>PC</sub> = 12.1 Hz), 138.60 d (PC=C, <sup>2</sup>J<sub>PC</sub> = 22.3 Hz), 142.32 d (PC=C, <sup>1</sup>J<sub>PC</sub> = 13.1 Hz). <sup>31</sup>P NMR spectrum: δ<sub>P</sub> –9.42 ppm. Found, %: C 83.61; H 5.65; P 10.75. C<sub>40</sub>H<sub>32</sub>P<sub>2</sub>. Calculated, %: C 83.62; H 5.57; P 10.80.

A Schlenk vessel was charged with a solution of 0.345 g (0.6 mmol) of (Z,Z')-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene in 5 ml of methylene chloride, a solution of bis(acetonitrile)palladium(II) dichloride in 10 ml of methylene chloride was added, and the mixture was kept for 1.5 h at 20°C. When the reaction was complete, the solvent was distilled off under reduced pressure, and the residue was recrystallized from methylene chloride–ethanol (1:5). Yield of [(Z,Z')-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene]palladium(II) dichloride 0.395 g (88%), mp 209.0–210.5°C. <sup>31</sup>P NMR spectrum: δ<sub>P</sub> 16.4 ppm. Found, %: C 63.48; H 4.16. C<sub>40</sub>H<sub>32</sub>Cl<sub>2</sub>P<sub>2</sub>Pd. Calculated, %: C 63.91; H 4.26.

A Schlenk vessel was charged with a solution of 0.153 g (0.5 mmol) of compound **Ia**, 0.11 g (1 mmol) of benzenethiol, and 0.123 g (1.1 mmol) of potassium *tert*-butoxide in 10 ml of toluene, a solution of 0.015 g (4 mol %) of [(Z,Z')-1,4-bis(diphenyl-λ<sup>3</sup>-phosphanyl)-1,4-diphenylbuta-1,3-diene]palladium(II) dichloride in 6 ml of toluene was added, and the mixture was heated for 2 h at 100–110°C. When the reaction was complete, the precipitate was filtered off and washed with hexane (2 × 5 ml), the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield of compound **IIIa** 0.130 g (96%), mp 63.5–64.0°C (from hexane).

**Catalytic system (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>.** An ampule was flushed with argon and charged with 0.153 g (0.5 mmol) of compound **Ia**, 0.11 g (1.0 mmol) of benzenethiol, 0.123 g (1.1 mmol) of potassium *tert*-butoxide, and 0.018 g (5.1 mol %) of (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> in 6 ml of toluene. The ampule was sealed, heated for 10 h at 110–115°C, cooled, and opened, the precipitate

was filtered off and washed with hexane (2×5 ml), the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield of **IIIa** 0.113 g (84%), mp 63.5–64.5°C (from hexane).

**Catalytic system Ni(cod)<sub>2</sub>**. A Schlenk vessel was charged with 0.153 g (0.5 mmol) of compound **Ia**, 0.007 g (5 mol %) of Ni(cod)<sub>2</sub>, 0.28 g (2.0 mmol) of K<sub>2</sub>CO<sub>3</sub>, 2 ml of DMF, and 0.11 g (1 mmol) of benzenethiol. The mixture was heated for 23 h at 110–115°C and cooled, the precipitate was filtered off, the solvent was distilled off under reduced pressure, and the residue was recrystallized from hexane. Yield of **IIIa** 0.120 g (89%), mp 63.5°C.

**Catalytic system Ni[P(OEt)<sub>3</sub>]<sub>4</sub>**. A Schlenk vessel was charged with 0.018 g (5 mol %) of tetrakis(triethyl phosphite)nickel(0), 0.28 g (2.0 mmol) of K<sub>2</sub>CO<sub>3</sub>, 0.153 g (0.5 mmol) of compound **Ia**, 2 ml of DMF, and 0.11 g (1 mmol) of benzenethiol. The mixture was heated for 12 h at 110–120°C and cooled, the precipitate was filtered off and washed with benzene, the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield of **IIIa** 0.105 g (78%), mp 64.0–64.5°C (from hexane).

**Catalytic system NiBr<sub>2</sub>**. Following a similar procedure, the reaction was carried out with 0.005 g (5 mol %) of nickel(II) bromide, 0.28 g (2.0 mmol) of K<sub>2</sub>CO<sub>3</sub>, 0.153 g (0.5 mmol) of compound **Ia**, and 0.11 g (1 mmol) of benzenethiol in 2 ml of DMF. The mixture was heated for 12 h at 120°C. Yield of **IIIa** 0.128 g (95%), mp 63.5–64.0°C (from hexane).

**Catalytic system Ni(acac)<sub>2</sub>**. Likewise, a mixture of 0.006 g (5 mol %) of nickel(II) acetylacetonate, 0.28 g (2.0 mmol) of K<sub>2</sub>CO<sub>3</sub>, 0.153 g (0.5 mmol) of compound **Ia**, and 0.11 g (1 mmol) of benzenethiol in 2 ml of DMF was heated for 4 h at 120°C. Yield of **IIIa** 0.130 g (97%), mp 64.0–64.5°C.

**Catalytic system CuI**. A Schlenk vessel was charged with 0.010 g (10 mol %) of copper(I) iodide, 0.28 g (2.0 mmol) of K<sub>2</sub>CO<sub>3</sub>, 0.153 g (0.5 mmol) of compound **Ia**, 2 ml of isopentyl alcohol, 0.11 g (1 mmol) of benzenethiol, and 0.124 g (0.1 ml, 2.0 mmol) of ethylene glycol. The mixture was heated for 9 h at 120°C. When the reaction was complete, the precipitate was filtered off and washed with benzene, the solvent was removed under reduced pressure, and the residue was recrystallized. Yield of **IIIa** 0.123 g (90%), mp 63.5–64.0°C (from hexane).

**(E,E′)-1,4-Bis(hexylsulfanyl)buta-1,3-diene (IIIb)**. *a. Catalytic system Ni(acac)<sub>2</sub>*. A Schlenk vessel

was charged with 0.153 g (0.5 mmol) of compound **Ia**, 0.120 g (1.0 mmol) of hexane-1-thiol, 0.28 g (2 mmol) of K<sub>2</sub>CO<sub>3</sub>, and 0.006 g (5 mol %) of nickel(II) acetylacetonate in 2 ml of DMF, and the mixture was heated for 50 h at 120°C. When the reaction was complete, the precipitate was filtered off, the solvent was distilled under reduced pressure, and the residue was recrystallized. Yield 0.097 g (69%), mp 67–68°C (from hexane). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 0.89 t (6H, CH<sub>3</sub>), 1.26–1.65 m (16H, CH<sub>2</sub>), 2.68 t (4H, CH<sub>2</sub>S), 6.07 m (2H, =CHS), 6.13 m (2H, =CHCH=). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 13.95, 22.48, 29.65, 31.32, 32.78, 37.97 (C<sub>6</sub>H<sub>13</sub>), 125.23 (=CC=), 127.39 (=CS). Found, %: C 66.92; H 10.62. C<sub>16</sub>H<sub>30</sub>S<sub>2</sub>. Calculated, %: C 67.13; H 10.49.

*b. Catalytic system CuI*. Following a similar procedure, a mixture of 0.153 g (0.5 mmol) of compound **Ia**, 0.120 g (1.0 mmol) of hexane-1-thiol, 0.28 g (2 mmol) of potassium carbonate, 0.010 g (10 mol %) of copper(I) iodide, 2 ml of isopentyl alcohol, and 0.124 g (0.1 ml, 2 mmol) of ethylene glycol was heated for 50 h at 120°C and subjected to appropriate treatment to isolate 0.136 g (96%) of compound **IIIb** with mp 67–68°C (from hexane).

**(E,E′)-1,4-Bis(benzylsulfanyl)buta-1,3-diene (IIIc)**. *a. Catalytic system Ni(acac)<sub>2</sub>*. A Schlenk vessel was charged with 0.153 g (0.5 mmol) of compound **Ia**, 0.124 g (1.0 mmol) of phenylmethanethiol, 0.28 g (2 mmol) of potassium carbonate, and 0.006 g (5 mol %) of nickel(II) acetylacetonate in 2 ml of DMF, and the mixture was heated for 32 h at 120°C. When the reaction was complete, the precipitate was filtered off, the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield 0.142 g (96%), mp 56–57°C (from hexane). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 3.81 s (4H, CH<sub>2</sub>S), 5.98 m (2H, =CHS), 6.10 m (2H, =CHCH=), 7.20 m (10H, Ph). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 38.30 (CH<sub>2</sub>S), 125.06 (=CC=), 129.07 (=CS), 128.65, 128.81, 129.03, 138.18 (Ph). Found, %: C 72.65; H 6.10. C<sub>18</sub>H<sub>18</sub>S<sub>2</sub>. Calculated, %: C 72.48; H 6.04.

*b. Catalytic system CuI*. Likewise, a mixture of 0.153 g (0.5 mmol) of compound **Ia**, 0.124 g (1.0 mmol, 0.12 ml) of phenylmethanethiol, 0.28 g (2 mmol) of potassium carbonate, 0.010 g (10 mol %) of copper(I) iodide, 2 ml of isopentyl alcohol, and 0.124 g (0.1 ml, 2 mmol) of ethylene glycol was heated for 50 h at 120°C. Yield of **IIIc** 0.127 g (86%), mp 56–57°C (from hexane).

**(Z,Z′)-1,4-Diphenyl-1,4-bis(phenylsulfanyl)buta-1,3-diene (IIId)**. A Schlenk vessel was charged with

0.010 g (10 mol %) of copper(I) iodide, 0.28 g (2.0 mmol) of potassium carbonate, 0.229 g (0.5 mmol) of (*Z,Z'*)-1,4-diiodo-1,4-diphenylbuta-1,3-diene, 2 ml of isopropyl alcohol, 0.11 g (1 mmol) of benzenethiol, and 0.124 g (0.1 ml, 2.0 mmol) of ethylene glycol. The mixture was heated for 30 h at 80°C and cooled, the precipitate was filtered off and washed with benzene, the solvent was removed under reduced pressure, and the residue was recrystallized. Yield 0.205 g (97%), mp 128–128.5°C (from hexane). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 125.80 (=CC=), 127.83, 128.25, 128.25, 128.65, 128.74, 133.35, 135.54, 138.12 (C<sub>6</sub>H<sub>5</sub>), 139.57 (=CS). Found, %: C 79.38; H 5.22. C<sub>28</sub>H<sub>22</sub>S<sub>2</sub>. Calculated, %: C 79.62; H 5.21.

**(*Z,Z'*)-1,4-Bis(benzylsulfanyl)-1,4-diphenylbuta-1,3-diene (IIIe).** A Schlenk vessel was charged with 0.229 g (0.5 mmol) of (*Z,Z'*)-1,4-diiodo-1,4-diphenylbuta-1,3-diene, 0.124 g (1.0 mmol) of phenylmethanethiol, 0.28 g (2 mmol) of potassium carbonate, 0.010 g (10 mol %) of copper(I) iodide, 2 ml of isopentyl alcohol, and 0.124 g (0.1 ml, 2 mmol) of ethylene glycol, and the mixture was heated for 40 h at 120°C. When the reaction was complete, the precipitate was filtered off, the solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield 0.174 g (78%), mp 116–117°C (from hexane); published data [8]: mp 117–118°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 3.59 s (4H, CH<sub>2</sub>S), 7.13 s (=CH), 7.02 m (4H, Ph), 7.20 m (6H, Ph), 7.50 m (4H, Ph). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 37.5 (SCH<sub>2</sub>), 132.1 (=CH), 140.0 (C=), 126.8, 128.0, 128.2, 128.3, 128.5, 128.7, 138.2, 139.2 (Ph).

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