JOC Article

The First Broad Application of Alkynyl Sulfides as Dienophiles in Cobalt(I)-Catalyzed Diels−Alder Reactions

Gerhard Hilt,* Steffen Lüers, and Klaus Harms

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35043 Marburg, Germany

hilt@chemie.uni-marburg.de

Received September 15, 2003

The cobalt(I)-catalyzed Diels−Alder reaction of nonactivated aryl alkynyl sulfides with acyclic 1,3-dienes generates dihydroaromatic vinyl sulfides under very mild reaction conditions, and these products can be oxidized with mild oxidants to the corresponding diaryl sulfides in good overall yields. The steric and electronic effects of substituents on the aryl, as well as on the alkynyl, moieties of the aryl alkynyl sulfide are discussed. While the cobalt catalyst system is quite efficient in converting alkynyl sulfides to the Diels−Alder adducts, the transformation of the corresponding aryl alkynyl sulfoxides and sulfones under similar mild reaction conditions gave only moderate yields of the desired adducts.

Introduction

The synthetic utility of the Diels−Alder reaction for the synthesis of complex structures is well documented.[1] Predominantly, thermal Diels−Alder reactions of starting materials with normal electron demand are used in synthetic applications. In such reactions, the reactivity of dienophiles with electron-withdrawing substituents can generally be enhanced by the addition of Lewis acids to enable reactions to take place under milder conditions. However, when nonactivated starting materials are used in a Diels−Alder reaction with neutral electron demand, these substrates first cannot be activated by the classical Lewis acid strategy and second need harsh reaction conditions to undergo the thermal Diels−Alder reactions. Therefore, the desired products are generally obtained in low yield, accompanied by oligomers, polymers, and other side products.

To circumvent these problems, the Diels−Alder reaction of nonactivated starting materials can be accomplished by the use of low-valent transition metal catalysts where multiple free coordination sides on the metal center allow the coordination of the starting materials and thus enable the cycloaddition to proceed in a stepwise fashion via metallacycles within the coordination sphere of the transition metal (transition metal catalyzed Diels−Alder reactions).[2] Such alternative reaction pathways might even proceed at ambient temperatures and atmospheric pressure, so that very mild reaction conditions can be realized for such neutral electron demand cycloadditions.

In the series of sulfur-functionalized alkynes, the thermal Diels−Alder reaction can be accomplished for alkynyl sulfoxides or alkynyl sulfones as starting materials[3] (normal electron demand), while for alkynyl sulfides only a few examples are described where the thermal Diels−Alder reaction of such nonactivated substrates was achieved.[4]

Herein we report our investigations regarding cobalt(I)-catalyzed Diels−Alder reactions of acyclic 1,3-dienes with an alkynyl sulfide as the dienophile. The products (dihydroaromatic thioenol ethers) are generated under very mild reaction conditions by a catalyst mixture consisting of $CoBr_2$(dppe), ZnI_2, and zinc dust and the cycloadducts are converted into the diaryl sulfides by mild DDQ oxidation.

---

[1] For recent reviews on the application of Diels−Alder reactions in total synthesis see: (a) Corey, E. J. *Angew. Chem.* **2002**, *114*, 1724; *Angew. Chem., Int. Ed.* **2002**, *41*, 1650. (b) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. E. *Angew. Chem.* **2002**, *114*, 1743; *Angew. Chem., Int. Ed.* **2002**, *41*, 1668.

[2] For selected examples of metal-catalyzed [4+2] cycloadditions see: (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (b) tom Dieck, H.; Diercks, R. *Angew. Chem.* **1983**, *95*, 801; Angew. *Chem., Int. Ed. Engl.* **1983**, *22*, 778. (c) Bakhtiar, R.; Drader, J. J.; Jacobsen, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 8304. (d) Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432. (e) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1995**, *60*, 2962. (f) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (g) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843. (h) Brunner, H.; Reimer, A. *Bull. Chem. Soc. Fr.* **1997**, *134*, 307. (i) Lautens, M.; Tam, W.; Lautens, J. C.; Edwards, L. G.; Crudden, C. M.; Smith, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6863.

[3] (a) Lee, A. W. M.; Chan, W. H. *Top. Curr. Chem.* **1997**, *190*, 103. (b) Lee, A. W. M.; Chan, W. H.; Zhang, H. K.; Xia, P. F. *Curr. Org. Chem.* **2003**, *7*, 573. (c) Parham, W. E.; Motter, R. F.; Mayo, G. L. O. *J. Am. Chem. Soc.* **1959**, *81*, 3386. (d) Lee, A. W. M.; Chan, W. H.; Wong, M. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1585. (e) Maignan, K.; Belkasmioni *Bull. Soc. Chim. Fr.* **1989**, *126*, 695. (f) Shen, M.; Schultz, A. G. *Tetrahedron Lett.* **1981**, *22*, 3347. (g) De Lucchi, O.; Licini, G.; Pasquato, L.; Senta, M. *Tetrahedron Lett.* **1988**, *29*, 831. (h) Zhang, C.; Ballay, J., II; Trudell, M. L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 675. (i) Back, T. G.; Bethell, R. J.; Parvez, M.; Taylor, J. A.; Wehrli, D. *J. Org. Chem.* **1999**, *64*, 7426.

[4] (a) Sauer, J.; Heldmann, D. K.; Hetzenegger, J.; Krauthan, J.; Sichert, H.; Schuster, J. *Eur. J. Org. Chem.* **1998**, 2885. (b) Feldman, K. S.; Ruckle, R. E., Jr.; Ensel, S. M.; Weinreb, P. H. *Tetrahedron Lett.* **1992**, *33*, 7101. (c) Haas, A.; Krächter, H. U. *Chem. Ber.* **1988**, *121*, 1833. (d) Nakayama, J.; Yamaoka, S.; Nakanishi, T.; Hoshino, M. *J. Am. Chem. Soc.* **1988**, *110*, 6598. (e) Meier, H.; Stavridou, E.; Storek, C. *Angew. Chem.* **1986**, *98*, 838; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 809.

10.1021/jo0302915 CCC: $27.50

SCHEME 1

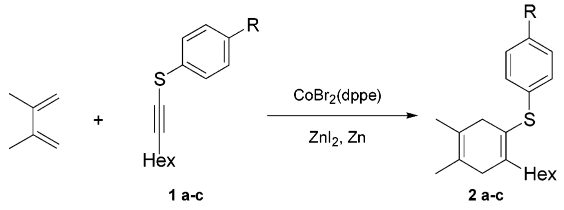


TABLE 1.

	R	mol % of catalyst	% yield **2a−c**
1a	H	10	52
1b	OMe	20	77
1c	CO_2Me	10	80

Results and Discussion

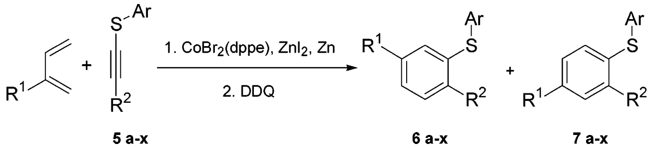
For our investigation we initially choose alkyl alkynyl sulfides and aryl alkynyl sulfides as substrates. However, we soon recognized that the conversions of acyclic 1,3-dienes with the aryl alkynyl sulfide substrates proceeded under comparably mild conditions (ambient temperature) with our cobalt(I)-catalyst system with higher conversions and yields and better regioselectivities for unsymmetrical starting materials than for the alkyl alkynyl sulfides. Accordingly, the subsequent investigation was conducted with various substituted aryl alkynyl sulfides and their use as dienophiles in cobalt(I)-catalyzed Diels−Alder reactions is described below.

While in previous reports various nonactivated alkynes could be reacted with 1,3-dienes generally with less than 5.0 mol % of the catalyst under mild conditions to the corresponding dihydroaromatic compounds,[5] we quickly recognized that the cobalt(I)-catalyzed conversions of alkynyl sulfides proceeded with unsatisfying results only when less than 5.0 mol % of the catalyst was used. This effect can be rationalized by coordination of the sulfur atom to the catalyst, diminishing its activity. Nevertheless, with few exceptions, the use of 10−20 mol % of the catalyst gave reasonable conversion rates to the desired products. However, the diydroaromatic products generated in the conversion of alkynyl sulfides with 1,3-dienes are quite difficult to separate from small amounts of accompanied oxidized material (diaryl sulfides) by column chromatography. Nevertheless, we were able to isolate and characterize some of the dihydroaromatic products (Scheme 1, Table 1), while in the further course of our investigation the dihydroaromatic intermediates were oxidized under mild conditions to the corresponding stable aromatic diaryl products.

As can be seen from Table 1, modification of the para substituent of the arene moiety results in little difference in the reactions. While the rate of the reactions was comparable, reaching complete conversion within 20 h, acceptable yields were obtained for the neutral substituted alkynyl sulfide (**1a**, R = H), which could be increased by using higher catalyst loadings (compare Table 2, entry 1). The reaction with an electron-withdrawing-substituted alkynyl sulfide (**1c**, R = CO_2Me) gave the best results. Higher catalyst loadings had to be applied for the electron-donating-substituted alkynyl sulfide (**1b**, R = OMe), where the reactivity was somewhat diminished.

SCHEME 2

SCHEME 3



In the following series of reactions, we tested the reactivity of differently substituted aryl alkynyl sulfides in the Diels−Alder reaction with 2,3-dimethyl-1,3-butadiene (Scheme 2). The dihydroaromatic intermediates were detected by GC-MS and immediately oxidized with DDQ to the corresponding aromatic products, which were isolated and characterized. The steric effects upon the reactivity and the formation of the desired diaryl products can be seen from Table 2. When sterically hindered arene substituents are used, the reaction still proceeds with relatively low catalyst loadings (10−20 mol %) in good yields for the two-step reactions and cannot be substantially increased over 85% for **4a** when 50 mol % (65% yield with 20 mol % of catalyst) of catalyst is used.[6] The best results in this series of experiments were obtained with the electron-withdrawing-substituted arene derivative (**4f**). However, when the corresponding ortho- and meta-substituted esters were used, lower yields (of **4i** and **4j**) were obtained and the introduction of a nitro substituent gave only traces of the desired compound **4k** (GC-MS analysis).[7] Variation of the R substituent (alkyl, aryl, silyl, or thienyl substituents; **4*l*−o**) gave the desired compounds in reasonable yields. However, the introduction of an alkoxy functionality in the propargylic position led to diminished yields of (**4m**) even when the protecting group on the oxygen was altered from a methyl ether to a THP ether.[8] In previous investigations we had already recognized that this type of substituent changed the reactivity of the catalyst, most likely by coordination to the cobalt center.[9] This effect seems to be less marked when the alkoxy substituent is located at a nonpropargylic position (**4n**). Similar results could be obtained when the

---

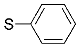
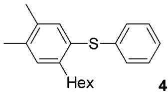
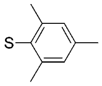
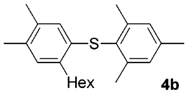
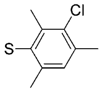
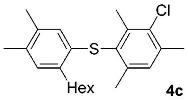
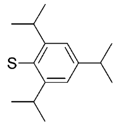
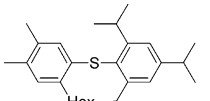
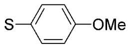
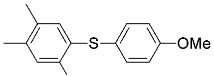
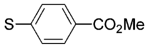
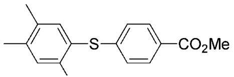
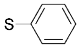
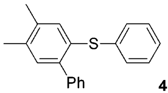
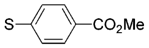
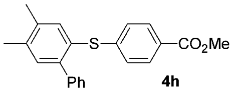
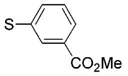
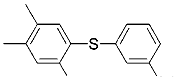
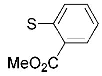
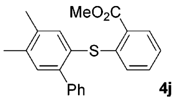
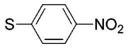
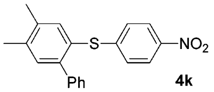
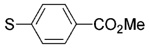
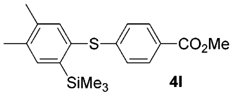
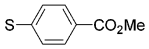
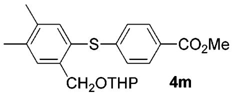
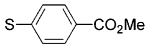
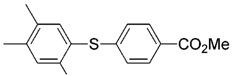
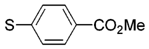
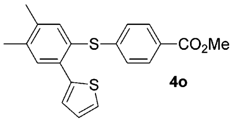
(5) For the latest applications of our cobalt-catalyst system see: (a) Hilt, G.; Smolko, K. I. *Angew. Chem.* **2003**, *115*, 2901; *Angew. Chem., Int. Ed.* **2003**, *43*, 2795. (b) Hilt, G.; Lüers, S. *Synthesis* **2003**, 1784.

(6) The chlorinated arene (Table 1, entry 3) is generated when mesitylene thiol is reacted with an excess of $SOCl_2$ for the synthesis of the aryl sulfenyl chloride (Ar−SCl) overnight.

(7) Nitrogen-containing functional groups, even far away from the reaction center, inhibit the cycloaddition. Only recently we identified a protecting group for the nitrogen functionality (phthalimide) that allows the cycloaddition to proceed.

(8) The reaction with the methoxy ether derivative (R = CH_2OMe) gave 37% yield and reaction with the benzyl ether derivative (R = CH_2OCH_2Ph) gave 11% yield of contaminated products, while other side products were not identified. The formation of a cobalt-stabilized propargylic cation could be the rational for the low yield and the formation of the side products. For reviews concerning the Nicholas reaction see: (a) Teobald, B. J. *J. Med. Chem.* **2002**, *58*, 4133. (b) Green, J. R. *Curr. Org. Chem.* **2001**, *5*, 809. (c) Müller, T. J. J. *Eur. J. Org. Chem.* **2001**, 2021.

TABLE 2.

Entry	S-Ar	R	Product (4)	Mol% catalyst	Time (h)	Yield (%)
1		Hex	 **4a**	50	3	86
2		Hex	 **4b**	18	20	67
3		Hex	 **4c**	20	20	73
4		Hex	 **4d**	10	20	77
5		Hex	 **4e**	23	3	50
6		Hex	 **4f**	10	20	85
7		Ph	 **4g**	50	3	61
8		Ph	 **4h**	10	20	69
9		Ph	 **4i**	20	20	56
10		Ph	 **4j**	26	20	74
11		Ph	 **4k**	50	20	traces
12		$SiMe_3$	 **4l**	10	20	71
13		CH_2OTHP	 **4m**	20	20	27
14		$(CH_2)_4OBn$	 **4n**	10	20	69
15		2-Thienyl	 **4o**	50	2	68

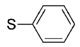
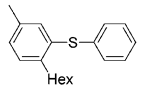
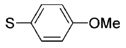
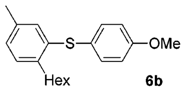
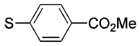
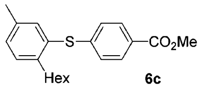
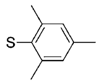
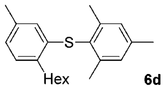
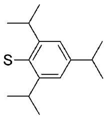
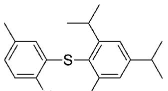
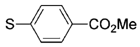
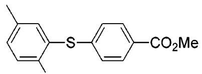
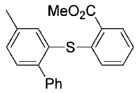
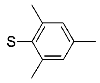
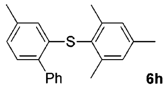
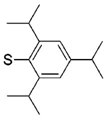
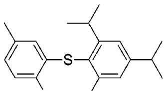
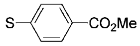
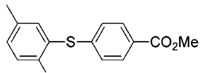
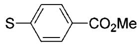
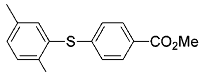
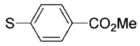
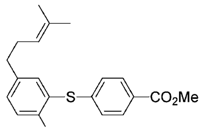
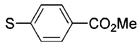
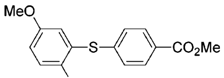
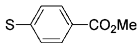
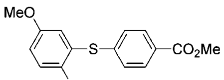
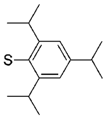
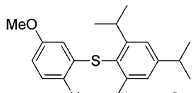
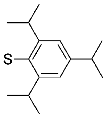
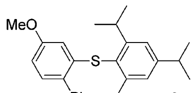
thienyl substituent was introduced (**4o**). In this case up to 50 mol % of catalyst was needed to generate the product in good yield, while keeping the reaction time comparably short. Lower catalyst loading, however, resulted in longer reaction times and diminished yields. This underlines the hypothesis that the coordination of heteroatoms to the cobalt center is the main reason for the low reactivity in these reactions.

At this point, we have shown that the reactivity of the system is only slightly dependent on electronic effects on

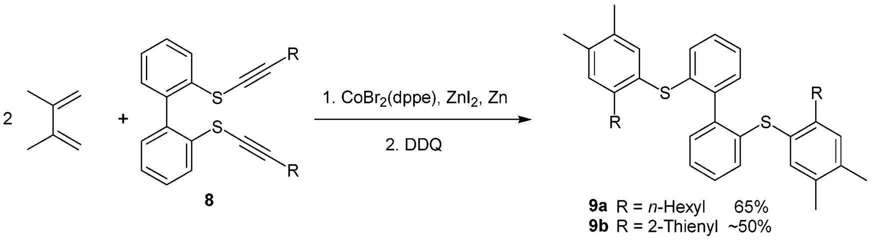
---

[9] (a) Lautens, M.; Tam, W.; Lautens, J. C.; Edwards, L. G.; Crudden, C. M.; Smith, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 6863. (b) Chen, Y.; Kiattansakul, R.; Ma, B.; Snyder, J. K. *J. Org. Chem.* **2001**, *66*, 6932.

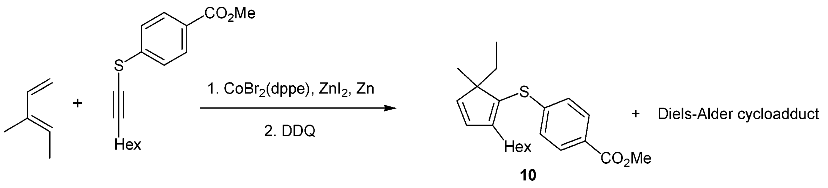
TABLE 3.

Entry	S-Ar in 5	R^1	R^2	Main Product (6)	Ratio 6 : 7	Yield (%)
1		Me	Hex	 **6a**	60 : 40	60
2		Me	Hex	 **6b**	65 : 35	61
3		Me	Hex	 **6c**	60 : 40	68
4		Me	Hex	 **6d**	81 : 19	82
5		Me	Hex	 **6e**	86 : 14	80
6		Me	Ph	 **6f**	89 : 11	80
7		Me	Ph	 **6g**	89 : 11	74
8		Me	Ph	 **6h**	87 : 13	73
9		Me	Ph	 **6i**	92 : 8	84
10		Me	$SiMe_3$	 **6j**	93 : 7	80
11		Me	2-Thienyl	 **6k**	90 : 10	91
12		Ph	$-CH_2-CH_2-$ $CH=C(CH_3)_2$	 **6l**	88 : 12	71
13		OMe	Hex	 **6m**	85 : 15	62
14		OMe	Ph	 **6n**	97 : 3	70
15		OMe	Hex	 **6o**	96 : 4	34
16		OMe	Ph	 **6p**	98 : 2	48

SCHEME 4



SCHEME 5



the arene substituent but very sensitive toward the presence of coordinating heteroatoms in the substrate. However, even for such (bis)sulfide substrates the catalyst system can be used to obtain acceptable results.

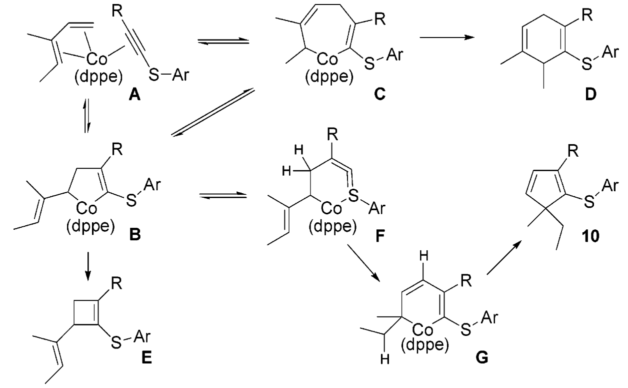
We next focused our attention on the regioselectivity when unsymmetrical 1,3-dienes are used as substrates (Scheme 3). As was expected, the electronic effect due to the substituent on the arene moiety showed little influence on the regioselectivity with which the two isomers **6** and **7** are formed. Interestingly, when the steric hindrance on the arene was increased the regioselectivity also increased, and for the trisisopropyl derivative, the regioselectivity was the best (Table 3, entry 16). In addition, when the steric bulkiness of the alkyne substituent (R^2) was then increased the regioselectivity became even higher for the aryl- and silyl-substituted alkynyl sulfides (Table 3, entries 9−12).

The main product (**6h**) of the reaction from mesitylene 2-phenylethynyl sulfide with isoprene was crystallized and the analysis of the X-ray structure verified the analysis of the two-dimensional NMR data that the sulfur atom of the alkynyl sulfide and the methyl group of the isoprene are in a meta relationship.

For alkoxy-substituted 1,3-dienes (Table 3, entries 13−16) the yields are still acceptable but the regioselectivities are substantially better for these alkoxy functionalized butadienes than for the reactions with isoprene. Accordingly, interesting alkoxy functionalized biaryl sulfides can be generated in a predictable regioselective fashion when either the alkyne has a bulky substituent (R^2) or the arene substituent on the sulfur is sterically hindered.

Although the reactvity of aryl alkynyl sulfides bearing an additional coordinating functionality was somewhat diminished, we attempted the conversion of a diphenyl (bis)sulfide derivative (**8**) in the cobalt(I)-catalyzed cycloaddition reaction (Scheme 4). With the octyne substrate (R = *n*-hexyl in Scheme 4), the desired product **9a** could be obtained in reasonable yield (65%), using 20 mol % of cobalt catalyst. Unfortunately, the reaction of the corresponding tetrasulfide derivative (R = 2-thienyl) proceeded only with very high catalyst loadings. Although 1 mol equiv of catalyst was used, the desired compound **9b** could only be obtained in around 50% yield. However, even after extended column chromatography, the desired product could not be obtained in analytically absolute pure form.

SCHEME 6

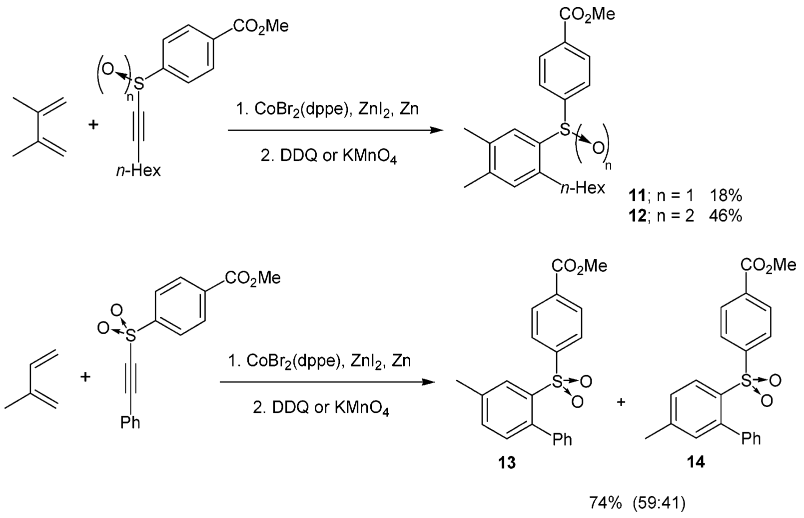


Finally, it is worthy of mention that we also found, for the first time in our cobalt(I)-catalyzed cycloaddition reactions of nonactivated substrates, a type of side product that was not observed in the previous investigations. The spectroscopic data suggest that a cyclopentadiene ring (**10**) is formed in 5−12% yield when 3-methyl-1,3-pentadiene is reacted with aryl alkynyl sulfides

However, this type of side product only occurred in detectable amounts in the above-mentioned case. In all other reactions of aryl alkynyl sulfides described above no such product was detected. However, the ratio of diaryl sulfides to cyclopentadiene derivatives varied (between 5 and 12%) for no obvious reason when the reaction was repeated several times under subjective identical conditions. At the moment we have not identified the reason the ratios vary and we could not find conditions where the alternative reaction pathway to the cyclopentadiene derivatives is favored over the pathway leading to the cyclohexadiene derivatives.

Proposed Mechanism. The lower reactivity of the alkynyl sulfides in the cobalt(I)-catalyzed Diels−Alder reaction compared to other nonactivated starting materials may originate from coordination of the sulfide atom to the catalyst. An incorporation of such a coordination could also be the reason for the generation of the cyclopentadiene side product. The starting materials coordinate to the low-valent cobalt center (**A**, Scheme 6) and

SCHEME 7



from here an insertion process leads to a five-membered cobaltacycle (**B**) and a seven-membered cobaltacycle (**C**), which are proposed to be in equilibrium via an allyl rearrangement. While a reductive elimination from **C** leads to the desired Diels–Alder adduct **D**, a reductive elimination from **B** would lead to a four-membered product (**E**).[10] A 1,2-cobalt shift to the sulfur atom expands the cobaltacycle to a geometrically congested six-membered ring (**F**).[11] A subsequent β-hydride elimination would be more favorable than in the corresponding five-membered-ring system (**B**) and would generate a Co–H moiety within the sulfur allene system. Readdition of this cobalt–hydride species then leads to the thermodynamically preferred cobaltacycle **G**, which represents the product of a formal 1,4-hydrogen shift. Finally, reductive elimination leads to the observed cyclopentadiene derivative **10**.

This overall cycle explains the existence of all observed byproducts through the equilibrated existence of key intermediates **B**, **C**, and **F**. Given the higher tendency of **C** over **B** to undergo reductive elimination, formation of **D** as the main product is a plausible consequence.

Cobalt(I)-Catalyzed Cycloaddition of Aryl Alkynyl Sulfoxides and Aryl Alkynyl Sulfones. In Diels–Alder reactions of the higher oxidation state sulfur derivatives, such as sulfoxides and sulfones, the cycloaddition process takes place under thermal conditions and the process can be promoted by Lewis acids, so that transformations at room temperature are even possible. The cobalt(I)-catalyzed cycloaddition of the corresponding aryl alkynyl sulfoxides and aryl alkynyl sulfones with 20 mol % of the cobalt catalyst is complete within 3 h at ambient temperature and the dihydroaromatic products can be oxidized under mild conditions to the corresponding diaryl sulfur derivatives **11**–**14** (Scheme 7). The control experiment with ZnI_2 and Zn dust in the absence of the cobalt complex gave no conversion (GCMS analysis).

Although the products are obtained under relatively mild conditions, the yields are sometimes drastically lower than for the corresponding aryl alkynyl sulfides and the regioselectivity of the cycloaddition of aryl alkynyl sulfone with isoprene is only moderate. Therefore, the reversed reaction sequence of cobalt(I)-catalyzed cycloaddition followed by oxidation to the sulfoxide or sulfone is preferable. However, with further improvements of the catalyst system an interesting alternative to the thermal Diels–Alder reaction of alkynyl sulfoxides and alkynyl sulfones might be realized, so that under mild reaction conditions the transformation can be performed in the presence of thermally labile functional groups.

Summary

The cobalt catalyst mixture [$CoBr_2$(dppe)/ZnI_2/Zn] represents the first catalyst that is able to efficiently convert aryl alkynyl sulfide dienophiles in a metal-catalyzed Diels–Alder reaction with acyclic 1,3-dienes. The dihydroaromatic products can either be isolated or easily oxidized to the corresponding polysubstituted diaryl sulfides in acceptable to good yields. The regioselectivity of the cycloaddition is controlled by steric parameters, while in the presence of potentially coordinating heteroatoms in the substrate, the reactivity is reduced. While the catalyst system converts aryl alkynyl sulfides under mild reaction conditions smoothly into the cycloaddition products, the yields for the corresponding alkynyl sulfoxides and alkynyl sulfones are substantially lower. Therefore, further improvements on the catalyst system could result in an alternative pathway for the Diels–Alder reaction of alkynyl sulfur compounds in the future, and such investigations are currently underway in our laboratory.

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Dichloromethane was distilled under argon from P_4O_{10} and ZnI_2 was dried in vacuo at 150 °C prior to use. Commercially available materials were used without further purification.

Starting Materials. The alkynyl sulfides,[12] as well as the alkynyl sulfoxides and the alkynyl sulfones,[12a,13] were prepared according to adopted literature procedures.

General Procedure for the Synthesis of Dihydroaromatic Sulfides (2a–c). In a 10-mL Schlenk tube $CoBr_2$(dppe) (40 mg, 0.065 mmol), anhydrous zinc iodide (100 mg,

---

[10] A fraction containing a side product whose ^{1}H NMR data fit to a cyclobutene derivative could be isolated in trace amounts (<2%).

[11] (a) Meier, H.; Stavridou, E.; Storek, C. *Angew. Chem.* **1986**, *98*, 838; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 809.

0.313 mmol), and zinc powder (15 mg, 0.229 mmol) were suspended in dry dichloromethane (1.0 mL) under a nitrogen atmosphere. Then 0.65 mmol of the alkynyl sulfide and 1.3 mmol of the 1,3-diene were added. After an induction period where a color change from green to brown was observed, the reaction mixture was stirred at room temperature overnight. After completion of the reaction, diethyl ether (5.0 mL) was added and the mixture was filtered through a small amount of silica gel (eluent: pentane:diethyl ether = 2:1). Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel to obtain the desired dihydroaromatic and air-sensitive product.

1-((2-Hexyl-4,5-dimethyl-1,4-cyclohexadien-1-yl)sulfanyl)-4-methoxybenzene (2b). Column chromatography with pentane:diethyl ether = 20:1 (R_f 0.26) as eluent affords the desired product in 77% yield (82 mg, 0.248 mmol) as a colorless oil, which contained small amounts of the corresponding diaryl sulfide.

^{1}H NMR (600 MHz, C_6D_6): δ 7.39−7.34 (m, 2 H), 6.68−6.63 (m, 2 H), 3.21 (s, 3 H), 2.88 (t, J = 7.2 Hz, 2 H), 2.67 (t, J = 7.2 Hz, 2 H), 2.60 (t, J = 7.9 Hz, 2 H), 1.58−1.51 (m, 2 H), 1.52 (s, 3 H), 1.42−1.35 (m, 2 H), 1,40 (s, 3 H), 1.34−1.26 (m, 4 H), 0.90 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (151 MHz, C_6D_6): δ 159.2 (C), 140.0 (C), 132.6 (2 CH), 126.5 (C), 123.9 (C), 123.4 (C), 122.5 (C), 115.0 (2 CH), 54.8 (OCH_3), 39.5 (CH_2), 39.2 (CH_2), 34.9 (CH_2), 32.2 (CH_2), 29.8 (CH_2), 28.8 (CH_2), 23.1 (CH_2), 18.0 (CH_3), 17.9 (CH_3), 14.4 (CH_3). MS(EI): m/z (%) 107 (36), 119 (51), 140 (85), 191 (30), 330 (100, M^+). HRMS: m/z calculated for $C_{21}H_{30}OS$ 330.2017, found 330.2005. IR (neat): ν 3001, 2955, 1593, 1493, 1254 cm^{-1}.

Methyl 4-((2-Hexyl-4,5-dimethyl-1,4-cyclohexadien-1-yl)sulfanyl)benzoate (2c). Column chromatography with pentane:diethyl ether = 50:1 (R_f 0.19) as eluent affords the desired product in 80% yield (187 mg, 0.522 mmol) as a colorless oil.

^{1}H NMR (300 MHz, C_6D_6): δ 8.02−7.94 (m, 2 H), 7.24−7.16 (m, 2 H), 3.47 (s, 3 H), 2.85 (t, J = 6.8 Hz, 2 H), 2.63 (t, J = 7.2 Hz, 2 H), 2.42 (t, J = 7.7 Hz, 2 H), 1.51 (s, 3 H), 1.47−1.36 (m, 2 H), 1.40 (s, 3 H), 1.35−1.15 (m, 6 H), 0.85 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (75 MHz, C_6D_6): δ 166.4 (C), 146.2 (C), 144.1 (C), 130.5 (2 CH), 127.6 (C), 126.9 (2 CH), 123.9 (C), 122.4 (C), 120.3 (C), 51.5 (OCH_3), 39.9 (CH_2), 39.0 (CH_2), 35.0 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 28.7 (CH_2), 23.0 (CH_2), 18.0 (CH_3), 17.8 (CH_3), 14.3 (CH_3). MS (EI): m/z (%) 107 (61), 119 (65), 137 (38), 168 (18), 191 (79), 225 (15), 358 (100, M^+). HRMS: m/z calculated for $C_{22}H_{30}O_2S$ 358.1966, found 358.1965. IR (neat): ν 2952, 1723, 1594, 1434, 1274 cm^{-1}.

General Procedure for the Synthesis of Diaryl Sulfides, Diaryl Sulfoxides, and Diaryl Sulfones. In a 10-mL Schlenk tube $CoBr_2$(dppe) (20 mg, 0.032 mmol), anhydrous zinc iodide (50 mg, 0.157 mmol), and zinc powder (8 mg, 0.122 mmol) were suspended in dry dichloromethane (0.5 mL) under a nitrogen atmosphere. Then the alkynyl sulfide (alkynyl sulfoxide or alkynyl sulfone, respectively) and the 1,3-diene (∼2 equiv) were added. After an induction period where a color change from green to brown was observed the reaction mixture was stirred at room temperature. After completion of the reaction, diethyl ether (5.0 mL) was added and the mixture was filtered through a small amount of silica gel (eluent pentane:diethyl ether = 2:1). Then the solvent was removed in vacuo and the residue was dissolved in benzene and the dihydroaromatic intermediate was oxidized with DDQ (1.5 equiv). The solution was then filtered through a small pad of silica gel with pentane:diethyl ether (1:1) as eluent and the solvents were then removed in vacuo. The residue was purified by column chromatography on silica gel to obtain the desired diaryl sulfides (diaryl sulfoxide or diaryl sulfone, respectively).

1-Hexyl-4,5-dimethyl-2-(phenylsulfanyl)benzene (4a). Column chromatography with pentane (R_f 0.35) as eluent affords the desired product in 86% yield (59 mg, 0.198 mmol) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17−7.09 (m, 3 H), 7.06−6.99 (m, 3 H), 6.97 (s, 1 H), 2.61 (t, J = 8.0 Hz, 2 H), 2.17 (s, 3 H), 2.10 (s, 3 H), 1.51−1.38 (m, 2 H), 1.28−1.12 (m, 6 H), 0.77 (t, J = 6.6 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5 (C), 138.7 (C), 137.5 (C), 136.4 (CH), 135.3 (C), 131.4 (CH), 129.0 (2 CH), 128.8 (C), 128.1 (2 CH), 125.5 (CH), 34.0 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 22.7 (CH_2), 19.6 (CH_3), 19.2 (CH_3), 14.2 (CH_3). MS (EI): m/z (%) 211 (26), 225 (100), 298 (94, M^+). HRMS: m/z calculated for $C_{20}H_{26}S$ 298.1755, found 298.1772. IR (neat): ν 2955, 1583, 1478, 1440 cm^{-1}.

2-((2-Hexyl-5-methylphenyl)sulfanyl)-1,3,5-triisopropylbenzene (6e) and 2-((2-Hexyl-4-methylphenyl)sulfanyl)-1,3,5-triisopropylbenzene (7e). Column chromatography with pentane (R_f 0.79) as eluent affords the desired product in 80% yield (80 mg, 0.195 mmol) as a colorless oil consisting of an inseparable regioisomeric mixture (86:14).

^{1}H NMR (600 MHz, $CDCl_3$) for **6e**: δ 7.13 (s, 2 H), 7.02 (d, J = 7.6 Hz, 1 H), 6.76 (d, J = 7.6 Hz, 1 H), 6.21 (s, 1 H), 3.62 (sept, J = 7.3 Hz, 2 H), 2.96 (sept, J = 6.8 Hz, 1 H), 2.79 (t, J = 7.8 Hz, 2 H), 2.09 (s, 3 H), 1.77−1.70 (m, 2 H), 1.49−1.43 (m, 2H), 1.41−1.32 (m, 4 H), 1.32 (d, J = 6.8 Hz, 6 H), 1.16 (d, J = 7.3 Hz, 12 H), 0.93 (t, J = 7.0 Hz, 3 H). Partial ^{1}H NMR data for **7e**: δ 6.96 (s, 1 H), 6.74 (d, J = 8.3 Hz, 1 H), 6.29 (d, J = 8.3 Hz, 1 H), 2.25 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) for **6e**: δ 153.9 (2 C), 150.6 (C), 138.5 (C), 135.9 (C), 135.8 (C), 128.9 (CH), 125.7 (CH), 125.3 (C), 125.0 (CH), 122.3 (2 CH), 34.5 (CH), 33.4 (CH_2), 32.0 (CH_2), 31.8 (2 CH), 30.0 (CH_2), 29.4 (CH_2), 24.4 (4 CH_3), 24.1 (2 CH_3), 22.8 (CH_2), 21.2 (CH_3), 14.3 (CH_3) (additional signals for **7e** are not resolved). MS (EI): m/z (%) 149 (9), 410 (100, M^+). HRMS: m/z calculated for $C_{28}H_{42}S$ 410.3007, found 410.3031. IR (neat): ν 2961, 1599, 1563, 1463 cm^{-1}.

Methyl 4-((5-Methyl-2-(trimethylsilyl)phenyl)sulfanyl)benzoate (6j) and Methyl 4-((4-Methyl-2-(trimethylsilyl)phenyl)sulfanyl)benzoate (7j). Column chromatography with pentane:diethyl ether = 20:1 (R_f 0.29) as eluent affords the desired product in 80% yield (80 mg, 0.242 mmol) as a colorless oil consisting of an inseparable regioisomeric mixture (93:7).

^{1}H NMR (600 MHz, $CDCl_3$) for **6j**: δ 7.87 (d, J = 8.6 Hz, 2 H), 7.53 (d, J = 7.5 Hz, 1 H), 7.33 (s, 1 H), 7.22 (d, J = 7.5 Hz, 1 H), 7.05 (d, J = 8.6 Hz, 2 H), 3.88 (s, 3 H), 2.32 (s, 3 H), 0.29 (s, 9 H). Partial ^{1}H NMR data for **7j**: δ 7.44 (s, 1 H), 7.40 (d, J = 7.9 Hz, 1 H), 7.01 (d, J = 8.4 Hz, 2 H), 2.40 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) for **6j**: δ 166.9 (C), 146.9 (C), 142.8 (C), 140.8 (C), 137.4 (C), 137.3 (CH), 135.9 (CH), 130.1 (2 CH), 129.6 (CH), 126.8 (C), 126.3 (2 CH), 52.1 (OCH_3), 21.2 (CH_3), 0.2 (3 CH_3). Partial ^{13}C NMR data for **7j**: δ 137.1 (CH), 136.8 (CH), 131.5 (CH), 125.8 (2 CH), 21.5 (CH_3). MS (EI): m/z (%) 241 (12), 299 (17), 315 (100), 330 (41, M^+). HRMS: m/z calculated for $C_{18}H_{22}O_2SSi$ 330.1110, found 330.1125. IR (neat): ν 2952, 1723, 1594, 1259, 1109 cm^{-1}.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Characterization data for compounds **2a**, **4b**−**j**, **4*l***−**o**, **6a**−**d**, **6f**−**i**, **6k**−**p**, **9a**, **9b**, and **10**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for **6h** are available under CCDC 218514. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

JO0302915

---

(12) (a) Kabanyane, S., T.; MaGee, D. I. *Can. J. Chem.* **1992**, *70*, 2758. (b) Harpp, D. N.; Friedlander, B. T.; Smith, R. A. *Synthesis* **1979**, 181. (c) Maruyama, H.; Shiozaki, M.; Oido, S.; Hiraoka, T. *Tetrahedron Lett.* **1985**, *26*, 4521. (d) Baudin, J. B.; Julia, S. A.; Lorne, R. *Bull. Soc. Chim. Fr.* **1987**, 181.

(13) Clive, D. L. J.; Bergstra, R. J. *J. Org. Chem.* **1990**, *55*, 1786.