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Palladium-Catalyzed Regio- and Stereoselective Carbothiolation of Terminal Alkynes with Azolyl Sulfides

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Supporting Information

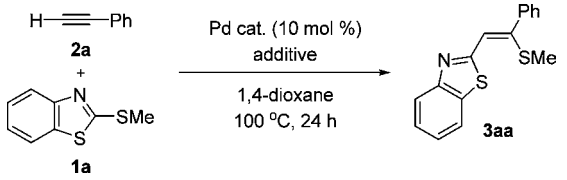
ABSTRACT: Palladium-catalyzed carbothiolation of terminal alkynes with azolyl sulfides affords various 2-(azolyl)alkenyl sulfides with perfect regio- and stereoselectivities. The present addition reaction proceeded through a direct cleavage of carbon−sulfur bonds in azolyl sulfides. The resulting adducts that are useful intermediates in organic synthesis are further transformed to multisubstituted olefins containing azolyl moieties.

Carbothiolation of alkynes has been regarded as the ideal approach to the highly substituted alkenyl sulfides in organic synthesis, which can generate carbon−carbon and carbon−sulfur bonds simultaneously.[1] Regio- and stereoselective addition of various carbon−sulfur bonds to alkynes has been achieved by using transition metal catalysts: thioesterification,[2] cyanothiolation,[3] allylthiolation,[4] alkenylthiolation,[5] acylthiolation,[6] iminothiolation,[7] alkynylthiolation,[8] and alkylthiolation.[9,10] Although only decarbonylative addition reaction of thioesters is known,[11] the atom-economical arylthiolation across alkynes has yet to be disclosed to date because carbon−sulfur bonds in aryl sulfides tend to cause a reversible oxidative addition.[12] While it was previously found that aryl sulfides underwent cross-coupling with organometallic reagents[13] probably because of the high reactivity of the once formed oxidative adducts for subsequent transmetalation, arylthiolation of alkynes is unprecedented.

Recently, Weller and Willis have reported rhodium-catalyzed addition of aryl sulfides bearing unique activating groups to terminal alkynes as a specific case.[14] On the other hand, the addition reaction of heteroaryl sulfides with alkynes, which can construct the ubiquitous skeletons in pharmaceuticals and agrochemicals,[15] is significantly limited despite its utility. Although only platinum-catalyzed furylthiolation,[11b,16] thienylthiolation,[17] and pyridylthiolation[18] of terminal alkynes with thioesters or with heteroaryl halides and arenethiolate salts are known, those reactions produce toxic carbon monoxide or undesired byproducts. We recently disclosed the regio- and stereocontrolled chlorothiolation of alkynes with transition metal catalysts through the chlorine−sulfur bond cleavage of sulfenyl chlorides.[19] During the course of our research on selective addition of organosulfur compounds to alkynes, we investigated carbothiolation with a direct activation of heteroaryl sulfides. Herein, we report that a palladium complex ligated with an *N*-heterocyclic carbene (NHC) catalyzed regio- and stereoselective addition of azolyl sulfides to terminal alkynes.

The reaction of 2-(methylthio)benzothiazole (**1a**) with phenylacetylene (**2a**) was carried out in 1,4-dioxane at 100 °C for 24 h. The results employing various palladium catalysts are summarized in Table 1. In the presence of $Pd(PPh_3)_4$, the

Table 1. Palladium-Catalyzed Addition of 2-(Methylthio)benzothiazole (1a) to Phenylacetylene (2a)[a]



entry	Pd cat.	additive	yield (%)[b]
1	$Pd(PPh_3)_4$	none	28
2	$Pd(OAc)_2/PPh_3$ (1/4)	none	10
3	$Pd(dba)_2/PCy_3$ (1/2)	none	7
4	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	none	75
5	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	H_2O	89
6	Pd-PEPPSI-IPr/LiOH·H_2O (1/4)	none	84
7	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	MeOH	95 (93)
8[c]	Pd-PEPPSI-IPr/^{n}BuLi (1/4)	MeOH	80

[a]Conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), Pd catalyst (0.10 mmol), ^{n}BuLi (0.40 mmol), additive (0.25 mL), in 1,4-dioxane (8.0 mL) at 100 °C for 24 h, unless otherwise stated. [b]NMR yields. An isolated yield is shown in parenthesis. [c]Microwave irradiation at 160 °C for 40 min.

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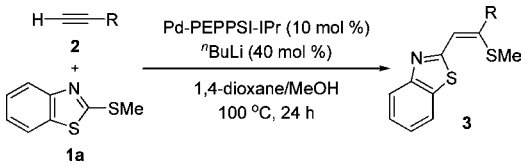
desired carbothiolation proceeded to yield the adduct **3aa** as a single product in 28% yield, while no reaction occurred without the catalyst (entry 1). The conventional palladium/phosphine catalytic systems were found to be less active (entries 2 and 3). Further screening of palladium catalysts revealed that Pd-PEPPSI-IPr ([1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridine)palladium(II) dichloride)[20] was the most effective (entry 4). Unexpectedly, the addition of a small amount of water improved the product yield (entry 5). The effect of water is unclear at this stage, but we presume that the *in situ* formed LiOH from ^{n}BuLi and water might act as an efficient reductant of a palladium(II) precursor. This assumption was strongly supported by the reaction with LiOH·H_2O, affording **3aa** in comparable yield (entry 6). Among the additives examined, MeOH gave the best result (entry 7).[21] It is of note that the present reaction was complete within 40 min under microwave irradiation at 160 °C (entry 8).

With the optimized conditions in hand, various aromatic and aliphatic terminal alkynes **2** were examined for the reaction with **1a**, as shown in Table 2. The reaction of electron-rich

Table 2. Palladium-Catalyzed Addition of 2-(Methylthio)benzothiazole (1a) to Terminal Alkynes 2[a]



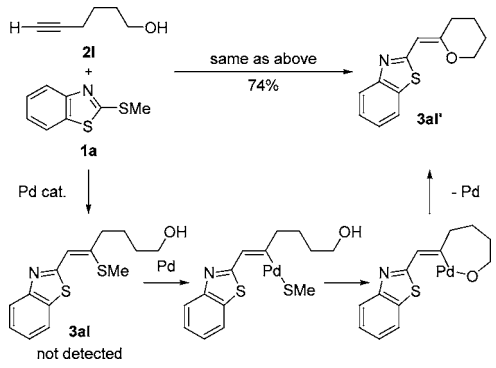
entry	R	2	3	yield (%)[b]
1	*p*-$MeOC_6H_4$	**2b**	**3ab**	81
2	*p*-MeC_6H_4	**2c**	**3ac**	91
3[c]	*p*-$CF_3C_6H_4$	**2d**	**3ad**	44
4[c]	1-naphthyl	**2e**	**3ae**	34
5[c]	Hex	**2f**	**3af**	67
6[c]	^{n}Bu	**2g**	**3ag**	70
7	^{t}Bu	**2h**	**3ah**	60
8[c]	$CH(OEt)_2$	**2i**	**3ai**	75
9	*p*-(HC≡C)C_6H_4	**2j**	**3aj**	52
10	$HC{\equiv}C(CH_2)_3$	**2k**	**3ak**	30

[a]Reaction conditions: **1a** (1.0 mmol), **2** (2.0 mmol), Pd-PEPPSI-IPr (0.10 mmol), ^{n}BuLi (0.40 mmol), in 1,4-dioxane (8.0 mL) and MeOH (0.125 mL) at 100 °C for 24 h. [b]Isolated yields. [c]Microwave irradiation at 160 °C for 40 min.

arylacetylenes **2b** and **2c** proceeded smoothly to provide the corresponding adducts **3ab** and **3ac** in 81% and 91% yields, respectively (entries 1 and 2). In contrast, the reaction was slightly affected by a coordination ability of alkynes to a palladium center: carbothiolation of electron-poor or bulkier arylacetylenes **2d** and **2e** gave the products **3ad** and **3ae** in moderate yields (entries 3 and 4). In addition, internal alkynes such as diphenylacetylene and dimethyl acetylenedicarboxylate did not undergo the desired reaction, recovering the starting substrates quantitatively. Moreover, alkylacetylenes **2f** and **2g** were applicable to the reaction, providing **3af** and **3ag** in 67% and 70% yields, respectively (entries 5 and 6). The steric congestion of **2h** did not influence the efficiency of the reaction (entry 7). 3,3-Diethoxyl-1-propyne (**2i**) also reacted with **1a** to give **3ai** with the acetal moiety remaining intact (entry 8). Furthermore, when an excess amount of diynes **2j** and **2k** on **1a** was employed, carbothiolation selectively occurred at one of two alkyne moieties to afford the 1:1 adducts **3aj** and **3ak**, albeit in low yields (entries 9 and 10). The reactions of diynes gave only a trace amount of 1:2 adducts because the high-yielding reaction required an excess amount of alkynes on **1a**.

As a small variant of the terminal alkynes, 5-hexyn-1-ol (**2l**) was employed in the reaction of **1a** (Scheme 1). The expected

Scheme 1. Carbothiolation of 5-Hexyn-1-ol (2l) with 1a



carbothiolation adduct **3al** was not obtained, while carboetherification product **3al′** was obtained in 74% yield. After the formation of carbothiolation adduct **3al**, palladium-catalyzed etherification of alkenyl sulfide **3al** might give **3al′** through oxidative addition of **3al**, ligand exchange between thiolate and alkoxide, and reductive carbon−oxygen bond formation.[22] To the best of our knowledge, there are no reports on etherification of alkenyl sulfides with alcohols despite their seeming simplicity. The configuration of **3al′** was determined by NOESY analysis.[21]

Next, we explored the scope of heteroaryl sulfides **1** in the reaction with phenylacetylene (**2a**) (Table 3). The addition of 2-benzothiazolyl phenyl sulfide (**1b**) gave **3ba** as a sole product through chemoselective cleavage of the C(2-benzothiazolyl)−S bond rather than the C(phenyl)−S bond (entry 1). The stereochemistry of **3ba** was unambiguously determined by X-ray crystallographic analysis, which provides clear evidence of the regio- and stereoselective carbothiolation process.[23] In addition to naphthothiazolyl sulfide **1c**, thiazolyl sulfides **1d** and **1e** were also amenable to the reaction (entries 2−4). Carbothiolation adduct **3fa** was obtained from benzoxazolyl sulfide **1f**, while the reaction of benzothienyl sulfide **1g** gave the product **3ga** in 12% yield. In the case giving the products **3** in low yields, the starting azoryl sulfides **1** were recovered. The increase of catalyst loading did not improve the product yields. It is of note that methyl 2-pyridyl sulfide and methyl phenyl sulfide did not undergo the reaction. Further optimization of carbothiolation with versatile heteroaryl sulfides is necessary for the efficient reaction.

A plausible reaction mechanism of the present carbothiolation is shown in Scheme 2. Oxidative addition of **1** to the palladium(0) species occurs to generate the (2-benzothiazolyl)-palladium(II) thiolate **A**. A cleavage of the C(heteroaryl)−S bond would occur in preference to those of C(methyl)−S and C(phenyl)−S bonds, which would result from a favorable coordination of heteroatoms in **1** to a palladium center prior to oxidative addition.[12,13] The subsequent regio- and stereoselective insertion of terminal alkynes **2** into the palladium−sulfur bond affords alkenyl(2-benzothiazolyl)palladium(II) intermediate **B**. The regioselectivity can be rationalized as follows. During migratory insertion of **A** with terminal alkynes

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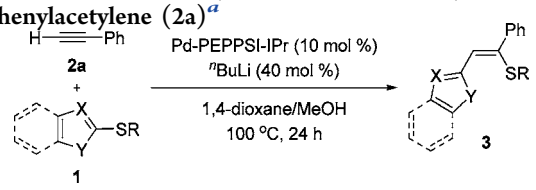
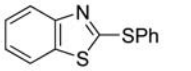
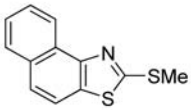
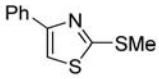
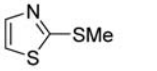
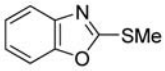
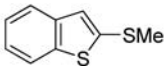
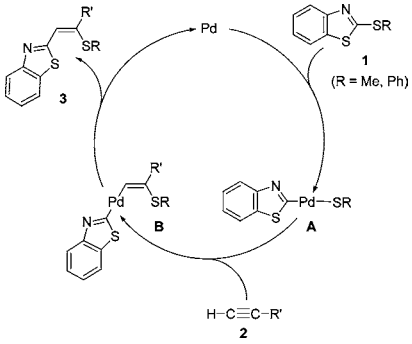
Table 3. Palladium-Catalyzed Addition of Azolyl Sulfides 1 to Phenylacetylene (2a)[a]



entry	heteroaryl sulfide	1	3	yield (%)[b]
1		1b	3ba	82
2		1c	3ca	75
3[c]		1d	3da	79
4[c]		1e	3ea	57
5[c]		1f	3fa	43
6		1g	3ga	12

[a]Conditions: **1** (1.0 mmol), **2a** (2.0 mmol), Pd-PEPPSI-IPr (0.10 mmol), ^{n}BuLi (0.40 mmol), in 1,4-dioxane (8.0 mL) and MeOH (0.125 mL) at 100 °C for 24 h. [b]Isolated yields. [c]Microwave irradiation at 160 °C for 40 min.

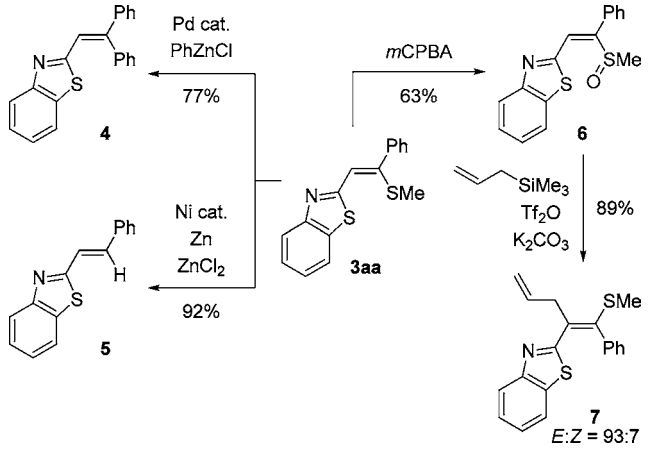
Scheme 2. Plausible Reaction Mechanism



2, bulkier carbene-ligated palladium avoids a steric repulsion with the substituents of the alkyne **2**. The proposed mechanism is consistent with a previous observation of an alkyne insertion into the metal–sulfur bond,[24] but an alternative pathway through carbopalladation of alkyne cannot be ruled out. Finally, reductive elimination proceeds to furnish **3**, regenerating the initial palladium complex.

The synthetic utility of the carbothiolation adduct **3** as synthetic intermediates was successfully demonstrated as shown in Scheme 3. Alkenyl methyl sulfide **3aa** can act as an alkenyl pseudohalide in cross-coupling: palladium-catalyzed Negishi coupling of **3aa** with phenylzinc chloride occurred to give **4** in 77% yield.[13] Nickel-catalyzed reduction of **3aa** with zinc provided 2-(phenethyl)benzothiazole (**5**) in 92% yield.[25] Oxidation of **3aa** with *m*-chloroperbenzoic acid (*m*CPBA) proceeded with a retention of stereochemistry to afford the corresponding sulfoxide **6**. The configuration of **6** was

Scheme 3. Transformations of 3aa



confirmed by X-ray crystallographic analysis.[23] Pummerer-type reaction of alkenyl sulfoxide **6** with allyltrimethylsilane in the presence of Tf_2O and K_2CO_3 furnished the allylated product **7** in 89% yield with a high stereoselectivity.[8b,26,27] It is noteworthy that allylation proceeded with an inversion of configuration and the formation of the *E*-isomer predominated, which was determined by NOESY analysis.[21]

In summary, the palladium/NHC complex Pd-PEPPSI-IPr catalyzed the addition of azolyl sulfides to terminal alkynes to afford (*Z*)-2-(azolyl)alkenyl sulfides with perfect regio- and stereoselectivities. The reaction proceeds with a direct cleavage of heteroaryl–sulfur bonds, which is widely applicable to substrates with various functionalities. The present method can be utilized for the construction of the highly functionalized olefin skeletons, which are often found in natural products and biologically active compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00503.

Details of all experiments procedures and spectroscopic data of new compounds (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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elemental analyses and SC-NMR Laboratory of Okayama University for the NMR spectral measurements.

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(23) CCDC-1455018 (**3ba**) and - 1455019 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See the Supporting Information for details.

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(27) Mechanism of regio- and stereoselective allylation is shown in the Supporting Information.

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