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Pd-NHC Catalytic System for the Efficient Atom-Economic Synthesis of Vinyl Sulfides from Tertiary, Secondary, or Primary Thiols

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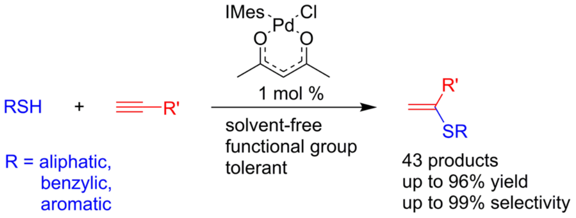
Supporting Information



ABSTRACT: Vinyl sulfides represent an important class of compounds in organic chemistry and materials science. Atom-economic addition of thiols to the triple bond of alkynes provides an excellent opportunity for environmentally friendly processes. We have found that well-known and readily available Pd-NHC complex (IMes)Pd(acac)Cl is an efficient catalyst for alkyne hydrothiolation. The reported technique provides a general one-pot approach for the selective preparation of Markovnikov-type vinyl sulfides starting from tertiary, secondary, or primary aliphatic thiols, as well as benzylic and aromatic thiols. In all the studied cases, the products were formed in excellent selectivity and good yields.

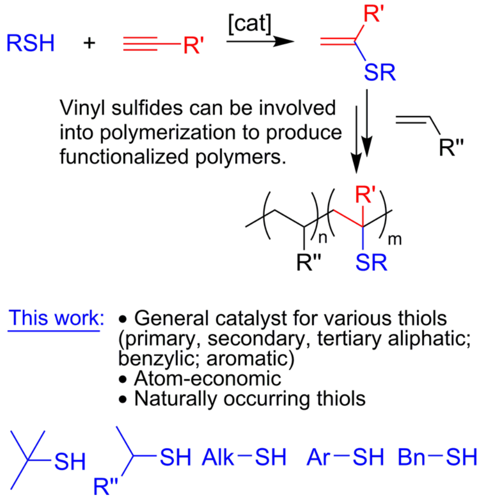
KEYWORDS: *atom economy, hydrothiolation, vinyl sulfides, palladium, N-heterocyclic carbene, catalysis*

Tremendous developments in materials science have caused the emergence of outstanding practical applications of organic compounds.[1−3] Of special importance are vinyl monomers that contain the C_{sp2}−heteroatom bond. The monomers can be easily involved in well-known polymerization routes to produce functionalized polymers.[2−5] Heteroatom-functionalized polymers represent a demanding class of new materials that are useful in a wide range of applications, such as high-performance engineering plastics, optics, optoelectronics, network polymers, fuel cell membranes, proton-conducting electrolytes, and photochemical materials.[2] Some polymers have applications in biomedicine, especially sulfopolymers that are used as biomembranes; polysulfates and polysulfonates exhibit antithrombotic and antiviral activities.[2] The incorporation of a sulfur atom into the polymer structure (Scheme 1) provides outstanding possibilities for changing its physical and chemical properties[3,4] to increase the refractive index,[6] improve elastic behavior,[7] enhance thermal properties,[8] and provide sorption activity for Au, Ag, Pt, Pd, and Hg salts.[9]

From a practical point of view, an atom-economic addition of thiols to alkynes opens outstanding possibilities to access vinyl sulfides. Application of the metal-complex catalysis allows one to obtain products with high yields and selectivity.[10] This catalytic approach was utilized for the preparation of the demanding Markovnikov-type vinyl sulfides (Scheme 1) and has demonstrated excellent tolerance to the nature of the functional group in the alkyne.

Surprisingly, the reaction is strongly sensitive to the nature of the R substituent in the thiol. Several [Ni]-based,[11] [Pd]-based,[12] [Rh]-based,[13] [Zr]-based,[14] lanthanide-based (where the lanthanide is [Sm], [La], or [Lu]),[15] actinide-based (where the actinide is [U] or [Th]),[16] and [In]-based[17] catalytic systems have been developed for the selective synthesis of Markovnikov-type vinyl sulfides.

Scheme 1. Selective Synthesis and Application of the Vinyl Sulfides



However, the addition of aliphatic thiols, especially branched ones, was much more challenging.[18] Indeed, from a practical

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point of view, the reaction with secondary and tertiary thiols is of high interest. On the one hand, the steric bulk provides flexible control over the properties of the resulting polymeric material. On the other hand, these alkanethiols are naturally occurring in crude oil and readily available, thus potentially providing a great opportunity to access inexpensive vinyl sulfide monomers, especially on the industrial scale.

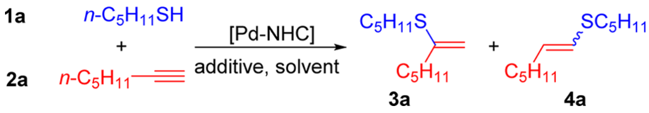
In the current study, we describe the first example of the Pd-NHC-catalyzed addition for a wide range of thiols and alkynes. (Here, NHC represents *N*-heterocyclic carbene.) The prepared catalyst precursor allowed us to conduct the reaction with tertiary, secondary, and primary aliphatic thiols, as well as with aromatic and benzylic thiols. The developed catalytic system has essential advantages, such as air and moisture stability.

The optimization of the reaction conditions was carried out using a model reaction involving 1-pentanethiol (**1a**) and 1-heptyne (**2a**). Several Ni, Pd, Pt, Cu, Fe, and Co metal complexes have been evaluated in the hydrothiolation reaction, and the Pd complexes exhibited the best performance (see the Supporting Information). Many different phosphine, nitrogen, and NHC ligands were evaluated in the reaction involving Pd complexes (see Tables S1 and S2 in the Supporting Information) with a superior outcome observed for (NHC)-Pd(acac)Cl. The application of the NHC = IPr ligand resulted in the formation of a mixture of Markovnikov and anti-Markovnikov products (**3a**:**4a** = 2:1), while the closely related IMes-bearing complex allowed for the selective preparation of the Markovnikov-type product (**3a**) (Table S2). (Here, IMes represents *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene and IPr represents *N*,*N*′-bis(2,6-diisopropylphenyl)imidazole-2-ylidene.) Therefore, the (IMes)Pd(acac)Cl complex was employed as the catalyst of choice for further optimization.

In the next step, we optimized the reaction conditions (see Table 1). The goal of the optimization was to increase the selectivity and yield toward the formation of product **3a**, while minimizing the formation of byproducts *Z*-**4a** and *E*-**4a**. Initially, the reaction was performed under solvent-free conditions, which furnished 9% yield of **3a** and 30% yield of byproducts **4a** (entry 1). The addition of γ-terpinene as a radical reaction inhibitor prevented the formation of byproducts **4a** (entry 2), because of suppression of the radical side reactions. The addition of triethylamine increased the yield of the desired product to 54% (entry 3). To determine the optimal conditions, the triethylamine amount was varied from 1 mol % to 100 mol % (entries 3−6). A catalytic amount of 4 mol % was found to be optimal for the studied reaction (entry 4). The use of pyridine as a base afforded lower yields, compared to triethylamine (entry 7). In the experiment with both triethylamine and γ-terpinene additives, product **3a** was selectively obtained in high yield (entry 8). The application of solvents, such as benzene, tetrahydrofuran, and 1,2-dichloroethane (entries 9−11), did not improve the yield of the product **3a**. The best results were obtained under solvent-free conditions (entry 8).

Variations in the temperature revealed an important advantage of the developed catalytic system. High selectivity toward the formation of desired product **3a** was retained over a wide temperature range from room temperature (rt) to 100 °C (entries 13−16). Reaction at higher temperature of 120 °C also gave a good product yield; however, some amount of byproducts was found (entry 12). For a particular combination of reagents (**1a** and **2a**), a temperature of 100 °C was the optimal choice (entry 13).

Table 1. Optimization of the Reaction Conditions[a]



entry		value	yield of 3(4) [%][b]
	Additives		
1	none		9(30)
2	γ-terpinene	1 equiv	26(<1)
3	Et$_3$N	1 mol %	54(22)
4	Et$_3$N	4 mol %	87(4)
5	Et$_3$N	10 mol %	79(6)
6	Et$_3$N	100 mol %	77(2)
7	pyridine	10 mol %	19(27)
8	Et$_3$N + γ-terpinene	4 mol % + 1 equiv	88(<1)
	Solvents[c]		
9	benzene	0.5 mL	75(<1)
10	tetrahydrofuran, THF	0.5 mL	73(<1)
11	dichloroethane, DCE	0.5 mL	32(<1)
	Temperatures[c]		
12	120 °C		86(4[d])
13	100 °C		88(<1)
14	80 °C		81(<1)
15	50 °C		47(<1)
16	room temperature		36(<1)

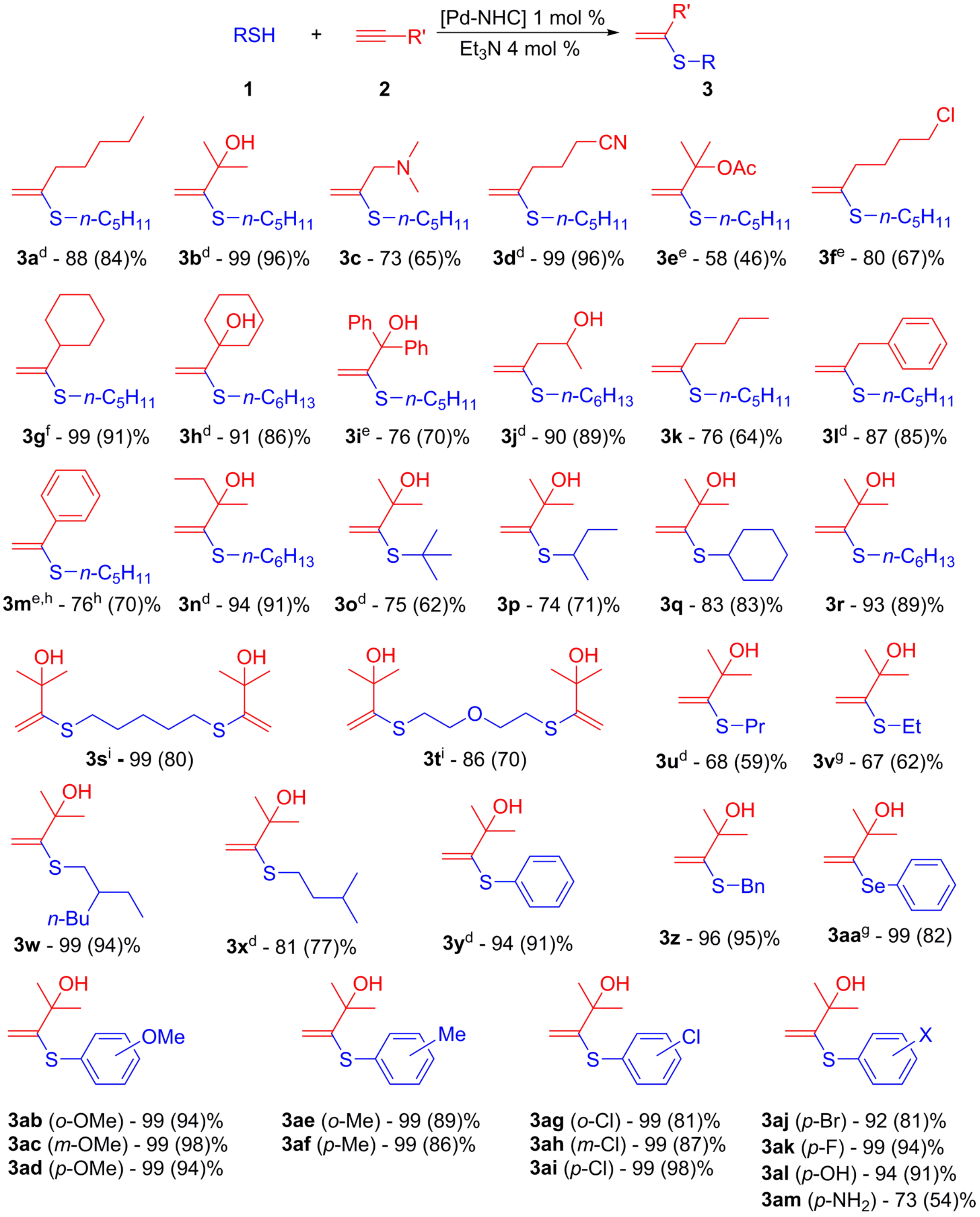
[a] Reaction conditions: **1a** (0.5 mmol) and **2a** (0.5 mmol) were added to (IMes)Pd(acac)Cl (1 mol %). The reaction mixture was stirred for 4 h at 100 °C (entries 1−11). [b] The yields were determined by ^{1}H NMR and calculated based on the initial thiol amount. [c] Et$_3$N (4 mol %), and γ-terpinene (1 equiv) were added. [d] Unidentified mixture of byproducts.

Once the optimal reaction conditions were established, we explored the scope of alkynes for the synthesis of vinyl sulfides (Scheme 2). All of the reactions proceeded with good to excellent yields. The various potentially reactive functional groups in the alkynes were well tolerated in this reaction. These groups include alcohols, amines, nitriles, esters, and chlorides (**3b**, **3c**, **3d**, **3e**, **3f**). To study alkyne steric effects, various R′ substituents were employed and exhibited excellent yields for **3a**, **3g**, **3h** (88%, 99%, and 91%, respectively). Even bulky product **3i** was formed in good yield (76%). Benzylic and aromatic alkynes also selectively yielded desired Markovnikov products **3l** and **3m**.

The developed catalytic system was tolerant to a wide range of thiols. First, the most challenging tertiary and secondary thiols were studied, and the products were obtained in very good yields of 74%−83% (**3o**, **3p**, **3q**). The developed catalytic system exhibited very good performance for various primary thiols (**3r**−**3x**) with product yields of 67%−99%.

Aromatic and benzylic thiols provided high yields (73%−99%) of the desired products (**3y**, **3z**, **3ab**−**3am**). A series of experiments with aromatic thiols, containing electron-withdrawing or electron-donating groups, were examined, and very good functional group tolerance was observed (**3ab**−**3am**). Phenylselenol has also reacted with a high yield of 99% (**3aa**). The developed catalytic system has shown excellent regioselectivity. A minor amount of byproducts was observed in one case only (**3m**:**4m** = 5:1). In all of the other cases, compound **3** was obtained as a single product (controlled by ^{1}H NMR), and amount of the byproducts was below the trace level. The catalyst operation in a wide temperature range is a key factor for optimizing the outcome of the addition process. Temper-

Scheme 2. Catalytic Regioselective Addition of Thiols to Alkynes^{a,b,c}

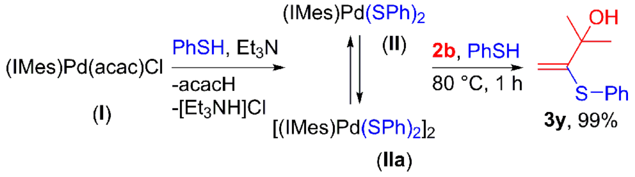


[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), Et_3N (4 mol %), (IMes)Pd(acac)Cl (1 mol %), γ-terpinene 1 equiv at 50 °C 18 h. [b]Yields by ^1H NMR and isolated yields shown in parentheses. [c]For additional substrate scope see also Scheme S1 in the Supporting Information. [d]Conditions: 100 °C, 8 h. [e]Conditions: 100 °C, 4 h. [f]Conditions: 50 °C, 8 h. [g]Conditions: 35 °C, 24 h. [h]**3m**:**4m** ratio = 5:1. [i]Two equivalents (2 equiv) of alkyne **2** were used. [j]PhSeH was used instead of thiol.

atures ranging from 35 °C to 100 °C were utilized to render the selective transformation, depending on the reactivity of thiol and alkyne (Scheme 2). The ability to vary the temperatures is important for reagents that have a low boiling point or thiols that are prone to generate disulfides at high temperatures.

To investigate the reaction mechanism, we performed a sequence of stoichiometric reactions (see Scheme 3). The ^1H NMR monitoring of the reaction between the catalyst precursor (**I**), 1 equiv of thiophenol (**1b**), and Et_3N was carried out in benzene-d_6. The appearance of a set of new signals was observed: half of the initial (IMes)Pd(acac)Cl was converted to a new NHC-containing complex, with the liberation of acetylacetone. The addition of a second equivalent of PhSH (**1b**) led to complete conversion of the initial precatalyst (**I**) into $[(IMes)Pd(SPh)_2]_n$, indicating the substitution of both the acac and Cl ligands in **I**. The crystals of the $[(IMes)Pd(SPh)_2]_2$

Scheme 3. Stoichiometric Reaction of Pd-Mediated PhSH (1b) Addition to Alkyne (2b)



dimer (**IIa**) were grown, and its molecular structure was determined by X-ray analysis (see Figure 1). In the last step of stoichiometric transformations, product **3y** was formed in high yield after heating with PhSH (Scheme 3). In the reaction of alkyne **2b** and isolated complex **IIa**, product formation was detected only in the presence of PhSH.

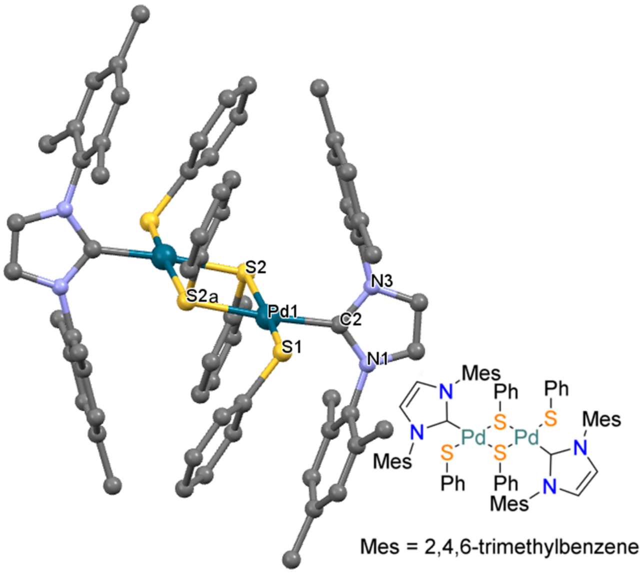


Figure 1. X-ray crystal structure of the catalyst resting state (**IIa**). Selected bond distances: Pd1−C2, 2.0212(17) Å; Pd1−S1, 2.3190(5) Å; Pd1−S2, 2.3431(4) Å; Pd1−S2a, 2.3648(4) Å; N1−C2, 1.362(2) Å; C2−N3, 1.360(2) Å. Selected bond angles: C2−Pd1−S1, 91.22(5)°; C2−Pd1−S2, 95.93(5)°; C2−Pd1−S2a, 174.92(5)°; S1−Pd1−S2, 170.822(18)°; S1−Pd1−S2a, 88.665(17)°; S2−Pd1−S2a, 83.699(16)°; Pd1−S2−Pd1a, 96.303(16)°; and N1−C2−N3, 103.73(15)°.

Compound **IIa** (Figure 1) is a centrosymmetric binuclear complex formed by two bridging phenylthiolato ligands. Because of the intrinsic inversion center, the central Pd_2S_2 four-membered ring is strictly planar. The Pd•••Pd separation in **IIa** was 3.5070(3) Å, which indicates the absence of a bonding interaction. Each Pd(II) atom adopts an approximately square planar geometry that is coordinated by three S atoms from the PhS ligands and one C atom from the NHC ligand. The distortion of the square planar configuration is manifested in the slight deviation of the Pd atoms from the mean planes that pass through the four coordinated atoms by 0.1032(5) Å. Both the bridging and terminal thiolate ligands are arranged *anti*, relative to the central four-membered ring, and the carbene ligands occupy the mutually *trans* positions. The phenyl rings of the terminal and bridging PhS ligands are nearly parallel with a dihedral angle of 11.22(14)°. The bridging Pd−S bond lengths were similar to each other, and the differences between these bond lengths may be due to the relative effects of the *trans* influence, as well as steric effects.

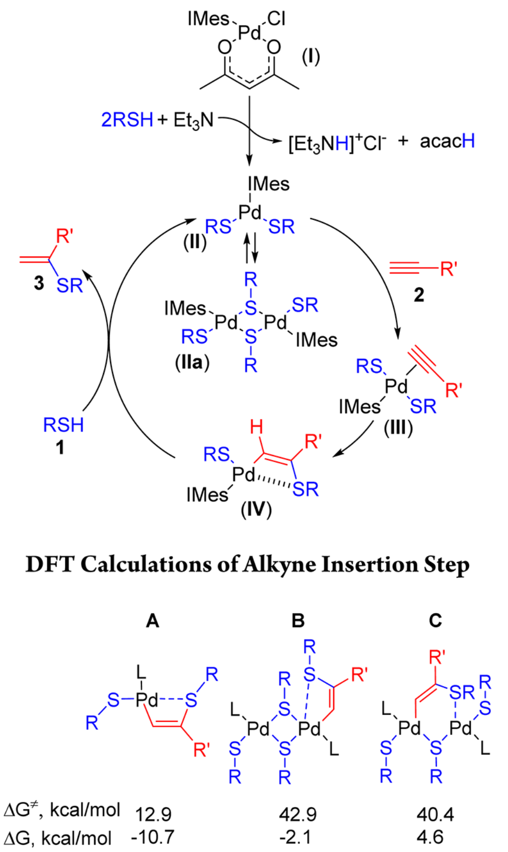
It is interesting to note that, in contrast to complex **IIa**, the two Pd_2S_2 four-membered rings in the related trinuclear complex, (IPr)(SPh)Pd−(μ-SPh)$_2$-Pd-(μ-SPh)$_2$−Pd(SPh)(IPr) has a *butterfly* conformation, and the square planar geometry of the terminal Pd atoms was distorted to a greater extent.[19] Regardless of these facts, the Pd−C and corresponding Pd−S distances in both complexes are very similar. Complex **IIa** can also be compared with related structures containing PPh_3[19b] or P(O-*i*Pr)[19c] ligands. Complex with triisopropyl phosphite has a *trans* configuration and the distance between Pd and S2a atom is shorter than Pd−S2, in contrast to **IIa**.

The catalytic activity of the isolated dimeric complex was also examined. The addition of alkyne (**2b**) and PhSH to the catalytic amount of complex **IIa**, followed by heating at 80 °C for 4 h, resulted in formation of the product **3y** in 90% NMR yield. Isolated complex **IIa** was found less reactive and the catalytic addition reaction was rather slow at rt or at 50 °C. Hydrothiolation of the alkyne was initiated upon heating of the reaction mixture up to 80 °C.

The overall catalytic transformation starts with the activation of the precatalyst **I** by replacement of the Cl and acac ligands with SR ligands (see Scheme 4). The resulting Pd complexes may exist in a monomeric (**II**) or dimeric (**IIa**) forms. The ligand replacement reactions were confirmed by a step-by-step stoichiometric sequence (see Scheme 3), and structure **IIa** was established by X-ray analysis (see Figure 1).

To define the nature of the catalytic species, kinetic studies and theoretical calculations were performed (see the Support-

Scheme 4. Plausible Mechanism of Alkyne Hydrothiolation



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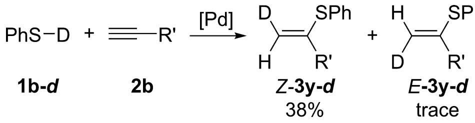
ing Information). Under catalytic conditions, the reaction was approximately first order, with respect to (IMes)Pd(acac)Cl. Therefore, we assume that a monomeric complex (**II**) is involved in the catalytic cycle as an intermediate, and complex **IIa** is a resting state (see Scheme 4).

Theoretical modeling of the alkyne insertion into Pd−S bond was carried out using DFT calculations at the PBE1PBE/6-311G(d) and SDD levels (see the Supporting Information). The monomeric complex is three-coordinated and provides the necessary option for binding of the alkyne and formation of π-complex **III** with further transition into complex **IV** after alkyne insertion (see Scheme 4). A relatively small activation barrier of $\Delta G^{\ddagger}$ = 12.9 kcal/mol and favorable thermodynamic driving force with ΔG = −10.7 kcal/mol were found in the calculations (Scheme 4A). Pd atoms in the dimeric complex are four-coordinated and do not have coordination vacancy for strong binding of alkyne and activation of the triple bond. Rather high activation barriers were calculated for alkyne insertion into the terminal $\Delta G^{\ddagger}$ = 42.9 kcal/mol (Scheme 4B) and bridging $\Delta G^{\ddagger}$ = 40.4 kcal/mol (Scheme 4C) Pd−S bonds. In total agreement with the experimental findings monomeric complex is more reactive toward alkynes, compared to the dimeric palladium complex.

The nature of the insertion step and observed selectivity of the reaction were confirmed by performing deuterium labeling experiments (see Scheme 5 and the Supporting Information).

Scheme 5. Isotope Labeling in the Hydrothiolation with PhSD



Using PhSD (**1b**-***d***) as the thiol, deuterium incorporation was observed only in the *cis*-position to the sulfur group Z-**3y**-***d*** (Scheme 5), with R′ and SR groups located at the same C atom. The observed reaction outcome is in good agreement with the literature data for the alkyne insertion step.[12,20] The location of the R′ substituent in the β position, with respect to Pd in complex **IV**, explains the high functional group tolerance of alkynes in the studied process, since R′ is located far from the metal center and the interactions between Pd and R′ is minimized. Such geometry arrangements may be stabilized via the coordination of sulfur to the metal center in **IV**, as evident from the DFT calculations.

The reaction of complex **IV** with thiols leads to the product formation and regeneration of intermediate complex **II**. Involvement of RSH in the last protonolysis step was confirmed by stoichiometric reactions (Scheme 3), because the formation of **3** does not occur without the presence of the thiol.

Thus, in the current study, we have solved the problem of selective synthesis of demanding vinyl sulfides starting from various thiols. We have demonstrated that the developed palladium catalytic system is efficient for a wide range of thiols including tertiary, secondary, and primary aliphatic thiols, as well as benzylic and aromatic thiols. The catalyst exhibits high functional group tolerance. It is important to note that the catalyst precursor is readily available and can be synthesized in a straightforward fashion by a simple reaction of $Pd(acac)_2$ and the IMes·HCl imidazolium salt.[21] The catalytic complex is stable in air, and this approach avoids the use of complicated experimental techniques. In summary, a simple and efficient catalytic system has been developed for the atom-economic preparation of vinyl sulfides with excellent selectivity and very good yields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01815.

> Mechanistic study, kinetic measurements, theoretical calculations, experimental procedures, spectral data, details of the X-ray analysis (PDF)
>
> Crystallographic data for $C_{66}H_{68}N_4Pd_2S_4$ (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Roncali, J.; Blanchard, P.; Frère, P. *J. Mater. Chem.* **2005**, *15*, 1589−1610. (b) Dou, L.; You, J.; Hong, Z.; Xu, Z.; Li, G.; Street, R. A.; Yang, Y. *Adv. Mater.* **2013**, *25*, 6642−6671. (c) Jeffries-EL, M.; Kobilka, B. M.; Hale, B. J. *Macromolecules* **2014**, *47*, 7253−7271. (d) Lee, I.-H.; Shin, S.; Choi, T.-L. *Science* **2015**, *347*, 1310−1311.

(2) (a) Ebewele, R. O. *Polymer Science and Technology*; CRC Press LL: New York, 2000. (b) Kultus, A. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, 2002.

(3) (a) Nakabayashi, K.; Abiko, Y.; Mori, H. *Macromolecules* **2013**, *46*, 5998−6012. (b) Abiko, Y.; Nakabayashi, K.; Mori, H. *Macromol. Symp.* **2015**, *349*, 34−43.

(4) Kausar, A.; Zulfiqar, S.; Sarwar, M. I. *Polym. Rev.* **2014**, *54*, 185−267.

(5) Lowe, A. B. *Polymer* **2014**, *55*, 5517−5549.

(6) (a) Liu, J.; Ueda, M. *J. Mater. Chem.* **2009**, *19*, 8907−8919. (b) Jang, J. Y.; Do, J. Y. *React. Funct. Polym.* **2015**, *91−92*, 28−34.

(7) Kilcher, G.; Wang, L.; Duckham, C.; Tirelli, N. *Macromolecules* **2007**, *40*, 5141−5149.

(8) Abiko, Y.; Matsumura, A.; Nakabayashi, K.; Mori, H. *Polymer* **2014**, *55*, 6025−6035.

(9) Anpilogova, G. R.; Vorob'eva, A. I.; Onina, S. A.; Khisamutdinov, R. A.; Murinov, Y. I.; Monakov, Y. B. *Russ. J. Appl. Chem.* **2006**, *79*, 1593−1599.

(10) (a) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108−5114. (b) Ogawa, A. *J. Organomet. Chem.* **2000**, *611*, 463−474. (c) Bichler, P.; Love, J. A. In *C−X Bond Formation*; Vigalok, A., Ed.; Topics in Organometallic Chemistry, Vol. *31*; Springer: Berlin, Heidelberg, Germany, 2010; pp 39−64. (d) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596−1636. (e) Ogawa, A. In *Hydrofunctionalization*; Ananikov, V. P., Tanaka, M., Eds.; Topics in Organometallic Chemistry, Vol. *43*; Springer: Berlin, Heidelberg, Germany, 2013; pp 325−360. (f) Dondoni, A.; Marra, A. *Eur. J. Org. Chem.* **2014**, *2014*, 3955−3969.

(11) (a) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *Adv. Synth. Catal.* **2005**, *347*, 1993−2001. (b) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P.; April, R. V. *Organometallics* **2006**, *25*, 4462−4470. (c) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970−1977.

(d) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2007**, *26*, 740−750.

(12) (a) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902−5903. (b) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y.; Timofeeva, T. V. *J. Am. Chem. Soc.* **2007**, *129*, 7252−7253. (c) Ananikov, V. P.; Orlov, N. V.; Zalesskiy, S. S.; Beletskaya, I. P.; Khrustalev, V. N.; Morokuma, K.; Musaev, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 6637−6649. (d) Gerber, R.; Frech, C. M. *Chem.—Eur. J.* **2012**, *18*, 8901−8905.

(13) (a) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614−17615. (b) Yang, J.; Sabarre, A.; Fraser, L. R.; Patrick, B. O.; Love, J. A. *J. Org. Chem.* **2009**, *74*, 182−187. (c) Yang, Y.; Rioux, R. M. *Chem. Commun.* **2011**, *47*, 6557−6559. (d) Di Giuseppe, A.; Castarlenas, R.; Pérez-Torrente, J. J.; Crucianelli, M.; Polo, V.; Sancho, R.; Lahoz, F. J.; Oro, L. A. *J. Am. Chem. Soc.* **2012**, *134*, 8171−8183. (e) Kankala, S.; Nerella, S.; Vadde, R.; Vasam, C. S. *RSC Adv.* **2013**, *3*, 23582−23588. (f) Palacios, L.; Artigas, M. J.; Polo, V.; Lahoz, F. J.; Castarlenas, R.; Pérez-Torrente, J. J.; Oro, L. A. *ACS Catal.* **2013**, *3*, 2910−2919.

(14) Weiss, C. J.; Marks, T. J. *J. Am. Chem. Soc.* **2010**, *132*, 10533−10546.

(15) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *Organometallics* **2010**, *29*, 6308−6320.

(16) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 2062−2063.

(17) Sarma, R.; Rajesh, N.; Prajapati, D. *Chem. Commun.* **2012**, *48*, 4014−4016.

(18) Such tendencies are usually connected with increasing bond dissociation energy in the row AlkSH > BnSH > PhSH and larger acidity of aromatic thiols over aliphatic.[12b] The low reactivity of secondary and tertiary thiols is connected to steric encumbrance: the bulkier thiols exhibit retarded activity. Great rate reduction during transitioning from primary to secondary thiols, and no reaction with tertiary thiols, were observed for the [Zr] complex.[14]

(19) (a) Sayah, M.; Lough, A. J.; Organ, M. G. *Chem.—Eur. J.* **2013**, *19*, 2749−2756. (b) Nakanishi, I.; Tanaka, S.; Matsumoto, K.; Ooi, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1994**, *50*, 58−61. (c) Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y. *Organometallics* **2005**, *24*, 1275−1283.

(20) (a) Ishii, A.; Nakata, N. In *Hydrofunctionalization*; Ananikov, V. P., Tanaka, M., Eds.; Topics in Organometallic Chemistry, Vol. *43*; Springer: Berlin, Heidelberg, Germany, 2011; pp 21−50. (b) Ananikov, V. P.; Beletskaya, I. P. In *Hydrofunctionalization*; Ananikov, V. P., Tanaka, M., Eds.; Topics in Organometallic Chemistry, Vol. *43*; Springer: Berlin, Heidelberg, Germany, 2012; pp 1−19. (c) Ishii, A.; Kamon, H.; Murakami, K.; Nakata, N. *Eur. J. Org. Chem.* **2010**, *2010*, 1653−1659. (d) Ishii, A.; Yamaguchi, Y.; Nakata, N. *Dalton Trans.* **2010**, *39*, 6181−6183. (e) Nakata, N.; Uchiumi, R.; Yoshino, T.; Ikeda, T.; Kamon, H.; Ishii, A. *Organometallics* **2009**, *28*, 1981−1984. (f) Ishii, A.; Nakata, N.; Uchiumi, R.; Murakami, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2661−2664. (g) Castarlenas, R.; Di Giuseppe, A.; Pérez-Torrente, J. J.; Oro, L. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 211−222.

(21) Marion, N.; de Frémont, P.; Puijk, I. M.; Ecarnot, E. C.; Amoroso, D.; Bell, A.; Nolan, S. P. *Adv. Synth. Catal.* **2007**, *349*, 2380−2384.