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Copper-Catalyzed Monochalcogenation of Terminal Alkyne Using Dichalcogenide Compound via Cleavage of the Dichalcogenide Bond

Nobukazu Taniguchi*

Department of Chemistry, Fukushima Medical University, Fukushima 960-1295

Abstract: The methodology for a copper-catalyzed chalcogenation of terminal alkynes with dichalcogenide in air. Numerous alkynyl sulfides, selenides or tellurides can be synthesized by the use of a CuCl catalyst and N,N'-dialkyl ethylenediamine. The employed diamine serves as a ligand of CuCl and a base facilitating the chalcogenation of alkynes. Furthermore, the present reaction can efficiently take advantage of two chalcogenide–groups in the dichalcogenide.

Introduction

Alkynyl chalcogenides have found widespread utilization as convenient intermediates in organic syntheses. To furnish these compounds, the reaction of terminal alkynes with dichalcogenide under basic conditions has often been employed, whereas in the traditional system one chalcogenide-group in the dichalcogenide is not used. The cause is attributable to the generation of anion. Similarly, when the chalcogenation of alkyne using copper salt is carried out under basic conditions, copper(I) chalcogenide is produced together with alkynyl chalcogenide (Scheme 1). However, no copper-chalcogenide performs the chalcogenation of alkynes under usual conditions. Moreover, it is well known that the reactivity of this complex is lower owing to the stability of the metal-chalcogenide bond. Therefore, an approach using a transition-metal-catalyzed method which can use two chalcogenide–groups has been limited.

In this paper, a copper-catalyzed preparation of alkynyl chalcogenide from a terminal alkyne with dichalcogenide will be described.

Scheme 1. The chalcogenation of alkyne with dichalcogenide via copper-acetylide

Results and Discussion

Initial screening sulfidation of terminal alkyne was performed with copper(I) chloride as a catalyst (Table 1).

In air, when the phenylsulfidation of 1-octyne 1a with diphenyl disulfide 2a was executed using CuCl-bpy (10 mol%), 1-(phenylthio)-1-octyne was not detected at all (Table 1, entry 1). The employment of other diamines 7, 8b and 8c or triethylamine 5 also did not produce satisfactory results owing to the dimerization of alkynes (Table 1, entries 2, 3, 4, and 5).

Fortunately, the combination of CuCl and N,N'-diethylentetramine 8a (10 mol%) produced the corresponding sulfide 3aa in 71% yield with the formation of diyne 4a in 22% yield (Table 1, entry 6). Most notably, the reaction under nitrogen atmosphere using a balloon gave 3aa in 90% yield, and
succeeded in suppressing the yield of 4a (Table 1, entry 7).
A solvent such as DMF or toluene was unsuitable for the reaction (Table 1, entries 8 and 9). Although other copper catalysts were also examined, Cu' salts (CuI, CuBr and CuOAc) gave lower yields (Table 1, entries 10, 11, and 12), and CuI salts (CuCl2, CuBr2 and CuF2) could not advance the reaction (Table 1, entries 13, 14, and 15).

On the basis of the optimized result, we concurrently pursued the copper-catalyzed sulfidation and selenation of terminal alkynes using disulfide and diselenide (Table 2). When alkynes 1 (0.3 mmol), CuCl–8a or 8b (10 mol%) and disulfides 2a–c or diselenides 2d–e were stirred in dioxane (0.5 mL) at 100 °C, alkynyl sulfides or selenides 3 were obtained in 60–94% yields. Regrettably, when (nBuS)2 or propargyl amine was used, these yields decreased (Table 2, entries 3, 10 and 20). Thus this system could use the combination of miscellaneous alkynes with disulfides or diselenides.

Next, the synthesis of alkynyl tellurides was investigated. Unfortunately, employment of the previous conditions using the CuCl catalyst did not facilitate the telluridation owing to the dimerization of the alkyne (Table 3, entries 1, 2 and 3). To promote the expected reaction, the employment of other copper salts (CuBr, Cu, CuCl2 or CuBr2) was then examined, and, surprisingly, alkynyl telluride was produced in 47–60% yield (Table 3, entries 4, 5, 6 and 7). Furthermore, in the use of CuCl, the addition of nBu4NBr led effectively to completion of the reaction and produced 1-(phenyltelluro)-1-octyne (9af) in 85% yield without the formation of diyne (Table 3, entry 9). According developed procedure, a variety of alkynyl phenyl tellurides 9 could be synthesized in 70–92% yields by the mixture of terminal alkyne, (PhTe)2, CuCl–8b (5 mol%) and nBu4NBr (20 mol%) treated in dioxane at 100 °C (Table 4). In the present reaction, the production of 9 was not affected by the substrates.

Thus, the CuCl-catalyzed chalcogenation of terminal alkynes with dichalcogenides was achieved via cleavage of the dichalcogenide bond, and this system enabled the efficient use of two chalcogenide-groups in dichalcogenide.

Initially, to understand the reaction mechanism, the role of the copper catalyst was investigated in the case of sulfidation. The reaction of CuCl with diphenyl disulfide 2a could not be promoted at all (Scheme 3), although the reaction of copper(I) phenylacetylide (0.3 mmol) with 2a (0.15 mmol) produced the expected sulfide in 94% yield (Scheme 4). These results show that CuCl itself cannot cleave the disulfide bond, but the copper(I)-acetylide is formed in the first step of the catalytic cycle. Sequentially, both alkynyl sulfide and copper-sulfide were produced by the copper-acetylide reacting with disulfide.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]</th>
<th>Ligand</th>
<th>3aa− (%)</th>
<th>4a− (%)</th>
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<td>6</td>
<td>0</td>
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<tr>
<td>2a</td>
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</tr>
<tr>
<td>3a</td>
<td>7</td>
<td>29</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>8b</td>
<td>30</td>
<td>42</td>
<td></td>
</tr>
<tr>
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<td>8c</td>
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<td>8a</td>
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<td>8a</td>
<td>90</td>
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<td>8b,d</td>
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<td>0</td>
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<td>9b,e</td>
<td>8a</td>
<td>39</td>
<td>40</td>
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<td>10b</td>
<td>Cu</td>
<td>8a</td>
<td>16</td>
<td>41</td>
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<tr>
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<tr>
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<tr>
<td>14b</td>
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<td>8a</td>
<td>trace</td>
<td>47</td>
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<td>15b</td>
<td>CuF2</td>
<td>8a</td>
<td>trace</td>
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[a] Reaction was performed in air. [b] Reaction was performed under a nitrogen using the balloon. [c] Isolated yields after silica-gel chromatography. [d] DMF was used as a solvent. [e] PhCH3 was used as a solvent.
Table 2. Copper-catalyzed preparation of alkynyl sulfides or selenides from terminal alkynes with dichalcogenide

\[
\begin{array}{c}
\text{R}^1_2 + 1/2(\text{R}^2\text{Y})_2 \\
\text{CuCl-8a (10 mol%)} \\
\text{dioxane, 100 ºC} \\
\rightarrow \text{R}^1\text{YR}^2
\end{array}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Y</th>
<th>1</th>
<th>Time (h)</th>
<th>3a (%)</th>
<th>Entry</th>
<th>Y</th>
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<td>i-Pr3Si</td>
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<td>89</td>
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<td>Ph</td>
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<td>Ph</td>
<td>18</td>
<td>83</td>
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<td>Ph</td>
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<td>Ph</td>
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<td>HO</td>
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<td>17b</td>
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<tr>
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<td>S</td>
<td>i-Pr3Si</td>
<td>18</td>
<td>82</td>
<td>22b</td>
<td>Se</td>
<td>i-Pr3Si</td>
<td>18</td>
<td>88</td>
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</table>

[a] Isolated yields after silica-gel chromatography. [b] N,N’-Dimethylenediamine 7b (10 mol%) was used as a ligand.

In fact, the reaction in the sealed tube (condition A) gave the corresponding sulfide 3aa only in 11% yield in the presence of 10 mol% of CuCl, although the reaction under a nitrogen atmosphere using the balloon (condition B) resulted in 87% yield. Accordingly, it is clear that oxygen has been supplied in the balloon from the atmosphere.

Next, the role of the combination of CuSPh and diamine was surveyed (Table 5). The treatment of a mixture of CuSPh-8b (100 mol%) and 1-octyne 1a gave 3aa in 46% yield (Table 5, entry 1), and the use of CuSPh-8b (10 mol%) produced 3aa in 81% yield by the addition of hydrochloric acid (10 mol%) (Table 5, entries 3 and 4). Interestingly, the system in the absence of diamines 8b rarely had the reaction promoted (Table 5, entries 2 and 5), although the reaction of sodium acetylide with CuSPh gave 3aa in 38% yield (Scheme 6). From these results, it is presumed that CuSPh works for the phenylsulfidation of the terminal alkyne by 8b serving as a base and a ligand.

The CuSPh produced herein is necessary for oxygen in order to facilitate the sulfidation of alkynes. In fact, the reaction in the sealed tube (condition A) gave the corresponding sulfide 3aa only in 11% yield in the presence of 10 mol% of CuCl, although the reaction under a nitrogen atmosphere using the balloon (condition B) resulted in 87% yield. Accordingly, it is clear that oxygen has been supplied in the balloon from the atmosphere.

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of the terminal alkyne by \textbf{8b} serving as a base and a ligand.

**Table 3.** Copper-catalyzed chalcogenation of 1-octyne \textbf{1a} with (PhTe)\textsubscript{2} \textbf{2f} and \textbf{8b} serving as a base and a ligand.

\[
\begin{array}{cccc}
\text{Entry} & \text{[Cu]} & \text{Ligand} & \text{Additive} \\
\hline
1 & \text{CuCl} & 7 & \text{none} \\
2 & \text{CuCl} & \text{8a} & \text{none} \\
3 & \text{CuCl} & \text{8b} & \text{none} \\
4 & \text{CuBr} & \text{8b} & \text{none} \\
5 & \text{CuI} & \text{8b} & \text{none} \\
6 & \text{CuCl\textsubscript{2}} & \text{8b} & \text{none} \\
7 & \text{CuBr\textsubscript{2}} & \text{8b} & \text{none} \\
8 & \text{CuCl} & \text{8b} & \text{nBu}_{4}\text{NCl (20 mol\%)} \\
9 & \text{CuCl} & \text{8b} & \text{nBu}_{4}\text{NBr (20 mol\%)} \\
10 & \text{CuI} & \text{8b} & \text{nBu}_{4}\text{NBr (20 mol\%)} \\
11 & \text{CuBr} & \text{8b} & \text{nBu}_{4}\text{NBr (20 mol\%)} \\
12 & \text{none} & \text{none} & \text{nBu}_{4}\text{NBr (20 mol\%)} \\
\end{array}
\]

[a] Reaction was carried out under a nitrogen using the balloon. [b] Isolated yields after silica-gel chromatography.

**Table 4.** Copper-catalyzed preparation of alkynyltellurides \textbf{9} from terminal alkynes with diphenyl ditelluride

\[
\begin{array}{ccc}
\text{Entry} & \text{1} & \text{Time (h)} & \text{9} \\
\hline
1 & \text{Ph} & 24 & 82 \\
2 & \text{4-MeC}_6\text{H}_4 & 24 & 92 \\
3 & \text{n-C}_6\text{H}_{13} & 24 & 85 \\
4 & \text{HO} & 24 & 87 \\
5 & \text{Me}_2\text{N} & 24 & 78 \\
6 & \text{HO} & 24 & 81 \\
7 & \text{EtO}_2\text{C} & 24 & 85 \\
8 & \text{i-Pr}_3\text{Si} & 24 & 87 \\
9 & \text{EtO}_2\text{C} & 24 & 85 \\
10 & \text{EtO}_2\text{C} & 24 & 85 \\
\end{array}
\]

[a] Isolated yields after silica-gel chromatography.

**Scheme 3.** A reaction between (PhS)\textsubscript{2} with Cu(I)Cl

\[
\begin{array}{ccc}
\text{CuCl-} & \text{8b} & \text{none} \\
\hline
\end{array}
\]

Scheme 4. A reaction between copper(I) phenyl acetylide with \textbf{2a}

\[
\begin{array}{ccc}
\text{CuCl-} & \text{8b} & \text{none} \\
\hline
\end{array}
\]

A proposed mechanism is outlined in Figure 1. In the first step, the reaction of copper-acetylide \textbf{10} with disulfide produces alkynyl sulfide \textbf{3} and Cu\textsuperscript{1}SPh \textbf{11}. In the second step, a cuprate \textbf{12} as an intermediate is formed by the reaction of the generated \textbf{11} reacts with the terminal alkyne \textbf{1} in the presence of the diamines \textbf{8b}.\textsuperscript{[12]} Finally, the alkynyl sulfide \textbf{3} is produced again by the oxidation of \textbf{12} and Cu\textsuperscript{1}Cl is reproduced. Thus, this catalytic system can consume two chalcogenide-groups in the dichalcogenide.
Scheme 5. The large scale of sulfidation of 1a

\[
\begin{align*}
  &\text{CuCl-7a} \quad (0.3 \text{ mmol}) \\
  &\text{dioxane, 100 ºC, 30 h}
\end{align*}
\]

1a (3.0 mmol) 2a (1.5 mmol)

<table>
<thead>
<tr>
<th>Condition</th>
<th>3aa (%)</th>
<th>4a (%)</th>
<th>2a (%)</th>
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<td>A</td>
<td>11</td>
<td>8</td>
<td>71</td>
</tr>
<tr>
<td>B</td>
<td>87</td>
<td>3</td>
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</table>

A: in the sealed tube under N2
B: under N2 using the balloon

Conclusion
In conclusion, we have achieved a copper-catalyzed chalcogenation of a terminal alkyne with dichalcogenide under a nitrogen atmosphere using a balloon. The present reaction enables the efficient use of two chalcogenide-groups in the dichalcogenide by the diamines serving as a ligand and a base.

Scheme 6. A reaction of sodium acetylide with CuSPh

Table 5. Sulfidation of 1-octyne by Cu(I)SPh

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent (mol %)</th>
<th>CuSPh (mol %)</th>
<th>8a (mol %)</th>
<th>Additive (mol %)</th>
<th>3aa[a] (%)</th>
<th>4a[a] (%)</th>
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<td>100</td>
<td>100</td>
<td>none</td>
<td>46</td>
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<td>2</td>
<td>none</td>
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<td>none</td>
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<tr>
<td>3</td>
<td>(PhS)₂(50)</td>
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<td>none</td>
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<td>12</td>
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<td>4[c]</td>
<td>(PhS)₂(50)</td>
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<td>HCl(10)</td>
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<td>(PhS)₂(50)</td>
<td>10</td>
<td>none</td>
<td>HCl(10)</td>
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<td>trace</td>
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[a] Isolated yields after a silica-gel chromatography. [b] Reaction was carried out for 48 h in air. [c] Hydrochloric acid used 37 wt.% in water.

Figure 1. A plausible reaction mechanism in the synthesis of alkynyl sulfide or selenide

Experimental Section
General. All reactions were carried out under a nitrogen atmosphere using the balloon. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ¹H, 67.5 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ¹H NMR and chloroform-d (δ 77.0) for ¹³C NMR. IR spectra were measured by Perkin-Elmer Spectrum One FT-IR spectrometer. Melting points were measured on a BÜCHI Melting Point B-540 apparatus. Elemental analysis was performed at the Instrumental Analysis Center for Chemistry, Tohoku University (Japan).

Preparation of the alkynyl sulfides from terminal alkynes with disulfides
A typical procedure is given for the reaction of ethynylbenzene with diphenyl disulfide 2a giving phenylethynyl phenyl sulfide (entry 1 in Table 2): To the mixture of Cu(I)Cl (3.0 mg, 0.03 mmol), diphenyl disulfide (32.8 mg, 0.15 mmol), and N,N'-diethylethlenediamine 8a (3.5 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) were added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 24 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in Et₂O. The solution was washed with H₂O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel
(Hexane) gave 1-phenyl-2-(phenylthio) ethyne (59.1 mg, 94%) as a colorless oil.

1-Phenyl-2-(phenylthio) ethyne (Table 2, entry 1)[2b, a]:

1H NMR (CDCl3) δ 7.21 (t, J = 6.8 Hz, 1H), 7.31–7.36 (m, 5H), 7.45–7.52 (m, 4H); 13C NMR (CDCl3) δ 75.5, 97.9, 122.9, 126.2, 126.5, 128.4, 128.6, 129.2, 131.7, 132.9; IR (neat) 2170, 1584, 1479 cm⁻¹; elemental analysis calcd for C14H14S (214.33): C, 78.45; H, 6.58; found: C, 78.31; H, 6.59.

1-(Phenylthio)ethynyl-1-cyclohexanol (Table 2, entry 8)[a]:

1H NMR (CDCl3) δ 1.26–1.31 (m, 1H), 1.51–1.76 (m, 7H), 1.97–2.03 (m, 2H), 2.13 (s, 1H), 2.72 (t, J = 7.2 Hz, 1H), 3.41 (dd, J = 7.9 and 7.2 Hz, 2H); 13C NMR (CDCl3) δ 23.2, 25.1, 39.8, 69.7, 70.6, 102.5, 125.9, 126.4, 129.2, 132.8; IR (neat) 3400, 2923, 2175, 1584 cm⁻¹; elemental analysis calcd (%) for C14H16OS (232.34): C, 72.37; H, 6.94; found: C, 72.35; H, 6.94.

1-(Phenylthio)but-1-yn-4-ol (Table 2, entry 9)[a,b]:

1H NMR (CDCl3) δ 2.35 (s, 4H), 3.51 (s, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.9 and 7.2 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H); 13C NMR (CDCl3) δ 44.1, 49.2, 70.8, 94.6, 126.1, 126.3, 129.1, 133.0; IR (neat) 3390, 2941, 2855, 1582, 1478, 1440 cm⁻¹; elemental analysis calcd for C15H16OS (285.26): C, 75.78; H, 5.65; found: C, 75.69; H, 5.69.

1-(Phenylthio)-2-tri-isopropylsilyl ethyne (Table 2, entry 12)[a]:

1H NMR (CDCl3) δ 1.12 (s, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.32 (dd, J = 7.9 and 7.3 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H); 13C NMR (CDCl3) δ 11.4, 18.6, 91.1, 103.2, 126.0, 126.3, 129.1, 132.8; IR (neat) 2924, 2865, 2092, 1583, 1462 cm⁻¹; elemental analysis calcd for C21H18SiS (339.54): C, 70.28; H, 9.02; found: C, 70.45; H, 8.90.

Preparation of the alkyln selenides from terminal alkynes with diselenides

A typical procedure is given for the reaction of ethynylbenzene with diphenyl diselenide 2d giving phenylethynyl phenyl selenide (entry 13 in Table 2). To the mixture of Cu(II)Cl (3.0 mg, 0.03 mmol), diphenyl diselenide (46.8 mg, 0.15 mmol), and N,N' -dimethylacetylenediamine 8b (2.6 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) was added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 18 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in EtO. The solution was washed with H2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica
gel (Hexane) gave 1-phenyl-2-(phenylseleno) ethyne (64.0 mg, 83%) as a colorless oil.

1-Phenyl-2-(phenylseleno) ethyne (Table 2, entry 13\textsuperscript{8a})

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 6.23-7.35 (m, 6H), 7.48-7.51 (m, 2H), 7.57-7.60 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 69.2, 103.5, 123.2, 127.1, 128.3, 128.6, 129.0, 129.5, 131.7; IR (neat) \nu = 3057, 2159, 1576, 1476 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{14}H\textsubscript{16}OSe (279.24): C, 63.58; H, 5.32; found: C, 65.40; H, 4.17.}

1-Phenyl-2-(benzylseleno) ethyne (Table 2, entry 14)

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 4.10 (s, 2H), 7.25-7.37 (m, 10H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 32.6, 33.0, 101.2, 123.5, 127.5, 128.1, 128.2, 128.6, 129.0, 131.4, 137.5; IR (neat) 3060, 3028, 2156, 1599, 1493 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{14}H\textsubscript{18}Se (265.25): C, 63.39; H, 6.84; found: C, 63.56; H, 6.77.}

1-(4-tolyl)-2-(phenylseleno) ethyne (Table 2, entry 15\textsuperscript{10})

\[ \text{m.p. 43.8-44.0 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 2.35 (s, 3H), 7.13 (d, J = 7.9 Hz, 2H), 7.23-7.34 (m, 3H), 7.39 (d, J = 8.2 Hz, 2H) 7.57 (d, J = 7.9 Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 21.5, 103.1, 120.1, 126.9, 128.9, 129.0, 129.1, 129.5, 131.5, 137.8; IR (CHCl\textsubscript{3}) 3017, 2159, 1577, 1576 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{15}H\textsubscript{12}Se (271.22): C, 66.43; H, 4.46; found: C, 66.15; H, 4.67.}

1-(4-tolyl)-2-(phenylseleno) ethyne (Table 2, entry 21\textsuperscript{21})

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 1.11 (s, 21H), 7.25 (d, J = 7.2 Hz, 1H), 7.34 (dd, J = 7.9 and 7.2 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 11.4, 18.6, 85.1, 108.3, 126.8, 128.6, 128.9, 129.4; IR (neat) 2942, 2865, 2087, 1578, 1471, 1461 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{16}H\textsubscript{16}SeSi (337.44): C, 60.51; H, 7.77; found: C, 60.56; H, 7.71.}

Preparation of the alkynyl tellurides from terminal alkynes with ditellurides

A typical procedure is given for the reaction of ethynylbenzene with diphenyl ditelluride 2\textsuperscript{F} giving phenylethynyl phenyl telluride (entry 1 in Table 4): To the mixture of Cu(I)Cl (1.5 mg, 0.015 mmol), diphenyl ditelluride (61.4 mg, 0.15 mmol), nBu\textsubscript{3}NBr (19.3 mg, 0.06 mmol) and N,N-dimethylthelylenediamine 8\textsuperscript{b} (2.6 mg, 0.03 mmol) in dioxane (0.5 mL), ethynylbenzene (30.6 mg, 0.3 mmol) were added under a nitrogen atmosphere using the balloon. The mixture was stirred at 100 °C for 24 h. After the solvent was cooled to room temperature, the reaction mixture was dissolved in Et\textsubscript{2}O. The solution was washed with H\textsubscript{2}O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (Hexane) gave 1-phenyl-2-(phenyltelluro) ethyne (75.2 mg, 82%) as a pale yellow oil.

1-Phenyl-2-(phenyltelluro) ethyne (Table 4, entry 1\textsuperscript{10,11})

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 7.24-7.34 (m, 6H), 7.44-7.48 (m, 2H), 7.73-7.75 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 47.2, 113.1, 114.2, 123.3, 127.9, 128.2, 128.6, 129.7, 131.9, 135.1; IR (neat) 2140, 1574, 1487 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{16}H\textsubscript{16}Te (305.83): C, 54.98; H, 3.30; found: C, 54.94; H, 3.21.}

1-(4-Tolyl)-2-(phenyltelluro) ethyne (Table 4, entry 2\textsuperscript{11})

\[ \text{m.p. 73.6-74.0 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 2.35 (s, 3H), 7.12 (d, J = 8.5 Hz, 2H), 7.26-7.28 (m, 3H), 7.36 (d, J = 8.5 Hz, 2H), 7.70-7.73 (m, 2H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \delta 21.4, 46.1, 113.2, 114.4, 120.3, 127.8, 129.7, 131.8, 134.7, 134.9, 138.8; IR (CHCl\textsubscript{3}) 3019, 1574, 1507 cm\textsuperscript{-1}; elemental analysis calculated for C\textsubscript{16}H\textsubscript{16}Te (319.86): C, 56.33; H, 3.78; found: C, 56.22; H, 3.93.}

1-(Phenyltelluro)-1-octyne (Table 4, entry 3\textsuperscript{10})

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}) \delta 0.88 (t, J = 6.8 Hz, 3H), 1.26-1.31 (m,}
C17H26TeSi (386.08): C, 52.89; H, 6.79; found: C, 52.97; H, 5.78; found: C, 52.58; H, 5.88.

1-(Phenyltelluro)but-1-yn-3-ol (Table 4, entry 4): 1H NMR (CDCl3) δ 1.50 (d, J = 6.6 Hz, 3H), 2.04 (br, 1H), 4.75 (q, J = 6.6 Hz, 1H), 7.21–7.31 (m, 3H), 7.66–7.70 (m, 2H); 13C NMR (CDCl3) δ 25.3, 39.9, 69.9, 112.8, 118.9, 127.7, 129.6, 134.7; IR (neat) ν = 3390, 2931, 2149, 1574 cm−1; elemental analysis calcd for C14H14Te (309.86): C, 54.27; H, 4.55; found: C, 54.03; H, 4.64.

1-(Phenyltelluro)but-1-yn-4-ol (Table 4, entry 6): 1H NMR (CDCl3) δ 1.52–1.68 (m, 4H), 2.12–2.20 (m, 2H), 3.75 (br, 2H), 7.22–7.28 (m, 3H), 7.64–7.70 (m, 2H); 13C NMR (CDCl3) δ 24.3, 42.2, 59.5, 112.3, 116.8, 128.0, 129.7, 135.3; IR (neat) 3390, 2931, 2149, 1574 cm−1; elemental analysis calcd for C14H14Te (309.86): C, 54.03; H, 4.64.

1-(Phenyltelluro)-3-dimethylamino propyne (Table 4, entry 7): m.p. 64.0–64.8 °C; 1H NMR (CDCl3) δ 2.32 (s, 6H), 3.58 (s, 2H), 7.22–7.27 (m, 3H), 7.64–7.71 (m, 2H); 13C NMR (CDCl3) δ 41.3, 44.0, 49.7, 110.5, 112.7, 127.7, 129.6, 135.1; IR (neat) ν = 3390, 2931, 2149, 1574 cm−1; elemental analysis calcd for C11H13N2Te (286.83): C, 46.06; H, 4.57; found: C, 46.84; H, 4.69.

1-(Phenyltelluro)-4-cyclohexanol (Table 4, entry 8): 1H NMR (CDCl3) δ 1.52–1.68 (m, 4H), 2.12–2.20 (m, 2H), 3.64–16.4 (m, 4H), 7.17–7.27 (m, 3H), 7.63–7.70 (m, 2H); 13C NMR (CDCl3) δ 21.4, 22.5, 25.9, 29.2, 43.2, 113.5, 116.5, 121.2, 127.6, 129.6, 134.6, 137.9; IR (neat) ν = 3051, 2928, 1573, 1474, 1434 cm−1; elemental analysis calcd for C19H20O2Te (339.86): C, 54.27; H, 4.55; found: C, 54.03; H, 4.64.

References


7 For selected examples of the use of organosulfur derivative as a ligand of copper or other metals, see: a) G. Murray, F. R. Hartley, Chem. Rev. 1981, 81, 365.
In condition A, the formation of a yellow precipitate was observed. Although in condition B this compound was formed, it gradually disappeared.