Experimental and theoretical studies on formal σ-bond metathesis of silyl tellurides with alkyl halides

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Abstract

Silyl tellurides reacted with alkyl halides under mild thermal conditions to give the corresponding alkyl tellurides and silyl halides in good to excellent yields. Substitution took place much faster in polar solvents, such as acetonitrile, than that in non-polar solvents. After removal of the volatile silyl halides and solvent under vacuum, the essentially pure divalent organotellurium compounds were obtained. Theoretical calculations were performed to understand the reaction mechanism, and a stepwise pathway involving tetravalent organotellurium intermediate was obtained. Since the intermediate as well as the rate-determining step leading to the intermediate from the reactants possess highly polar character, they would be stabilized in polar solvents.
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1. Introduction

While silyl sulfides and silyl selenides have proved to be valuable synthetic reagents [1], a little is known for the synthetic use of silyl tellurides [2]. We have recently disclosed trimethylsilyl phenyl telluride (**1**) and triethoxysilyl phenyl telluride promote radical coupling reaction of carbonyl compounds or imines with isonitriles and alkynes [3]. We also found that **1** undergoes reductive bis-silylation of quinones [4]. During the course to investigate the new reactivity of silyl tellurides, we found that they react with alkyl halides in polar solvents to give alkyl phenyl tellurides and silyl halides (Scheme 1).

Since two σ-bonds, namely carbon–halogen bond in alkyl halides and silicon–tellurium bond in silyl tellurides, were substituted for new two σ-bonds, namely carbon–tellurium bond and silicon–halogen bond, this reaction can be looked upon as a formal σ-bond metathesis reaction. As far

as we know, only a few examples have been reported so far on the similar formal σ-bond metathesis of organochalcogen compounds which proceeds under mild thermal conditions. Ogura and coworkers reported that thermal reaction of alkyl phenyl tellurides with halogens to give alkyl halides and phenyl tellanyl halides [5]. We also reported the reaction of sugar-derived divalent selenides and tellurides with bromine produce alkyl bromide and corresponding selenyl- and tellanyl-bromide, respectively [6]. These unique reactivities of organochalcogenides compounds prompted us to investigate the reaction of silyl tellurides and alkyl halides in detail. Preliminary results have already been reported [7], and we report here the full details of the studies including the theoretical calculations.

2. Results and discussion

2.1. Synthesis of divalent organotellurium compounds using group 14-metaltellurides

Effects of substituents on the silicon atom in silyl tellurides have been firstly examined. The reaction of trimethyl-

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$$R_3Si-TePh \ + \ R'-X \xrightarrow[\text{rt - 60 °C}]{\text{MeCN}} R'-TePh \ + \ X-SiR_3$$
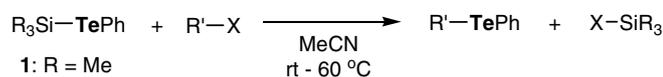
1: R = Me

Scheme 1. Reaction of silyl tellurides with alkyl halides.

silyl phenyl telluride (**1**, R = Me, 1.0 equiv.) and benzyl bromide in acetonitrile-d_3 was monitored by ^{1}H NMR at room temperature. The reaction completed within 1 h, and the formation of benzyl phenyl telluride and trimethylsilyl bromide was observed by ^{1}H NMR. After solvent and trimethylsilyl bromide were removed under reduced pressure, virtually pure benzyl phenyl telluride was obtained in quantitative yield (Table 1, run 1). The reactions of *t*-butyldimethylsilyl phenyl telluride, triethoxysilyl phenyl telluride, and tris(trimethylsilyl)silyl phenyl telluride with benzyl bromide were slow at room temperature, but benzyl phenyl telluride was eventually formed in moderate to good yields after 24 h at room temperature (runs 2–4). Low reactivity of these silyl tellurides compared to **1** might be attributed to the steric bulkiness and/or electronic effects of substituents on the silicon atom. We also examined the reaction of trimethylgermyl phenyl telluride and trimethylstannyl phenyl telluride. While the both reagents showed lower reactivity than **1**, benzyl phenyl telluride formed in excellent yields after 24 h at room temperature (runs 5 and 6). We used **1** for the following studies due to its high reactivity.

The effects of solvent and leaving group were also investigated using **1** and *n*-decyl halides, and the results are summarized in Table 2. The reaction of **1** with *n*-decyl bromide in acetonitrile completed within 12 h at 60 °C to give *n*-decyl phenyl telluride in quantitative yield (run 2). The formation of trimethylsilyl bromide was also characterized by ^{1}H NMR in the experiments carried out in acetonitrile-d_3. The progress of the reaction was found to be strongly influenced by the polarity of the solvent. Thus, the reaction took place efficiently in polar solvents, e.g., acetonitrile, DMF, pyridine, and the ionic liquid (1-butyl-3-methyl-1-imidazolium tetrafluoroborate), while no reaction occurred in non-polar solvents, e.g., THF, toluene, and hexane under similar conditions (runs 3–8). Acetonitrile was selected as the solvent for the following investigations due to its high volatility.

Table 1
Reaction of Group 14-metaltellurides with benzylbromide in acetonitrile-d_3[a]

Run	Metaltelluride	Time (h)	Yield (%)[b]
1	Me$_3$SiTePh (**1**)	1	100
2	*t*-BuMe$_2$SiTePh	24	82
3	(EtO)$_3$SiTePh	24	77
4	(Me$_3$Si)$_3$SiTePh	24	45
5	Me$_3$GeTePh	24	88
6	Me$_3$SnTePh	24	91

[a] Typical experimental procedures: a mixture of benzylbromide and metaltelluride (1.0 equiv.) in acetonitrile-d_3 (ca. 0.5 M solution) was stirred at room temperature.
[b] The yields were determined by ^{1}H NMR of the crude mixture after adding an internal standard.

Table 2
Reaction of **1** with 1-decylhalides[a]

Run	*n*-Decylhalide	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	*n*-C$_{10}$H$_{21}$Br	Acetonitrile	r.t.	12	25
2		Acetonitrile	60	12	100 (84)[b]
3		Pyridine	60	3	88
4		DMF	60	3	63
5		Ionic liquid[c]	60	3	37
6		THF	60	3	0
7		Toluene	60	3	0
8		Hexane	60	3	0
9	*n*-C$_{10}$H$_{21}$Cl	Acetonitrile	60	24	87 (57)[b]
10	*n*-C$_{10}$H$_{21}$I	Acetonitrile	60	24	41 (23)[b]

[a] Typical experimental procedures: a mixture of alkyl halide and **1** (1.0 equiv.) in acetonitrile was stirred at 60 °C. After removal of the volatile materials under vacuum, the product was analyzed by ^{1}H NMR.
[b] Yield corresponding to the reaction at 60 °C for 3 h.
[c] 1-Butyl-3-methyl-1-imidazolium tetrafluoroborate was used.

The effects of leaving groups were also examined. We surprisingly found that alkyl bromides were most reactive followed by alkyl chlorides, and that alkyl iodides were the least reactive. Thus, even though the reaction of *n*-decyl chloride had not completed after 24 h at 60 °C, the desired product formed in 87% yield (run 9). Conversely, only half the amount of *n*-decyl iodide was converted to the product under similar conditions (run 10).

The scope and efficiency of the present reaction are summarized in Table 3. Benzyl halides are especially good substrates, and several substituted benzyl chlorides reacted with **1** to give the corresponding tellurides in quantitative yields (runs 1–3). Substitution took place exclusively at the sp^3 carbon–chlorine bond over the sp^2 carbon–chlorine bond (runs 2 and 3). The secondary benzyl bromide also afforded the desired product in good yield (run 4). Allyl halides were equally good substrates, and gave the desired products in excellent yields (runs 5–7). Primary alkyl bromide and chloride were also quite reactive (runs 8 and 9). 1-Hexenyl-6-bromide did not give the cyclized product (run 8), and this result suggests that a mechanism involving free 1-hexenyl radical is unlikely [8]. Secondary alkyl bromides were found to be moderately reactive (run 10), and tertiary alkyl bromides resulted in low conversion (run 11). Aryl halides, such as phenyl bromide and iodide did not react under similar conditions, whereas 2-pyridyl bromide reacted to give the corresponding telluride in moderate yield (run 12). This is probably because the strong directing effect of the 2-pyridinyl group enhances the reactivity.

A synthetic advantage of the current method is the ease of workup. Many of organotellurium compounds, in particular compounds having sp^3-carbon tellurium bond, are unstable under air or silica gel chromatography conditions, and they are often used in the following step without purification. As the side product formed in this reaction was the volatile trimethylsilyl halides, the essentially pure products could be easily obtained after removal of the silyl halides and the solvent under vacuum. Therefore, the crude products could then be used for further synthetic transformations

Table 3
Synthesis of organotellurium compounds from organic halides and **1**[a]

Run	RX	Temperature (°C)	Time (h)	Product	Yield (%)[b]
1	PhCH$_2$Cl	r.t.	3	PhCH$_2$TePh (**2**)	100
2	o-ClC$_6$H$_4$CH$_2$Cl	r.t.	0.5	o-ClC$_6$H$_4$CH$_2$TePh	100
3	m-ClC$_6$H$_4$CH$_2$Cl	r.t.	0.5	m-ClC$_6$H$_4$CH$_2$TePh	100
4	PhCH(CH$_3$)Br	60	6	PhCH(CH$_3$)TePh	72
5	H$_2$C=CHCH$_2$Br	r.t.	1.5	H$_2$C=CHCH$_2$TePh	98
6	H$_2$C=CHCH$_2$Cl	r.t.	3	H$_2$C=CHCH$_2$TePh	100
7	trans-PhCH=CHCH$_2$Cl	r.t.	3.5	trans-PhCH=CHCH$_2$TePh	90
8	CH$_2$=CH(CH$_2$)$_4$Br	60	4	CH$_2$=CH(CH$_2$)$_4$TePh	91
9	(benzotriazole-CH$_2$-Cl)	r.t.	1.5	(benzotriazole-CH$_2$-TePh)	95[c]
10	c-C$_6$H$_{11}$Br	60	24	c-C$_6$H$_{11}$TePh	60
11	t-BuBr	100	24	t-BuTePh	36
12	(methylpyridine-Br)	60	48	(methylpyridine-TePh)	48
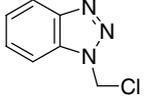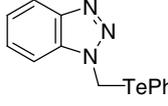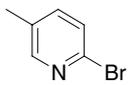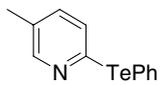
[a] Typical experimental procedures: a mixture of alkyl halide and **1** (1.0–1.1 equiv.) in acetonitrile (ca. 0.5 M solution) was stirred at the temperature indicated in the Table. After removal of the volatile materials under vacuum, the product was analyzed by ^{1}H and ^{13}C NMR.

[b] As the products formed were unstable under the conditions of silica gel chromatography, the yields were determined by ^{1}H NMR of the crude mixture after adding an internal standard.

[c] Slight excess of **1** (1.5 equiv) was used.

as precursors for carbon-centered radicals [9], carbanions [10], and carbocations [11].

2.2. Possible reaction pathways

Three mechanisms would be envisaged to account for the experimental results. The first is the nucleophilc attack of phenyltellanyl anion or its equivalent derived from silyl telluride to alkyl halides (Scheme 2a). In this mechanism, polar solvent such as acetonitrile may coordinate to silicon atom thus enhancing the nucleophilicity of the phenyltellanyl anion species. However, the reactivity of organoiodines is usually highest followed by organobromines and then organochlorides in the nucleophilic substitution reaction, but the experimental data did not follow this reactivity order. Therefore, we believe that this possibility would be rigorously excluded.

The second is the σ-bond metathesis involving four-centered transition state (Scheme 2b), and the third is the oxidative addition/reductive elimination mechanism involving tetravalent organotellurium intermediate or transition state (Scheme 2c). Theoretical investigations revealed the existence of the oxidative addition/reductive elimination path-

way involving tetravalent tellurium intermediate, while several attempts to locate the σ-bond metathesis pathway were so far unsuccessful.

Morokuma and coworkers already reported on the theoretical study on the reductive elimination reaction (the ligand coupling reaction) of tetrahydrochalcogenide to dihydrochalcogenide and hydrogen at the MP2 level of theory [12]. They reported that the transition state of the equatorial–equatorial coupling is less polar and higher in energy than that of the apical–equatorial coupling. Since the activation energies of two pathways are sufficiently large (39 kJ/mol for tellurium) and the latter pathway should be more stabilized in polar medium than the former, we only calculated the apical–equatorial coupling pathway throughout this study.

2.3. Theoretical studies

The reactions of trihydrosilyl methyl telluride (**2**) and methyl chloride, bromide, and iodide leading to dimethyl telluride (**6**) and trihydrosilyl chloride, bromide, and iodide, respectively, were selected as a model reaction. Geometry optimizations were performed with the hybrid B3LYP density functional [13] with a Hey–Wadt effective core potential (ECP) and outermost valence electron basis set (LANL2DZ) [14] for silicon, chlorine, bromine, tellurium, and iodine and 6-31G(d) basis set [15] for hydrogen and carbon. While the d polarization functions are important for hypervalent species to obtain more accurate energy values [16], we believe that the calculation without the

(a) Neucleophilic attack   (b) σ-Bond metathesis   (c) Oxidative addition/ Reductive elimination.
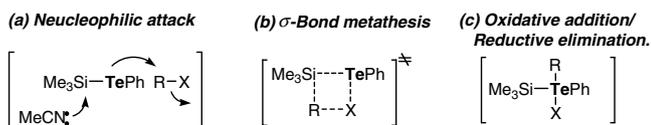
Scheme 2. Possible reaction pathways.

d polarization would reasonably reproduce relative reactivity difference of alkyl halides towards silyl tellurides.

The reaction of **2** and methyl chloride was calculated to proceed through two transition states **3** and **5**, which lead to tetravalent tellurium intermediate **4** and the products, respectively. Transition state **3**, namely oxidative addition of methyl chloride to tellurium atom in **2** requires 203 kJ/mol of activation energy leading to **4**. This is an endothermic process, and intermediate **4** locates 48 kJ/mol of higher in energy than the starting reactants. Subsequent reductive elimination from **4** to **6** is highly exothermic (90 kJ/mol) with low activation barrier (9 kJ/mol) through transition state **5**. The calculation clearly indicates that the oxidative addition is the rate determining step. As the reaction of alkyl chloride with trimethylsilyl phenyl telluride proceeded at 60 °C for 1 day, the calculated activation energy of the rate determining step seems to be in good agreement with the experimental data. As the activation energy of the reductive elimination is considerably low, this step should proceed spontaneously from intermediate **4**. The overall reaction is 43 kJ/mol of exothermicity, which must be responsible to drive the reaction (see Fig. 1).

Mulliken charge analyses indicate that transition states **3** and **5** as well as intermediate **4** possess highly polar character compared to the reactants and products. Intermediate **4** is most polar among them; the tellurium atom bears 0.77 positive charge and negative charges are localized mainly on the chloride atom (-0.59) and the apical carbon atom (-0.23). The observed charge distributions are in good agreement with the well known character of hypervalent heteroatom compounds bearing electron negative apical ligand [16]. As both the transition states and intermediate should be stabilized in a polar solvent, the calculated charge distributions are consistent with the experimentally observed solvent effects.

The reactions of **2** with methyl bromide and methyl iodide were also calculated, and similar transition states and tetravalent tellurium intermediates were obtained in both cases (Figs. 2 and 3). Transition states **7** and **10** leading to intermediates **8** and **11**, respectively, are calculated to be higher in energy than transition state **9** and **12** leading to the final products, respectively. Therefore, the oxidative addition is also the rate determining steps in both cases. The transition states and intermediates also possess considerable polar character compared to the reactants and products. Therefore, these reactions should be also strongly accelerated in a polar solvent.
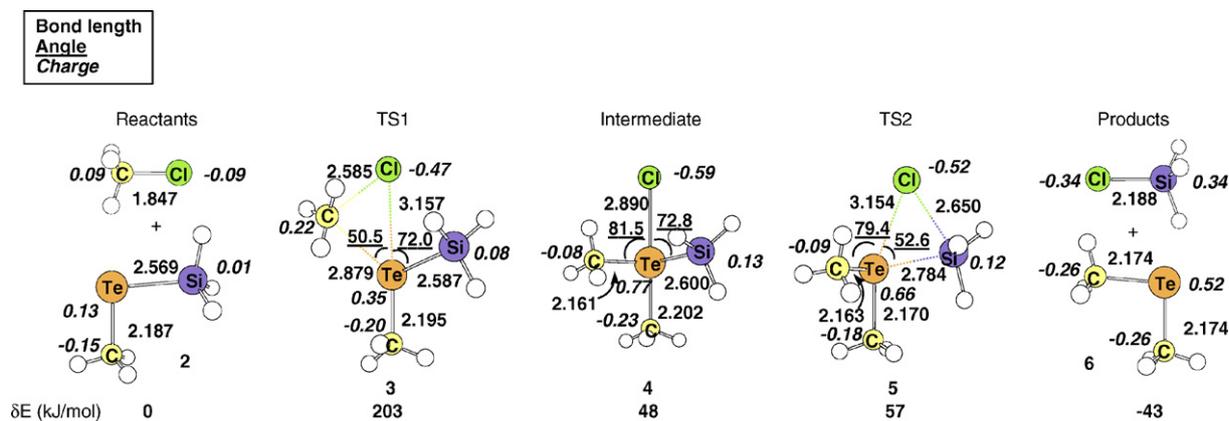
Fig. 1. Geometry (Å, °) and relative energies (total energy + ZPE, kJ/mol) of the reactants, TSs, intermediate, and products for the reaction of methyl chloride with **2**. Mulliken charges of the heavy atoms are shown as italic.
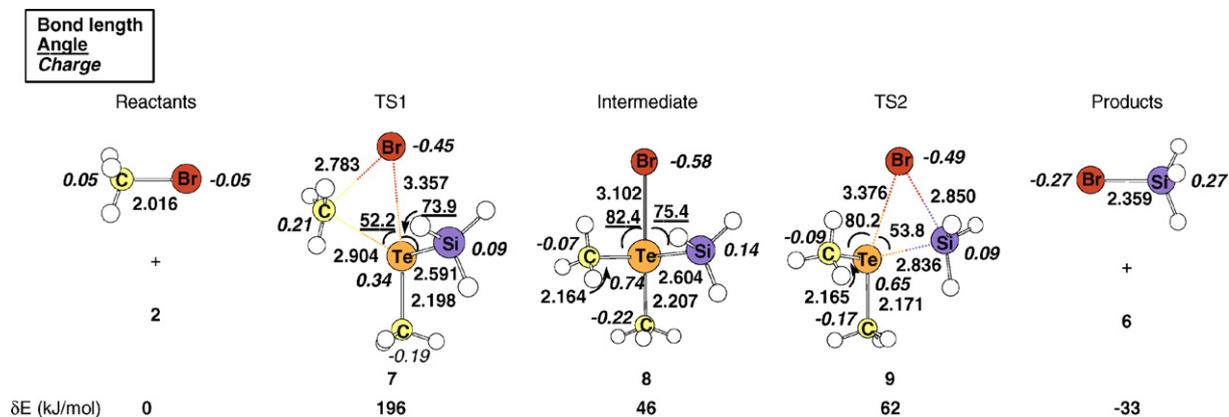
Fig. 2. Geometry (Å, °) and relative energies (total energy + ZPE, kJ/mol) of the reactants, TSs, intermediate, and products for the reaction of methyl bromide with **2**. Mulliken charges of the heavy atoms are shown as italic.
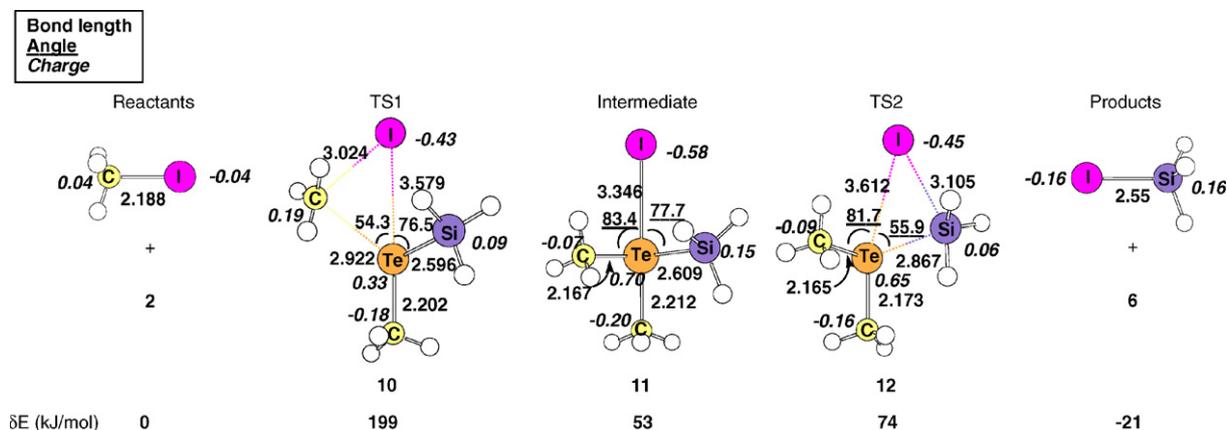
Fig. 3. Geometry (A, °) and relative energies (total energy + ZPE, kJ/mol) of the reactants, TSs, intermediate, and products for the reaction of methyl iodide with **2**. Mulliken charges of the heavy atoms are shown as italic.

The calculated activation energy of the rate determining step is lowest in the reaction of methyl bromide followed by that of methyl iodide and then methyl chloride, though the differences are very small. Therefore, several factors, e.g., charge distributions, would also contribute the reactivity difference of halogen atoms in polar solvent, and more studies are obviously needed to clarify this point.

3. Conclusion

We have demonstrated that several group14-metal tellurides, especially trimethylsilyl phenyl telluride (**1**), react with organic halides to give the corresponding organotellurium compounds and group 14-metal halides in good to excellent yields. After the volatile metal halides and solvent are removed under reduced pressure, the essentially pure organotellurium compounds can be easily obtained. Since many of the organotellurium compounds are unstable under purification conditions, this method would provide a new and practical synthetic route to divalent organotellurium compounds.

Theoretical calculations revealed that the reaction proceeds through oxidative addition/reductive elimination pathway involving highly polarized tetravalent organotellurium intermediate. This reaction pathway is rather insensitive to the nature of halogen atom of alkyl halides, and the oxidative addition of alkyl halides on the tellurium atom of silyl telluride is the rate determining step in all cases. While more studies are needed, we believe that the current work provides a new insight into the reactivity of hypervalent chalcogen species.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were measured on Varian Gemini 2000 (300 MHz for ^{1}H and 75 MHz for ^{13}C) instru-ment, and are reported in parts per million (δ) from tetra-methylsilane. IR spectra were recorded on a Shimadzu FTIR-8200, and are reported in cm^{-1}. FAB-MS spectra were recorded on JEOL IMS-300 spectrometer. 3-Nitrob-enzyl alcohol was used as a matrix for FAB-MS.

4.2. Materials

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Ethereal solvents were distilled from benzophenone ketyl immediately under argon atmosphere before use. Benzyl-phenyl telluride, allyl phenyl telluride, and cimnamyl phenyl telluride were identified by comparison of its ^{1}H NMR spectrum with that reported in the literature because of sensitivity to oxidation. Trimethylsilyl phenyl telluride (**1**) [2a,17], tris(trimethylsilyl)silyl phenyl telluride [18], trim-ethylgermyl phenyl telluride [2a], and trimethylstannyl phe-nyl telluride [2a] were prepared according to the literature method. These metal tellurides are moisture sensitive, but they can be stored for long period under inert atmosphere.

4.3. t-Butyldimethylsilylphenyltelluride

Phenyllithium (52.9 mL, 1.04 M solution in diethyl ether, 55 mmol) was slowly added to a suspension of tellu-rium powder (6.38 g, 50 mmol) in 50 mL of THF over 20 min at room temperature. The resulting mixture was stirred for 20 min until tellurium powder was completely disappeared. A THF solution of t-butyldimethylsilyl chlo-ride (8.29 g, 55 mmol) was added at room temperature, and the resulting solution was stirred for 18 h at this tem-perature followed by 3 h at 50 °C. The solvent was removed under reduced pressure, followed by distillation under reduced pressure (bp. 90.0–91.2 °C/0.1 mmHg) to give the title compound as slightly yellow oil in 54 % yield (8.64 g, 27.0 mmol). ^{1}H NMR (300 MHz, CDCl$_3$) 0.43 (s, 6H), 0.10 (s, 9H), 7.08–7.14 (m, 2H), 7.26–7.31 (m, 1H),

7.75–7.79 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) – 1.35, 19.20, 26.70, 127.29, 128.79, 141.61.

4.4. Triethoxysilylphenyltelluride

Phenyllithium (1.04 M in cyclohexane/ether, 106 mL, 110 mmol) was slowly added to a suspension of tellurium powder (12.8 g, 100 mmol) in THF (100 mL) over 30 min at room temperature, and the resulting mixture was stirred for 1 h. Chlorotriethoxysilane (21.9 g, 110 mmol) was added dropwisely over 15 min at room temperature, and the resulting mixture was stirred for 2 h. Solvent was removed under reduced pressure followed by distillation (bp. 83–109 °C/0.55 mmHg) afforded the title compound in 62% yield (22.8 g) as orange oil. IR (neat) 1476, 1435, 1391, 1165, 1076, 1017, 997, 785, 733, 693, 486, 455; ^{1}H NMR (300 MHz, CDCl$_3$) 1.19 (t, $J = 7.1$ Hz, 9H), 3.85 (q, $J = 7.0$ Hz, 6H), 7.07–7.16 (m, 2H), 7.20–7.30 (m, 1H), 7.72–7.82 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) 17.61, 59.65, 104.27, 127.37, 129.13, 140.22.

4.5. Typical experimental procedure for the synthesis of organotellurium compounds from alkyl halides and trimethylsilylphenyltelluride (1). Synthesis of n-decylphenyltelluride

A solution of n-decyl bromide (68.1 mg, 0.30 mmol) and 1 (83.3 mg, 0.30 mmol) in acetonitrile (1.0 mL) was stirred at 60 °C for 12 h. After the solvent was removed under reduced pressure, the product was obtained in 100% yield (45.5 mg) as yellow oil. The product was sufficiently pure as judged by NMR spectroscopy. As the product was unstable toward air, further purification was not attempted. IR (KBr) 1455, 1277, 1192, 887; ^{1}H NMR (300 MHz, CDCl$_3$) 2.17 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) 102.54, 113.37, 128.82, 151.34; HRMS (FAB) m/z: Anal. Calc. for C$_{16}$H$_{26}$Te (M)$^+$, 348.1097. Found 348.1097%.

4.6. Benzylphenyltelluride [19]

^{1}H NMR (300 MHz, CD$_3$CN) 4.25 (s, 2H), 7.06–7.13 (m, 8H), 7.65 (d, $J = 9$ Hz, 2H); ^{13}C NMR (75 MHz, CD$_3$CN) 0.77, 124.52, 144.61.

4.7. c-Hexylphenyltelluride [20]

^{1}H NMR (300 MHz, CDCl$_3$) 0.26 (s, 9H), 0.31 (s, 9H), 6.77 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) 0.07, 0.67, 120.06, 126.57, 143.29, 149.01.

4.8. tert-Butylphenyltelluride [21]

^{1}H NMR (300 MHz, CDCl$_3$) 1.59 (s, 9H), 7.23–7.47 (m, 5H), 7.89 (d, $J = 9.0$ Hz 1H), 3.79 (s, 3H), 3.82 (s, 3H), 6.39 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) 35.36, 127.15, 128.74, 141.19.

4.9. o-Chrolobenzylphenyltelluride

^{1}H NMR (300 MHz, CD$_3$CN) 4.24 (s, 2H), 6.97–7.12 (m, 3H), 7.16–7.23 (m, 2H), 7.28–7.31 (m, 2H), 7.66 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, CD$_3$CN) 10.33, 113.88, 128.39, 129.32, 129.64, 130.70, 130.97, 131.50, 140.61, 140.93.

4.10. m-Chrolobenzylphenyltelluride

^{1}H NMR (300 MHz, CD$_3$CN) 4.16 (s, 2H), 6.98–7.33 (m, 7H), 7.63 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (75 MHz, CD$_3$CN) 11.65, 113.92, 127.40, 128.22, 129.59, 130.73, 130.87, 131.31, 134.74, 139.08, 140.67, 145.52.

4.11. Allylphenyltelluride

^{1}H NMR (300 MHz, CD$_3$CN) 0.32 (s, 9H), 0.33 (s, 9H), 7.13 (d, $J = 8.7$ Hz, 1H), 7.31–7.49 (m, 3 H), 7.73–7.79 (m, 1H), 8.01–8.08 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) 0.39, 0.68, 121.59, 122.00, 122.14, 123.99, 125.32, 127.59, 129.60, 130.30, 140.57, 141.81.

4.12. Cimnamylphenyltelluride [22]

^{1}H NMR (300 MHz, CDCl$_3$) 3.76 (d, $J = 8.1$ Hz, 2H), 5.96 (d, $J = 15.6$ Hz, 1H), 6.44 (dt, 1H), 7.10–7.37 (m, 8H) 7.70–7.76 (m, 2H).

4.13. Computational study

All theoretical calculations were carried out with GAUSSIAN 98 program [23]. Geometry optimizations were performed with the hybrid B3LYP density functional [13] with a Hey-Wadt effective core potential (ECP) and outermost valence electron basis set (LANL2DZ) [14] for chlorine, bromine, iodine, silicon, and tellurium and 6-31G(d) [15] basis set for carbon and hydrogen. Intrinsic reaction coordinate (IRC) analysis [24] was performed near the transition structure at the same level. Atomic charges were derived from Mulliken population analysis of the Kohn–Sham orbitals.

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