

Functionalized Tellurols: Synthesis, Spectroscopic Characterization by Photoelectron Spectroscopy, and Quantum Chemical Study

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Ethene-, cyclopropane-, 3-butene-, and cyclopropanemethanetellurol have been synthesized by reaction of tributyltin hydride with the corresponding ditellurides and characterized by ¹H, ¹³C, and ¹²⁵Te NMR spectroscopy and high-resolution mass spectrometry. The tellurols of this series, with a gradually increasing distance between the tellurium atom and the unsaturated group, have been studied by photoelectron spectroscopy and quantum chemical calculations. Two stable conformations of ethenellurol and cyclopropanetellurol, five of allyltellurol, and four of cyclopropanemethanetellurol were found. In the photoelectron spectrum of vinyltellurol, the huge split between the first two bands indicates a direct interaction between the tellurium lone electron pair and the double bond. In the allyl derivative, a hyperconjugation effect was found for the most stable conformers. In contrast to the vinyl compounds, no direct interaction between the lone electron pair of X (X = O, S, Se, and Te) and the three-membered ring could be observed in the cyclopropyl derivatives. A hyperconjugation-like effect, which is independent of the relative orientation of the X–H group, is found to increase from S to Te. Thus, the type and extent of the interaction between the TeH group and an unsaturated or cyclopropyl moiety are clarified while the first comparison of interactions between the nonradioactive unsaturated chalcogen derivatives is performed.

Introduction

The study by UV photoelectron spectroscopy (PES) and quantum chemical calculations of alkenylselenols^{1,2} with gradually increasing distance between the selenium atom and the unsaturated group has recently clarified the nature of interactions between the SeH group and the unsaturated moiety.^{3,4} The unavailability of the corresponding tellurium derivatives makes a similar study difficult, and it is essential to have such compounds at hand to determine their physicochemical properties. Although the synthesis of some alkyltellurols and aryltellurols was described in the literature

a long time ago,⁵ only a few functionalized compounds have been reported, and little is known of the tellurols.⁶ The toxicity and expected kinetic instability of these ill-smelling compounds have probably discouraged the investigations. However, the first unsaturated aliphatic tellurols, the vinyltellurols, were synthesized in 2000,¹ and thus, for example, the gas-phase acidity of vinyltellurol has been measured.⁷

Here, we report the first photoelectron spectroscopy study devoted to aliphatic tellurols. To the best of our knowledge, only the tris(trimethylsilyl)silyltellurol was investigated by photoelectron spectroscopy.^{6c} Since even the spectrum of

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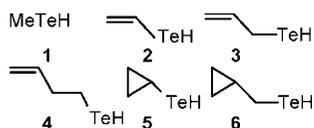
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the simplest alkyl derivative, methanetellurol **1**, has never been described, this spectrum is added to this work for use as a reference. With the so-called banana bonds along the edges of the cyclopropyl ring, cyclopropyl derivatives present properties intermediate between those of alkyl and alkenyl compounds, and cyclopropyl tellurols were also studied. Thus, methane **1**, vinyl **2**, allyl **3**, homoallyl **4**, cyclopropane **5**, and cyclopropanemethanetellurol **6** have been investigated from a theoretical and experimental point of view. The aim of this work was to study the structural and electronic properties of the simplest functionalized tellurols. The result of this study would also lead to a complete understanding of the differences or similarities between unsaturated alcohols, thiols, selenols, and tellurols.

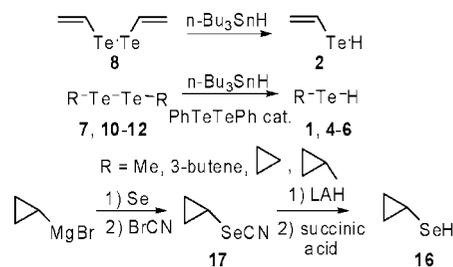


Results and Discussion

Synthesis of Tellurols. Ethenetellurol (vinyltellurol) **2** was prepared starting from divinyl ditelluride **8**,¹ and as such we tried to extend this approach starting from ditellurides to the other compounds. Dimethylditelluride **7** was thus synthesized as previously reported,⁸ and this preparation has been extended to the di-3-butenylditelluride **10** and dicyclopropylmethylditelluride **12**. However, all our attempts to prepare the diallylditelluride **9** were unsuccessful: only unidentified decomposition products were obtained in the reaction of sodium telluride on allyl bromide. That could be attributed to the possible kinetic instability of these products.⁹ Several attempts to find another precursor of allyltellurol **3** were unsuccessful. Dicyclopropylditelluride **11** was prepared by addition of cyclopropyllithium¹⁰ on tellurium followed by oxidation of the formed salt with bubbling oxygen. Compounds **10–12** are kinetically stable at room temperature.

The synthesis of tellurols was then investigated. Vinyltellurol was prepared¹ by slow addition of tributyltin hydride on compound **8** and continuous extraction of the product from the reaction mixture to avoid any decomposition. However, the extension of this approach to ditellurides **7**, **10–12** led to very low yields of the corresponding tellurols. The efficacy of the reaction was thus correlated to the nature of the ditelluride. This hypothesis was confirmed in a reaction starting from the ditelluride **7**, **10**, and small amounts of divinyl ditelluride **8**. In these experiments, good yields of the corresponding tellurols **1** and **4** were obtained. Nevertheless, to avoid the presence of a low-boiling impurity (vinyltellurol **2**) in the products, we replaced ditelluride **8** by small amounts (0.2 equiv) of diphenylditelluride **13**. A similar activation

Scheme 1



of the reaction was observed, but the high boiling point of the formed phenyltellurol **14** allowed the isolation of pure products **1**, **4–6** in good yields (Scheme 1). Characterization was performed by ¹H, ¹³C, and ¹²⁵Te NMR spectroscopy and high-resolution mass spectrometry. On the ¹H NMR spectrum, the signal of the hydrogen on the tellurium atom is typical of such compounds. It is observed at $\delta_{\text{H}} -5.3$ ppm for a saturated compound (**1**) and moves to $\delta_{\text{H}} -2.97$ ppm for the vinyl derivative (**2**).¹ The chemical shift at $\delta_{\text{H}} -3.85$ ppm of the cyclopropanetellurol **5** ranges between those of compounds **1** and **2** and shows, once again, the particular role played by the cyclopropane ring. Similarly, the corresponding chemical shift of the cyclopropanemethanetellurol **6** ($\delta_{\text{H}} -4.66$ ppm) should range between those of methanetellurol **1** and of the unknown allyltellurol **3**. Lacking tellurol **3**, we added cyclopropanethiol **15** and cyclopropaneselenol **16** to the series to complete the comparison. In both cases, the chemical shifts of compounds **15** and **16** range between those of the corresponding saturated and allylic derivatives.² In the ¹²⁵Te NMR spectra, the chemical shifts of vinyltellurol **2** and cyclopropanetellurol **5** are observed at low fields (70.4 and 109 ppm, respectively), while those of cyclopropanemethanetellurol **6** and 3-butenetellurol **4** are observed downfield (-101 and -111 ppm, respectively). The half-life of tellurols **4** and **6** diluted in deuteriochloroform is comparable to that of alkyltellurols and ranges between 30 and 40 h at room temperature. The half-life decreases somewhat for cyclopropanetellurol **5** (20 h) and a lot for vinyltellurol **2** (1 h)¹ under similar experimental conditions. However, in the presence of small amounts of duroquinone, a radical inhibitor, the half-life of these compounds increases. The corresponding ditellurides **10–12** are the main products observed in the decomposition products.

Structure. The calculated geometrical parameters of the investigated tellurols are given in Table 1. All the “stable” conformers, associated with minima on the potential-energy hypersurface of the molecules, are shown in Figures 1 and 2. The calculated total energies and relative energies of alkenyl and cyclopropyl tellurols are compiled in the Table S1 of the Supporting Information.

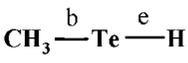
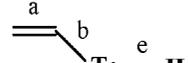
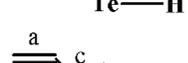
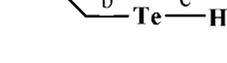
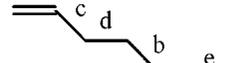
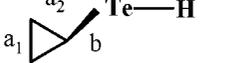
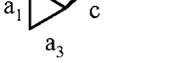
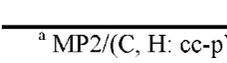
On the basis of the calculated bond lengths in vinyltellurol **2**, a conjugation interaction is expected between the π system and the lone electron pair of tellurium. The double bond slightly elongates (1.337 Å) compared to ethene (1.332 Å) or butenetellurol **4** (1.335 Å). The Te–C bond considerably shortens (2.130, 2.138, and 2.086 Å in methanetellurol, butenetellurol **4**, and **2a**, respectively). A similar effect can be observed in the corresponding Se derivatives.³

(8) Chen, M. T.; George, J. W. *J. Organomet. Chem.* **1968**, *12*, 401–403.

(9) The decomposition of diallylic diselenide into the corresponding diallylic monoselenide has been reported. Even with the diallylditelluride at hand, to isolate a pure sample of compound **3** would be particularly challenging: the kinetic stability dramatically decreases between thiols and selenols as well as between selenols and tellurols, and allylic selenols are very reactive compounds (ref 2).

(10) Seyferth, D.; Cohen, H. M. *J. Organomet. Chem.* **1963**, *1*, 15–21.

Table 1. Calculated Bond Lengths of Alkenyl and Cyclopropyl Tellurols [in Å]^a

Molecule	Conformation	Geometrical Parameter					
		a	a ₁ / a ₂ / a ₃	b	c	d	e
	1			2.130 (2.145)			1.645 (1.649)
	2a	1.337 (1.326)		2.086 (2.095)			1.646 (1.649)
	2b	1.337 (1.327)		2.080 (2.089)			1.645 (1.649)
	3a	1.337 (1.329)		2.150 (2.174)	1.485 (1.485)		1.645 (1.648)
	3b	1.336 (1.329)		2.152 (2.178)	1.486 (1.486)		1.646 (1.649)
	3c	1.337 (1.329)		2.153 (2.180)	1.488 (1.486)		1.648 (1.651)
	3d	1.334 (1.325)		2.142 (2.162)	1.494 (1.495)		1.645 (1.649)
	3e	1.334 (1.325)		2.135 (2.155)	1.498 (1.499)		1.646 (1.649)
	4	1.335 (1.326)		2.138 (2.158)	1.494 (1.499)	1.530 (1.533)	1.644 (1.648)
	5a		1.502 (1.501)/ 1.507 (1.504)/ 1.512 (1.508)	2.095 (2.115)			1.648 (1.652)
	5b		1.511 (1.510)/ 1.502 (1.500)/ 1.502 (1.500)	2.105 (2.124)			1.647 (1.650)
	6a		1.508 (1.506)/ 1.502 (1.502)/ 1.508 (1.510)	2.144 (2.166)	1.498 (1.502)		1.646 (1.649)
	6b		1.508 (1.506)/ 1.499 (1.500)/ 1.509 (1.511)	2.146 (2.168)	1.498 (1.502)		1.646 (1.650)
	6c		1.507 (1.505)/ 1.505 (1.506)/ 1.506 (1.509)	2.148 (2.173)	1.500 (1.502)		1.647 (1.650)
	6d		1.508 (1.507)/ 1.501 (1.501)/ 1.501 (1.502)	2.140 (2.160)	1.509 (1.513)		1.645 (1.649)

^a MP2/(C, H: cc-pVTZ; Te: SDB-aug-cc-pVQZ). Data of B3LYP level (using the same basis set) are in bracket.

Two stable conformations of vinyltellurol can be found: the nonplanar **2a** and the planar **2b**. The energy difference between them is only a few tenths of a kilocalorie per mole, the rotation barrier is only 1.04 kcal mol⁻¹; therefore, the TeH group rotates almost freely. The dihedral angle of H–Te–C=C in **2a** is 139.6° (in the corresponding O, S, and Se compounds, the H–X–C=C dihedral angle is 180°, 159.6°, and 151.4°, respectively). In contrast to **2**, in vinylalcohol, vinylthiol, and vinylselenol, conformation **b** is more stable than **a**.

The five stable allyltellurol conformations (**3a–e**) can be divided into two groups depending on the position of the TeH group. In the three lowest-energy structures (referred to **A** conformations), the tellurium atom is out of the plane with the allylic group (**3a–c**). In **3d** and **3e** (**B** conformations), the skeleton of the molecules is planar. Hyperconjugation between the double bond and the C–Te σ bond can be assumed only in the **A** conformers, which are indeed more stable than **B**. Also, both the C=C and the C–Te bonds are somewhat longer, while the C–C bond is somewhat shorter in **A** than in **B**.

In 3-butenetellurol **4**, it can be assumed that the interaction with the distant tellurium atom is negligible; therefore, the whole potential energy surface of 3-butenetellurol was not investigated. The conformations of the corresponding selenium derivative were previously studied using microwave spectroscopy and quantum chemical calculations;¹¹ thus, we supposed that the geometry of the most stable 3-butenetellurol was similar to the analogous selenol.

Two minima were found on the potential surface of cyclopropanetellurol **5** (Figure 2). The energy difference between the conformations is 1.5–1.7 kcal mol⁻¹ depending on the computational method. Since the rotation barrier between the two conformers **5a** and **5b** is almost zero, the Te–H group is assumed to rotate almost freely.

In **5a**, the a₁ bond of the three-membered ring is shorter than a₂ and a₃; in **5b**, however, a₂ and a₃ are shorter than a₁ (see Table 1). This fact indicates different interactions between the cyclopropyl group and the tellurium in the two cases. In both conformations, the C–Te bond shortens

(11) Petitprez, D.; Demaison, J.; Włodarczyk, G.; Guillemin, J.-C.; Møllendal, H. *J. Phys. Chem. A* **2004**, *108*, 1403–1408.

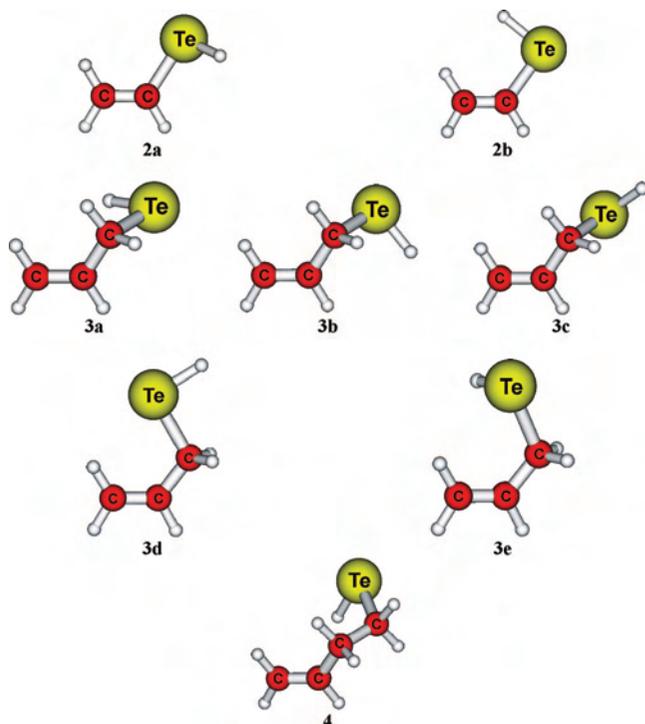


Figure 1. Stable alkenyl tellurols.

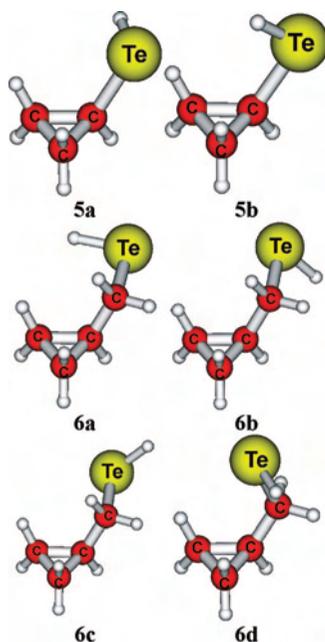


Figure 2. Stable cyclopropyl tellurols.

(2.130 Å in methanetellurol, 2.095 Å in **5a**, and 2.105 Å in **5b**).

Three of the four stable cyclopropanemethanetellurols (**6**) are geometrically similar: the tellurium atom and the cyclopropyl group are far from each other (**6a–c**). In the **6d** conformation, the tellurium is situated above the cyclopropyl ring. Interactions between the $\sigma(\text{C–Te})$ orbital and the cyclopropane ring are also possible in all conformations.

Photoelectron Spectroscopy. The positions of the most important photoelectron bands of alkenyl and cyclopropyl tellurols and the calculated vertical ionization energies using the ROVGF method^{12,13} are given in Table 2. The observed

photoelectron spectra are collected in the Supporting Information (Figure S1). The calculated results fit very well (within 0.1–0.2 eV) to the experimental data.

The photoelectron spectra of alkenyl tellurols can be characterized by their three lowest energy bands, which can be attributed to the lone electron pair of the tellurium atom (n_{Te}), the π bond, and the C–Te σ bond. To interpret the spectra, we have to consider the possible interactions between the unsaturated moiety and the tellurium atom.

In 3-butenetellurol **4**, the conjugation can be excluded due to the considerable distance between the nonbonding orbital of the tellurium atom and the π system. The first two experimental ionization potentials which can be assigned to the n_{Te} and the π orbitals confirm this assumption, as they are very close to the values observed in methanetellurol and propene (Figure 3). Only a small inductive effect of the alkyl group is observed in the spectrum that destabilizes the bands by 0.2–0.4 eV compared to the parent compounds.

Since we could not synthesize allyltellurol **3**, only the calculated ionization energies are compared to the experimental spectra of other tellurol derivatives (Figure 4). According to the data, there is no significant difference in the first ionization energy in all the conformations (Table 2). This fact suggests that the n_{Te} orbital does not interact with other molecular orbitals. The position of the following two bands is, however, different in the **A** and **B** conformations. While in **A** due to the considerable hyperconjugation the second π band is destabilized and the third C–Te band is stabilized (relative to those in **4**), in **B** only a slight shift of the same direction can be observed. Since conformation **A** is about 2.5 kcal/mol more stable than **B**, it is assumed that the experimental spectrum would resemble **A**.

The photoelectron spectra of cyclopropyl tellurols **5** and **6** can be characterized by their four lowest energy bands, which are attributed to the lone electron pair of the tellurium atom, the two lowest energy orbitals of the ring (e_1 and e_2), and the C–Te σ bond. Since the ring orbitals considered are degenerated (“e” symmetry) in the unsubstituted cyclopropane **5** (see Figure S2 in the Supporting Information), the splitting of these orbitals may give information on the interaction and effect of the substituent. It is well-known that the cyclopropyl ring displays unique properties such as conjugative interaction with π -electron systems.¹⁵ In our case, we have to study the interactions between n_{Te} , $\sigma(\text{Te–C})$, and the two lowest-energy MOs of the ring (Figure 4).

On the basis of their mutual orientation, it can easily be concluded that in **5** the lone electron pair of tellurium can only interact with the e_1 orbital in the **b** orientation. On the other hand, the out-of-(ring) plane $\sigma(\text{Te–C})$ bonding orbital may interact with the e_2 orbital in both **a** and **b**. The two different effects result in different consequences (Figure 4, Table 2). In position **a**, n_{Te} and e_1 are unchanged relative to

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(13) (a) Zakrzewski, V. G.; von Niessen, W. *J. Comput. Chem.* **1993**, *14*, 13–18. (b) Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1995**, *53*, 583–590. (c) Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **1994**, *28*, 23–27.

Table 2. Experimental and Calculated Ionization Energies [eV]

No.	Molecule	IE_{exptl}	IE_{exptl}		IE_{calcd}			Assignment
			a	b	c	d	e	
1	MeTeH	8.46	8.41				n_{Te}	
		11.00	11.13				$\sigma(\text{C-Te})$	
2	$\text{H}_2\text{C}=\text{CHTeH}$	8.41	8.35	8.21			$n_{\text{Te}}-\pi$	
		10.66	10.67	10.94			$n_{\text{Te}}+\pi$	
		11.18	11.20	11.22			$\sigma(\text{C-Te})$	
		12.50	12.77	12.57			σ	
		14.12	14.40	14.51			σ	
3	$\text{H}_2\text{C}=\text{CHCH}_2\text{TeH}$	-	8.33	8.30	8.34	8.34	8.37	n_{Te}
		-	9.51	9.54	9.59	10.10	9.97	π
		-	11.55	11.57	11.35	10.81	10.87	$\sigma(\text{C-Te})$
		-	12.65	12.49	12.50	12.33	12.32	σ
		-	12.83	12.82	13.06	13.08	12.88	σ
4	$\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{TeH}$	8.27	8.21				n_{Te}	
		9.86	9.85				π	
		10.59	10.61				$\sigma(\text{C-Te})$	
		11.84	11.97				σ	
5		8.38	8.33	8.14			n_{Te}	$n_{\text{Te}} - e_1$
		10.29	10.50	10.34			$e_2 - \sigma(\text{C-Te})$	$e_2 - \sigma(\text{C-Te})$
		10.86	10.78	11.40			e_1	$n_{\text{Te}} + e_1$
		11.65	11.74	11.83			$e_2 + \sigma(\text{C-Te})$	$e_2 + \sigma(\text{C-Te})$
		12.56	12.79	12.42				
		13.01						
6		8.22	8.22	8.22	8.21	8.34		n_{Te}
		9.75	9.81	9.77	9.87	10.34		$e_2 - \sigma(\text{C-Te})$
		10.68	10.69	10.67	10.75	10.36		e_1
		11.48	11.58	11.71	11.37	10.94		$e_2 + \sigma(\text{C-Te})$

cyclopropane and MeTeH, respectively, while in **b**, the first orbital ($n_{\text{Te}} - e_1$ combination) is destabilized, and the third one ($n_{\text{Te}} + e_1$ combination) is strongly stabilized. In both cases, however, the $\sigma(\text{C-Te}) \pm e_2$ combinations form the second and fourth bands. Compared to the observed and the calculated ionization energies, it is clearly seen that the molecule takes place mainly in **a** conformation.

Compared to the observed and calculated photoelectron bands of cyclopropanemethanetellurol, it is clear that the experimental ionization potentials fit to the more stable conformations **6a-c**. It can also be found that the $\sigma(\text{C-Te})$ and e_2 orbitals combine again, and the lone electron pair of tellurium and the e_2 orbital of cyclopropane do not. The hyperconjugation is definitely stronger than in **5**. As a result, the C-Te bond elongates and the geometry of the ring is slightly deformed.

Comparison between Oxygen, Sulfur, Selenium, and Tellurium Derivatives. In Figures 5–8, the different conjugative effects are demonstrated and compared in the respective O, S, Se, and Te derivatives. We investigated the

splitting of the interacting orbitals as well as the variation of the C-X (X = O, S, Se, Te) bond distances.¹⁴

In the case of vinyl compounds, both the C-X bond shortening (relative to the respective Me-XH bond length) and the splitting of the first two PES bands (relative to the respective bands of propene and Me-XH) indicate a decreasing conjugation effect of the lone pair from oxygen to tellurium (Figure 5).

To estimate the hyperconjugation in the allyl derivatives, we compared the splitting of the interacting second and third PE bands in the allyl-XH (X = O, S, Se, Te) relative to the respective noninteracting bands of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{XH}$ (Figure 6). The splitting from the oxygen to the Te compound increases. The trend is similar in the C-X bond distances. (Δr was also calculated as the C-X bond length difference between the actual compound and Me-XH.) As the relative geometrical orientation between the C-X bond and the C=C bond is similar, the increasing hyperconjugation from O to Te

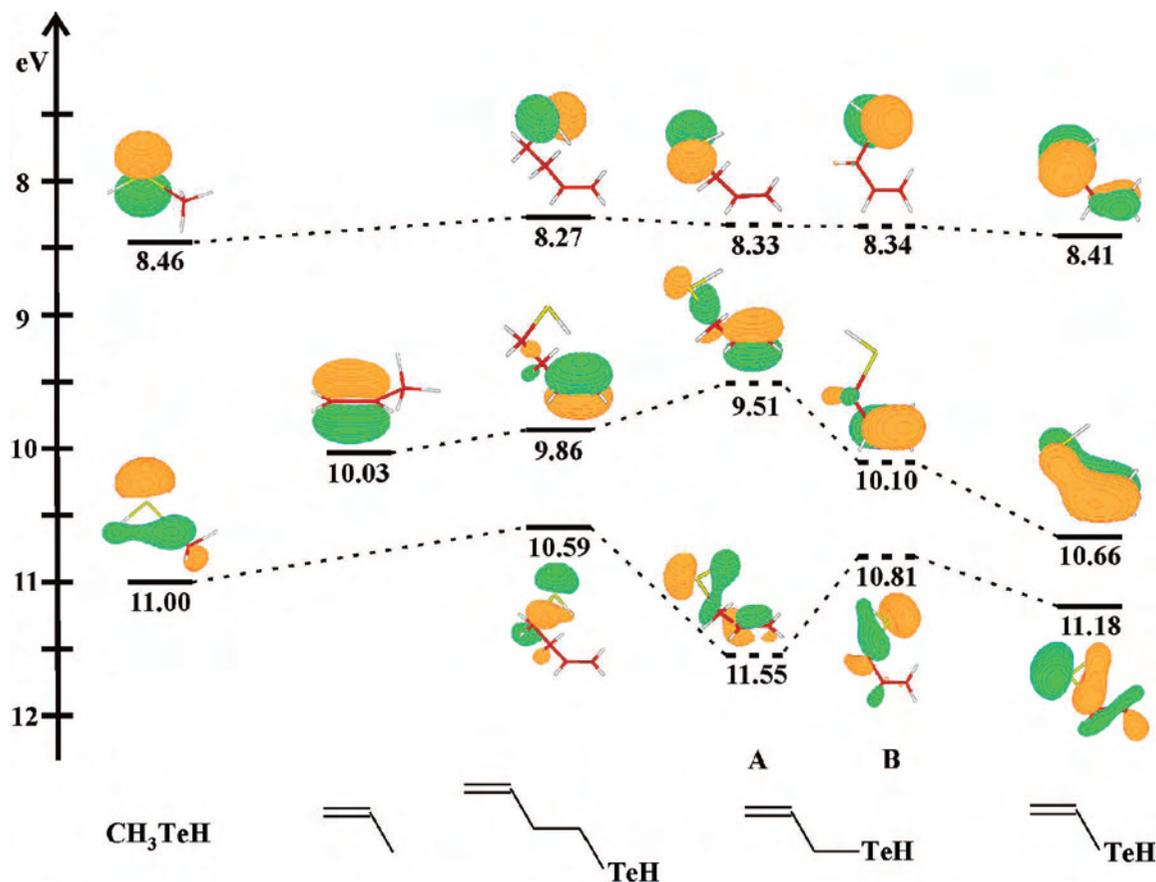


Figure 3. Correlation between the observed photoelectron bands in alkenyl tellurols.

derivatives can be interpreted by the decreasing C–X bond energy from oxygen to tellurium.

In contrast to the vinyl compounds, no direct interaction between the lone electron pair of X (X = S, Se, Te) and the three-membered ring could be observed in the cyclopropyl derivatives. Instead, an interaction between the $\sigma(\text{C}-\text{Te})$ and e_2 orbitals (second and fourth bands) could be shown. According to the C–X bond distance (relative to the respective Me–XH bond) and the PES results, this hyperconjugation-like effect increases from S to Te (Figure 7).

Finally, similarly to the cyclopropyl compounds, in cyclopropylmethane derivatives an increasing hyperconjugation is observed from S to Te (Figure 8). This finding is supported by the increasing split between the $\sigma(\text{C}-\text{Te})$ and e_2 orbitals (second and fourth PE bands) and the increasing Δr values.

- (14) (a) The PES of propene, cyclopropane, methanol and methanethiol were taken from: Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo; Halsted Press: New York, 1981. (b) See ref 3. (c) The PES of vinyl alcohol was taken from: Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrupt, P. A. *Helv. Chim. Acta* **1984**, *67*, 216–219. (d) The PES of ethenethiol was taken from: Chin, W. S.; Mok, C. Y.; Huang, H. H. *J. Electron Spectrosc. Relat. Phenom.* **1994**, *67*, 173–179. (e) The PESs of allyl mercaptan and allyl alcohol were taken from: Katrib, A.; Rabalais, J. W. *J. Phys. Chem.* **1973**, *77*, 2358–2363. (f) The first four IPs of cyclopropanethiol are: 9.27, 10.91, 11.49, and 12.5 eV: Bajor, G.; Veszprémi, T. Unpublished results..
- (15) (a) Kimura, S.; Ito, S.; Yoshifuji, M.; Veszprémi, T. *J. Org. Chem.* **2003**, *68*, 6820–6823. (b) de Meijere, A. *Methoden der Organischen Chemie (Houben Weyl)*; Thieme: Stuttgart, Germany, 1996; Vol. E17 Carbocyclic Three- and Four-Membered Ring Compounds. (c) de Meijere, A. *Angew. Chem., Int. Ed.* **1979**, *18*, 809–826.

Conclusion

Vinyl-, homoallyl-, cyclopropane-, and cyclopropanemethanetellurols have been prepared in good yields by reaction of tributyltin hydride on the corresponding ditellurides. Characterization was performed by ^1H , ^{13}C , and ^{125}Te NMR spectroscopy and mass spectrometry.

All the stable conformers of **2–6** have been located on the potential energy surface. The interaction of the alkenyl and cyclopropyl groups with the TeH group was investigated using photoelectron spectroscopy and quantum chemical calculations.

Strong interactions exist in the vinyl derivative between the C=C double bond and the lone electron pair of the tellurium. On the other hand, the hyperconjugation between the Te–C bond and the double bond is the ruling effect in allyl compound **3**. In cyclopropanetellurol **5**, different interactions were clarified in the conformations **a** and **b**. Although the rotational barrier is almost zero between **5a** and **5b**, from the observed PE spectrum, it was clearly seen that the molecule is mainly in conformation **a**. A stronger hyperconjugation was observed in **6** than in **3**.

Similarities and differences between these systems and the corresponding alcohols, thiols, and selenols have been clearly demonstrated. In the vinyl compounds, a decreasing conjugation from O to Te was found. However, no direct interaction between the lone electron pair of X (X = S, Se, Te) and the three-membered ring could be observed in the cyclopropyl derivatives. Instead, an interaction between the $\sigma(\text{C}-\text{Te})$ and

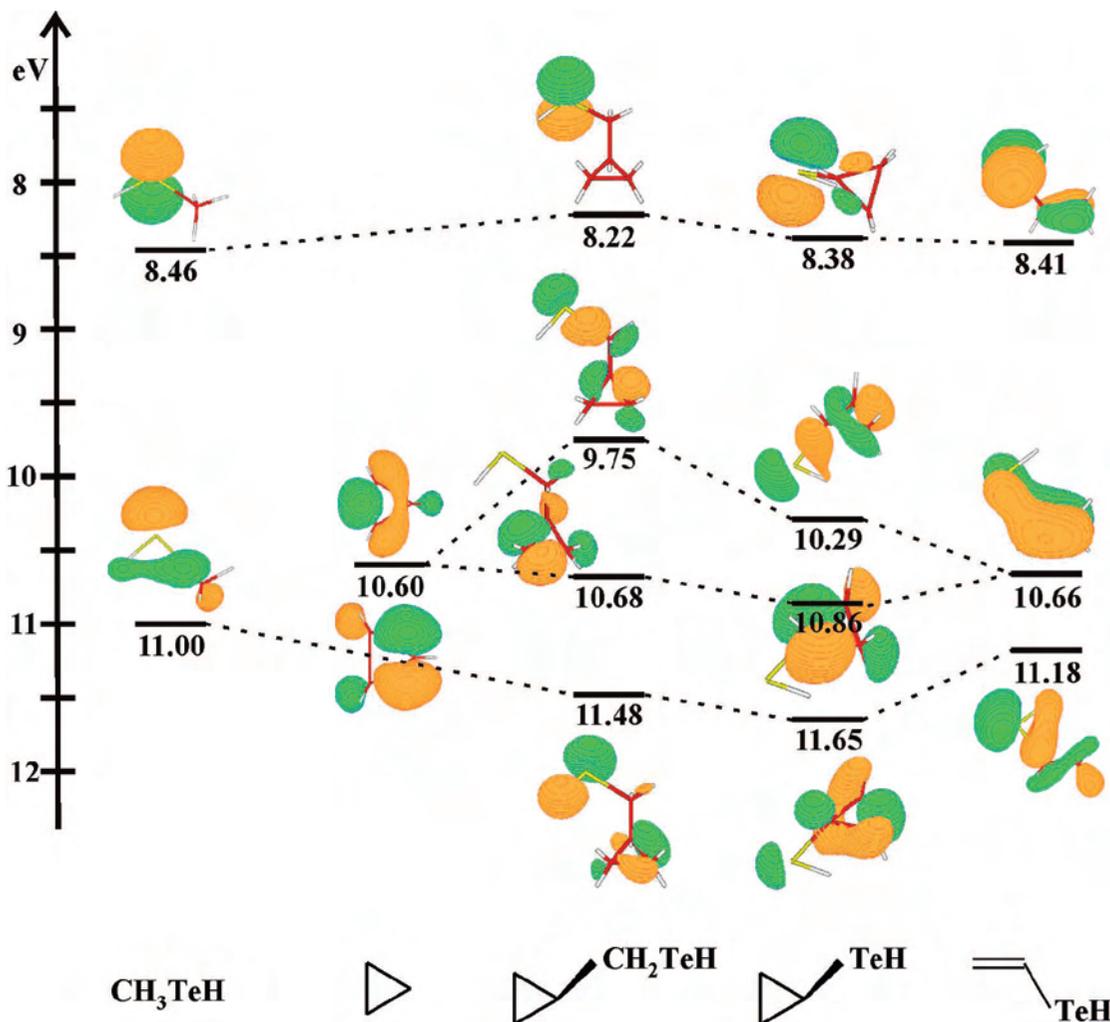


Figure 4. Correlation between the observed photoelectron bands in cyclopropyl tellurols.

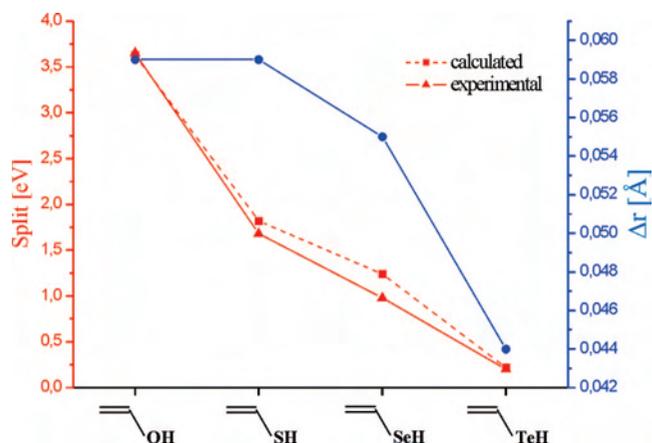


Figure 5. Trend of the C-X bond shortening (Δr) and split of the first two photoelectron (PE) bands in the vinyl-XH ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) derivatives.

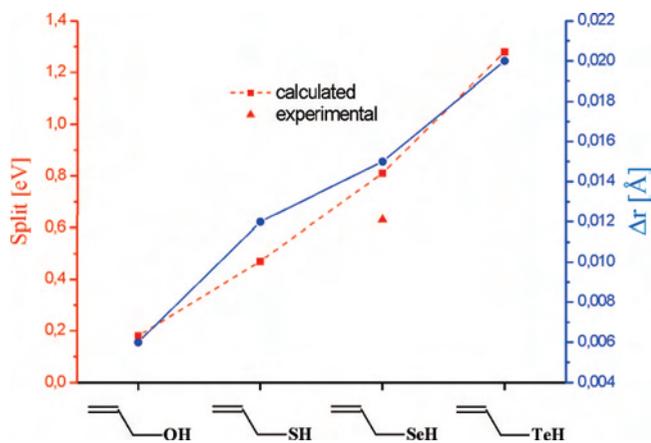


Figure 6. Trend of the C-X bond shortening (Δr) and split of the second and third PE bands in the allyl-XH ($X = \text{O}, \text{S}, \text{Se}, \text{Te}$) derivatives.

e_2 orbitals has been shown. This hyperconjugation-like effect increases from S to Te. Also, an increasing hyperconjugation could be observed from S to Te in compounds **3** and **6**.

Experimental Section

Caution! Low-boiling tellurols smell bad and are potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.

General. Diphenylditelluride, tellurium powder, 4-bromo-1-butene, cyclopropyl bromide, and (bromomethyl)cyclopropane were purchased from ACROS. Dimethylditelluride **7**⁸ and diethenylditelluride **8**¹⁶ were prepared as previously reported. Di-3-butenylditelluride **10** and di(cyclopropylmethyl)ditelluride **12** were prepared using the synthesis of Chen and George reported for compound **7**.⁸

(16) Dabdoub, M. J.; Comasseto, J. V. *J. Organomet. Chem.* **1988**, *344*, 167–173.

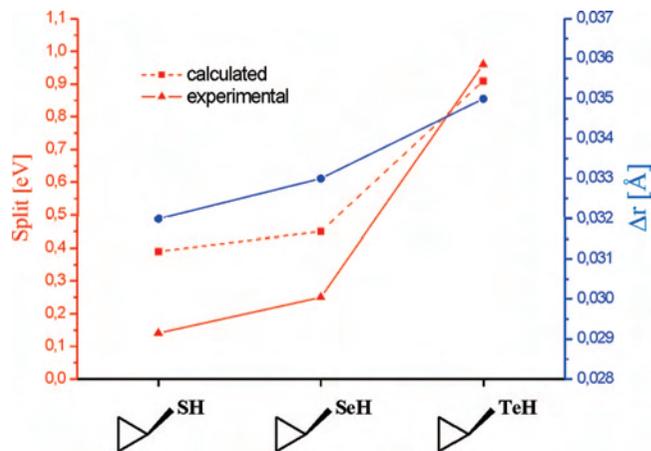


Figure 7. Trend of the C–X bond length difference (Δr) and the split of the second and fourth PE bands (relative to Me–XH and cyclopropane) in the cyclopropyl–XH (X = S, Se, Te) derivatives.

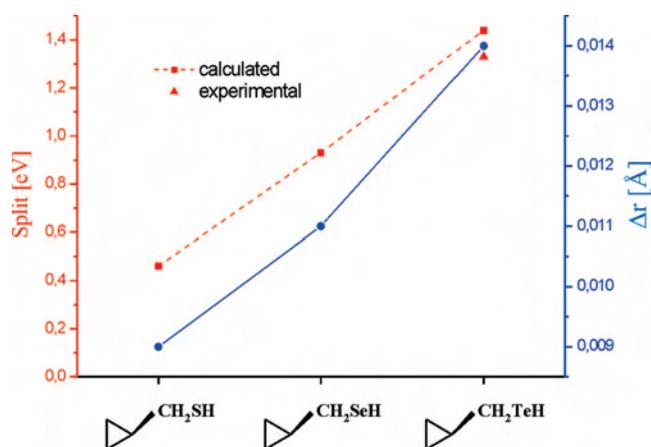


Figure 8. Trend of the C–X bond length difference (Δr) and the split of the second and fourth PE bands (relative to Me–XH and cyclopropane) in the cyclopropylmethane–XH (X = S, Se, Te) derivatives.

He I photoelectron spectra were recorded on an instrument described earlier.¹⁷ The resolution at the Ar $2P_{1/2}$ line was 40 meV during the measurements. For internal calibration, the N₂ and the He⁺ peaks were used. Quantum chemical calculations were performed for all the investigated molecules by the Gaussian 03 program package.¹⁸ All the structures were optimized with MP2 and B3LYP methods using the cc-pVTZ basis set for H and C atoms and the SDB-aug-cc-pVQZ basis set for the Te atom. The stationary points were characterized by second-derivative calculations using the same model chemistry. The relative energies were corrected using the zero-point vibrational energies. To interpret the PE spectra, we proceeded in two ways. We compared the shape and position of the bands to those of related molecules whose PE bands have been assigned, and we compared the recorded vertical ionization energies with quantum chemical results obtained at the ROVGF/ (C, H: cc-pVTZ; Te: SDB-aug-cc-pVQZ) level of theory on the optimized geometry. Molecules and molecular orbitals were visualized with the Molden 4.0 visualization program.¹⁹

Synthesis of Ditellurides. Di-3-butenylditelluride (10) and di(cyclopropylmethyl)ditelluride (12). General Procedure. Sodium metal (0.46 g, 20 mmol) was added to 50 mL of anhydrous ammonia at -78 °C in a 250 mL three-necked flask equipped with a nitrogen inlet and a stirring bar. After stirring the mixture for 1 h, tellurium powder (2.55 g; 20 mmol) was added in 0.5 g

portions. 4-Bromo-1-butene or (bromomethyl)cyclopropane (2.7 g; 20 mmol) was added dropwise over 20 min. The cold bath was then removed, and the flask was slowly allowed to warm to room temperature to remove ammonia. Diethyl ether (30 mL) and water (50 mL) were added, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (2×30 mL). The combined organic layers were dried on MgSO₄, and the solvent was removed in vacuo. The crude ditelluride was evacuated at 0.1 mbar for 15 min and used in the following step without further purification.

Di-3-butenylditelluride (10). Yield: 1.31 g, 7.2 mmol, 36%. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 2.53 (m, ³J_{HH} = 7.5 Hz, ³J_{HH} = 6.6 Hz, 2H, CH₂–CTe), 3.16 (t, ³J_{HH} = 7.5 Hz, ²J_{TeH} = 31.0 Hz (d), 2H, CH₂Te), 5.08 (dm, ³J_{HHcis} = 10.2 Hz, 1 H of CH₂=C), 5.12 (dm, ³J_{HHtrans} = 16.8 Hz, 1H of CH₂=C), 5.82 (m, ³J_{HHtrans} = 16.8 Hz, ³J_{HHcis} = 10.2 Hz, ³J_{HH} = 6.6 Hz, 1H, C=CH). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ 2.6 (t, ¹J_{CH} = 142.6 Hz, ¹J_{TeC} = 171.8 Hz (d), CH₂–Te), 37.5 (t, ¹J_{CH} = 130.1 Hz, CH₂CH₂Te), 115.3 (dd, ¹J_{CH} = 159.8 Hz, ¹J_{CH} = 154.2 Hz, CH₂=C), 138.3 (d, ¹J_{CH} = 153.4 Hz, CH₂=CH). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 293 K): δ 130. HRMS calcd for C₈H₁₄¹²⁸Te₂: 365.9185. Found: 365.922.

Di(cyclopropylmethyl)ditelluride (12). Yield: 1.64 g, 9.0 mmol, 45%. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 0.23 (m, ³J_{HH} = 4.9 Hz, ³J_{HH} = 4.9 Hz, ²J_{HH} = 6.0 Hz, 2H cycle), 0.66 (m, ³J_{HH} = 7.7 Hz, ³J_{HH} = 4.9 Hz, ²J_{HH} = 6.0 Hz, 2H of cycle), 1.18 (tddd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 7.7 Hz, ³J_{HH} = 7.7 Hz, ³J_{HH} = 4.9 Hz, ³J_{HH} = 4.9 Hz, 1H, CH), 3.15 (d, ³J_{HH} = 7.5 Hz, ²J_{TeH} = 28.3 Hz (d), 2H, CH₂Te). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ 8.8 (t, ¹J_{CH} = 159.4 Hz, ¹J_{TeC} = 161.3 Hz (d), CH₂Te), 11.3 (t, ¹J_{CH} = 141.8 Hz, CH₂ cycle), 15.6 (d, ¹J_{CH} = 162.2 Hz, CH). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 293 K): δ 138. HRMS calcd for C₈H₁₄¹²⁸Te₂: 365.9185. Found: 365.922.

Dicyclopropylditelluride (11). Lithium (0.28 g; 40 mmol) and dry diethyl ether (100 mL) were introduced into a 250 mL three-necked flask equipped with a stirring bar and a nitrogen inlet. The flask was immersed in a cold bath, and bromocyclopropane (2.42 g; 20 mmol) diluted in dry diethyl ether (10 mL) was added over 1 h to form the cyclopropyllithium.¹⁰

Tellurium powder (2.55 g; 20 mmol) and dry THF (50 mL) were introduced into another 250 mL three-necked flask. The suspension was cooled at 0 °C, and the solution of cyclopropyllithium was added slowly. The mixture was stirred for 35 min at 0 °C and then for 15 min at room temperature. It was cautiously poured into an Erlenmeyer flask containing water (100 mL), and pure dioxygen

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(19) Molden: a pre- and post-processing program for molecular and electronic structures: Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

(17) Veszprémi, T.; Zsombok, Gy. *Magy. Kem. Foly.* **1986**, *92*, 39–40.

was bubbled for 15 min.²⁰ The organic phase was then separated, and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The organic phases were combined and washed with a saturated solution of NH₄Cl (50 mL) and then brine (50 mL) and dried with MgSO₄. The solvent was removed in vacuo. The crude ditelluride was evacuated at 0.1 mbar for 15 min and used in the following step without further purification. Yield: 1.28 g, 7.6 mmol, 38%. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 0.63 (m, ³J_{HH} = 5.1 Hz, ²J_{HH} = 5.8 Hz, 2 H cycle), 1.15 (m, ³J_{HH} = 8.2 Hz, ²J_{HH} = 5.8 Hz, 2H cycle), 2.13 (dddd, ³J_{HH} = 8.2 Hz, ³J_{HH} = 8.2 Hz, ³J_{HH} = 5.1 Hz, ³J_{HH} = 5.1 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃, 293 K): δ -23.8 (t, ¹J_{CH} = 173.4 Hz, ¹J_{TeC} = 300.1 Hz (d), CHTe), 12.0 (t, ¹J_{CH} = 163.0 Hz, 2 CH₂ cycle). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 293 K): δ 343. HRMS calcd for C₆H₁₀¹²⁸Te₂: 337.8872. Found: 337.889.

Synthesis of Telluroles. Ethenetellurol (2). Ethenetellurol **2** was prepared as previously reported.¹ Yield: 30.7 mg, 0.2 mmol, 67%. $\tau_{1/2}$ (5% in CDCl₃, 20 °C) ≈ 1 h. ¹H NMR (400 MHz, CDCl₃, 233 K): δ -2.94 (d, ³J_{HH} = 4.9 Hz, ¹J_{TeH} = 30.6 Hz (d),* 1H, TeH), 6.04 (dd, ³J_{HH} = 17.7 Hz, ⁴J_{HH} = 1.0 Hz, 1H of CH₂=C), 6.36 (d, ³J_{HH} = 10.0 Hz, 1H of CH₂=C), 6.94 (ddd, ³J_{HH} = 17.7 Hz, ³J_{HH} = 10.0 Hz, ³J_{HH} = 4.9 Hz, 1H, HC-Te). ¹³C NMR (CDCl₃, 233 K): δ 100 (d, ¹J_{CH} = 173.8 Hz, ¹J_{TeC} = 255.8 Hz (d), CH), 130.5 (t, ¹J_{CH} = 159.2 Hz, CH₂). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 233 K): δ 70.4. *The data previously reported for ¹J_{Te-H} (25.6 Hz)¹ is erroneous (ref 1).

Synthesis of 3-butenetellurol (4), Cyclopropanetellurol (5), and Cyclopropanemethanetellurol (6). General Procedure. In a 25 mL two-necked flask equipped with a septum, the ditellurides **7**, **10–12** (0.3 mmol); diphenylditellure (24 mg; 0.06 mmol); and tetraglyme (6 mL) were introduced. The flask and two traps equipped with stopcocks were attached to a vacuum line. The flask was degassed, and tributylstannane (317 mg; 1 mmol) was slowly added (1 h) by portions with a syringe. The formed telluroles **1**, **4–6** were continuously removed by distillation in vacuo from the reaction mixture. The first trap, cooled at -20 °C, selectively removed the less-volatile products, and the tellurol was selectively condensed in the second trap cooled at -90 °C. When the dark red color of the reaction mixture had disappeared, the cell was disconnected from the vacuum line by stopcocks and the product was kept in liquid nitrogen. This cell was directly connected to the mass or photoelectron spectrometer. To prepare the NMR sample, the tellurol and an NMR solvent were vaporized in vacuo and condensed on a coldfinger (77 K) before introduction of the solution under nitrogen in an NMR tube.

3-Butenetellurol (4). Yield: 43.0 mg, 0.23 mmol, 78%. $\tau_{1/2}$ (5% in CDCl₃, 20 °C) ≈ 30 h. bp ≈ -30 °C (0.1 mmHg). ¹H NMR (400 MHz, CDCl₃, 233 K): δ -4.73 (t, ³J_{HH} = 5.7 Hz, ¹J_{TeH} = 47.1 Hz (d), 1H, TeH), 2.57 (m, ³J_{HH} = 6.7 Hz, ³J_{HH} = 6.0 Hz, 2H, CH₂-CTe), 2.67 (m, ³J_{HH} = 6.7 Hz, ³J_{HH} = 5.7 Hz, 2H, CH₂Te), 5.06 (dm, ³J_{HHcis} = 11.5 Hz, 1 H of CH₂=C), 5.07 (dm, ³J_{HHtrans} = 15.9 Hz, 1H of CH₂=C), 5.73 (m, ³J_{HHtrans} = 15.9 Hz, ³J_{HHcis} = 11.5 Hz, ³J_{HH} = 6.0 Hz, 1H, C=CH). ¹³C NMR (100 MHz, CDCl₃, 233 K): δ -2.7 (t, ¹J_{CH} = 143.5 Hz, ¹J_{TeC} = 123.5 Hz (d), CH₂Te), 38.1 (t, ¹J_{CH} = 126.1 Hz, CH₂CH₂Te), 115.7 (dd, ¹J_{CH} = 158.2 Hz, ¹J_{CH} = 155.0 Hz, CH₂=C), 138.2 (d, ¹J_{CH} = 154.2 Hz, CH₂=CH). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 233 K): δ -111. HRMS calcd for C₄H₈¹³⁰Te: 185.9688. Found: 185.969.

Cyclopropanetellurol (5). Yield: 36.6 mg, 0.22 mmol, 72%. $\tau_{1/2}$ (5% in CDCl₃, 20 °C) ≈ 20 h. bp ≈ -45 °C (0.1 mmHg). ¹H NMR (400 MHz, CDCl₃, 233 K): δ -3.85 (m, ³J_{HH} = 1.1 Hz,

⁴J_{HH} = 0.9 Hz, ¹J_{TeH} = 51.1 Hz (d), 1H, TeH), 0.67 (m, ³J_{HH} = 5.1 Hz, ²J_{HH} = 5.0 Hz, 2 H cycle), 1.08 (m, ³J_{HH} = 8.0 Hz, ²J_{HH} = 5.0 Hz, ⁴J_{HH} = 0.9 Hz, 2H cycle), 1.81 (dddd, ³J_{HH} = 8.0 Hz, ³J_{HH} = 8.0 Hz, ³J_{HH} = 5.1 Hz, ³J_{HH} = 5.1 Hz, ³J_{HH} = 1.1 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃, 233 K): δ -26.6 (t, ¹J_{CH} = 177.5 Hz, ¹J_{TeC} = 220.9 Hz (d), CH₂Te), 9.1 (t, ¹J_{CH} = 163.0 Hz, CH₂ cycle). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 233 K): δ 109. HRMS calcd for C₃H₆¹³⁰Te: 171.9532. Found: 171.954.

Cyclopropanemethanetellurol (6). Yield: 44.6 mg, 0.24 mmol, 81%. $\tau_{1/2}$ (5% in CDCl₃, 20 °C) ≈ 40 h. bp ≈ -30 °C (0.1 mmHg). ¹H NMR (400 MHz, CDCl₃, 233 K): δ -4.66 (t, ³J_{HH} = 5.6 Hz, ¹J_{TeH} = 48.6 Hz (d), 1H, TeH), 0.13 (ddd, ²J_{HH} = 6.2 Hz, ³J_{HH} = 4.9 Hz, ³J_{HH} = 4.9 Hz, 2H cycle), 0.69 (m, ³J_{HH} = 7.7 Hz, ²J_{HH} = 6.2 Hz, 2H cycle), 1.15 (dddd, ³J_{HH} = 7.7 Hz, ³J_{HH} = 7.7 Hz, ³J_{HH} = 7.5 Hz, ³J_{HH} = 4.9 Hz, ³J_{HH} = 4.9 Hz, 1H, CH), 2.57 (dd, ³J_{HH} = 7.5 Hz, ³J_{HH} = 5.6 Hz, ²J_{TeH} = 28.5 Hz (d), 2H, CH₂Te). ¹³C NMR (100 MHz, CDCl₃, 233 K): δ 5.2 (t, ¹J_{CH} = 143.8 Hz, ¹J_{TeC} = 116.6 Hz (d), CH₂Te), 9.9 (t, ¹J_{CH} = 160.6 Hz, CH₂ cycle), 16.4 (d, ¹J_{CH} = 159.8 Hz, CH). ¹²⁵Te NMR (94.7 MHz, CDCl₃, 233 K): δ -101. HRMS calcd for C₄H₈¹³⁰Te: 185.9688. Found: 185.968.

Selenocyanic Acid, Cyclopropane Ester (17). Cyclopropylmagnesium bromide was prepared by slow addition of cyclopropyl bromide (6.05 g, 50 mmol) in THF (30 mL) to Mg (1.2 g, 50 mmol) in THF (20 mL) at 0 °C. The solution was then warmed to 50 °C for 20 min and then cooled to 0 °C, at which time selenium powder (3.95 g; 50 mmol) was added by portions over 10 min and then stirred at room temperature for 30 min. The solution was introduced into a dropping funnel and poured into a 250 mL flask containing a cooled (-40 °C) solution of cyanogen bromide (5.1 g, 48 mmol) in THF (20 mL). The solution was then allowed to warm to room temperature and stirred for 20 min. Water (20 mL) was added, and the organic phase was separated; the aqueous layer was extracted with diethyl ether (2 × 30 mL). The organic phases were combined and dried with MgSO₄. The solvent was removed in vacuo. Purification was performed by distillation in vacuo. bp: 40 °C (0.1 mmHg). Yield: 3.31 g, 22.5 mmol, 45%. ¹H NMR (400 MHz, CDCl₃): δ 0.93 (m, ²J_{HH} = 6.6 Hz, ³J_{HH} = 4.3 Hz, 2H cycle). 1.16 (m, ³J_{HH} = 7.4 Hz, ²J_{HH} = 6.6 Hz, 2H cycle), 2.53 (dddd, ³J_{HH} = 7.4 Hz, ³J_{HH} = 7.4 Hz, ³J_{HH} = 4.3 Hz, ³J_{HH} = 4.3 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃): δ 8.55 (d, ¹J_{CH} = 187.9 Hz, CH), 9.13 (t, ¹J_{CH} = 164.6 Hz, CH₂), 101.6 (s, CN). ⁷⁷Se NMR (57.2 MHz, CDCl₃): δ 322.4. HRMS calcd for C₄H₅N⁸⁰Se: 146.9587. Found: 146.959. IR (KBr): 3009 (w), 2153 (s, ν_{CN}), 1262, 1032, 863 cm⁻¹.

Cyclopropaneselenol (16). LiAlH₄ (0.1 g; 2.4 mmol) and dry tetraglyme (20 mL) were introduced into a 50 mL two-necked flask equipped with a stirring bar and a nitrogen inlet. The reaction mixture was cooled to -10 °C and stirred for 5 min. Compound **17** (456 mg, 3.0 mmol) diluted in dry tetraglyme (10 mL) was then added dropwise over about 5 min, and the mixture was stirred for 5 min at -10 °C. Succinic acid (4.72 g; 40 mmol) and tetraglyme (20 mL) were introduced into a 100 mL two-necked round-bottomed flask equipped with a stirring bar and a septum. The flask was attached to a vacuum line equipped with two cells, degassed, and then immersed in a cold bath (-10 °C). The mixture containing the aluminum selenolate was slowly added using a syringe through the septum into the flask containing the succinic acid. During and after the addition, selenol **16** was distilled off in vacuo (10⁻¹ mbar) from the reaction mixture. The first trap cooled at -50 °C removed selectively the less volatile products, and compound **16** was condensed in the second trap equipped with two stopcocks and cooled at -100 °C. At the end of the reaction, this second cell was

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Functionalized Tellurols

disconnected from the vacuum line by stopcocks and adapted to the PE or mass spectrometer. On the other hand, to record the NMR spectra, this second trap was allowed to warm to room temperature, and the products were condensed on a coldfinger ($-196\text{ }^{\circ}\text{C}$) connected at the bottom to a NMR tube immersed in liquid nitrogen. A cosolvent (CDCl_3) was added at this step. After disconnection from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The products were collected in the NMR tube and kept at low temperatures ($<-30\text{ }^{\circ}\text{C}$) before analysis at room temperature. Yield 73%. bp $\approx -60\text{ }^{\circ}\text{C}$ (0.1 mmHg). $\tau_{1/2}$ (5% in CDCl_3 at room temperature) ≈ 20 h. ^1H NMR (400 MHz, CDCl_3): δ 0.19 (m, $^3J_{\text{HH}} = 1.0$ Hz, $^1J_{\text{SeH}} = 45.2$ Hz (d), 1H, SeH), 0.60 (m, $^2J_{\text{HH}} = 6.1$ Hz, $^3J_{\text{HH}} = 4.3$ Hz, 2H cycle), 0.93 (m, $^2J_{\text{HH}} = 6.1$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 2H cycle), 1.91 (dddd, $^3J_{\text{HH}} = 6.1$ Hz, $^3J_{\text{HH}} = 6.1$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, CH). ^{13}C NMR (100 MHz, CDCl_3): δ -2.2 (d, $^1J_{\text{CH}} = 179.3$ Hz, CH), 8.9 (t, $^1J_{\text{CH}} = 166.3$

Hz, CHSe). ^{77}Se NMR (57.2 MHz, CDCl_3): δ 96.4. HRMS calcd for $\text{C}_3\text{H}_6^{80}\text{Se}$: 121.9634. Found: 121.962. IR (KBr): 2934 (vs), 2250 (m, ν_{SeH}), 1717 (s), 1448 (s), 1263 (s), 1194 (s), 1036 (s), 823 (s) cm^{-1} .

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Supporting Information Available: Synthesis and spectroscopic characterization of cyclopropanethiol **15**, the photoelectron spectra of tellurols **2**, **4–6** (Figure S1), the shape of the degenerated HOMOs of cyclopropane (Figure S2), and the calculated total energies (au) and relative energies (kcal/mol) of alkenyl and cyclopropyl tellurols (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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