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Hydrozirconation of Acetylenic Chalcogenides. Synthesis and Reactions of Zirconated Vinyl Chalcogenide Intermediates

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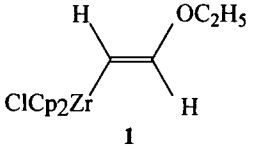
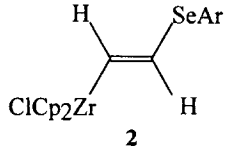
Abstract: *Acetylenic tellurides react with $Cp_2Zr(H)Cl$ in THF at room temperature to give the α-zirconated vinyl telluride intermediates **39**, which react with a wide range of electrophiles to give several types of trisubstituted olefins, such as α-halo vinyl tellurides, ketene telluro(seleno) acetals, ketene telluro acetals, and vinylic tellurides of **Z** configuration. Acetylenic selenides undergo similar reactions, but a lack of regioselectivity results in the formation of a mixture of α-zirconated **19** and β-zirconated **20** vinylic selenide intermediates. After a detailed study was established that the use of 2.0 equivalents of $Cp_2Zr(H)Cl$ is crucial to perform the total hydrozirconation of acetylenic selenides or tellurides.*

Hydrozirconation of unsymmetrical disubstituted alkynes ($CH_3C{\equiv}CAlkyl$) produces regioselectively a mixture of the two possible regio-isomers.[1] Lipshutz et al[2] have shown that the regiochemistry of the hydrozirconation of trialkylstannyl acetylenes ($RC{\equiv}CSnR_3$) is such that zirconium is localized only on the resulting sp^2 carbon bearing the R_3Sn moiety. Hydrozirconation of tributylstannylethyne ($HC{\equiv}CSnBu_3$) was also studied and protonolysis of the dimetallo intermediate involved resulted in the formation of the corresponding vinylstannane,[3] although, the 1,1-dimetallo or 1,2-dimetallo nature of this specific intermediate was not established by these authors.[4] Tucker and Knochel[5] obtained 1,1-dimetalloalkenes of zinc and zirconium by hydrozirconation of alkynylzinc bromides, but the ethynylzinc bromide compound was not studied. Ethoxyacetylene was regioselectively converted into the (***E***)-2-ethoxyethenylzirconium derivative **1** *via* hydrozirconation using $Cp_2Zr(H)Cl$.[6]



1



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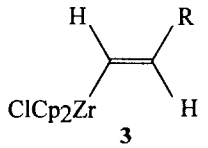

3

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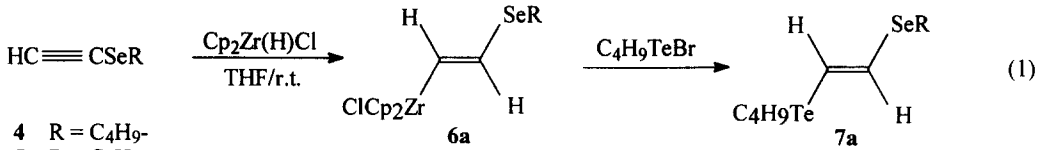
The same regioselectivity was observed in the reaction of arylseleno analogue compounds by Huang et al.[7] These authors described in several communications published in 1996 that exclusive formation of β-zirconated vinyl selenide **2** occurred by reaction of arylselenoethyne and 1.0 equivalent of $Cp_2Zr(H)Cl$.

We believe that formation of these intermediates occurs because the terminal alkoxy- or seleno-acetylenes were used since terminal alkynes (aryl or alkylsubstituted) generally undergo easy and exclusive formation of terminally (*E*)-Zr-substituted alkenes of type **3**.[1] However, hydrozirconation of tributylstannylethyne[4] and (trimethylsilyl)acetylene[8] yield the β-zirconated heteroatom-substituted ethene while a similar reaction with the (trimethylsilyl) phenylacetylene[8c] affords the corresponding α-zirconated silylalkene.

We have special interest in the study of the reactivity of an organyltellurium moiety in the presence of another organochalcogene group (Te, Se, S) attached at one double bond since tellurium removal using several types of reagents is expected to be an extremely selective reaction. However, few compounds containing these difunctionalizations are known.[9-13] Previous attempts to prepare the 1-butyltelluro-2-phenylselenoethenes by the telluroalumination/selenenylation of acetylenes were unsuccessful.[14] More recently we described the synthesis of ketene butyltelluro(phenylseleno)acetals by the Al/Te exchange reaction[13] showing that the addition of DIBAL-H to the carbon-carbon triple bond of acetylenic selenides is *syn*. Al is always added to the carbon bearing the selenium moiety and hydride is transferred to the adjacent carbon. The ketene telluro(seleno) acetals were obtained in low yields (22-50 %) because the Al/Te exchange reaction is very slow in the α-aluminated vinyl selenide intermediates and vinyl selenides of *Z* configuration are formed as side-products.[13]

We report here our results of a detailed study on the regio and stereochemistry of hydrozirconation of terminal and substituted acetylenic selenides and acetylenic tellurides followed by capture of the corresponding zirconated vinyl chalcogenide intermediates with electrophiles to permit the preparation of 1,1 or 1,2 dichalcogenoethenes, (*Z*)-vinyl chalcogenides and 1-halo(iodo or bromo)-1-butyltelluroethenes.

The hydrozirconation of the butylseleno or (phenylseleno)ethyne **4** and **5** followed by treatment of the intermediates **6a-b** with butyltellurenylbromide studied in this paper results in the formation of the (*E*)-1-butyltelluro-2-butylseleno (or 2-phenylseleno) ethene **7a** and **7b** in 81% and 66% yield, respectively (entries 1 and 2; Table 1) as the only product (Eq. 1). Although in this example the reaction was 100% regioselective in agreement with the result described by Huang et al,[7] our studies with a wide range of other selenoacetylenes have shown that this regioselectivity is not general.

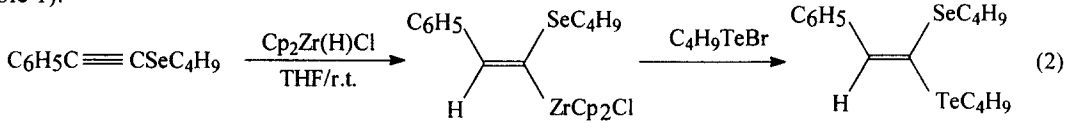


(1)

4 R = C_4H_9-
5 R = C_6H_5-

6a **6b** **7a** **7b**

Total inversion of regioselectivity was observed when a phenyl group is linked at the triple bond as in the (butylseleno)phenylacetylene **8**. In this case, the α-zirconated selenoalkene **9** was the intermediate formed and after treatment with butyltellurenylbromide, the ketene butylseleno(butyltelluro) acetal **10** (Eq. 2) was isolated as the sole product in 63% yield (entry 7; Table 1).

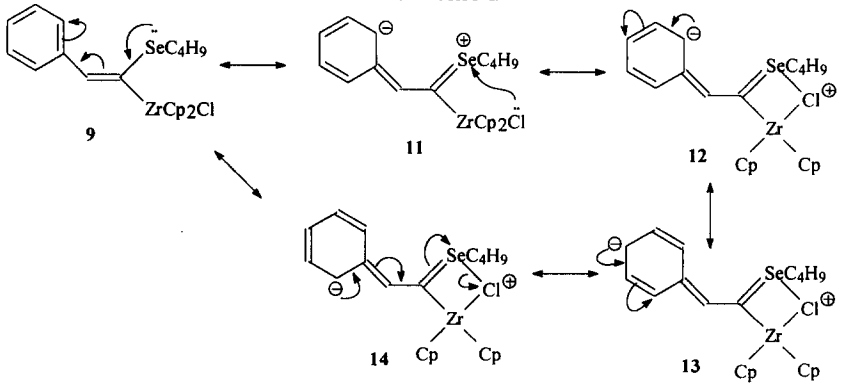


(2)

8 **9** **10**

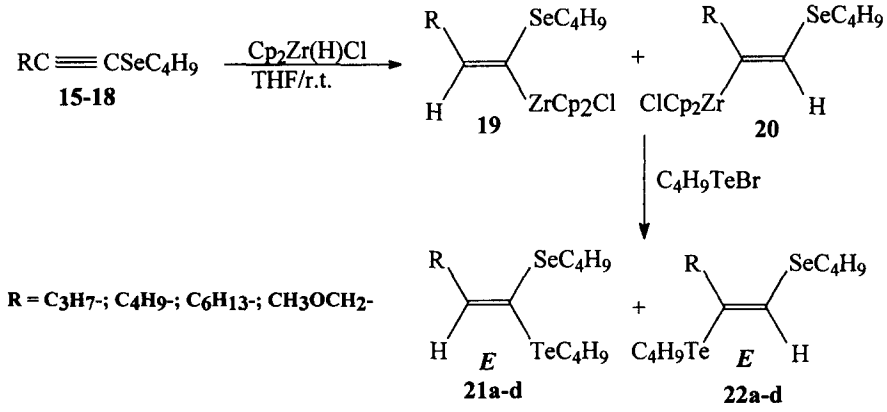
In the hydrozirconation of compound **8** (entry 7, Table 1) the total regioselectivity is probably explained in terms of the presence of a phenyl group attached at the β-carbon of the triple bond, which permits the formation of intermediate **9** and **12** to give the electronically controled regiochemistry (Scheme 1). We believe that the mechanism basically involves the formation of the Se-Cl bond by electron deslocalization as shown in Scheme 1. The empty orbital in the selenium atom (structure **11**) is filled by the electron pair donated by the chloro atom, as shown in **11** and **12**. Electronic deslocalization occur with the formation of several other canonical structures such as **12-14**, which are also responsible for the intermediate stabilization, justifying the formation of the α-zirconated vinylic selenide **9** rather than the β-zirconated analogue. However, the present mechanism is hypothetical and further studies examining a series of para-substituted phenyl groups are necessary for a final conclusion.

Scheme 1



On the other hand, the hydrozirconation of 1-butylseleno-2-alkylethynes **15-18** results in the formation of mixtures of the regioisomers α-zirconated **19** and β-zirconated vinylselenides **20** that by reaction with butyltellurenyl bromide afforded a mixture of seleno(telluro)ethenes **21** and **22** as depicted in Scheme 2. The isomers of type **21** were the major products (see ratios in entries 3-6; Table 1) indicating that the organoselenium moiety is responsible for a partial preference for the attachment of zirconium to the α-position, although the formation of the cyclic intermediate is less favored when an alkyl group is attached at the β-position compared with an aryl group (Scheme 1).

Scheme 2



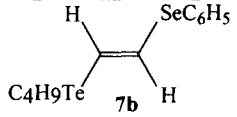
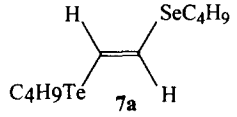
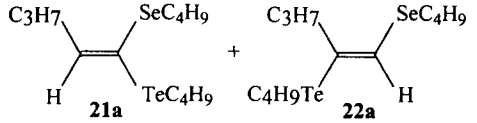
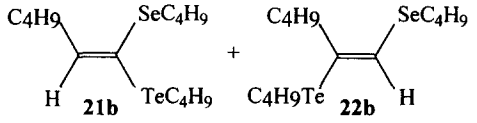
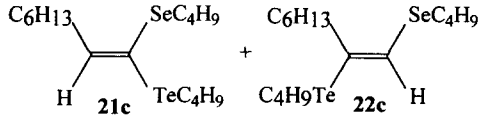
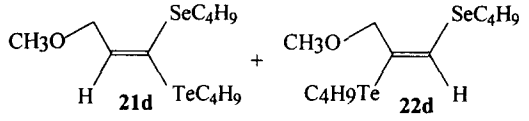
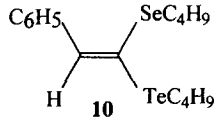
Compounds **21a-c** and **22a-c** (entries 3-5; Table 1) were easily separated by column chromatography, with the methyl ether derivatives **21d** and **22d** (entry 6; Table 1) being one exception. Only the *E* isomer of compound **21** and one of compound **22** were formed, showing that in this case the Zr/Te exchange reaction occurs with total retention of configuration.

It is known that hydrozirconation of unsymmetrically substituted alkynes provides mixtures of regioisomers with the major alkenyl zirconocene placing the zirconium at the carbon bearing the sterically less hindered group.[1] However, excess of $ZrCp_2(H)Cl$ readily isomerizes the adduct obtained, presumably *via* a dimetalated alkane to give improved thermodynamically controled regioselectivity.[1] We believe that in the case of 1-butylseleno-2-alkylethynes the use of excess of $Cp_2Zr(H)Cl$ may be responsible for some isomerization of the initial mixture formed in the reaction with 1.0 equivalent *via* a similar dimetalated alkane **23**.

However, the ratio of **21** and **22** obtained from **19** and **20** using only 1.0 equivalent was not determined because reactions of compounds **8** and **15-18** with this amount of pure $Cp_2Zr(H)Cl$ are

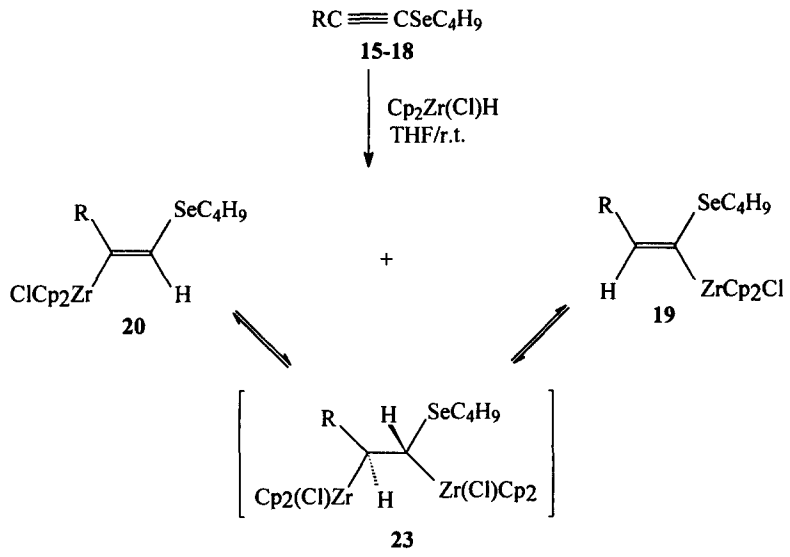
very slow and detailed experimentation in which the hydrozirconation reactions were monitored by TLC showed that only with the use of 2.0 equivalents of this reagent, total conversion of the starting material was achieved after the time indicated in Table 2.

Table 1. Selenotelluroethenes obtained from selenoalkynes.

Entry	selenoalkyne	Product	ratio 21:22	Yield (%)
1	$HC{\equiv}CSeC_6H_5$ **5**	 **7b**	100:0	66[a]
2	$HC{\equiv}CSeC_4H_9$ **4**	 **7a**	100:0	81[a]
3	$C_3H_7C{\equiv}CSeC_4H_9$ **15**	 **21a** + **22a**	70:30	65[b]
4	$C_4H_9C{\equiv}CSeC_4H_9$ **16**	 **21b** + **22b**	90:10	70[b]
5	$C_6H_{13}C{\equiv}CSeC_4H_9$ **17**	 **21c** + **22c**	92:8	66[b]
6	$CH_3OCH_2C{\equiv}CSeC_4H_9$ **18**	 **21d** + **22d**	64:34	64[c]
7	$C_6H_5C{\equiv}CSeC_4H_9$ **8**	 **10**	100:0	63[a]

a. Only one isomer formed. b. Isomers separated by column chromatography. c. Unseparable mixture by chromatography or distillation.

Scheme 3

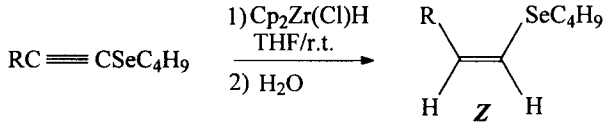


The reactions employing the terminal butylseleno and phenylseleno acetylenes **4** and **5** were carried out with 1.0 equivalent of the Schwartz's reagent in accordance with previous work based on the use of phenylselenoethyne[7] but we observed that the use of 2.0 equivalents of $Cp_2Zr(H)Cl$ in these reactions is crucial to allow the reaction to reach completion. When the reactions using 2.0 equivalents of $Cp_2Zr(H)Cl$ were carried out at 0 °C or at room temperature, the phenylseleno ethene **24** (entry 1, Table 2) and the butylseleno ethene **25** (entry 2; Table 2) were isolated in 64 and 81% yield respectively. However, in both cases no formation of dibutyl or diphenyl diselenide was observed, in contrast to the data reported by Huang et al.[7c] The reaction of **5** at room temperature with 1.0 equivalent followed by aqueous quench results in the formation of phenylselenoethene **24** in 45% isolated yield and 55% phenylselenoethyne **5** recovery, i.e., with no change compared to determination by TLC, GC and ^1H NMR.

The zirconated vinyl selenide intermediates **6a, 6b, 9, 19** and **20** were also treated with water resulting in the formation of the (*Z*)-vinylic selenides **24-31** in very good yields (Eq. 3; Table 2). The stereochemistry of the obtained products was easily determined by the coupling constant data analysis in the ^1H NMR spectra. It should be noted that the butylselenobutadiene **29** was obtained pure as determined by ^1H NMR. However, this compound is stereoisomerically unstable since undergoes isomerization after some time.[15] There has been a remarkable interest in the preparation of vinylic selenides and their utilization in organic synthesis.[16] Thus, considering the excellent yields, mild

reaction conditions, simple procedures and readily available reagents, the transformation developed here is a convenient approach to (*Z*)-vinyl selenides and an alternative to the known methods.[16]

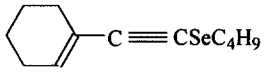
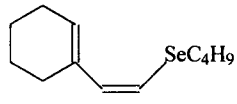
These facts show that hydrozirconation of acetylenic selenides using 2.0 equivalents of $Cp_2Zr(H)Cl$ is 100% stereoselective (Table 2), although the regiochemistry in this reaction is highly dependent on the structure of the employed substrate (Table 1).



(3)

R = C_6H_5-, alkyl or alkenyl **26-31**

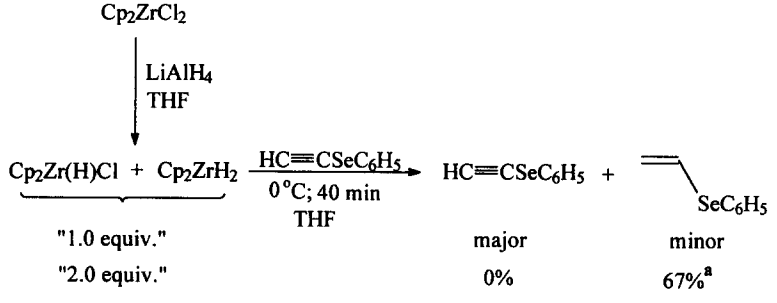
Table 2. (*Z*)-Vinylic selenides obtained from selenoalkynes.

Entry	Acetylenic selenide	Product	reaction time[a] (h)	Yield (%)
1	$HC{\equiv}CSeC_6H_5$ **5**	SeC_6H_5 **24**	0.66	64
2	$HC{\equiv}CSeC_4H_9$ **4**	SeC_4H_9 **25**	0.33	81
3	$C_3H_7C{\equiv}CSeC_4H_9$ **15**	C_3H_7, SeC_4H_9 **26**	2.0	82
4	$C_4H_9C{\equiv}CSeC_4H_9$ **16**	C_4H_9, SeC_4H_9 **27**	2.0	86
5	$C_6H_{13}C{\equiv}CSeC_4H_9$ **17**	C_6H_{13}, SeC_4H_9 **28**	2.0	89
6		 **29**	2.0	83[ref. 15]
7	$CH_3OCH_2C{\equiv}CSeC_4H_9$ **18**	CH_3O, SeC_4H_9 **30**	1.0	87
8	$C_6H_5C{\equiv}CSeC_4H_9$ **19**	C_6H_5, SeC_4H_9 **31**	3.0	81

[a] Using 2.0 equiv. of $Cp_2Zr(H)Cl$.

We also performed the hydrozirconation of **5**, using a mixture of $Cp_2Zr(H)Cl$ and Cp_2ZrH_2 (Scheme 4) obtained by reaction of Cp_2ZrCl_2 with $LiAlH_4$ as described by Buchwald et al[17] for the synthesis of $Cp_2Zr(H)Cl$, but the mixture was not washed with CH_2Cl_2. In this case the mixture of the hydride and dihydride was used considering the molecular weight of the $Cp_2Zr(H)Cl$, however the formation of diphenyl diselenide never was observed, even using 1.0 or 2.0 "equivalents" of the reducing mixture (Scheme 4).

Scheme 4



a. Isolated Yield (sole product)

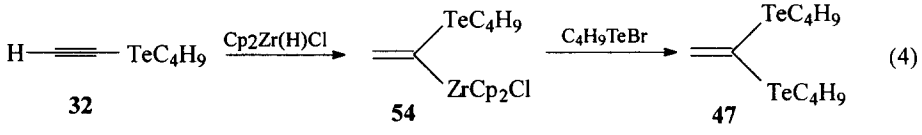
Recent reports by our group[18] and others[19] have shown that the Zr/Te exchange reaction on (*E*)-vinyl zirconates with organyltellurenyl halides occurs with total retention of configuration, producing (*E*)-vinylic tellurides in good yields. In a previous communication we reported that vinylic tellurides of *Z* configuration were obtained by us *via* hydrozirconation of acetylenic tellurides.[20] We also studied the synthesis of (*Z*)-vinylic tellurides by the hydroalumination of acetylenic tellurides with DIBAL-H.[14] However, the yields of the (*Z*)-vinylic tellurides obtained by hydroalumination are only moderate since the Csp-Te bond of the telluroalkynes undergoes partial cleavage.[14]

In the present paper we also described our results on the study of the regio and stereoselective hydrozirconation of acetylenic tellurides **32-38** using the Schwartz's reagent and the transformation of the zirconate intermediates **39** into different types of highly functionalized trisubstituted olefins (Scheme 5). We first observed that the reaction of 1-butyltelluro-1-hexyne **34** with $Cp_2Zr(H)Cl$ in THF at room temperature followed by treatment of the intermediate **39** with water gives the corresponding vinylic telluride of *Z* configuration **42** in 91 % yield (entry 3; Table 3). This reaction was successfully extended to other acetylenic tellurides and yields of the isolated products **40-46** obtained are listed in Table 3. As for selenides **26-31**, the *Z* geometry of products **41-46** was determinated by the analysis of the coupling constant data in the ^1H NMR spectra.

It is noteworthy that, as for acetylenic selenides, total conversion of the starting acetylenic tellurides was only achieved using 2.0 equivalents of $Cp_2Zr(H)Cl$, with the formation of an intense

red solution in the last cases. The reactions of acetylenic tellurides are faster than reactions of acetylenic selenides, as determined by monitoring the acetylenic telluride or selenide disappearance by TLC (see reactions time in Tables 2 and 3), generally using hexane as eluent.

The addition of the Zr-H across the acetylene occurs in a *cis* fashion, placing the zirconium atom at the α-position relative to the butyltellurium moiety. The proposed regiochemistry and the intermediacy of **39** was confirmed by performing the Zr/Te exchange reaction with C_4H_9TeBr, that affords exclusively the corresponding ketene bis(butyltelluro) acetals **47-53** in 70-79 % yield (Scheme 5; Table 3). In the same way, an interesting result was obtained when performing the hydrozirconation of the butyltelluro ethyne **32** since the 1,1-dimetallo nature of the intermediate exclusively formed was established by us, capturing **54** with butyltellurenyl bromide to afford the ketene bis(butyltelluro) acetal **47** in 79% yield (Eq. 4; entry 1; Table 3). The assignment determining that **47** is the 1,1-isomer and not the 1,2-isomer was made by ^{13}C NMR spectroscopy because two signals are observed in the olefinic carbon region (one in 106.5 and another in 117.3 ppm) while for the 1,2-isomer only one signal would be expected in the same region. A DEPT experiment was an additional evidence to confirm this assignment. The observed regiochemistry in this case is contrary to that observed for butylselenoethyne (or phenylselenoethyne[7]), ethoxyacetylene[6] and terminal alkynes,[1] but similar to boron alkynyl,[21] tributylstannylethyne[4] or zinc alkynyl derivatives.[5]



32 **54** **47** (4)

During the preparation of the present manuscript, Oh et al.[22a] described the hydrozirconation of three acetylenic tellurides[22a] obtaining five different ketene telluroacetals and using 1.1 equivalents of the Schwartz's reagent, but our experience has shown that total transformation of the starting materials is only achieved using 2.0 equivalents of this reagent, which was commercially available or prepared in accordance with a procedure described in the literature.[17]

Contrary to reports made by Oh et al,[22] the disappearance of the insoluble hydride (1.1[22a] or 1.2[22b] equivalents) and the formation of a clear solution is not sufficient evidence that hydrozirconation of acetylenic tellurides was complete,[22a] as occurs for alkynes that do not contain selenium or tellurium.[17-19] At the beginning of our studies (three years ago) described here, we attempted to perform the hydrozirconation of several acetylenic tellurides using 1.0 up to 1.5 equivalents of $Cp_2Zr(H)Cl$ in THF and observed by TLC that the clear solution obtained after total

solubilization of the hydride (~15-20 min) consists of a mixture of the α-zirconated vinylic telluride and the starting material. For example, performing the quench with water of the mixture obtained by hydrozirconation of **35**, with 1.1 equivalent of $Cp_2Zr(H)Cl$, components of the mixture analyzed by TLC, were quantified after separation by column chromatography and identification by ^1H NMR. The (*Z*)-vinylic telluride **43** was isolated in 58% yield and 41% of the acetylenic telluride was recovered unchanged.

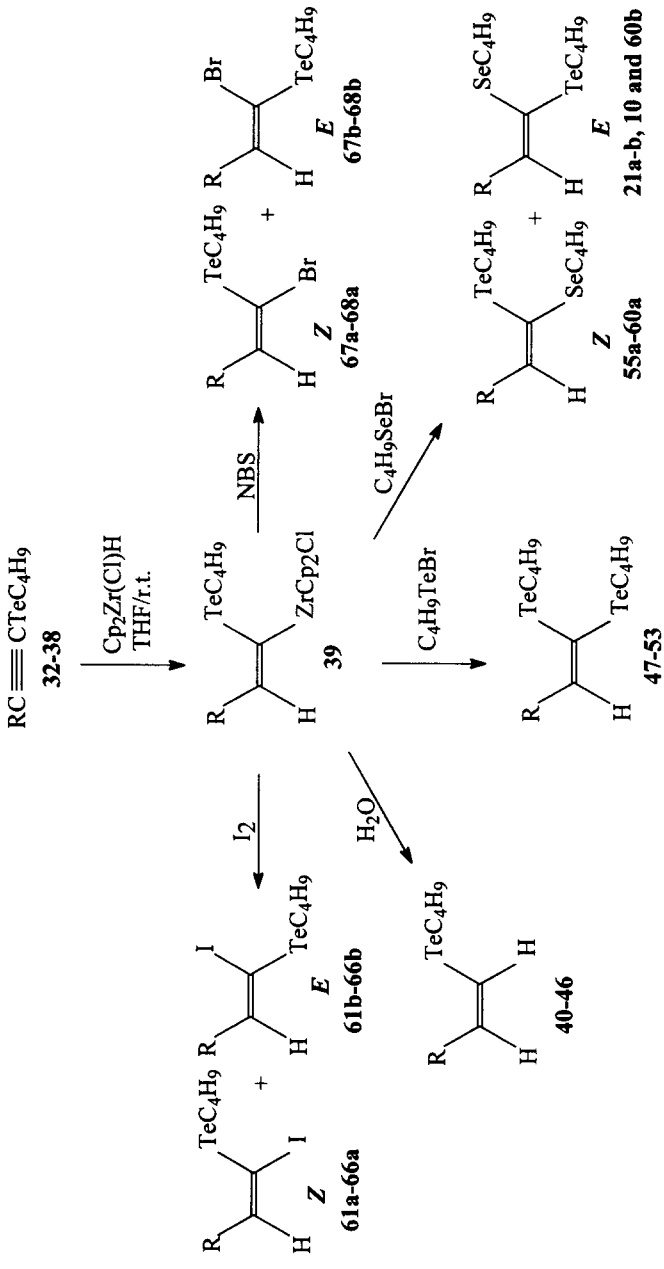
Oh et al used two different procedures to perform the hydrozirconation of acetylenic tellurides: with 1.1 mmol of $Cp_2Zr(H)Cl$ and 7.0 mL of THF/mmol of acetylenic telluride[22a] and 1.2 mmol of $Cp_2Zr(H)Cl$ and 4.0 mL of THF/mmol of acetylenic telluride[22b] and the only difference between the procedures described by Oh et al[22] and our procedure is the volume of THF and the amounts of the Schwartz's reagent employed. However, the reactions were repeated by us using all three procedures monitoring the reactions by TLC, showing that hydrozirconation of tellurides is complete only using 2.0 equivalents of the Schwartz's reagent, after the time indicated in Table 3 and with the formation of an intermediate that is responsible for the intense red color of the solution which turned pale yellow only after treatment with water.

During prior studies by our group[14,24] on the reactivity of vinylic and acetylenic tellurides we observed that the Csp-Te bond is extremely labile against hydrides, Grignard reagents, alkyl lithiums, hydroxides and others. This bond is only partially cleaved by DIBAL-H[14] and we now observed that it is not cleaved by $Cp_2Zr(H)Cl$ in the case of butyltelluro ethyne (entry 1; Table 3) or butyltelluro alkylacetylenes (entries 2-4; Table 3), while for butyltelluro aryl (or alkenyl and methoxymethyl) acetylenes (entries 5-7; Table 3) cleavage occurs, but only to a minor extent (<15%).

We are able to obtain the vinylic telluride **45** in 81% isolated yield and the ketene bis(butyltelluro) acetal **52** in 73% yield by the hydrozirconation of butyltelluro phenylacetylene **37** (entry 6; Table 3), while other authors[22b] reported that the same compound undergoes preferably Csp-Te bond cleavage affording dibutylditelluride in 35% yield and only 6% of the corresponding vinylic telluride **45**.

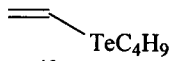
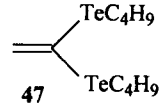
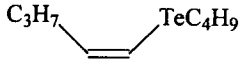
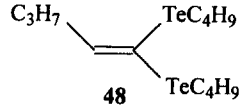
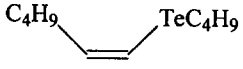
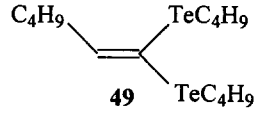
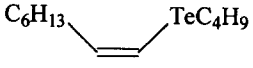
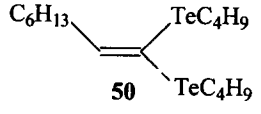
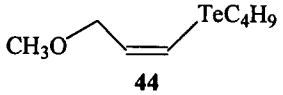
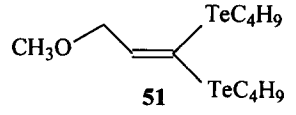
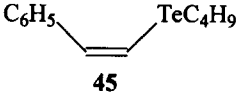
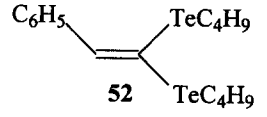
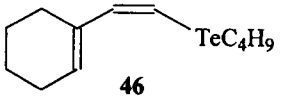
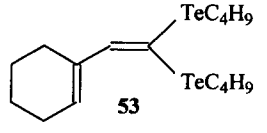
Several attempts to reproduce the Csp-Te bond cleavage in **37** using zirconium hydrides as described in literature[22b] were made by us, but always the major product was the vinylic telluride **45**. However, when the $Cp_2Zr(H)Cl$ employed is prepared from Cp_2ZrCl_2 and $LiAlH_4$ as described in literature[17] experimental details described in this report must be caustiosly followed to avoid the presence of $LiAlH_4$ which promotes the Csp-Te bond cleavage.[24] In this way, we also studied this reaction employing "1.1 equivalent" of the mixture of $Cp_2Zr(H)Cl$ and Cp_2ZrH_2 obtained as

Scheme 5


RC≡CTeC4H9
32-38
Cp2Zr(Cl)H
THF/r.t.
TeC4H9
ZrCp2Cl
39
NBS
C4H9SeBr
C4H9TeBr
I2
H2O
67a-68a
Z
67b-68b
E
55a-60a
Z
21a-b, 10 and 60b
E
47-53
61a-66a
Z
61b-66b
E
40-46

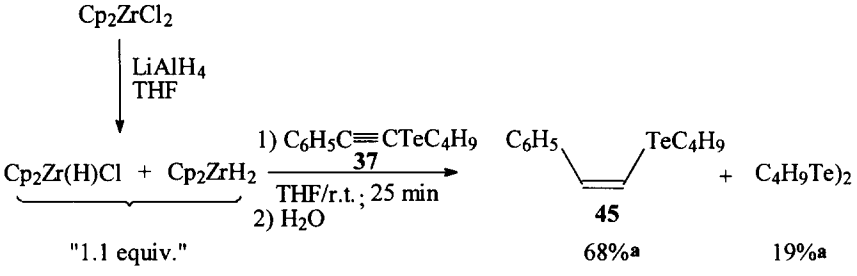
described above (Cp_2ZrCl_2 + $LiAlH_4$; no washing the mixture with CH_2Cl_2). In this case the reaction of **37** is total because the cleavage of the Csp-Te bond occurs and more active hydrides are present in the reaction due to the Cp_2ZrH_2. The products were isolated by column chromatography on SiO_2 using hexane as eluent showing that **45** and the dibutylditelluride were formed in 68% and 19% isolated yield respectively (Scheme 6). The results discussed above show that hydrozirconation follows a different pathway reaction than hydroalumination[14] of the same compound.

Table 3. (Z)-Vinylic tellurides and ketenetelluroacetals obtained from telluroalkynes.

Entry	Vinylic telluride	reaction time (min)	Yield (%)[a]	Ketenetelluro acetal	Yield (%)[a]
1	 **40**	10	92[ref. 23]	 **47**	79
2	 **41**	15	91	 **48**	74
3	 **42**	15	91	 **49**	70
4	 **43**	15	90	 **50**	74
5	 **44**	15	86	 **51**	77
6	 **45**	18	81[ref. 14,23]	 **52**	73
7	 **46**	30	80[ref.14,15]	 **53**	70

[a]Isolated yields.

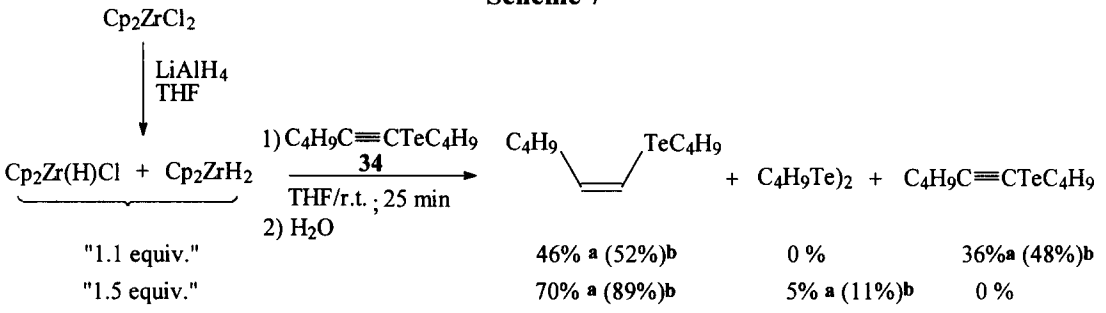
Scheme 6



a. Isolated Yield.

A similar reaction was performed employing the 1-butyltelluro-1-hexyne **34** (Scheme 7) and this compound was less reactive as observed using "1.1 equivalent" of the mixture of hydrides. In this case the acetylenic telluride was recovered in 36% and the vinylic derivative was isolated in 46% yield by column chromatography (Scheme 7) indicating that the Csp-Te bond was no cleaved to form dibutylditelluride. Employing "1.5 equivalents" of the same mixture the starting material undergoes total transformation and the vinylic telluride derivative was isolated in 70% yield. Only under the last conditions, the partial cleavage of the Csp-Te bond of a butyltelluro alkylacetylene was observed. In this case the dibutylditelluride was isolated in 5 % yield (Scheme 7).

Scheme 7

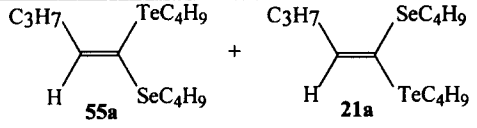
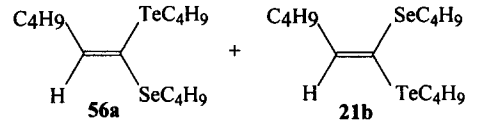
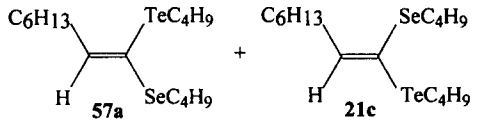
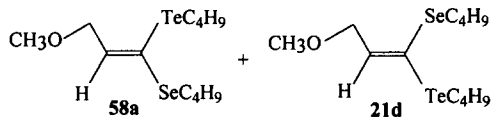
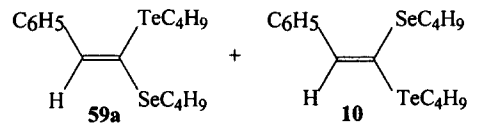
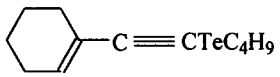
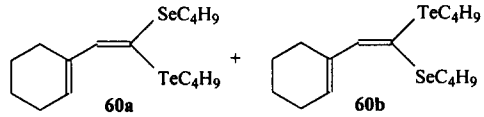


a. Isolated Yield. b. Determined by GC.

The α-zirconated vinyl tellurides **39** were also reacted with butylselenenyl bromide prepared *in situ* giving the ketene butyltelluro(butylseleno) acetals **55a-60a, 21a-21d, 10 and 60b** in 61-69 % yield (Table 4). In the last reaction only one regioisomer was formed, but two stereoisomers (***E*** and ***Z***) were detected, showing that in contrast to the Zr/Te exchange reaction discussed above which occurs with total retention of configuration, the retention of configuration in the Zr/Se exchange reaction on intermediates of type **39** is only partial and the compound formed with inversion of configuration was the major product, the phenyl derivative being one exception (Table 4, entry 5).

Contrary to the regioisomers **21** and **22 (a-c)** obtained by the hydrozirconation of acetylenic selenides, followed by the Zr/Te exchange reaction, the stereoisomers ***E*** and ***Z*** of compounds obtained by the hydrozirconation of acetylenic tellurides followed by the Zr/Se exchange reaction (Table 4) were unseparable by chromatography on silica gel using a variety of solvents as eluent.

Table 4. Selenotelluroketeneacetals obtained from telluroalkynes.

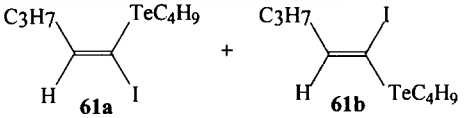
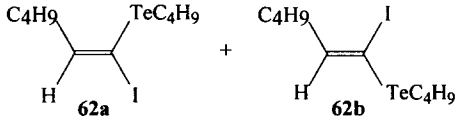
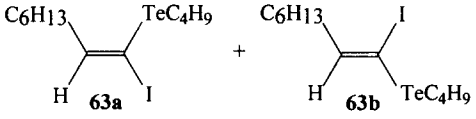
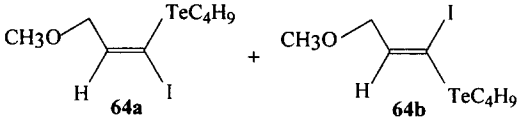
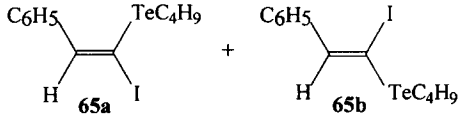
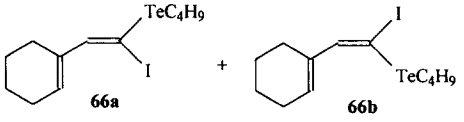
entry	Acetylenic telluride	Selenotelluroketeneacetals	Z:E ratio[a]	Yield (%)[b]
1	$C_3H_7C\equiv CTeC_4H_9$ **33**	 **55a** + **21a**	**35:65**	**65**
2	$C_4H_9C\equiv CTeC_4H_9$ **34**	 **56a** + **21b**	**36:64**	**69**
3	$C_6H_{13}C\equiv CTeC_4H_9$ **35**	 **57a** + **21c**	**40:60**	**66**
4	$CH_3OCH_2C\equiv CTeC_4H_9$ **36**	 **58a** + **21d**	**30:70**	**64**
5	$C_6H_5C\equiv CTeC_4H_9$ **37**	 **59a** + **10**	**65:35**	**66**
6	 **38**	 **60a** + **60b**	**37:63**	**61**

[a]Ratio determined by GC. [b]Yield of the stereoisomeric mixture

On the other hand, iodinolysis of the Csp^2-Zr bond in **39** with I_2 affords the 1-iodo-1-butyltelluro-1-alkenes **61-66(a,b)** in 73-81 % yield, as mixtures of ***E:Z*** isomers (Scheme 5) in ratios determined by ^1H NMR as shown in Table 5. In all cases, the isomers formed with retention of configuration **61a-66a** were the principal products. In all cases the crude products were treated with a saturated sodium thiosulphate solution[25] or with $NaBH_4$[26] to remove the iodine excess. Analytical

samples of products were obtained by purification using preparative thin layer chromatography and hexane as eluent, but the stereoisomers obtained were unseparable.

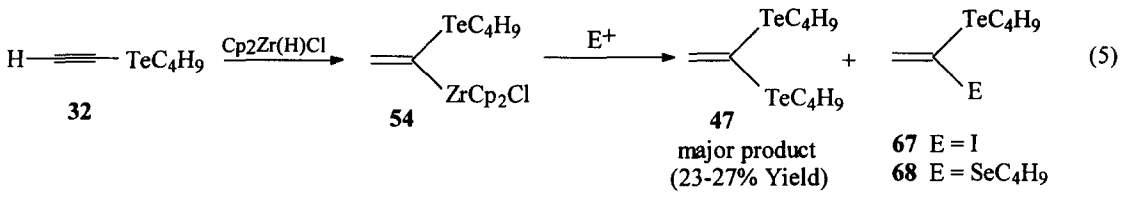
Table 5. 1-Telluro-1-iodoethenes obtained from telluroalkynes.

entry	Products	a:b ratio[a]	Yield (%)[b]
1	 **61a** + **61b**	**90:10**	**80**
2	 **62a** + **62b**	**86:14**	**77**
3	 **63a** + **63b**	**80:20**	**80**
4	 **64a** + **64b**	**90:10**	**76**
5	 **65a** + **65b**	**95:5**	**81**
6	 **66a** + **66b**	**100:0**	**73**

[a]Ratio determinated by ^{1}H NMR. [b]Yield of the stereoisomeric mixture

Reaction of intermediate **54** (obtained by hydrozirconation of **32**) with iodine or butylselenenyl bromide as electrophiles (Eq. 5) result in a mixture of the ketenetelluroacetal **47** as the major product and the expected 1-iodo-1-butyltelluroethene **67** or 1-butylseleno-1-butyltelluroethene **68**. The presence of **67** or **68** was detected using a thiosulphate solution during extraction, to remove the iodine excess and/or to transform the dihalogenated tellurium species formed due to the presence of halogens sources in both reactions, but using $NaBH_4$ to perform the same operation, the exclusive formation of **47** was observed in the two cases.

It should be noted that an extra tellurium atom is incorporated in the major product, and there is no source of tellurium in the reaction other than the starting material **32**. In this way, the maximum yield for this transformation is 50%. However, the mechanism pathway for this transformation is unknown to us.

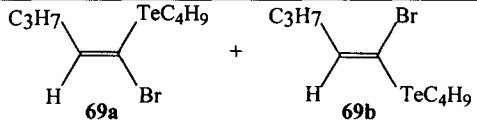
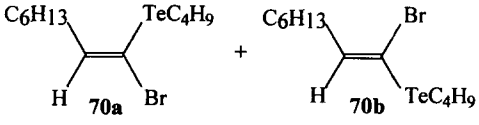


(5)

The brominolysis of the Csp^2-Zr bond on intermediates of type **39** was conveniently achieved with N-bromosuccinimide (NBS) to produce the corresponding 1-bromo-1-butyltelluro-1-ethenes **69-70 (a,b)** in 69-73% yield since reaction with bromine gives a complex mixture of products. In this case two stereoisomers were also formed, and we believe that this occurs during the halogenolysis step. Compounds **69-70** were obtained as a mixture of ***Z/E*** isomers as determined by ^1H NMR (Table 6).

The fact that only (***Z***)-vinylic tellurides were obtained by treatment with water and that different ratios of the isomers were obtained in reactions with I_2, NBS and C_4H_9SeBr are evidence that only intermediates of type **39** are formed, and the lack of retention of configuration in reactions with I_2, NBS and C_4H_9SeBr as electrophiles is responsible for the formation of mixtures.

Table 6. 1-Telluro-1-bromoethenes obtained from telluroalkynes.

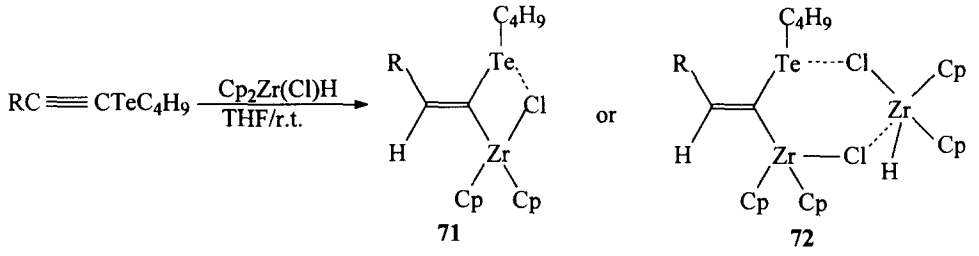
entry	Products	a:b ratio[a]	Yield (%)[b]
1	 **69a** + **69b**	**55:45**	**80**
2	 **70a** + **70b**	**56:44**	**77**

[a]Determinated by ^1H NMR. [b]Isolated yields of the stereoisomeric mixture.

A plausible mechanism to explain the exclusive formation of the α-zirconated vinyl telluride **39** is based on the great affinity of tellurium for halogens.[27,28] Thus, by analogy with the formation of a cyclic intermediate in hydrozirconation of alkynylzinc bromides,[5] we believe that reaction of alkynyltellurides with $ZrCp_2(H)Cl$ proceeds *via* a cyclic intermediate such as **71** or **72** (Scheme 8). Although the proposed mechanism is hypothetical, both intermediates could be formed by the great affinity of tellurium for halogens[27,28] and the formation of a six member cyclic intermediate **72** can explain better why two equivalents of $ZrCp_2(H)Cl$ are necessary. If similar cyclic intermediates are

formed during the hydrozirconation of selenoacetylenes, they are not as efficient as the tellurium analogous compounds.

Scheme 8



EXPERIMENTAL SECTION

General remarks. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 80 MHz, 300 MHz or a 400 MHz spectrometer as noted. Chemical shifts are expressed as parts per million (ppm) with respect to tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/GC HP-5988A spectrometer. Elemental analyses were performed at the Instrumental Analysis Center of the Chemistry Institute of São Paulo University. Reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Analytical TLC of all reactions was performed using E. M. Merck prepared plates (silica gel 60 F-254 on aluminum). Merck silica gel (230-400 mesh) was used for flash chromatography. Tetrahydrofuran (THF) was distilled over sodium/benzophenone immediately before use. The 1-alkynes, n-butyllithium (2.5 M in hexanes) and Cp_2ZrCl_2 and $Cp_2Zr(H)Cl$ were purchased from Aldrich Chemical Co., Inc. Dibutylditelluride,[29] $Cp_2Zr(H)Cl$,[17] acetylenic tellurides[24] and selenides[30] were prepared by methods reported in the literature.

Preparation of the butyltellurenyl bromide or butylselenenyl bromide solution. To a solution of dibutyl ditelluride[29] (0.369 g; 1.0 mmol) in THF (10 mL) cooled at 0 °C a solution of bromine (0.16 g; 1.0 mmol) in benzene (10 mL) was added, after stirring for 10 min, the solution of butyltellurenyl bromide was transferred *via* syringe to the chalcogenovinyl zirconium derivatives as described below.

General procedure for the synthesis of telluroseleno ethenes from acetylenic selenides. To a mixture of $Cp_2Zr(H)Cl$ (0.51 g; 2.0 mmol) in THF (6.0 mL) under nitrogen, a solution of the corresponding butylselenoacetylene (1.0 mmol) in THF (2.0 mL) was added *via* syringe. The reaction

was stirred at room temperature for the time indicated in Table 2 until the total transformation of the starting material was confirmed following the reaction by TLC on SiO_2 using hexane as eluent. Then the resulting clear yellow solution formed was cooled at 0 °C and a solution of butyltellurenyl bromide (2.0 mmol) prepared separately as described above was transferred *via* syringe. The stirring was continued for an additional 15 min, the mixture transferred to an Erlenmeyer flask, diluted with ethyl acetate (10 mL), 95% ethanol (5 mL) and water (10 mL). Butylbromide (0.32 mL; 3.0 mmol) and finally $NaBH_4$ (0.09 g; 3.0 mmol) were added to transform the dibutylditelluride to the corresponding telluride which is more easily removed by distillation. After this treatment the product was extracted with ethyl acetate (5 x 20 mL) and washed with water (5 x 20 mL), the organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. The dibutyltelluride was removed by distillation of the crude product using a Kugelrohr apparatus. The residue is constituted by the telluroseleno ethenes described below which were obtained as yellow liquids after purification by flash chromatography using hexane as eluent in all cases.

(*E*)-1-butyltelluro-2-butylselenoethene 7a. Yield: 0.28 g (81%); GC/MS m/z 348 (19.87), 291 (16.35) 235 (26.72), 57 (100.00); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.92 (t, J = 7.5 Hz, 3H), 0.93(t, J = 7.5 Hz, 3H), 1.38 (sext., J = 7.5 Hz, 2H), 1.41(sext., J = 7.5 Hz, 2H), 1.70 (quint., J = 7.5 Hz, 2H), 1.78 (quint., J = 7.5 Hz, 2H), 2.74 (t, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 15.8 Hz, 1H), 7.04 (d, J = 15.8 Hz, 1H). ^{13}C NMR 7.4, 13.3, 13.5, 22.9, 24.9, 26.1, 32.4, 33.9, 95.3, 129.7; Anal Calcd. for $C_{10}H_{20}TeSe$: C 34.63, H 5.81. Found: C 35.02, H 5.44.

(*E*)-1-Butyltelluro-2-phenylselenoethene 7b. Yield: 0.24 g (66%); GC/MS m/z 368 (48.66), 366 (41.49), 285 (36.85), 283 (29.10), 208 (36.18), 103 (67.27), 77 (100.00); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.0 Hz, 3H), 1.39 (sext., J = 7.0 Hz, 4H), 1.78 (quint, J = 7.0 Hz, 2H), 2.77(t, J = 7.0 Hz, 2H), 7.01(d, J = 16.0 Hz, 1H), 7.08(d, J = 16 Hz, 1H), 7.2-7.3(m, 3H), 7.4-7.5(m, 2H); ^{13}C NMR 7.4, 13.3, 25.0, 33.9, 68.2, 100.1, 127.5, 127.8, 129.3, 132.8, Anal Calcd. for $C_{12}H_{16}TeSe$: C 39.29, H 4.40. Found: C 39.65, H 4.47.

(*E*)-1-butyltelluro-1-butylseleno-2-phenylethene 10. Yield: 0.26 g (63%); GC/MS m/z 426 (14.92), 290 (6.55), 238 (20.36), 102 (62.62), 57 (100.00); ^{1}H NMR (300 MHz) (δ in CDCl3) 0.85 (t, J = 7.20, 1H), 0.92 (t, J = 7.22 Hz, 3H), 1.34 (sext., J = 7.22, 2H), 1.42 (sext., J = 7.22 Hz, 2H), 1.61 (quint., J = 7.22 Hz, 2H), 1.79 (quint., J = 7.22 Hz, 2H), 2.76 (t, J = 7.22 Hz, 2H), 2.92 (t, J = 7.22 Hz, 2H), 7.2-7.4 (m, 3H), 7.5 (m, 2H), 7.71 (s, 1H); ^{13}C NMR 11.9, 13.5, 13.6, 23.1, 25.2, 32.2, 33.11, 33.6,

102.29, 127.3, 128.3, 128.8, 138.9, 145.8; Anal Calcd. for $C_{16}H_{24}TeSe$: C 45.44, H 5.72. Found: C 45.63, H 5.58.

(*E*)-1-butyltelluro-1-butylseleno-1-pentene 21a. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.93 (t, J = 7.3, 6H), 1.3-1.5 (m, 4H), 1.62 (quint., J = 7.3 Hz, 2H), 1.79 (quint., J = 7.3 Hz, 2H), 2.31 (q, J = 7.1, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 6.68 (t, J = 7.1 Hz, 1H); ^{13}C NMR 10.9, 14.1, 14.3, 22.9, 23.5, 25.7, 31.8, 33.0, 33.1, 34.2, 37.2, 98.6, 152.1; Anal Calcd. for $C_{13}H_{26}TeSe$: C 40.15, H 6.74. Found: C 40.48, H 6.82.

(*E*)-1-butylseleno-2-butyltelluro-1-pentene 22a. GC/MS m/z 392 (47.12), 322 (62.15), 266 (81.45), 208 (43.10), 57 (100.00). ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.9-1.0 (m, 9H), 1.39 (sext., J = 7.3 Hz, 2H), 1.42 (sext., J = 7.3 Hz, 2H), 1.55 (sext., J = 7.3 Hz, 2H), 1.69 (quint., J = 7.3 Hz, 2H), 1.77 (quint., J = 7.3 Hz, 2H), 2.34 (t, J = 7.3 Hz, 2H), 2.73 (t, J = 7.3 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H), 6.78 (s, 1H); ^{13}C NMR 8.2, 14.0, 14.1, 14.2, 22.9, 23.4, 25.7, 27.5, 33.6, 34.5, 43.1, 115.6, 126.5; Anal Calcd. for $C_{13}H_{26}TeSe$: C, 40.15, H 6.74. Found: C 40.52, H 6.83.

(*E*)-1-butyltelluro-1-butylseleno-1-hexene 21b. MS/GC m/z 406 (5.09), 267 (6.96), 202 (16.46), 149 (98.50), 57 (100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.85-0.95 (m, 9H), 1.3-1.5 (m, 8H), 1.62 (quint., J = 7.3 Hz, 2H), 1.78 (quint., J = 7Hz, 2H), 2.33 (q, J = 7.3 Hz, 2H), 2.73 (t, J = 7.3 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H); Anal Calcd. for: $C_{14}H_{28}TeSe$: C 41.73, H 7.00. Found: C 41.99, H 6.67.

(*E*)-1-butylseleno-2-butyltelluro-1-hexene 22b. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.92 (t, J = 7.7 Hz, 9H), 1.25-1.60 (m, 8H), 1.60-1.80 (m, 4H), 2.36 (t, J = 7.7 Hz, 2H), 2.72 (t, J = 7.7 Hz, 2H), 2.75 (t, J = 7.7Hz, 2H), 6.75 (s, 1H); ^{13}C NMR 8.2, 14.0, 14.1, 14.6, 22.7, 23.4, 25.7, 27.5, 31.8, 33.6, 34.5, 40.9, 115.8, 129.1; Anal Calcd. for $C_{14}H_{28}TeSe$: C 41.73, H 7.00. Found: C 41.91, H 6.64.

(*E*)-1-butyltelluro-1-butylseleno-1-octene 21c. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.8-1.0 (m, 9H), 1.2-1.5 (m, 8H), 1.63 (quint. J = 7.3 Hz, 2H), 1.81 (quint, J = 7.3 Hz, 2H), 2.31 (q, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H); ^{13}C NMR 10.8, 14.1, 14.3, 14.7, 23.2, 23.5, 25.7, 29.4, 29.6, 31.7, 32.3, 33.1, 34.2, 35.3, 98.4, 152.4; Anal Calcd. for $C_{16}H_{32}TeSe$: C 44.59, H 7.48. Found: C 44.92, H 7.32.

(*E*)-1-butylseleno-2-butyltelluro-1-octene 22c. MS/GC m/z 434 (26.21), 375 (7.79), 322 (8.57), 247 (4.53) 109 (73.17), 57 (83.76), 41 (100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.9-1.2 (m, 9H), 1.10-

1.25 (m, 12H), 1.70 (quint, J = 7.3 Hz, 2H), 1.76 (quint, J = 7.3 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 2.72 (t, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 6.75 (s, 1H); ^{13}C NMR 8.2, 14.0, 14.1, 14.6, 23.2, 23.4, 25.7, 27.5, 29.2, 29.5, 32.3, 33.6, 34.5, 41.0, 115.9, 126.5; Anal Calcd. for $C_{16}H_{32}TeSe$: C 44.92, H 7.48. Found: C 44.30, H 7.23.

(*E*)-1-butyltelluro-1-butylseleno-2-methoxymethyl ethene 21d and 1-butylseleno-2-butyltelluro-2-methoxymethyl ethene 22d. These isomers were not separated. MS/GC m/z for the first isomer: 394 (30.92), 335 (52.58), 247 (100.00), 57 (80.23), for the second isomer: 392 (22.87), 249 (28.30), 177 (77.73), 57 (57.56), 41 (100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) the presence of two isomers was confirmed by the following signals: two peaks corresponding to the methoxy groups (at 3.34 ppm and 3.35 ppm), allylic and vinylic protons in compound **21d**: 4.17 (d, J = 6.0 Hz, 2H), 6.73 (t, J = 6.0 Hz, 1H) and in compound **22d**: 4.13 (d, J = 1.7 Hz, 2H), 6.82 (t, J = 1.7 Hz, 1H); ^{13}C NMR only vinylic carbons, for **21d**: 103.1, 145.8 and for **22d**: 112.3, 128.3; Anal Calcd. for $C_{12}H_{24}TeSeO$: C 36.87, H 6.19. Found: C 36.97, H 6.04.

General procedure for the synthesis of (*Z*)-vinylchalcogenides from acetylenic chalcogenides. To a mixture of $Cp_2Zr(H)Cl$ (0.51 g; 2.0 mmol) in THF (6.0 mL) under nitrogen, a solution of the corresponding acetylenic chalcogenide (1.0 mmol) in THF (2.0 mL) was added *via* syringe. The reaction was stirred at room temperature for the time indicated in Table 2 (for selenides) or Table 3 (for tellurides). The total transformation of the starting material was confirmed following the reaction by TLC on SiO_2 using hexane as eluent. Then, the reaction mixture was treated with water (2.0 mL), diluted with ethyl acetate (150 mL) and washed with a saturated solution of ammonium chloride (3 x 50 mL). The organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. After purification by flash chromatography using hexane as eluent, the products were obtained as yellow oils in yield listed in Table 2 (for selenides) and Table 3 (for tellurides).

Butylseleno ethene 25. Yield: 0.13 g (81%); GC/MS m/z 164(32.79), 162(14.47), 119(13.66), 117(11.72), 108(100.0), 57(52.20), 41(83.82); ^1H NMR (400 MHz) (δ in $CDCl_3$) 0.93 (t, J = 7.0 Hz, 3H), 1.43 (sext., J = 7.0 Hz, 2H), 1.70(quint., J = 7.0 Hz, 2H), 2.74 (t, J = 7.0 Hz, 2H), 5.43 (d, J = 17 Hz, 1H), 5.66 (d, J = 10.0 Hz, 1), 6.769 (dd, J = 17.0 Hz, J = 10.0 Hz, 1H). ^{13}C NMR 13.5, 22.9, 24.9, 32.2, 116.6, 126.9.

Phenylseleno ethene 24. Yield: 0.12 g (64%); GC/MS m/z 184(93.38), 183(100.00), 182(51.17), 157(17.97), 104(41.66); ^1H NMR (300 MHz) (δ in $CDCl_3$) 5.55 (d, J = 16Hz, 1H); 5.78 (d, J = 9.0

Hz, 1H); 6.85 (dd, J = 16 Hz, J = 9.0 Hz, 1H); 7.3 (m, 3H), 7.5(m, 2H); ^{13}C NMR 119.4, 126.7, 127.6, 128.9, 132.5, 133.0; Anal Calcd. for C_8H_8Se: C 52.48, H 4.40. Found: C 52.86, H 4.64.

(*Z*)-1-Butylseleno-1-pentene 26. Yield: 0.17 g (82%). GC/MS m/z 206(29.50), 204(15.30), 177(16.63), 175(9.29), 150(12.99), 149(19.10), 121(49.15), 119(24.47), 69(100.00); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.91(t, J = 7.0 Hz, 6H), 1.4-1.5(m, 4H), 1.73(quint., J = 7.0 Hz, 2H), 2.70 (t, J = 7.0 Hz, 2H), 5.90 (dt, J= 9.0 Hz, J = 6.0 Hz, 1H), 6.24(d, J = 9.0 Hz, 1H); ^{13}C NMR 13.4, 20.4, 21.1, 21.9, 22.4, 26.0, 32.9, 120.2, 132.6; Anal Calcd. for $C_9H_{18}Se$: C 52.68, H, 8.84. Found: C 53.05, H 8.99.

(*Z*)-1-Butylseleno-1-hexene 27. Yield: 0.19 g (86%). GC/MS m/z 383(1.18), 381(3.82), 301(3.00), 299(1.59), 81(23.66), 57(40.46), 41(100.00); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.90(t, J = 7.2 Hz, 3H), 0.92(t, J = 7.2 Hz, 3H), 1.2-1.5(m, 6H), 1.6-1.8(m, 2H), 2.10(dq, J = 7.2 Hz, J = 1.3 Hz, 2H), 2.66(t, J = 7.2 Hz, 2H), 5.86(dt, J = 8.9 Hz, J = 6.8 Hz, 1H), 6.20(dt, J = 8.9 Hz, J = 1.3 Hz, 1H); ^{13}C NMR 13.5, 13.9, 22.3, 22.8, 26.2, 30.9, 31.0, 33.0, 120.1, 133.1; Anal Calcd. for $C_{10}H_{20}Se$: C 54.79, H 9.20. Found: C 54.47, H 8.92.

(*Z*)-1-Butylseleno-1-octene 28. Yield: 0.22 g (89%). GC/MS m/z 248(15.41), 191(9.84), 177(11.65), 135(20.86), 121(35.91), 69(100.00), 57(33.40); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.88(t, J = 7.4 Hz, 3H), 0.92(t, J = 7.4 Hz, 3H), 1.2-1.5(m, 10H), 1.68(quint., J = 7.4 Hz, 2H), 2.07(dq, J = 7.4 Hz, J = 1.23 Hz, 2H), 2.66(t, J = 7.4 Hz, 2H), 5.86(dt, J = 8.98 Hz, J = 7.0 Hz, 1H), 6.20(dt, J = 8.98 Hz, J = 1.23 Hz, 1H), ^{13}C NMR 13.6, 14.1, 22.6, 23.1, 26.2, 28.8, 28.9, 31.3, 31.7, 33.0, 120.1, 133.1; Anal Calcd. for $C_{12}H_{24}Se$: C 58.29, H 9.78. Found: C 58.33, H 9.70.

(*Z*)-1-Butylseleno-2-cyclohexenyl ethene 29. Yield: 0.2 g (83%). GC/MS m/z 244(16.37), 187(100.00), 145(36.15), 105(21.30); ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.89(t, J = 3H), 1.1-2.4(m, 12H), 2.65(t, J = 7.0 Hz, 2H), 5.71(m, 1H), 6.09(d, J = 11.0 Hz, 1H), 6.30(d, J = 11.0 Hz, 1H). Compound **29** undergoes isomerization after some time.[15]

(*Z*)-1-Butylseleno-3-methoxy-1-propene 30. Yield: 0.18 g (87%). GC/MS m/z 210(1.09), 208(6.13), 151(9.97), 71(100.00), 41(77.39); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.4 Hz, 3H), 1.41(sext, J = 7.4 Hz, 2H), 1.68(quint, J = 7.4 Hz, 2H), 2.69(t, J = 7.4 Hz, 2H), 3.35(s, 3H), 3.98(d, J = 5.7 Hz, 2H), 6.02(dt, J =9.7 Hz, J = 5.7, 1H), 6.49(d, J = 9.7 Hz, 1H); ^{13}C NMR 13.5, 22.7, 26.9, 32.9, 58.0, 70.9, 124.1, 128.5; Anal Calcd. for $C_8H_{16}SeO$: C 46.15, H 7.75. Found: C 45.96, H 7.34.

(*Z*)-1-Butylseleno-2-phenyl ethene 31. Yield: 0.19 g (81%). GC/MS m/z 240(90.97), 238(38.77), 184(85.78), 183(100.0), 182(61.40), 181(56.23), 103(18.99), 102(31.69); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.4 Hz, 3H), 1.42(sext., J = 7.4 Hz, 2H), 1.72(quint., J = 7.4 Hz, 2H), 2.76(t, J = 7.4 Hz, 2H), 6.59(d, J = 10.66 Hz, 1H), 6.86(d, J = 10.66 Hz, 1H), 7.20(t, J = 7.3 Hz, 1H), 7.33(t, J = 7.3 Hz, 2H), 7.40(d, J = 7.3 Hz, 2H); ^{13}C NMR 13.5, 22.7, 28.7, 32.8, 123.2, 126.8, 128.2, 129.3; Anal Calcd. for $C_{12}H_{16}Se$: C 60.25, H 6.74. Found: C 60.30, H 6.58.

(*Z*)-1-Butyltelluro ethene 40. Yield: 0.19 g (92%). ^{1}H NMR (60 MHz) (δ in $CDCl_3$) 0.93(t, J = 7.0 Hz, 3H), 1.1-2.1(m, 4H), 2.25(dd, J ~ 1.5 Hz, J ~ 1.0 3H), 2.80(t, J = 7.0 Hz, 2H), 5.38(q, J ~1Hz, 1H), 5.85(q, J ~1.5 Hz, 1H). Reference 23.

(*Z*)-1-Butyltelluro-1-pentene 41. Yield: 0.23 g (91%). GC/MS m/z 256(25.12), 254(25.37), 252(15.06), 200(14.18), 198(13.14), 69(100.0), 57(32.63); ^{1}H NMR (400 MHz) (δ in $CDCl_3$) 0.91(t, J = 7.0 Hz, 3H), 0.93(t, J = 7.0 Hz, 3H), 1.3-1.5(m, 4H), 1.77(quint., J = 7.0 Hz, 2H), 2.02(q, J = 7.0 Hz, 2H), 2.68(t, J = 7.0 Hz, 2H), 6.17(dt, J = 9.0 Hz, J = 6.0 Hz, 1H), 6.56(d, J = 9.0 Hz, 1H); ^{13}C NMR 5.8, 13.2, 13.7, 22.0, 24.9, 34.2, 37.6, 102.5, 140.4; Anal Calcd. for $C_9H_{18}Te$: C 42.59, H 7.15. Found: C 42.22, H 6.91.

(*Z*)-1-Butyltelluro-1-hexene 42. Yield: 0.24 g (91%). GC/MS m/z 270(10.69), 268(9.88), 214(4.07), 212(3.92), 171(6.97), 169(6.68), 57(34.58), 55(73.90), 41(100.00); ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.87 (t, J = 7.0 Hz, 3H), 0.91(t, J = 7.0 Hz, 3H), 1.1-2.2(m, 10H), 2.65(t, J = 8.0 Hz, 2H), 6.11 (dt, J = 9.6 Hz, J = 6.6 Hz, 1H), 6.55(dt, J = 9.3 Hz, J ~0.5 Hz, 1H); ^{13}C NMR 13.3, 22.2, 25.8, 38.4, 34.1, 102.2, 140.4; Anal Calcd. for $C_{10}H_{20}Te$: C 44.44, H 7.40. Found: C 44.33, H 7.24.

(*Z*)-1-Butyltelluro-1-octene 43. Yield: 0.26 g (90%). GC/MS m/z 270(100.00), 212(25.7, 171(49.6), 158(36.0), 130(20.3), 83(34.6), 55(81.2); ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.88(t, J = 7.0 Hz, 3H), 0.91(t, J = 7.0 Hz, 3H), 1.1-2.2(m, 14H), 2.68(t, J = 7.0 Hz, 2H), 6.12(dt, J = 9.3 Hz, J = 6.7 Hz, 1H), 6.56(dt, J = 9.3 Hz, J ~0.5 Hz, 1H); ^{13}C NMR 5.8, 22.4, 24.8, 29.7, 34.6, 102.1, 140.4; Anal Calcd. for $C_{12}H_{24}Te$: C 48.81, H 8.13. Found: C 49.12, H 8.01.

(*Z*)-1-Butyltelluro-3-methoxy-1-propene 44. Yield: 0.22 g (86%). GC/MS m/z 258(9.10), 256(11.81), 201(9.64), 199((7.94), 170(6.69), 168(9.58), 130(12.84), 128(11.81), 85(28.71), 83(25.13), 71(100.00), 57(71.92); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.2 Hz, 3H), 1.39(sext, J = 7.2 Hz, 2H), 1.78(quint, J = 7.2 Hz, 2H), 2.64(t, J = 7.2 Hz, 2H), 3.35(s, 3H), 3.91(d, J = 1.2 Hz, 2H), 6.37(dt, J = 10.1 Hz, J = 5.6 Hz, 1H), 6.88(dt, J = 10.1 Hz, J = 1.2 Hz, 1H); ^{13}C NMR

7.0, 13.4, 24.9, 33.9, 58.0, 73.9, 106.2, 134.7; Anal Calcd. for $C_8H_{16}TeO$: C 37.56, H 6.30. Found: C 37.58, H 6.24.

(*Z*)-1-Butyltelluro-2-phenyl ethene 45. Yield: 0.23 g (81%). GC/MS m/z 290(35.0), 233(7.7), 231(9.7), 104(100.0), 57(8.0); ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.85(t, J = 6.7 Hz, 3H), 1.32(sext. J = 6.7 Hz, 2H), 1.75(quint., J = 6.7 Hz, 2H), 2.62(t, J = 7.0 Hz, 2H), 6.90(d, J = 10.6 Hz, 1H), 7.25(, 5H), 7.35(d, J = 10.6 Hz, 1H); ^{13}C NMR 9.6, 13.1, 24.5, 33.5, 105.1, 128.3, 127.9, 138.2, 135.5. References 14 and 23.

(*Z*)-1-Butyltelluro-2-cyclohexenyl ethene 46. 0.23 g (80%). GC/MS m/z 294(15.2), 237(44.9), 233(25.2), 185(9.8), 145(13.0), 129(12.3), 107(100.0), 79(57.6); ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.95(t, J = 6.6 Hz, 3H), 1.1-2.3(m, 11H), 2.72(t, J = 6.6 Hz, 2H), 5.3(m, 1H), 6.45(d, J = 10.7 Hz, 1H), 6.76(d, J = 10.7, 1H); ^{13}C NMR 13.4, 22.6, 24.9, 33.5, 98.7, 122.9, 138.3, 146.4, 153.5. Anal Calcd. for $C_{12}H_{20}Te$: C 49.38, H 6.91. Found: C 49.56, H 6.97. Reference 15.

General procedure for the synthesis of bis(butyltelluro)ketene acetals. To a mixture of $Cp_2Zr(H)Cl$ (0.51 g; 2.0 mmol) in THF (6.0 mL) under nitrogen, a solution of the corresponding butyltelluroacetylene (1.0 mmol) in THF (2.0 mL) was added *via* syringe. The reaction was stirred at room temperature for the time indicated in Table 3. The total transformation of the starting material was confirmed following the reaction by TLC on SiO_2 using hexane as eluent. Then the resulting dark red solution formed was cooled at 0 °C and a solution of butyltellurenyl bromide (2.0 mmol) prepared separately as described above was transferred *via* syringe. The stirring was continued for an additional 15 min, the mixture transferred to an Erlenmeyer flask, diluted with ethyl acetate (10 mL), 95% ethanol (5 mL) and water (10 mL). Butylbromide (0.32 mL; 3.0 mmol) and finally $NaBH_4$ (0.09 g; 3.0 mmol) were added to transform the dibutylditelluride to the corresponding telluride which is more easily removed by distillation. After this treatment, the product was extracted with ethyl acetate (5 x 20 mL) and washed with water (5 x 20 mL), the organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. The dibutyltelluride was removed by distillation of the crude product using a Kugelrohr apparatus (100 °C/0.6 mmHg). The residue is constituted by the bis(telluroketene) acetals described below which were obtained as yellow liquids after purification by flash chromatography using hexane as eluent in all cases.

1,1-Bis(butyltelluro)ethene 47. Yield: 0.31 g (79%). GC/MS m/z 400 (7.37), 396 (13.47), 341 (6.96), 339 (7.74), 285 (5.56), 283 (5.54), 57 (100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.92 (t, J = 7.0 Hz,

6H), 1.38 (sext, J = 7.0 Hz, 4H), 1.80 (quint, J = 7.0 Hz, 4H), 2.79 (t, J = 7.0 Hz, 4H), 7.44 (s, 2H); ^{13}C NMR 7.6, 13.4, 25.1, 33.9, 106.5, 117.3; Anal Calcd. for $C_{10}H_{20}Te_2$: C 30.37, H 5.10. Found: C 30.45, H 5.03.

1,1-Bis(butyltelluro)pentene 48. Yield: 0.32 g (74%). ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.93 (t, J = 7.0 Hz, 9H), 1.34-1.52 (m, 6H), 1.78 (quint, J = 7.0 Hz, 2H), 1.83 (quint, J = 7.0 Hz, 2H), 2.23 (q, J = 7.0 Hz, 2H), 2.78 (t, J = 7.0 Hz, 4H), 6.72 (t, J = 7.0 Hz, 1H); ^{13}C NMR 12.4, 14.1, 14.3, 22.8, 25.8, 34.0, 34.5, 42.0, 126.5, 155.0; Anal. Calcd. for $C_{13}H_{26}Te_2$: C 35.29, H 5.93. Found: C 35.41, H 5.77.

1,1-Bis(butyltelluro)hexene 49. Yield: 0.31 g (70%). GC/MS m/z 456 (12.15), 454 (20.24), 452(23.00), 315(40.47), 313(42.45), 258(22.38), 256(23.85), 169 (19.63), 81(100.00, 57(61.38); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.93 (t, J = 7.2 Hz, 9H), 1.3-1.5 (m, 6H), 1.7-1.9 (m, 4H), 2.26(q, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H); ^{13}C NMR 14.2, 14.7, 15.8, 23.2, 25.7, 26.2, 29.0, 29.4, 32.3, 34.2, 39.9, 49.2, 126.5, 155.6; Anal Calcd. for $C_{14}H_{28}Te_2$: C 37.24, H 6.25. Found: C 37.38, H 6.04.

1,1-Bis(butyltelluro)octene 50. Yield: 0.35 g (74%). GC/MS m/z 482(3.00), 480(3.19), 406(2.04), 315(2.30), 313(2.99), 109(39.37), 57(100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.8-1.0 (m, 9H), 1.2-1.5(m, 12H), 1.78 (quint, J = 7.2 Hz, 2H), 1.82(quint, J = 7.2 Hz, 2H), 2.24 (q, J = 7.22 Hz, 2H), 2.78 (t, J = 7.2 Hz, 4H), 6.71 (t, J = 7.2 Hz, 1H); ^{13}C NMR 11.8, 13.4, 13.5, 13.7, 14.1, 22.6, 25.0, 25.2, 28.8, 31.7, 33.4, 33.9, 34.2, 39.4, 102.4, 154.6; Anal Calcd. for $C_{16}H_{32}Te_2$: C 40.07, H 6.72. Found: C 40.45, H 6.70.

1,1-Bis(butyltelluro)-3-methoxy-1-propene 51. Yield: 0.34 g (77%). GC/MS m/z 444(5.39), 441(10.74), 440(11.05), 383(3.51), 299(6.36), 297(7.50), 295(5.98), 171(10.33), 169(14.11), 167(10.33), 57(100.00); ^{1}NMR (80 MHz) (δ in $CDCl_3$) 0.90 (t, J = 7.0 Hz, 6H), 1.1-2.1 (m 8H), 2.79(t, J = 7.0 Hz, 4H), 3.32 (s, 3H), 4.05 (d, J = 5.8 Hz, 2H), 6.82 (t, J = 5.8 Hz, 1H); ^{13}C NMR 13.3, 14.1, 14.8, 25.7, 25.8, 33.9, 34.4, 58.5, 81.1, 114.5, 147.7; Anal Calcd. for $C_{12}H_{24}Te_2O$: C 32.79, H 5.50. Found: C 33.09, H 5.0.

1,1-Bis(butyltelluro)-2-phenyl ethene 52. Yield: 0.34 g (73%). GC/MS m/z 476(6.66), 474(11.75), 472(13.22), 290(15.83), 288(17.69), 233(15.68), 231(16.51), 104(38.72), 103(33.58), 57(100.00); ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.91(t, J = 7.0 Hz, 6H), 1.1-2.1(m, 8H), 2.73(t, J = 7.0 Hz, 2H), 2.92 (t, J = 7.0 Hz, 2H), 7.25(s, 5H), 7.95(s, 1H); ^{13}C NMR 13.4, 13.9, 16.1,25.4, 25.4, 25.6, 33.8, 34.1; Anal Calcd. for $C_{16}H_{24}Te_2$: C 40.75, H 5.13. Found: C 40.86, H 5.10.

1,1-Bis(butyltelluro)-2-cyclohexenyl ethene 53. Yield: 0.33 g (70%). GC/MS m/z 479(2.25), 475(2.05), 423(12.78), 421(23.31), 419(25.87), 315(6.10), 313(5.90), 235(8.65), 233(6.26), 107(24.15), 57(100.00); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.0 Hz, 6H), 1.3-1.5(m, 4H), 1.5-1.7(m, 4H), 1.7-1.9(m, 4H), 2.0-2.2(m, 4H), 2.80(t, J = 7.0 Hz, 2H), 2.82(t, J = 7.0 Hz, 2H), 5,.57(m, 1H), 7.30(s, 1H); ^{13}C NMR 12.5, 14.1, 14.2, 15.7, 22.6, 23.1, 25.8, 25.9, 28.7, 33.9, 34.4, 128.8, 141.0, 154.4; Anal Calcd. for $C_{16}H_{28}Te_2$: C 40.00, H 5.88. Found: C 39.89, H 5.64.

General procedure for the synthesis of telluroseleno ethenes from acetylenic telurides. To a mixture of $Cp_2Zr(H)Cl$ (0.51 g; 2.0 mmol) in THF (6.0 mL) under nitrogen, a solution of the corresponding butyltelluroacetylene (1.0 mmol) in THF (2.0 mL) was added *via* syringe. The reaction was stirred at room temperature for the time indicated in Table 2. The total transformation of the starting material was confirmed following the reaction by TLC on SiO_2 using hexane as eluent. Then the resulting dark red solution formed was cooled at 0 °C and a solution of butylselenenyl bromide (2.0 mmol) prepared separately as described above was transferred *via* syringe. The stirring was continued for an additional 15 min, the mixture transferred to an Erlenmeyer flask, diluted with ethyl acetate (10 mL), 95% ethanol (5 mL) and water (10 mL). Butylbromide (0.32 mL; 3.0 mmol) and finally $NaBH_4$ (0.09 g; 3.0 mmol) were added to transform the dibutyldiselenide to the corresponding selenide which is more easily removed by distillation. After this treatment the product was extracted with ethyl acetate (5 x 20 mL) and washed with water (5 x 20 mL), the organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under vacuum. The dibutylselenide was removed by distillation of the crude product using a Kugelrohr apparatus (70 °C/0.6 mmHg). The residue is constituted by the ketene telluroseleno acetals described below which were obtained as yellow liquids after purification by flash chromatography using hexane as eluent in all cases.

(*Z*)-1-Butyltelluro-1-butylseleno-1-butene 55a. Isomer **55a** was not separated from **21a**. GC/MS 392(47.12), 390(57.88), 324(49.14), 322(62.15), 268(58.29), 266(81.45), 147(45.97), 57(100.00); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.92 (t, J = 7.0 Hz, 9H), 1.3-1.5 (m, 6H), 1.7-1.9 (m, 4H), 2.21 (q, J = 7.0 Hz, 2H), 2.78 (t, J = 7.0 Hz, 2H), 2.82(t, J = 7.0 Hz, 2H), 6.30 (t, J = 7.0 Hz, 1H); ^{13}C NMR only vinylic carbons: 127.0, 147.0.

(*Z*)-1-Butyltelluro-1-butylseleno-1-hexene 56a. Isomer **56a** was not separated from **21b**. ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.91 (t, J = 7.1 Hz, 9H), 1.3-1.5 (m, 6H), 1.7-1.9 (m, 4H), 2.22 (q, J = 7.3

Hz, 2H), 2.78 (t, J = 7.1 Hz, 2H), 2.82 (t, J = 7.1 Hz, 2H), 6.30 (t, J = 7.3 Hz, 1H); ^{13}C NMR only vinylic carbons: 147.1, 155.2.

(*Z*)-1-Butyltelluro-1-butylseleno-1-octene 57a. Isomer **57a** was not separated from **21c**. GC/MS m/z 434(4.28), 432(5.87), 177(25.45), 109(100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.88 (t, J = 7.5 Hz, 9H), 1.2-1.5 (m, 12H), 1.6-1.9(m, 4H), 2.22 (q, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 2.82 (t, J = 7.5 Hz, 2H), 6.29 (t, J = 7.5 Hz, 1H); ^{13}C NMR only vinylic carbons: 147.1, 155.4.

(*Z*)-1-Butyltelluro-1-butylseleno-3-methoxy-1-propene 58a. Isomer **58a** was not separated from **21d**. GC/MS m/z 394(18.23), 392(23.85), 251(25.48), 249(36.90), 179(19.14), 177(88.32), 121(63.55), 119(100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.5 Hz, 6H), 1.3-1.5 (m, 4H), 1.7-1.9 (m, 4H), 2.79 (t, J = 7.5 Hz, 2H), 2.81 (t, J = 7.5 Hz, 2H), 3.35 (s, 3H), 4.05(d, J = 5.6 Hz, 2H), 6.34 (t, J = 5.6 Hz, 1H); ^{13}C NMR only olefinic carbons: 138.3, 147.6; Anal Calcd. for $C_{12}H_{24}TeSeO$: C 36.89, H 6.19. Found: C 37.30, H 5.86.

(*Z*)-1-butyltelluro-1-butylseleno-2-phenyl ethene 59a. Isomer **59a** was not separated form **10**. GC/MS m/z 422(2.05), 258(2.18, 102(29.71), 57(100.00); ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.90 (t, J = 7.0 Hz, 6H), 1.1-2.1(m, 8H), 2.68(t, J = 7.0 Hz, 2H), 2.82(t, J = 7.0 Hz, 2H), 7.0-7.4(m, 5H), 7.94(s, 1H).

(*Z*)-1-butyltelluro-1-butylseleno-2-cyclohexenyl ethene 60. Isomer **60a** was not separated from **60b**. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.89(t, J = 7.0 Hz, 6H), 1.3-2.3(m, 8H), 2.82(t, J = 7.0 Hz, 2H0, 2.84(t, J = 7.0Hz, 2H), 5.55(m, 1H), 6.84(s, 1H).

(*E*)-1-butyltelluro-1-butylseleno-2-cyclohexenyl ethene 60b. Isomer **60b** was not separated from **60a**. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.89(t, J = 7.0 Hz, 6H), 1.3-2.3(m, 8H), 2.82(t, J = 7.0 Hz, 2H0, 2.84(t, J = 7.0Hz, 2H), 5.72(m, 1H), 7.12(s, 1H).

General procedure for the synthesis of 1-halo-1-telluro ethenes from acetylenic telurides. To a mixture of $Cp_2Zr(H)Cl$ (0.51 g; 2.0 mmol) in THF (6.0 mL) under nitrogen, a solution of the corresponding butyltelluroacetylene (1.0 mmol) in THF (3.0 mL) was added *via* syringe. The reaction was stirred at room temperature for the time indicated in Table 3. The total transformation of the starting material was confirmed following the reaction by TLC on SiO_2 using hexane as eluent. Then, the resulting dark red mixture formed was treated at room temperature with a solution of iodine or NBS (3.0 mmol) in THF (5.0 mL), transferred *via* syringe. The stirring was continued for an

additional 30 min, the mixture transferred to an Erlenmeyer flask, diluted with ethyl acetate (10 mL), 95% ethanol (10 mL) and water (5 mL) and finally $NaBH_4$ (0.09 g; 3.0 mmol) was added to remove the electrophile excess and to perform the dehalogenation of the tellurium atom. After this treatment the product was extracted with ethyl acetate (5 x 30 mL) and washed with water (5 x 50 mL), the organic phase was dried over anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure. The residue is constituted by the 1-butyltelluro-1-halo ethenes described below which were obtained as yellow liquids after purification by flash chromatography using hexane as eluent in all cases.

1-Iodo-1-butyltelluro-1-pentenes 61a and 61b. These isomers were not separated. GC/MS m/z 383(4.72), 382(53.56), 380(44.69), 257(67.13), 255(100.00), 253(70.05), 199(33.09), 197(38.333), 185(31.72), 183(28.08), 57(39.95); ^1H NMR (300 MHz) ($CDCl_3$) 0.91(t, J = 7.0 Hz, 3H), 0.94(t, J = 7.0 Hz, 3H), 1.45(sext., J = 7.0 Hz, 4H), 1.85(quint., J = 7.0 Hz, 2H), 2.01(q, J = 7.0 Hz, 2H), 2.90(t, J= 7.0 Hz, 2H), olefinic protons are differents, for **61a**: 7.03(t, J = 7.0 Hz, 1H) while for **61b**: 6.62(t, J = 7.0 Hz, 1H); Anal calcd. for $C_9H_{17}TeI$: C 28.47, H 4.51. Found: C 28.85, H 4.55.

1-Iodo-1-butyltelluro-1-hexenes 62a and 62b. These isomers were not separated. GC/MS m/z 396(46.64), 395(42.12), 392(25.77), 257(48.17), 255(47.92), 253(28.38), 81(100.00), 57(36.19); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.90(t, J = 7.0 Hz, 3H), 0.95(t, J = 7.0 Hz, 3H), 1.3-1.4(m, 6H), 1.82(sext, J = 7.0 Hz, 2H), 2.03(q, J = 7.0 Hz, 2H), 2.88(t, J = 7.0 Hz, 2H), olefinic protons are differents, for **62a**: 7.03(t, J = 7.0 Hz, 1H), while for **62b**: 6.61(t, J = 7.0 Hz, 1H). Anal Calcd. for $C_{10}H_{19}TeI$: C 30.50, H 4.86. Found: C 30.89, H 4.88.

1-Iodo-1-butyltelluro-1-octenes 63a and 63b. These isomers were not separated. GC/MS m/z 424(4.87), 422(4.26), 295(2.08), 257(3.81), 109(96.13), 57(72.50), 41(100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.89(t, J = 7.0 Hz, 3H), 0.97(t, J = 7.0 Hz, 3H), 1.2-1.5(m, 10H), 1.84(sext, J = 7.0 Hz, 2H), 2.02(q, J = 7.0 Hz, 2H), 2.89(t, J = 7.0 Hz, 2H), olefinic protons are differents, for **63a**: 7.02(t, J = 7.0 Hz, 1H), while for **63b**: 6.60(t, J = 7.0 Hz, 1H). Anal Calcd. for $C_{12}H_{23}TeI$: C 34.17, H 5.50. Found: C 33.87, H 5.55.

1-Iodo-1-butyltelluro-3-methoxy-1-propenes 64a and 64b. These isomers were not separated. GC/MS m/z 384(47.44), 382(40.82), 327(8.44), 325(7.36), 227(73.48), 225(70.77), 171(81.48), 169(100.00), 167(75.49); ^1H NMR (80 MHz) (δ in $CDCl_3$) for **64a**: 0.92(t J = 7.0 Hz, 3H), 1.43(sext, J = 7.0 Hz, 2H), 1.85(quint, J = 7.0 Hz, 2H), 2.89(t, J = 7.0 Hz, 2H), 3.32(s, 3H), 3.81(d, J = 5.8 Hz, 3H), 7.26(t, J = 5.8 Hz, 1H); for **64b**: 0.92(t, J = 7.0 Hz, 3H), 1.43(sext, J = 7.0 Hz, 2H), 1.85(quint, J

= 7.0 Hz, 2H), 2.89(t, J = 7.0 Hz, 2H), 3.36(s, 3H), 3.96(d, J = 5.3 Hz, 2H), 6.83(t, J = 5.3 Hz, 1H); Anal Calcd. for $C_8H_{15}TeIO$: C 25.01, H 3.54. Found: C 25.05, H 4.10.

1-Iodo-1-butyltelluro-2-phenylethene 65a and 65b. These isomers were not separated. GC/MS m/z 416(10.55), 414(9.49), 412(6.02),233(21.35), 231(19.37), 103(26.14), 102(86.38), 57(100.00); 1H NMR (80 MHz) (δ in $CDCl_3$) for 61a 0.91(t, J = 7.0 Hz, 3H), 1.39(sext, J = 7.0 Hz, 2H), 1.78(quint, J = 7.0 Hz, 2H), 2.88(t, J = 7.0 Hz, 2H), 7.27(m, 5H), olefinic protons are diferents, for **65b**: 7.78(s, 1H), for **65a**: 8.29(s, 1H); Anal Calcd. for $C_{12}H_{15}TeI$: C 34.84, H 3.65. Found: C 35.25, H 3.52.

1-Iodo-1-butyltelluro-2-cyclohexenyl ethene 66a. GC/MS m/z 420(10.88), 418(9.88), 416(6.42), 363(53.26), 361(46.73), 359(29.27), 236(41.19), 234(36.91), 232(23.53), 106(50.87), 105(69.92), 57(82.77), 41(100.00); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.93(t, J = 7.7 Hz, 3H), 1.42(sext, J = 7.7 Hz, 2H), 1.61(m, 4H), 1.81(quint, J = 7.7 Hz, 2H), 2.07(m, 4H), 2.84(t, J = 7.7 Hz, 2H), 5.58(m, 1H), 7.55(s, 1H); Anal Calcd. for $C_{12}H_{19}TeI$: C 34.50, H 4.58. Found: C 34.24, H 4.43.

1-Bromo-1-butyltelluro-1-pentenes 69a and 69b. These isomers were not separated. GC/MS m/z 336(46.36), 334(100.00), 332(79.41), 330(39.21), 280(16.84), 278(31.43), 276(24.17), 211(25.30), 209(46.78), 207(37.95), 67(26.35; ^1H NMR (80 MHz) (δ in $CDCl_3$) 0.92(t, J = 7.7 Hz, 3H), 1.2-2.3(m, 8H), 2.95(t, J = 7.7 Hz, 2H), olefinic protons are diferents, for **69a**: 6.66(t, J = 7,2 Hz, 1H) and for **69b**: 6.54(t, J = 7.2 Hz, 1H); Anal Calcd. for $C_9H_{17}TeBr$: C 32.49, H 5.15. Found: C 32.26, H 5.22.

1-Bromo-1-butyltelluro-1-octenes 70a and 70b. These isomers were not separated. GC/MS m/z 374(20.78), 249(19.99), 247(16.45), 209(27.46), 207(20.56), 109(100.00), 67(84.58), 57(97.22); ^1H NMR (300 MHz) (δ in $CDCl_3$) **70a**: 0.91(t, J = 7.0 Hz, 3H), 0.96 (t, J = 7.0 Hz, 3H), 1.2-1.5(m, 10H), 1.82(quint., J = 7.0 Hz, 2H), 2.07(q, J = 7.0 Hz, 2H), 2.95(t, J = 7.0 Hz, 2H), 6.56(t, J = 7.0 Hz, 1H); **70b**: 0.91(t, J = 7.0 Hz, 3H), 0.96 (t, J = 7.0 Hz, 3H), 1.2-1.5(m, 10H), 1.71(quint., J = 7.0 Hz, 2H), 2.21(q, J = 7.0 Hz, 2H), 3.14(t, J = 7.0 Hz, 2H), 6.68(t, J = 7.0 Hz, 1H); Anal Calcd. for $C_{12}H_{23}TeBr$: C 38.45, H 6.19. Found: C 38.62, H 6.10.

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