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One-pot synthesis of telluroketene acetals and haloketene acetals using sp^2 geminated hetero organobismetallic intermediates

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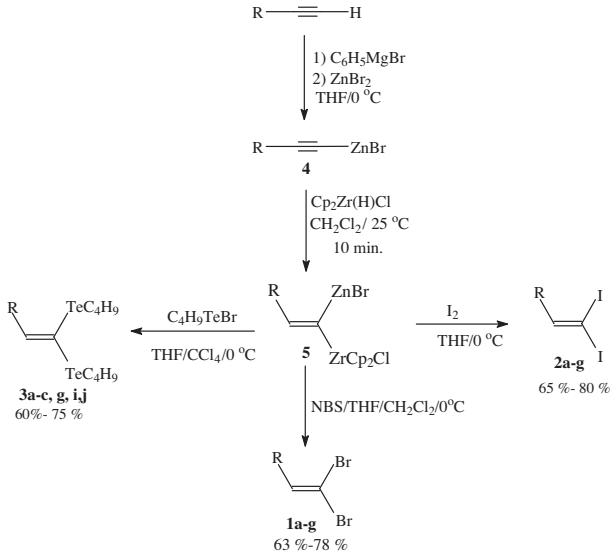
ABSTRACT

A novel one-pot synthesis of 1,1-dihalo-1-alkenes and 1,1-bis(butyltelluro)-1-alkenes was developed from hydrozirconation of alkynylzinc bromide with $Cp_2Zr(H)Cl$ and subsequent capture of the Zn/Zr 1,1-heterodimetallo-1-alkene intermediates with halogen and tellurium electrophiles. These protocols, which include multiple reactions in a one-pot procedure, allow the preparation of the potentially useful haloketene acetals and telluroketene acetals from terminal alkynes, under mild conditions and in a good yield.

New strategies for generation of 1,1-bisanions such as 1,1-sp^3 and 1,1-sp^2 bismetallic reagents have been the target of intense research, as reflected in a plethora of articles published in recent decades.[1,2] Vinyl geminated organobismetallic derivatives containing lithium,[3] boron,[4] magnesium,[5] aluminum,[6] copper,[7] titanium,[8] gallium,[9] and indium[10] have been applied as an efficient and useful alternative to prepare functionalized substituted olefins. The total synthesis of molecules with retinoidal activities[11a] such as Temarotene[11b,c] was performed by palladium catalyzed cross-coupling reactions of *gem*-borazirconocene alkenes.[4b] The synthesis and recent applications of trisubstituted olefins containing two functional groups attached to the same C-sp^2 such as haloketene acetals (1,1-dibromo-1-alkenes **1** and 1,1-diiodo-1-alkenes **2**)[12] and telluroketene acetals (1,1-bis(organylchalcogene)-1-alkenes)[13] **3** were investigated by our group and others. As representative examples, telluroketene acetals and haloketene acetals can be obtained by the hydrozirconation of telluroacetylenes[13a] and stannylacetylenes[12d] followed by subsequent quenching of the sp^2 1,1-heterobismetallic intermediates using butyltellurenyl bromide (C_4H_9TeBr) and halogen electrophiles, respectively. The 1,1-diiodo-1-alkenes can also be obtained by carbometalation of alkynyl alanate[6a] with $(CH_3)_3Al$ and Cl_2ZrCp_2 as catalyst. However, the published methodology to synthesize telluroketene acetals and haloketene acetals requires the preliminary preparation of



R = Alkyl, aryl, alkenyl, CH_2OBn, $CH_2(CH_2)_2Cl$, CH_2OTBS for compounds **1** and **2**
R = Alkyl, aryl, alkenyl, CH_2OCH_3 for compounds **3**

Scheme 1.

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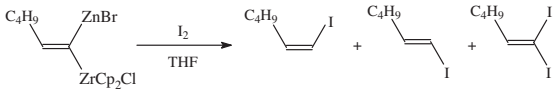
Table 1
Iodonolysis of C-Zr or C-Zn of 1,1-bismetallic-1-alkenes

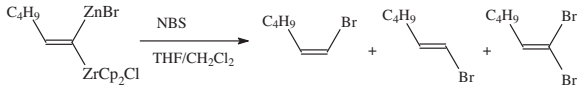


5a 6 7 2

Entry	Reactions and conditions	Ratio[a]		
		6:	**7:**	**2:**
1	1.0 equiv of I_2/THF, −78 °C	78	15	07
2	1.0 equiv of I_2/THF, 0 °C	61	30	09
3	1.5 equiv of I_2/THF, −78 °C	50	35	15
4	1.5 equiv of I_2/THF, 0 °C	48	30	22
5	2.0 equiv of I_2/THF, -78 °C	10	05	85
6	2.0 equiv of I_2/THF, 0 °C	09	07	84
7	2.5 equiv of I_2/THF, −78 °C	05	05	90
8	2.5 equiv of I_2/THF, 0 °C	—	—	100

[a] Ratio determined by ^{1}H NMR.

Table 2
Bromonolysis of C-Zr or C-Zn of 1,1-bismetallic-1-alkenes

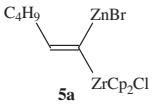
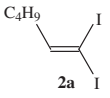
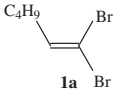
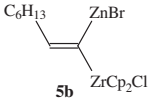
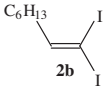
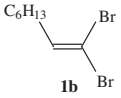
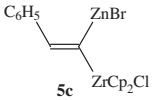
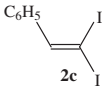
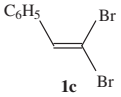
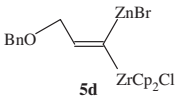
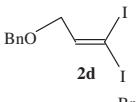
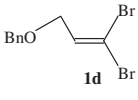
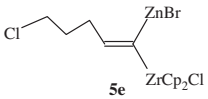
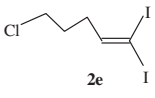
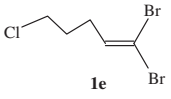
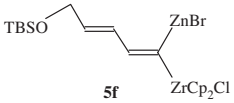
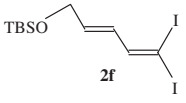


5a 8 9 1a

Entry	Reactions and conditions	Ratio[a]		
		8:	**9**:	**1a**:
1	1.0 equiv of NBS/THF/CH_2Cl_2, −78 °C	91	09	—
2	1.0 equiv of NBS/THF/CH_2Cl_2, 0 °C	90	10	—
3	1.5 equiv of NBS/THF/CH_2Cl_2, −78 °C	75	25	—
4	1.5 equiv of NBS/THF/CH_2Cl_2, 0 °C	75	25	—
5	2.0 equiv of NBS/THF/CH_2Cl_2, −78 °C	08	05	87
6	2.0 equiv of NBS/THF/CH_2Cl_2, 0 °C	08	05	87
7	2.5 equiv of NBS/THF/CH_2Cl_2, −78 °C	05	—	95
8	2.5 equiv of NBS/THF/CH_2Cl_2, 0 °C	—	—	100

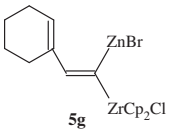
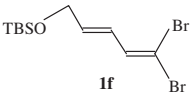
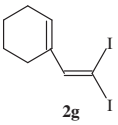
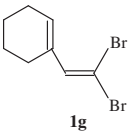
[a] Ratio determined by ^{1}H NMR.

Table 3
Synthesis of 1,1-dihalo-1-alkenes

Entry	1,1-Bimetallic reagent	Electrophile	Time (h)[a]	1,1-Dihalo-1-alkene[b]	Yield (%)[c]
1	 **5a**	I_2	1.0	 **2a**	76
		NBS	1.5	 **1a**	72
2	 **5b**	I_2	1.0	 **2b**	73
		NBS	1.5	 **1b**	75
3	 **5c**	I_2	1.0	 **2c**	65
		NBS	1.5	 **1c**	70
4	 **5d**	I_2	2.5	 **2d**	76
		NBS	3.0	 **1d**	75
5	 **5e**	I_2	2.0	 **2e**	80
		NBS	2.5	 **1e**	78
6	 **5f**	I_2	2.5	 **2f**	78

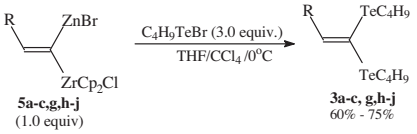
(*continued on next page*)

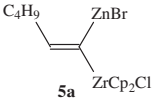
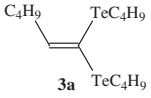
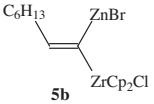
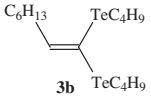
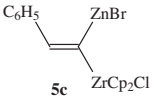
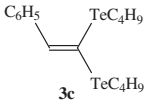
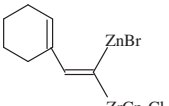
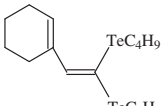
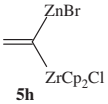
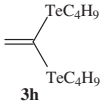
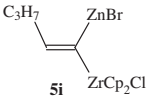
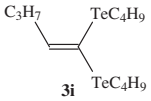
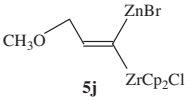
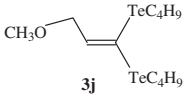
Table 3 (*continued*)

Entry	1,1-Bimetallic reagent	Electrophile	Time (h)[a]	1,1-Dihalo-1-alkene[b]	Yield (%)[c]
7	 **5g**	NBS	3.0	 **1f**	75
		I_2	3.0	 **2g**	70
		NBS	4.0	 **1g**	63

[a] Reaction time of the electrophile and 1,1-bismetallic-1-alkene reagent.
[b] Fully characterized by NMR (^{1}H and ^{13}C), HRMS.
[c] Isolated yields after purification by chromatography using silica gel (230–400 mesh). Mobile phase: hexane for **1a–c**, **1g**; **2a–c**, **2g** and a mixture of ethyl acetate/hexane (2:8 v/v) for **1d–f**, **2d–f**.

Table 4
Synthesis of telluroketene acetals[21]



Entry	1,1-Bimetallic reagent	Electrophile	Time (min)[a]	Product[b]	Yield[c] (%)
1	 **5a**	C_4H_9TeBr	30	 **3a**	70
2	 **5b**	C_4H_9TeBr	30	 **3b**	73
3	 **5c**	C_4H_9TeBr	50	 **3c**	67
4	 **5g**	C_4H_9TeBr	60	 **3g**	60
5	 **5h**	C_4H_9TeBr	20	 **3h**	65
6	 **5i**	C_4H_9TeBr	30	 **3i**	75
7	 **5j**	C_4H_9TeBr	45	 **3j**	65

[a] Reaction time of the electrophile and 1,1-bismetallic-1-alkene.
[b] Fully characterized by NMR (^{1}H and ^{13}C), GC/MS and microanalysis.
[c] Isolated yields after purification by chromatography using silica gel (230–400 mesh). Mobile phase: hexane for **3a-c, g, h–i** and a mixture of ethyl acetate/hexane (2:8 v/v) for **3j**.

telluroacetylenes[13a] or stannylacetylenes[12d] as starting material and the carbometalation of the alkynyl alanate[6a] to afford the iodoketene acetals, is carried out using the dangerous and pyrophoric reagent trimethyl-aluminum.

Knochel and co-workers[14] published a long time ago, the synthesis of polyfunctional olefins and allenes using Zn/Zr 1,1-sp^2 bismetallic reagents **5**. However, to the best of our knowledge, studies concerning the chemical reactivity involving the powerful intermediate type **5** with other electrophiles such as chalcogenes and halogen have not yet been reported. Considering that 1,1-dihalo-1-alkenes have been applied as important substrates in cross-coupling reactions,[12e,f] to prepare therapeutic agents such as heteroaryl ketones[12g] and anticancer polyketides,[12h] we describe herein our detailed study toward the one-pot synthesis of telluroketene acetals and haloketene acetals using a wide range of Zn/Zr alkylidene species.

Corey and Fuchs demonstrated that various aldehydes can be converted into 1,1-dibromo-1-alkenes using a Wittig-type reaction with carbon tetrabromide.[12a] Recently, the use of phosphorus reagents has been avoided because of their high toxicity and the tedious procedures involved in product purification which limits this protocol.[15] Bismetallic vinyl species of Sn[16] and In[17] generated from terminal acetylenes have been used to obtain 1,1-dihalo-1-alkenes of type **1**, **2**. However, these methodologies are not efficient, since only specific alkynes containing oxygen were used. Therefore, the development of new, versatile, and general alternatives to afford the synthesis of the useful 1,1-dihalo-alkenes and telluroketene acetals has been the target of great interest in organic synthesis.

Our approach to synthesize 1,1-dihalo-1-alkenes and telluroketene acetals from 1-alkynes using a one-pot procedure, which is described in Scheme 1, was realized as an extension of the work developed by Knochel,[14] who reported the reduction of alkynylzinc bromide **4** with $Cp_2Zr(H)Cl$ (Schwarts reagent)[18] in CH_2Cl_2.

We examined the chemical reactivity of the in situ generated 1,1-bismetallic-1-alkenes species **5a** as toward I_2 and NBS under several reaction conditions (Tables 1 and 2). A predominance of (***Z***)-vinyl halides **6**, **8** and low amounts of 1,1-dihalo-1-alkenes **1**, **2** (Tables 1 and 2, entries 1–4) were detected when a solution containing iodine in THF or NBS in THF/CH_2Cl_2 (1.0 and 1.5 equiv) was added at either 0 °C or −78 °C to a solution of the 1,1-bismetallic-1-alkenes **5** (1.0 equiv). These results allow us to observe that the halogenolysis of C-Zn is faster than C-Zr. Larger amounts of 1,1-dihalo-1-alkenes **1**, **2** and traces of vinyl halides **6–9** were observed after the addition of 2.0 equiv of I_2 or NBS to a solution of the intermediate **5** (Tables 1 and 2, entries **5–6**).

The (***Z***) and (***E***)-vinyl halides **6–9** are formed by hydrogen capture during the aqueous workup.

By adding 2.5 equiv of NBS in THF/CH_2Cl_2 or I_2 in THF at 0 °C to alkylidene species **5**, the 1,1-dibromo-1-alkenes[19] **1**, and 1,1-diiodo-1-alkenes[20] **2** were obtained exclusively and in good yields (Tables 1, 2 entry 8 and Table 3).

Exploiting our previous results to prepare the 1,1-dihalo-1-alkenes **1–2**, we studied the one-pot synthesis of telluroketene acetals type **3** by using butyltellurenyl bromide (C_4H_9TeBr) instead of iodine or NBS as electrophile. However, the addition of 2.5 equiv of C_4H_9TeBr to 1,1-hetero bismetallic intermediate **5a–b** leads to telluroketene acetals in low yields (15–20%), and an appreciable amount of telluroacetylene (50–65%) was detected.

To overcome these problems, the best result, as shown in Table 3, was achieved by the addition of butyltellurenyl bromide (C_4H_9TeBr; 3.0 equiv) at 0 °C to the Zn/Zr 1,1-dimetallo 1-alkenes **5** (1.0 equiv), leading to the one-pot preparation of the telluroketene acetals **3** in a good yield (Scheme 1, Table 4).

Assignments of the 1,1-dihalo-1-alkenes (Table 3)[12d] and 1,1-bis(butyltelluro)-1-alkenes (Table 4)[13a] are consistent with ^1H NMR, ^{13}C NMR, HRMS, GC/MS and microanalysis published previously by our group.

In summary, we describe a novel, efficient, and general one-pot synthesis of the useful 1,1-bis(organyltelluro)-1-alkenes, 1,1-diiodo-1-alkenes and 1,1-dibromo-1-alkenes by the reactions of Zn/Zr 1,1-bismetallic-1-alkenes with tellurium and halogen electrophiles. To the best of our knowledge, this is the first report in which telluroketene acetals and haloketene acetals are obtained directly from 1-alkynes via double halogenolysis reactions involving Zn/Zr 1,1-bismetallic-1-alkenes type **5** under mild conditions. This procedure tolerates various functional groups that are not compatible with some published procedures.

Further studies applying the telluroketene acetals and haloketene acetals toward rapid total synthesis of molecules with medicinal and biological activities, such as *gem*-enedyines, which have anticancer properties, and insect sex pheromones are presently underway in our laboratories.

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References and notes

1. Marek, I.; Normant, J. F. *Chem. Rev.* **1996**, *96*, 3241.
2. Marek, I. *Chem. Rev.* **2000**, *100*, 2887.
3. (a) Maercker, A.; Bos, B. *Main Group Met. Chem.* **1991**, *14*, 67; (b) Maercker, A. In *Lithium Chemistry*; Sapse, A. M., Schelyer, P., Eds.; Wiley & Sons: New York, 1995; p 490; (c) Seyferth, D.; Langer, P.; Doering, M. *Organometallics* **1995**, *14*, 4457.
4. (a) Cooke, M. P., Jr. *J. Org. Chem.* **1994**, *59*, 2930; (b) Deloux, L.; Srebnik, M.; Sabat, M. *J. Org. Chem.* **1995**, *60*, 3276; (c) Desurmont, G.; Dalton, S.; Giolando, D. M.; Srebnik, M. *J. Org. Chem.* **1997**, *62*, 8907.
5. (a) Duboudin, J. G.; Jousseaume, B. *Synth. Comm.* **1979**, *9*, 53; (b) Duboudin, J. G.; Jousseaume, B.; Saux, A. *J. Organometal. Chem.* **1979**, *168*, 1.
6. (a) Van Horn, D. E.; Valente, L. F.; Idacavage, M. J.; Negishi, E. I. *J. Organometal. Chem.* **1978**, *156*, C20; (b) Pelter, A.; Smith, K.; Parry, D. E.; Jones, K. D. *Aust. J. Chem.* **1992**, *45*, 57.
7. Janssen, M. D.; Kohler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817.
8. (a) Urabe, H.; Hamada, T.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 2931; (b) Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 1245.
9. Yamaguchi, M.; Tsukagoshi, T.; Arisawa, M. *J. Am. Chem. Soc.* **1999**, *121*, 4074.
10. Fujiwara, N.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4095.
11. (a) Mangelsdorf, D. J.; Umesono, K.; Evans, R. M. The Retinoid Receptors. In *The Retinoids*; Academic Press: Orlando, FL, 1994; (b) Ritter, S. J.; Smith, J. E. *Biochim. Biophys. Acta* **1996**, *1291*, 228; (c) Nankervis, R.; Davis, S. S.; Day, N. H.; Shaw, P. N. *Int. J. Pharm.* **1996**, *130*, 57.
12. For the synthesis of 1,1-dihalo-1-alkenes see: (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769; (b) Desai, N. B.; McKelvie, N.; Ramirez, F. *J. Am. Chem. Soc.* **2002**, *84*, 1745; (c) Bonnet, B.; Le Gallic, Y.; Plé, G.; Duhamel, L. *Synthesis* **1993**, 1071; (d) Dabdoub, M. J.; Dabdoub, V. B.; Baroni, A. C. M. *J. Am. Chem. Soc.* **2001**, *123*, 9694; For the applications of 1,1-dihalo-1-alkenes see (e) Rao, M. L. N.; Jadhav, D. N.; Dasgupta, P. *Org. Lett.* **2010**, *12*, 2048; (f) Chelucci, G.; Capitta, F.; Baldino, S. *Tetrahedron* **2008**, *64*, 10250; (g) Fan, X.; He, Y.; Zhang, X.; Guo, S.; Wang, Y. *Tetrahedron* **2011**, *67*, 6369; (h) Paterson, I.; Paquet, T.; Dalby, S. M. *Org. Lett.* **2011**, *13*, 4398.
13. For the synthesis of telluroketene acetals see: (a) Dabdoub, M. J.; Begnini, M. L.; Guerrero, P. G., Jr. *Tetrahedron* **1998**, *54*, 2371; (b) Silveira, C. C.; Perin, G.; Jacob, R. G.; Braga, A. L. *Phosphorus, Sulfur and Silicon* **2001**, *172*, 55; For the applications of telluroketene acetals see: (c) Zeni, G.; Perin, G.; Cella, R.; Jacob, R. G.; Braga, A. L.; Silveira, C. C.; Stefani, H. A. *Synlett* **2002**, 975.
14. (a) Tucker, C. E.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 9888; (b) Tucker, C. E.; Greve, B.; Klein, W.; Knochel, P. *Organometallics* **1994**, *13*, 94.
15. Wang, Z.; Campagna, S.; Yang, K.; Xu, G.; Pierce, M. E.; Fortunak, J. M.; Confalone, P. N. *J. Org. Chem.* **2000**, *65*, 1889.
16. Quayle, P.; Wang, J.; Xu, J.; Urch, C. J. *Tetrahedron Lett.* **1998**, *39*, 481.
17. Klaps, E.; Schmid, W. *J. Org. Chem.* **1999**, *64*, 7537.
18. Buchwald, S. L.; LaMarie, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
19. *Typical procedure for the preparation of 1,1-dibromo-1-alkenes*
To a two-neck flask under nitrogen atmosphere and equipped with a magnetic stirring bar, containing 1-alkyne (1.0 mmol) in THF (5.0 mL), a solution of phenyl magnesium bromide (1.1 mL; 1.1 mmol; 1.0 M in THF) was added dropwise at 0 °C. After 10 min, $ZnBr_2$ (0.22 g; 1.1 mmol) in THF (3.0 mL) was

added at -78 °C and the mixture was stirred for an additional 15 min. Next, the system was warmed to 25 °C and the THF was totally removed under vacuum and replaced by dry CH_2Cl_2 (5.0 mL). Then, $Cp_2Zr(H)Cl$ (0.26 g; 1.0 mmol) in CH_2Cl_2 (5.0 mL) was added slowly at 25 °C and the mixture was stirred for 10 min for generation of the 1,1-bismetallic intermediate **5**. Finally, the reaction mixture was cooled to 0 °C and NBS (0.44 g, 2.5 mmol) dissolved in THF (5.0 mL) and CH_2Cl_2 (5.0 mL) was transferred via syringe and the solution stirred for the time needed, as indicated in Table 2. The mixture was diluted with ethyl acetate (50.0 mL) the organic phase was washed with brine (4 × 20.0 mL) and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under vacuum by rotary evaporation and the crude products were purified by flash chromatography (using silica gel 230–400 mesh and the appropriate mobile phase as shown in Table 1), furnishing the 1,1-dibromo-1-alkenes as a pale yellow oil.

1,1-Dibromo-1-hexene ***1a***. Yield (72%). IR (cm^{-1}) 2958, 2929, 1623, 1465, 808. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.91 (t, *J* = 7.5 Hz, 3H), 1.2–1.7 (m, 4H), 2.12 (q, *J* = 7.2 Hz, 2H), 6.42 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz) 13.8, 22.2, 29.9, 32.6, 88.5, 138.9. HMRS Calcd for $C_6H_{10}Br_2$ (M^+): 239.9150 Found: 239.9143.

1,1-Dibromo-1-octene ***1b***. Yield (75%). IR (cm^{-1}) 2928, 2856, 1623, 1465, 779. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.90 (t, *J* = 7.5 Hz, 3H), 1.3-1.6 (m, 8H), 2.10 (q, *J* = 7.5 Hz, 2H), 6.40 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz) 14.1, 22.5, 27.8, 28.2, 31.6, 33.0, 88.5, 138.9. HMRS Calcd for $C_8H_{14}Br_2$ (M^+): 267.9465. Found: 267.9453.

20. *Typical procedure for the preparation of 1,1-diiodo-1-alkenes*
The reaction mixture containing the 1,1-bismetallic **5** intermediate was performed as described in the Ref[19], and cooled to 0 °C. Then, iodine (0.63 g; 2.5 mmol) dissolved in THF (5.0 mL) was transferred via syringe and the resulting dark-red solution was stirred for the time needed as indicated in Table 2. The resulting solution was transferred to an Erlenmeyer flask and a solution of sodium thiosulfate (5 g/100 mL) was added under stirring until the solution turned pale yellow. The mixture was diluted with ethyl acetate (50.0 mL) and the organic phase was washed with brine (4 × 20.0 mL) and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under vacuum by rotary evaporation and the crude products were purified by flash chromatography (using silica gel 230–400 mesh and the appropriate mobile phase as shown in Table 1), furnishing the 1,1-diiodo-1-alkenes as a yellow oil.
1,1-Diiodo-1-hexene ***2a***. Yield (76%). IR (cm^{-1}) 2955, 2925, 2856, 1589, 1463, 715. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.92 (t, *J* = 7.5 Hz, 3H), 1.38 (sext., *J* = 7.5 Hz, 2H), 1.43 (quint, *J* = 7.5 Hz, 2H), 1.92 (quart, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHZ) 11.5, 13.9, 22.1, 29.5, 39.3, 154.1. HRMS. Calc for $C_6H_{10}I_2$ (M^+) 335.8875. Found 335.8872.

1,1-Diiodo-1-octene ***2b***. Yield (73%). IR (cm^{-1}) 3166, 2924, 2854, 1589, 1464, 715. ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.95 (t, *J* = 7.2 Hz, 3H), 1.0-1.5 (m, 6H), 1.45 (quint, *J* = 7.5 Hz, 2H), 6.60 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHZ) 11.5, 14.1, 22.5, 27.4, 28.5, 31.5, 39.7,153.2. HMRS Calc for $C_8H_{14}I_2$ (M^+): 363.9186. Found: 363.9190.

21. *Typical procedure for the preparation of 1,1-bis(butyltelluro)-1-alkenes*
The reaction mixture containing the 1,1-bismetallic **5** intermediate was performed as described in the Ref[19], and cooled to 0 °C. Then, butyltellurenyl bromide [(C_4H_9TeBr; 3.0 mmol, prepared separately by the addition of bromine (0.24 g; 1.5 mmol) in CCl_4 (5.0 mL) to a solution of dibutyl ditelluride[22] (0.55 g; 1.5 mmol) in THF (10.0 mL)], was added dropwise via syringe. The stirring was continued for 30 min. at 0 °C, and the mixture was transferred to an Erlenmeyer flask (500 mL) and diluted with ethyl acetate (20.0 mL), water (50.0 mL) and 95% (v/v) ethanol (20.0 mL). Finally, butyl bromide (1.0 mL) and $NaBH_4$ (until the mixture turned pale yellow) were added to transform dibutyl ditelluride to the corresponding telluride, which is easily removed by distillation. After this treatment, the crude product was extracted with ethyl acetate (3 × 20.0 mL) and washed with brine (4 × 15.0 mL). The organic phase was dried over anhydrous $MgSO_4$, and the solvent was evaporated. After filtration through Celite using hexane as the eluent, the product was concentrated under vacuum. Dibutyl telluride was removed by distillation from the crude product using a Kugelrohr apparatus (80 °C/0.01 mmHg). Flash column chromatography (using silica gel 230–400 mesh and the appropriate mobile phase as shown in Table 1) of the residue furnished the telluroketene acetals as a yellow oil.
1,1-Bis(butyltelluro)-1-hexene ***3a***. Yield (70%). GC/MS *m*/*z* 456 (12.15), 454 (20.24), 452 (23.00), 315 (40.47), 313 (42.45), 258 (22.38), 169 (19.63), 81 (100.00), 57(61.38). ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.93 (t, *J* = 7.0 Hz, 9H), 1.3–1.5 (m, 6H), 1.7–1.9 (m, 4H), 2.26 (q, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 1H), 6.72 (t, H = 7.0 Hz, 1H); ^{13}C NMR (75 MHz) 14.2, 15.8, 23.2, 25.7, 26.2, 29.0, 32.3, 34.2, 39.9, 49.2, 126.5, 155.6. Anal. Calcd for $C_{14}H_{28}Te_2$: C 35.29, H 5.93. Found: C 35.41, H 5.77.
1,1-Bis(butyltelluro)-1-octene ***3b***. Yield (73%). 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* = 7.2 Hz, 3H), 2.78 (t, *J* = 7.2 Hz, 4H), 6.71 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (75 MHz) 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, 145.6. Anal. Calcd for $C_{16}H_{32}Te_2$: C 40.07, H 6.72. Found: C 40.45, H 6.70.

22. (a) Engman, L.; Cava, M. *Synth. Commun.* **1982**, *12*, 163; (b) de Araujo, M. A.; Raminelli, C.; Comasseto, J. V. *J. Braz. Chem. Soc.* **2004**, *15*, 358.