Hydrotelluration of Acetylenes: Synthesis of Vinylic Tellurides, Divinyl Tellurides, and 1-(Organyltelluro)-1,3-butadienes

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Organyltellurols generated in situ by reduction of diorganyl ditellurides by sodium borohydride react with acetylenes in ethanol under reflux to give vinylic tellurides $RCH{=}CHTeR^1$ of *Z* configuration [$R = C_6H_5$, $R^1 = C_4H_9$, 93%; $R = \overline{CH_2CH_2CH_2CH_2OC}H_2OCH_2$, $R^1 = n\text{-}C_4H_9$, 77%; $R = \overline{CH_2CH_2OCH_2C}$-$\overline{H_2N}CH_2$, $R^1 = n\text{-}C_4H_9$, 80%; $R = C_5H_{11}$, $R^1 = n\text{-}C_4H_9$, 36%; $R = C_6H_5$, $R_1 = CH{=}CH_2$, 76%; $R = 4\text{–}ClC_6H_4$, $R^1 = CH{=}CH_2$, 75%; $R = C_6H_5$, $R^1 = C(CH_3){=}CH_2$, 65%; $R = 4\text{–}BrC_6H_4$; $R^1 = C(CH_3){=}CH_2$, 77%]. The addition to aromatic acetylenes leads exclusively to the 1,2-substituted regioisomer, whereas the addition to the aliphatic ones furnished the 2,2-substituted regioisomer as a minor byproduct. 1-(Organyltelluro)-1,3–butadienes of *Z* configuration at C_1 [$RCH{=}C(R^1)CH{=}CHTeR^2$] were prepared analogously by addition of organyltellurols to conjugated enynes [(1*Z*,3*E*) $R = HOCH_2$, $R^1 = CH_3$, $R^2 = C_{12}H_{25}$, 80%; (1*Z*,3*Z*) $R = HOCH_2$, $R^1 = CH_3$; $R^2 = C_{12}H_{25}$, 65%; (1*Z*,3*E*) $R = HOCH_2$, $R^1 = CH_3$, $R^2 = 4\text{–}CH_3OC_6H_4$, 70%; (1*Z*,3*Z*) $R = HOCH_2$, $R^1 = CH_3$, $R^2 = 4\text{–}CH_3OC_6H_4$, 91%; (1*Z*,3*E*) $R = HOCH_2$, $R^1 = CH_3$, $R^2 = 2\text{-}CH_3C_6H_4$, 60%; R, $R^1 = CH_2(CH_2)_2CH_2$, $R^2 = C_{12}H_{25}$, 60%; R, $R^1 = CH_2(CH_2)_2CH_2$, $R^2 = 4\text{-}CH_3OC_6H_4$, 53%]. The hydrotelluration of acetylenes with a mixture of tellurium, sodium borohydride, and sodium hydroxide in ethanol/water at reflux temperature gave divinyl tellurides $(RCH{=}CH)_2Te$ of *Z* configuration [$R = C_6H_5$, 98%; $R = 4\text{-}ClC_6H_4$, 98%; $R = 4\text{-}BrC_6H_4$, 84%; $R = 4\text{-}CH_3C_6H_4$, 64%; $R = 4\text{-}CH_3OC_6H_4$, 65%; $R = (E)\text{-}HOCH_2CH{=}C(CH_3)$, 77%; $R = \overline{CH_2CH_2OCH_2CH_2N}CH_2$, 77%; $R = \overline{CH_2CH_2CH_2CH_2OC}H_2O$-$CH_2$, 94%; $R = \overline{CH_2CH_2CH_2CH_2CH{=}C}$–, 6%]. (*Z*)-1-(Butyltelluro)-2-phenylethene and (*Z*)-bis(2-phenylethenyl) telluride reacted with *n*-butyllithium at –78 °C to give the corresponding vinyllithium, which was captured with benzaldehyde to give (*Z*)-1-phenyl-1-hydroxy-3-phenylprop-2-ene in 85 and 80% yields, respectively.

Introduction

Hydrometallation of acetylenes is a widely used method for the synthesis of vinylic metal and metalloid derivatives. In spite of the growth of organic tellurium chemistry during the past years,[1-3] the reaction of tellurols with acetylenes have not been studied in detail. Only isolated examples of such reaction were published.[4-22]

As a part of our on going program in the synthesis of vinylic tellurides, we recently reported our preliminary results concerning the hydrotelluration of acetylenes.[23] In this paper we give a full account of our efforts toward the synthesis of vinylic tellurides, divinyl tellurides, and 1-(organyltelluro)-1,3-butadienes by means of the hydrotelluration of acetylenes.

Results and Discussion

The hydrotelluration of acetylenes was performed by reaction of diorganyl ditellurides with sodium borohydride in ethanol at room temperature in the presence of the acetylene, refluxing the mixture for 5 h.

In the reaction with phenylacetylene only the regioisomer 1 was observed. With alkylacetylenes the two possible regioisomers were formed with isomer 1 predominating (eq 1).

$$RC{\equiv}CH + (R'Te)_2 \xrightarrow[\text{2. reflux, 5 h}]{\text{1. NaBH}_4\text{/EtOH/room temp, N}_2} \underset{1}{RCH{=}CHTeR'} + \underset{2}{R'Te(R)C{=}CH_2} \quad (1)$$

In all cases the regioisomer 1 had *Z* stereochemistry. This high stereoselectivity is worth of note, since the addition of thiols[24] and selenols[25] to acetylenes under heating leads to mixtures of *Z* and *E* olefins. However in these cases the *Z*/*E* mixtures may be a result of a thermodynamic equilibration rather than of a kinetic preference for

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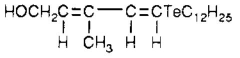
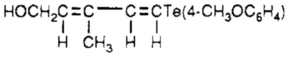
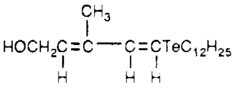
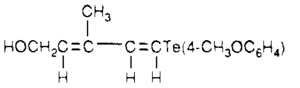
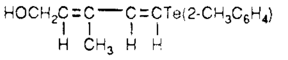
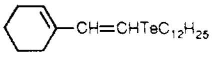
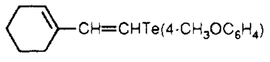
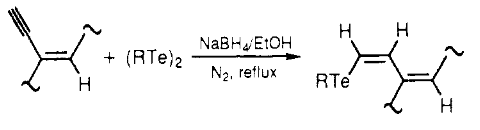
Table I. (Organyltelluro)-1,3-butadienes

	tellurobutadiene	yield,[a] % A	yield,[a] % B	eluent (hexane/ethyl acetate)	mp, °C	anal. found (calcd) H	anal. found (calcd) C	^1H NMR, ppm (*J*, Hz; TMS internal)
1.	 $HOC\underset{H}{H_2C}=\underset{CH_3}{C}-\underset{H}{C}=\underset{H}{C}TeC_{12}H_{25}$	74	80	80:20	70–71	8.84 (8.63)	54.94 (54.87)	0.87 (m, 3 H); 1.25 (m, 20 H); 1.84 (s, 3 H); 2.67 (t, *J* = 7, 2 H); 4.09 (d, *J* = 7, 2 H); 5.5 (t, *J* = 7, 1 H); 6.75 (d, *J* = 11, 1 H); 6.88 (d, *J* = 11, 1 H)[d]
2.	 $HOC\underset{H}{H_2C}=\underset{CH_3}{C}-\underset{H}{C}=\underset{H}{C}Te(4\text{-}CH_3OC_6H_4)$	65	70	80:20	49–50	4.88 (4.82)	46.91 (47.04)	1.89 (m, 3 H); 3.78 (s, 3 H); 4.16 (d, *J* = 7, 2 H); 5.56 (t, *J* = 7, 1 H); 6.78 (d, *J* = 8, 2 H); 6.8 (d, *J* = 11, 1 H); 6.98 (d, *J* = 11, 1 H); 7.78 (d, *J* = 8, 2 H)[d]
3.	 $HOC\underset{H}{H_2C}=\overset{CH_3}{C}-\underset{H}{C}=\underset{H}{C}TeC_{12}H_{25}$	55	65	90:10	38–40	8.78 (8.63)	55.53 (54.87)	0.88 (m, 3 H); 1.26 (m, 20 H); 1.81 (m, 3 H); 2.64 (t, *J* = 7, 2 H); 2.31 (s, 1 H); 4.23 (d, *J* = 7, 2 H); 5.52 (t, *J* = 7, 1 H); 6.62 (d, *J* = 11, 1 H); 6.81 (d, *J* = 11, 1 H)[d]
4.	 $HOC\underset{H}{H_2C}=\overset{CH_3}{C}-\underset{H}{C}=\underset{H}{C}Te(4\text{-}CH_3OC_6H_4)$	75	91	80:20	44–46	4.92 (4.82)	47.37 (47.04)	1.81 (m, 3 H); 2.86 (m, 1 H); 3.73 (s, 3 H); 4.16 (d, *J* = 7, 2 H); 5.43 (t, *J* = 7, 1 H); 6.53 (d, *J* = 11, 1 H) 6.63 (d, *J* = 8, 2 H); 6.78 (d, *J* = 11, 1 H); 7.55 (d, *J* = 8, 2 H)[c]
5.	 $HOC\underset{H}{H_2C}=\underset{CH_3}{C}-\underset{H}{C}=\underset{H}{C}Te(2\text{-}CH_3C_6H_4)$	62	75	75:25	*b*	5.25 (5.07)	49.25 (49.43)	1.77 (s, 1 H); 1.89 (m, 3 H); 3.78 (s, 3 H); 4.16 (d, *J* = 7, 2 H); 5.56 (t, *J* = 7, 1 H); 6.78 (d, *J* = 8, 2 H); 6.8 (d, *J* = 11, 1 H); 6.98 (d, *J* = 11, 1 H) 7.78 (d, *J* = 8, 2 H)[d]
6.		40	60	100:0	*b*	9.07 (8.91)	59.11 (59.40)	0.88 (m, 3 H); 1.26 (m, 20 H); 1.5–1.8 (m, 4 H); 1.9–2.3 (m, 4 H); 2.58 (t, *J* = 7, 2 H); 5.53 (m, 1 H); 6.3 (d, *J* = 10, 1 H); 6.66 (d, *J* = 10, 1 H)[d]
7.		33	53	100:0	*b*	5.28 (5.26)	52.30 (52.69)	1.6 (m, 4 H); 2.1 (m, 2 H); 3.73 (s, 3 H); 5.6 (m, 1 H); 6.51 (d, *J* = 11, 1 H); 6.73 (d, *J* = 8, 2 H); 6.75 (d, *J* = 11, 1 H); 7.64 (d, *J* = 8, 2 H)[d]

[a] A, 2.5 mmol of enyne/1 mmol of ditelluride; B, 4 mmol of enyne/1 mmol of ditelluride. [b] Yellow liquids. [c] Spectrum recorded in CCl_4 on a Varian T-60 spectrometer. [d] Spectrum recorded in $CDCl_3$ on a Bruker AC-80 spectrometer.

both isomers, since reaction of equimolar amounts of acetylenes and thiols[26] or selenols[25,27] at room temperature give the cis adducts preferentially. The greatest stereoselectivity with increasing the atomic number of the chalcogen has been previously reported.[16]

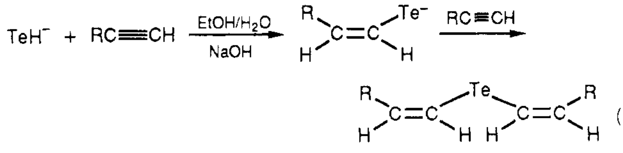
The hydrotelluration reaction was used to prepare 1-(organyltelluro)-1,3-butadienes, a new class of tellurium compounds. Addition of sodium borohydride to a mixture of a conjugated enyne and a dialkyl or diaryl ditelluride produced the 1-(organyltelluro)-1,3-butadienes in 33–75% yield with *Z* stereochemistry at the double bond formed (eq 2).



(2)

A 100% molar excess of the enyne made the yields to increase to 53–91% (see Table I).

Divinyl tellurides are infrequently investigated compounds. No general method for their preparation is available. These compounds were obtained when a mixture of elemental tellurium and potassium hydroxide in HMPA/H_2O was reacted with acetylene at 110–120 °C under pressure.[16] The hydrotelluration of acetylenes with a mixture of tellurium, sodium borohydride, and sodium hydroxide in ethanol/water at reflux temperature is a good method for the synthesis of divinyl tellurides (eq 3). The ethenetellurolate ion, formed from acetylene and the hydrogen telluride anion, attacks another molecule of acetylene leading to divinyl telluride (eq 3, Table II).

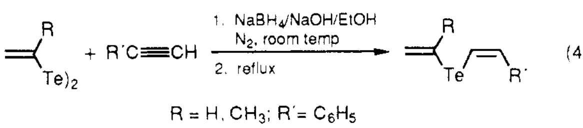


(3)

The products had predominantly *Z* stereochemistry. The nonconjugated acetylenes gave a small amount of the isomer substituted at C_2 as by-product (see Table II).

Attempts to synthesize divinyl ditellurides by hydroditelluration of acetylenes with disodium ditelluride generated from tellurium, sodium hydroxide, and sodium borohydride in aqueous ethanol were unsuccessful. Mixtures of divinyl tellurides, divinyl ditellurides, and elemental tellurium were obtained. Therefore, divinyl ditellurides used in this work were prepared from vinyl Grignard reagents and elemental tellurium followed by air oxidation of the reaction mixture.[28]

Unsymmetric divinyl tellurides were synthesized by hydrotelluration of acetylenes with ethenetellurolates generated by reacting divinyl ditellurides with sodium borohydride in aqueous ethanolic solution of sodium hydroxide at room temperature followed by refluxing the reaction mixture for 3 h (eq 4, Table III).



(4)

$R = H, CH_3; R' = C_6H_5$

The presence of sodium hydroxide is crucial for the

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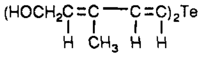
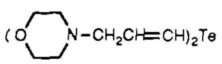
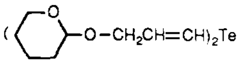
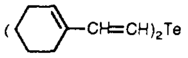
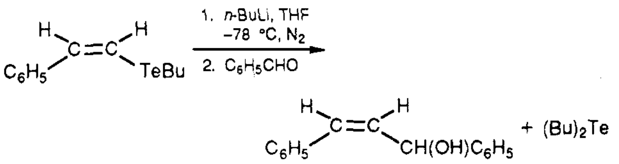
Table II. Symmetrical Divinyl Tellurides

telluride (Z)	yield, %	reactn time, h	eluent (hexane/ ethyl acetate)	mp, °C	anal. found (calcd) H	anal. found (calcd) C	^{1}H NMR, ppm (J, Hz; TMS internal)[a]
1. $(C_6H_5CH{=}CH)_2Te$	98	3	100:0	52–54	4.31 (4.19)	57.95 (57.55)	6.98 (d, J = 10.6, 2 H); 7.2–7.3 (m, 10 H); 7.44 (d, J = 10.6, 2 H)
2. $(4\text{-}ClC_6H_4CH{=}CH)_2Te$	98	6	95:5	84–86	2.95 (2.98)	47.48 (47.69)	6.82 (d, J = 10.6, 2 H); 7.1 (m, 4 H); 7.29 (m, 4 H); 7.24 (d, J = 10.6, 2 H)
3. $(4\text{-}BrC_6H_4CH{=}CH)_2Te$	84	6	95:5	105–107	2.52 (2.44)	38.92 (39.05)	6.98 (d, J = 10.7, 2 H); 7.1 (m, 4 H); 7.33 (d, J = 10.7, 2 H); 7.5 (m, 4 H)
4. $(4\text{-}CH_3C_6H_4CH{=}CH)_2Te$	64	6	95:5	77–78	5.11 (5.01)	59.81 (59.73)	2.30 (s, 6 H); 6.88 (d, J = 10.5, 2 H); 7.12 (s, 8 H); 7.38 (d, J = 10.5, 2 H)
5. $(4\text{-}CH_3OC_6H_4CH{=}CH)_2Te$	65	6	95:5	60–62	4.71 (4.61)	55.14 (54.88)	3.75 (s, 6 H); 6.82 (d, J = 10.5, 2 H); 6.9 (m, 4 H); 7.2 (m, 4 H); 7.36 (d, J = 10.5, 2 H)
6.  $(HOCH_2\underset{H}{C}{=}\underset{CH_3}{C}{-}\underset{H}{C}{=}\underset{H}{C})_2Te$	77	6	50:50	115–117	5.66 (5.64)	44.45 (44.78)	1.73 (s, 6 H); 4.1 (m, 4 H); 4.65 (m, 2 H); 5.42 (t, J = 6.4, 2 H); 6.68 (d, J = 10.5, 2 H); 6.88 (d, J = 10.5, 2 H)
7. 	77[b]	6	70:30	72–74	6.08 (6.32)	44.84 (44.25)	2.4–2.2 (m, 8 H); 2.83 (dd, J = 4.8, J = 1.3, 4 H); 3.6–3.7 (m, 8 H); 6.30 (dt, J = 9.9, J = 4.8 2 H); 6.88 (dt, J = 9.9, J = 1.3, 2 H)
8. 	94[c]	3	90:10	[d]	6.34 (6.39)	46.76 (46.87)	1.2–1.7 (m, 12 H); 3.4–3.6 (m, 2 H); 3.7–4.0 (m, 2 H); 3.92 (ddd, J = 13.7, J = 4.6, J = 1.3, 2 H); 4.28 (ddd, J = 13.7, J = 4.6, J = 1.3 2 H); 4.7 (m, 2 H); 6.46 (dt, J = 10.2, J = 4.6, 2 H); 6.84 (dt, J = 10.2, J = 1.3, 2 H)
9. 	6[e]	6	100:0	67–69	6.43 (6.44)	55.9 (56.2)	1.4–1.7 (m, 8 H); 1.9–2.2 (m, 8 H); 5.6 (m, 2 H); 6.45 (d, J = 10.5, 2 H); 6.78 (d, J = 10.5, 2 H)

[a] Spectra recorded in $CDCl_3$ on a Bruker AC-80 spectrometer. [b] ~10% of the 1,1-substituted vinylic telluride was formed. Products separated by flash chromatography on silica gel eluting with hexane/AcOEt (70:30). [c] Contaminated with ~10% of the 1,1-substituted vinylic telluride. [d] Yellow liquid. [e] This yield was obtained even at a larger scale reaction (8 mmol of Te).

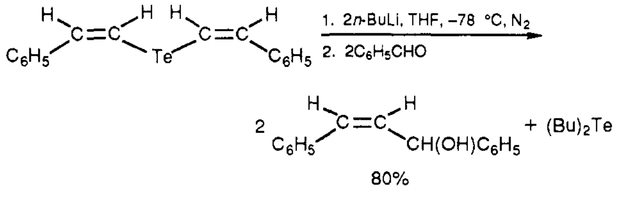
success of the reaction. Sodium hydroxide converts tellurols, which reduce the carbon–carbon double bonds in vinylic tellurium species,[28] to tellurolate anions that do not react with double bonds.

The vinylic tellurium compounds described in this paper can be used to prepare lithiovinyl compounds with retention of configuration. Treatment of (Z)-1-(butyltelluro)-2-phenylethene with n-butyllithium in THF at −78 °C, followed by addition of benzaldehyde, furnished (Z)-1-phenyl-1-hydroxy-3-phenylprop-2-ene in 85% yield (eq 5).



(5)

Similar treatment of bis(2-phenylethene) telluride with n-butyllithium, followed by capture of the intermediates vinyllithium with benzaldehyde, gave (Z)-1-phenyl-1-hydroxy-3-phenylprop-2-ene in 80% yield. In this case the tellurium compound is a source of two molecules of vinyllithium (eq 6).



(6)

These reactions could be a valuable alternative for generating vinyllithiums, since the reactions proceed rapidly with retention of configuration, and the dibutyl telluride can be easily separated from the reaction mixtures by column chromatography on silica gel.

Experimental Section

^{1}H NMR spectra were recorded on a Varian T-60 or on a Bruker AC-80 spectrometer. IR spectra were obtained with liquid films or Nujol mulls of the compounds on a Perkin-Elmer 457A or a Perkin-Elmer 1750-FT spectrometer. Merck silica gel 60 (70–230 mesh or 230–400 mesh) was used for column chromatography, and prepared plates (silica gel 60 F254 on aluminum) were used for TLC. Melting points (uncorrected) were determined on a Kofler hot plate. Bis(4-methoxyphenyl) ditelluride[3] and bis(dodecyl) ditelluride[29] were prepared by literature methods. Cyclohex-1-en-1-ylacetylene was obtained by dehydration of ethynylcyclohexan-1-ol with $POCl_3$ in pyridine.[30] (4-Methoxyphenyl)-, (4-methylphenyl)-, (4-bromophenyl)-, and (4-chlorophenyl)acetylene were prepared by reaction of the appropriate acetophenones with PCl_5 followed by dehydrohalogenation with potassium *tert*-butoxide in petroleum ether (30–60 °C) in the presence of dicyclohexyl 18-crown-6. Phenylacetylene, 1-heptyne, and (Z)- and (E)-3-methyl-2-penten-4-yn-1-ol were commercially available.

Reaction of Acetylenes with Diorganyl Ditelluride/Sodium Borohydride. To a solution of the acetylene (12.5 mmol) and the diorganyl ditelluride (5 mmol) in ethanol (30 mL) at room temperature under nitrogen was added in small portions sodium borohydride (0.53 g, 14 mmol). Toward the end of the addition,

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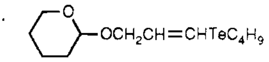
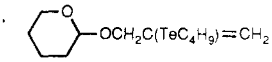
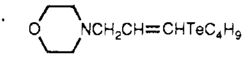
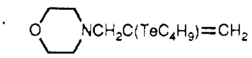
Table III. Unsymmetric Vinylic Tellurides

telluride (*Z*)	yield, %	isomer ratio	anal. found (calcd.)		^{1}H NMR, ppm (*J*, Hz; TMS internal)
			H	C	
1. $C_6H_5CH{=}CHTeC_4H_9$	93[a]	*g*		*j*	0.93 (t, *J* = 7, 3 H); 1.1–2.1 (m, 4 H); 2.76 (t, *J* = 7, 2 H); 7.00 (d, *J* = 11, 1 H); 7.33 (s, 5 H); 7.44 (d, *J* = 11, 1 H)[f]
2. 	77[b]	2/3 (86:14)		*j*	1.00 (t, *J* = 6.4, 3 H); 1.26–1.88 (m, 10 H); 2.65 (t, *J* = 6.7, 2 H); 3.5–3.9 (m, 2 H); 4.0–4.2 (m, 2 H); 4.6 (m, 1 H); 6.41 (dt, *J* = 10, *J* = 5, 1 H); 6.86 (dt, *J* = 10, *J* = 1.2, 1 H)[e]
3. 					*h*
4. 				*j*	0.91 (t, *J* = 6.3, 3 H); 1.1–2.0 (m, 4 H); 2.46 (m, 2 H); 2.35–2.50 (m, 4 H); 2.89 (dd, *J* = 4.9, *J* = 1.3, 2 H); 3.62–3.76 (m, 4 H); 6.32 (dt, *J* = 9.5, *J* = 4.9, 1 H); 6.90 (dt, *J* = 9.5, *J* = 1.3, 1 H)[e]
5. 	80[c]	4/5 (89:11)		*j*	0.7–2.1 (m, 7 H); 2.2–2.6 (m, 6 H); 3.2 (br s, 2 H); 3.4–3.8 (m, 4 H); 5.1 (br s, 1 H); 5.9 (br s, 1 H)[f]
6. $C_5H_{11}CH{=}CHTe(4\text{-}CH_3OC_6H_4)$	36[d]	6/7 (72:28)		*j*	0.89 (m, 3 H); 1.31 (m, 6 H); 1.94–2.40 (m, 2 H); 3.72 (s, 3 H); 6.23 (dt, *J* = 9.0, *J* = 6.0, H); 6.58–6.78 (m, 3 H); 7.54–7.65 (m, 2 H)[e]
7. $C_5H_{11}C(4\text{-}CH_3OC_6H_4Te){=}CH_2$					*i*
8. $C_6H_5CH{=}CHTeCH{=}CH_2$	76	*g*	4.04 (3.88)	46.14 (46.58)	5.83 (d, *J* = 17.7, 1 H); 6.22 (d, *J* = 10.2, 1 H); 6.93 (d, *J* = 10.5, 1 H); 7.02 (dd, *J* = 17.7, *J* = 10.2, 1 H); 7.1–7.3 (m, 5 H); 7.4 (d, *J* = 10.5, 1 H)[e]
9. $4\text{-}ClC_6H_4CH{=}CHTeCH{=}CH_2$	75	*g*	3.20 (3.08)	41.21 (41.08)	5.85 (d, *J* = 17.6, 1 H); 6.26 (d, *J* = 10.2, 1 H); 6.97 (d, *J* = 10.7, 1 H); 7.03 (dd, *J* = 17.6, *J* = 10.2, 1 H); 7.06 (m, 2 H); 7.27 (m, 2 H); 7.32 (d, *J* = 10.7, 1 H)[e]
10. $C_6H_5CH{=}CHTeC(CH_3){=}CH_2$	65	*g*	4.38 (4.45)	48.64 (48.61)	2.3 (m, 3 H); 5.5 (m, 1 H); 5.9 (m, 1 H); 7.07 (d, *J* = 10.6, 1 H); 7.2–7.3 (m, 5 H); 7.4 (d, *J* = 10.6, 1 H)[e]
11. $4\text{-}BrC_6H_4CH{=}CHTeC(CH_3){=}CH_2$	77	*g*	3.24 (3.16)	37.84 (37.67)	2.3–2.4 (m, 3 H); 5.48–5.49 (m, 1 H); 5.8–5.9 (m, 1 H); 7.01 (m, 2 H); 7.10 (d, *J* = 10.7, 1 H); 7.33 (d, *J* = 10.7, 1 H); 7.4 (m, 2 H)[e]

[a] Only one regioisomer formed. [b] Regioisomers not separated, ratio obtained by ^{1}H NMR. [c] Isolated regioisomer by preparative thin-layer chromatography on silica gel eluting with hexane/AcOEt (9:1). [d] Regioisomers not separated, ratio obtained by ^{1}H NMR. [e] Spectra recorded in $CDCl_3$ on a Bruker AC-80 spectrometer. [f] Spectra recorded in CCl_4 on a Varian T-60 spectrometer. [g] One single regioisomer. [h] The regioisomer was identified by a characteristic terminal olefin pattern at δ 6.1 (m, 1 H) and 5.4 (m, 1 H). [i] The regioisomer was identified by a characteristic terminal olefin pattern at δ 5.3 (m, 1 H) and 5.8 (m, 1 H). [j] Known compounds.[23]

when the red color of the solution had disappeared, the mixture was refluxed for 5 h. Then the mixture was cooled to room temperature and treated in sequence with water (2.5 mL) and 10% aqueous sodium hydroxide solution (2.5 mL). The mixture was diluted with ethyl acetate (100 mL) and washed with brine (4 × 30 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. The dry mixture was filtered and the solvent evaporated from the filtrate in a rotatory evaporator (20 mmHg). The residue was purified by flash chromatography on silica gel with hexane as the mobile phase (yields and physical data are given in Table III).

Reaction of Conjugated Enynes with Diorganyl Ditelluride/Sodium Borohydride. Synthesis of 1-(Organyltelluro)-1,3-butadienes. To a solution of the conjugated enyne (2.5 or 4.0 mmol, Table II) and the diorganyl ditelluride (1.0 mmol) in ethanol (6.0 mL) at room temperature under nitrogen atmosphere was added in small portions sodium borohydride (0.09 g, 2.5 mmol). Toward the end of the addition, when the red color of the mixture had disappeared, the mixture was refluxed for 5 h. After being cooled to room temperature, the mixture was treated with water (0.5 mL) and then with 10% aqueous sodium hydroxide solution (0.5 mL). The resulting mixture was diluted with diethyl ether (50 mL) and washed with brine (3 × 30 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. The dry mixture was filtered, and the filtrate was evaporated in a rotatory evaporator (20 mmHg). The residue was purified by flash chromatography on silica gel with heptane or a mixture of heptane and ethyl acetate as the mobile phase (Table I).

Reaction of Acetylenes with Tellurium/Sodium Borohydride/Sodium Hydroxide. Synthesis of Symmetric Divinyl Tellurides. Sodium borohydride (0.34 g, 9 mmol) was added in small portions to a stirred suspension of tellurium (0.383 g, 3 mmol) in ethanol (15 mL) kept under nitrogen. The mixture was heated. Sodium hydroxide (0.32 g, 8 mmol), water (15 mL), and tetrahydrofuran (5 mL) were added to the hot mixture, which was then refluxed for 15 min. The reaction mixture turned dark violet. The mixture was refluxed until all the tellurium had disappeared. The heat source was removed and the acetylene (7.8 mmol) added. The mixture was then refluxed and monitored by TLC. When the mixture had turned yellow, it was cooled to room temperature, diluted with ethyl acetate (50 mL), and washed first with a saturated solution of ammonium chloride (3 × 30 mL) and then with brine (3 × 30 mL). The organic phase was separated, dried with anhydrous magnesium sulfate, and filtered. The solvent was evaporated from the filtrate in a rotatory evaporator at 20 mmHg and the residue purified by flash chromatography on silica gel with hexane/ethyl acetate (ratios in Table II) as the mobile phase.

Synthesis of Unsymmetric Divinyl Tellurides. Sodium borohydride (0.26 g, 7.0 mmol) was added in small portions to a solution of the appropriate divinyl ditelluride (2.5 mmol), sodium hydroxide (0.56 g, 14 mmol) in water (10 mL), and the acetylene in ethanol (15 mL). The mixture was refluxed. After the dark red color of the ditelluride had disappeared (20–30 min), the reflux was continued for 3 h. The mixture was cooled to room temperature, treated with a saturated solution of ammonium chloride (20 mL), and extracted with ethyl acetate (3 × 20 mL). The extract was dried over anhydrous magnesium sulfate and then filtered. The solvent was removed from the filtrate in a rotatory evaporator at 20 mmHg and the residue purified by flash chromatography on silica gel with hexane as the mobile phase (Table III).

1-(Butyltelluro)-2-phenylethene from Phenyl(butyl-

telluro)acetylene. To a solution of sodium borohydride (1.9 g, 50 mmol) in ethanol (100 mL) in a 500-mL three-necked flask equipped with a dropping funnel, reflux condenser, and nitrogen inlet were added 2 mL of a solution prepared from phenyl(butyltelluro)acetylene (11.4 g, 40 mmol) and ethanol (40 mL). The reaction mixture was stirred and refluxed until the red color had disappeared and the gas evolution had ceased. Then the remaining ethanolic solution of phenyl(butyltelluro)acetylene (38 mL) was added dropwise. The rate of addition must be carefully adjusted to control foaming. When all the solution had been added, the mixture was refluxed for 3 h, cooled to room temperature, then treated with water (3 mL), diluted with diethyl ether (150 mL), and washed with brine (3 × 100 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated in a rotatory evaporator at 20 mmHg and the residue purified by flash chromatography on silica gel with hexane as mobile phase. The product (10.5 g, 92% yield) gave an ^{1}H NMR spectrum identical with published data.[29]

(*Z*)-1-Phenyl-1-hydroxy-3-phenylprop-2-ene from (*Z*)-1-(Butyltelluro)-2-phenylethene. To (*Z*)-1-butyltelluro-2-phenylethene (0.288 g, 1 mmol) in THF (3 mL) at −78 °C under nitrogen was added dropwise *n*-BuLi (0.67 mL, 1.5 M in hexane). The mixture was stirred at this temperature for 30 min, warmed to 0 °C, and then treated with benzaldehyde (0.106 g, 1 mmol). The mixture was stirred at 0 °C for 30 min, diluted with diethyl ether (40 mL), and washed with brine (4 × 15 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated in a rotatory evaporator at 20 mmHg. The product was purified by column chromatography on silica gel. Hexane eluted dibutyl telluride and ethyl acetate, the product (0.176 g, 85% yield). ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 1 H); 5.57 (d, J = 9.2 Hz, 1 H), 5.89 (dd, J = 9.2, J = 11.0 Hz, 1 H), 6.64 (d, J = 11.0 Hz, 1 H), 2.2–7.3 (m, 10 H). IR (film): 3351, 1601 cm^{-1}.

(*Z*)-Phenyl-1-hydroxy-3-phenylprop-2-ene from (*Z*)-Bis(2-phenylethenyl) Telluride. To a solution of (*Z*)-bis(2-phenylethenyl) telluride (0.334 g, 1 mmol) in THF (4 mL) at −78 °C under nitrogen was added dropwise a solution of *n*-BuLi (1.34 mL, 2 mmol, 1.5 M solution in hexane). After 40 min of stirring at this temperature, benzaldehyde (212 mg, 2 mmol) was added. The reaction mixture was allowed to reach room temperature (30 min), then diluted with ethyl acetate (40 mL), and washed with brine (4 × 15 mL). The organic layer was separated, dried with anhydrous magnesium sulfate, and filtered. The filtrate was evaporated in a rotatory evaporator at 20 mmHg. The residue was purified by column chromatography on silica gel. Elution with hexane removed dibutyl telluride, and elution with ethyl acetate yielded the product (334 mg, 80% yield).

Reaction of Sulfur Dioxide with the Unsaturated Triosmium–Platinum Clusters $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)$ (R = c-C_6H_{11}, C_6H_5). X-ray Crystal Structure of $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PCy_3)$

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Treatment of $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)$ (**1a**, R = Cy) in CH_2Cl_2 with excess SO_2 at ambient temperatures affords reasonable isolated yields of the 60-electron adduct $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PCy_3)$ (**3**), which has been characterized by multinuclear NMR and a single-crystal X-ray structure. Crystal data for **3**: monoclinic; space group $P2_1/n$; a = 13.254 (2), b = 15.893 (5), c = 17.079 (2) Å; β = 101.073 (9)°; V = 3531 (1) Å^3; Z = 4; final R (R_w) values 0.027 (0.036) for 4622 independent observed data ($I > 3.0\sigma(I)$). Complex **3** contains a tetrahedral Os_3Pt core with the SO_2 ligand bridging an Os–Os edge (Os(1)–Os(3) = 2.988 (1) Å). The two hydride ligands bridge the Os(2)–Os(3) edge (2.976 (1) Å) and the Pt–Os(2) vector (2.906 (1) Å). NMR studies on the reaction at 195 K suggest that the initially formed product is a butterfly Os_3Pt species with a Pt-bound SO_2 ligand. This product is unstable at ambient temperatures and rapidly converts to a mixture of complexes including **3**. Complex **3** exists as two isomers in solution, and in the absence of excess SO_2 cluster degradation readily occurs. Treatment of (**1b**, R = Ph) with SO_2 at ambient temperatures affords the analogous complex $Os_3Pt(\mu\text{-}H)_2(\mu\text{-}SO_2)(CO)_{10}(PPh_3)$ which in solution exists primarily as an isomer containing equivalent Os–Os edge-bridged hydrides.

Introduction

Numerous kinetic studies on the ligand substitution reactions of small homometallic carbonyl clusters have shown that both associative and dissociative mechanisms operate and that their relative rates depend both on the metal atom and on the nature of the ancilliary ligands.[1–4] Although fewer kinetic studies have been carried out on heterometallic clusters, it is well-known that these species may display metal site specificity in their substitution reactions with donor ligands.[5] In this context the re-

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