Dishart and Levine.[39] **α,α-Difluoroacetophenone**: bp 61–62 °C (8 mm); 50% yield. **α,α,α-Trifluoroacetophenone**: bp 43–44 °C (14 mm); 60% yield. **α,α-Difluoro-α-chloroacetophenone**: bp 57–59 °C (6 mm); 72% yield. **$\alpha,\alpha,\beta,\beta$-Pentafluoropropiophenone**: bp 58–59 °C (18 mm); 60% yield.

Preparation of Fluorinated Phenylethanols and Corresponding Tosylates. The ketones were reduced with sodium borohydride (Aldrich) in 90% aqueous dioxane as described by Depuy and Schultz.[10] The tosylates were prepared by reacting the alcohols with *p*-toluenesulfonyl chloride (Aldrich, recrystallized from petroleum ether–chloroform) in pyridine (Fisher, distilled). Reaction times were rather long (up to a week). **2,2-Difluoro-1-phenylethanol**: bp 97–99 °C (9 mm); 67% yield. **Tosylate**: mp 86–87 °C; 82% yield. **2,2,2-Trifluoro-1-phenylethanol**: bp 66–67 °C (5 mm); 86% yield. **Tosylate**: mp 114–115 °C; 85% yield. **2,2,3,3,3-Pentafluoro-1-phenyl-1-propanol**: bp 65–67 °C (3 mm); 73% yield. **Tosylate**: mp 58–58.5 °C; 67% yield. **2,2-Difluoro-2-chloro-1**-phenylethanol: bp 71–72 °C (3 mm); 80% yield. **Tosylate**: mp 111–112 °C; 80% yield.

Preparation of Phenylethanes. The desired fluorinated phenylethanes were obtained by hydrogenolysis of the tosylates using palladium on carbon (Alfa Products) in ethyl acetate (Fisher) under an atmosphere of hydrogen in an apparatus similar to that described by Depuy and Schultz.[10] **2,2-Difluoro-1-phenylethane (II)**: bp 58–59 °C (18 mm); 65% yield; NMR (CCl$_4$) δ 7.2 (s, 5 H), 5.8 (tt, 1 H, $J_{HH} = 5.0$ Hz, $J_{HF} = 58.0$ Hz), 3.1 (tt, 2 H, $J_{HH} = 5.0$ Hz, $J_{HF} = 17$ Hz). **2,2,2-Trifluoro-1-phenylethanol (III)**: bp 59–61 °C (49 mm); 63% yield; NMR (CCl$_4$) δ 7.3 (s, 5 H), 3.4 (q, 2 H, $J_{HF} = 10.0$ Hz). **2,2,3,3,3-Pentafluoro-1-phenylpropane** (V): bp 47–49 °C (20 mm); 73% yield; NMR (CCl$_4$) δ 7.3 (s, 5 H), 3.3 (t, 2 H, $J_{HF} = 18$ Hz). **2,2-Difluoro-2-chloro-1-phenylethane** (VI): bp 40–41 °C (10 mm); 85% yield; NMR (CCl$_4$) δ 7.2 (s, 5 H), 3.4 (t, 2 H, $J_{HF} = 13.8$ Hz).

Preparation of 2-Fluoro-1-phenylethane. 2-Fluoro-1-phenylethane (I) was prepared by the reaction of cesium fluoride (Alfa) in dimethylformamide with β-phenethyl tosylate (mp 39–40 °C) which was prepared in the usual manner from β-phenethyl alcohol (Aldrich). To a dry 100-mL three-neck creased round-bottom flask equipped with a Trubore stirrer, condenser, and stopper were charged 10 g of β-phenethyl tosylate (0.036 mol), 8.2 g of cesium fluoride (0.054 mol), and 40 mL of dimethylformamide (Aldrich, distilled and dried over molecular sieves). This was heated to 100 °C with a sand bath and stirred at that temperature for ca. 8 h, after which NMR analysis of an aliquot revealed that reaction was complete. The reaction mixture was worked up by pouring the contents of the flask into 300 mL of ice water (a dark oil separated). Extraction with pentane (5 × 75 mL) gave an organic layer which was washed with water (2 × 150 mL) and dried over magnesium sulfate. After removal of solvent by distillation through a 20-cm Vigreux column, the residue was vacuum distilled yielding 2.4 g (54%) of 99% pure β-phenethyl fluoride (bp 50–51 °C (8 mm)): NMR δ 7.2 (s, 5 H), 4.4 (dt, 2 H, $J_{HH} = 6.0$ Hz, $J_{HF} = 48$ Hz), 2.8 (dt, 2 H, $J_{HH} = 6.0$ Hz, $J_{HF} = 24$ Hz). Approximately 20% styrene was also formed, presumably by fluoride ion acting as a base in elimination of the tosylate. The distillation sufficed in separating this from the desired product.

Kinetics. Ethanolic ethoxide solutions were prepared by dissolving cleaned sodium metal in ethanol as previously described.[2]

Potassium *tert*-butoxide solutions were prepared by two methods. First, potassium metal which had been washed in *t*-BuOH was dissolved in *t*-BuOH (Aldrich) which had been distilled from potassium under a nitrogen atmosphere. The second procedure involved purifying the potassium metal by the procedure of Pearson and Keaton[40] in *tert*-amyl alcohol prior to dissolving it in *t*-BuOH which had been distilled twice from potassium metal (81 °C). The resulting solution was maintained under an inert atmosphere. These solutions were stable for several weeks after which they would become yellow in color. The kinetics run in *t*-BuOK/*t*-BuOH were identical for both methods of preparation.

The kinetic procedure has been described in the preceding paper.[2] The isotopic exchange studies were performed in EtOH-*O-d* (Aldrich Gold Label) and *t*-BuOH-*O-d* (Aldrich). A sufficient amount of either sodium or potassium was dissolved in their respective deuterated alcohols for preparation of the desired alkoxide solutions. Substrate (200 μL) was added via syringe to a 25-mL Erlenmeyer containing 20 mL of alkoxide/alcohol which was equilibrated to the desired temperature. The reaction was permitted to proceed to approximately 1 half-life and then quenched by charging the contents into a 125-mL separatory funnel containing 75 mL of 1 N HCl and CCl$_4$. The extent of elimination was determined by GLC. The starting material was recovered via preparatory GLC and the extent of deuterium incorporation was determined by mass spectrometry. A rate constant for exchange of III in ethanol-*O-d* was measured by sampling five points through 2 half-lives of elimination and analyzing the samples of starting material, which were isolated by preparative GLC, for deuterium content.

Acknowledgment. We are grateful to the Research Corporation for support of this research by a Cottrell College Science Grant.

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Extended Unsaturated Carbenes. Novel Silicon-, Germanium-, and Tin-Functionalized Cumulenes, $R_2C{=}C{=}C{=}CHMR'_3$, via Insertion of Alkadienylidenecarbenes into Group 4 Hydrides[1]

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Abstract: Interaction of alkadienylidenecarbenes, $R_2C{=}C{=}C{=}C{:}$, with group 4 hydrides results in the formation of novel Si, Ge, and Sn functionalized tetratrienes $R_2C{=}C{=}C{=}CHMR^1_3$. The reaction is general for alkyl- and aryl-substituted carbenes with isolated yields of 26–88%. The parent systems are too unstable to isolate, although IR evidence clearly indicates their formation. All cumulenes show a molecular ion with proper isotope distribution in the mass spectra, an intense IR absorption between 2015 and 2055 cm^{-1}, and a highly characteristic ^{13}C NMR with the two central sp-hybridized cumulenic carbons between 158 and 173 ppm and the two sp^2 olefinic carbons between 98 and 140 ppm. All new cumulenes are stable, isolable, but moderately oxygen-sensitive compounds that rearrange or polymerize upon prolonged standing at room temperature. No [4]radialene dimers were observed upon reaction with CuOSO$_2$CF$_3$, nor was isomerization to the terminally substituted enynes observed upon reaction with *t*-BuOK. Deuterium incorporation occurs in the presence of *t*-BuOD/*t*-BuOK. These results are discussed in detail.

Cumulenes are of considerable theoretical, structural, and synthetic interest.[2] The simplest cumulenes are allenes, first reported in 1888.[3] Although a large amount of research has been done on allene chemistry,[4] considerably less is known about the

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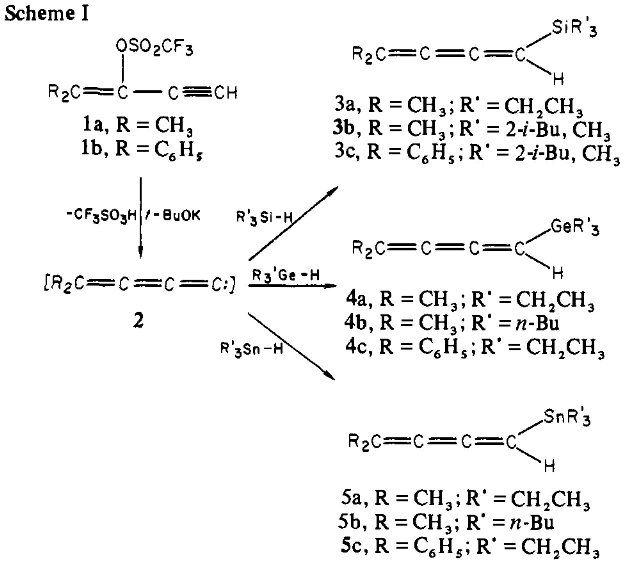
Scheme I



higher cumulenes. Butatrienes were first reported in 1921[5] and higher cumulenes subsequently.[2] Despite the fact that numerous allenes with a wide variety of substituents are known,[4] extended cumulenes, with very few exceptions, are restricted to alkyl- and aryl-substituted systems.[2] To the best of our knowledge, the only substituted tetratrienes known to date are perfluorobutatriene, an explosive gas,[6] and a few alkoxy and thioalkoxy tetratrienes reported by Brandsma and co-workers.[7] Hence in this paper we wish to report a simple, high-yield preparation, and the full spectral characterization of novel group 4 (i.e., Si, Ge, Sn) substituted tetratrienes, along with some of their preliminary chemistry.

It is well known that carbenes undergo addition as well as insertion reactions.[8] Moreover, divalent carbon insertions into group 4 hydrides and halides are well-established reactions.[9] Similarly, unsaturated carbenes are known to undergo addition as well as insertion reactions.[10] Recently, we reported on the generation, trapping, and nature of alkadienylidenecarbenes **2** with hydrogen, alkyl, or phenyl substituents.[11] Insertion of these species into group 4 hydrides provides a simple, general means of entry into the desired cumulenes.

Results and Discussions

Preparation of R_3Si-, R_3Ge-, and R_3Sn-Substituted Tetratrienes. Ethynylvinyl triflates **1** were prepared in three steps in good overall yields, as previously reported.[12] Reaction of ethynylvinyl triflates **1** with a mixture of excess group 4 hydride in 1,2-dimethoxyethane (DME) and t-BuOK at -50 °C under an Ar atmosphere proceeded as shown in Scheme I. Base-initiated elimination of triflic acid results in the formation of alkadienylidenecarbenes **2** which upon insertion into the appropriate group 4 hydride give the substituted tetratrienes **3–5** in yields of 26–88% as shown in Table I. The reaction is general vis-à-vis the carbene substitution; however the parent adducts proved to be too unstable to isolate (although cumulene formation is indicated by the characteristic IR band around 2040 cm^{-1} for the $GeEt_3$ and $SnEt_3$ compounds) and gave only tar upon workup. All other adducts are relatively stable, although somewhat air-sensitive, pale yellow oils. They may be stored in pure form under argon for several days at room temperature or several weeks at 0 °C.

Spectral Properties of R_3Si-, R_3Ge-, and R_3Sn-Substituted Tetratrienes. The spectral properties of functionalized tetratrienes **3–5** are listed in Table I. These spectral properties are fully consistent with the proposed structures. Specifically, each and every compound showed a molecular ion in the mass spectrum, including proper isotope distributions for the germanium and tin adducts, as well as a reasonable fragmentation pattern. The proton spectra are consistent with the proposed structures, with the cumulenic C–H in the expected region of 5.4–5.8 ppm for the methyl-substituted cumulenes and at 6.1 ppm for the phenyl-substituted isomers.

The most characteristic and valuable feature of the spectra of these substituted cumulenes are the infrared and C-13 NMR absorptions. Every single substituted tetratriene **3–5** has an intense, sharp absorption in the infrared spectrum between 2015–2055 cm^{-1}. This absorption is uniquely characteristic of unsymmetrically substituted cumulenes in general and tetratrienes in particular.[2] This absorption is sufficiently strong and characteristic that it can be observed even in the dilute reaction mixture and hence can be used to monitor the progress of the reaction and in particular the formation of cumulene. It is the appearance of this band in the infrared during the course of the reaction that indicates the formation of even the parent group 4 substituted cumulenes. A further spectral feature clearly indicating the cumulenic functionality is the characteristic alternating absorption of the cumulenic carbons in the C-13 spectrum.[13] Specifically, all olefinic carbons show up in the expected[14] downfield region of 100–175 ppm with the two central sp-hydridized carbons always at lower field (158–173 ppm) than the two outer sp^2-hydridized carbons (98–140 ppm). More specifically, the olefinic carbon (C-1) bearing the metal substituent is in all cases at 100 ± 2 ppm for the dimethyl tetratrienes, and at 111 ± 1 ppm for the diphenyl systems, regardless of the nature of the R_3M group. It is intersting to note that the effect of the metal (i.e., Si vs. Ge vs. Sn) is virtually nonexistent upon the chemical shift of C-1, whereas the δ-phenyl groups consistently cause a 10-ppm downfield shift. Similarly, C-4 is always at 120 ± 1 ppm for the methyl-substituted tetratrientes and at 139-147 ppm for the phenyl systems, regardless of the metal substitution. The two central cumulenic carbons in turn are remarkably insensitive to substitution with C-2, always at 170 ± 3 ppm and C-3 at 163 ± 5 ppm. Similarly, the UV shows a λ_{max} at 270 ± 2 nm for the dimethyl tetratrienes regardless of the R_3M group with a 60-nm bathochromic shift and λ_{max} 330 ± 3 nm for the diphenyl systems.

Chemistry of Group 4 Functionalized Tetratrienes. It is well known the cumulenes, in general, and butatrienes, in particular, readily dimerize.[2] We had previously reported on the dimerization of tetratrienes **6** to [4]radialenes **7**.[11] Interestingly, no such di-

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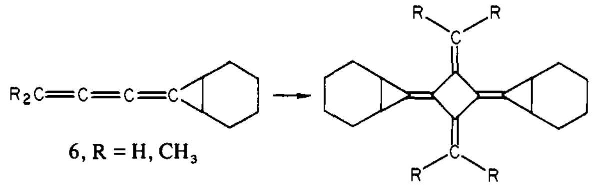
Table I. Spectral Properties of Group 4 Functionalized Tetratrienes 3–5

compound	yield[a]	mass spec (rel intensity)	UV[b] λ_{max}, nm (log ϵ)	IR[c] ν_{max}, cm^{-1} (intensity)	^{1}H NMR[d] δ (H's, mult)	^{13}C NMR[e], δ				
						C_1	C_2	C_3	C_4	others
$(CH_3)_2C{=}C{=}C{=}CHSi(C_2H_5)_3$ **3a**	52	194 (M^+, 75), 165 (100), 137 (61), 115 (45)	269 (4.20), 216 sh (3.66)	2055 (s, C=C=C=C) 1230, 730 (s, Si-C)	0.4–1.2 (15, m), 1.97 (6, s), 5.45 (1, s)	99.23	171.9	157.9	121.2	25.23, 6.39, 3.88
$(CH_3)_2C{=}C{=}C{=}CHSi(CH_3)[CH_2CH(CH_3)_2]_2$ **3b**	46	236 (M^+, 1.3), 235 (3), 221 (6), 180 (29), 165 (14), 124 (72), 123 (46), 109 (27), 83 (100)	268 (4.17), 217 sh (4.24)	2050 (s, C=C=C=C), 1235, 810 (s, Si–C)	0.19 (3, s), 0.69 (4, d), 0.98 (12, d), 1.80 (2, m), 2.0 (6, s), 5.54 (1, s)	102.0	172.7	159.3	120.6	26.6, 26.3, 25.3, −2.64
$(C_6H_5)_2C{=}C{=}C{=}CHSi(CH_3)[CH_2CH(CH_3)_2]_2$ **3c**	54	360 (M^+, 6), 304 (18), 250 (6), 249 (25), 248 (100), 233 (15), 203 (10)	328 (4.14), 260 sh (3.98), 252 (3.99)	2020 (s, C=C=C=C), 1250, 1220, 1095, 1040, 805, 780, 700 (all s)	0.21 (3, s), 0.82 (4, d), 0.98 (12, d), 1.80 (2, m), 6.13 (1, s) 7.35 (10, m)	111.5	169.7	163.5	139.1	129.1, 129.0, 128.1 128.0, 127.9, 26.31, 26.23, 25.83, 24.83, −2.69
$(CH_3)_2C{=}C{=}C{=}CHGe(C_2H_5)_3$ **4a**	84	240 (M^+, 44), 238 (32), 236 (24), 211 (100), 209 (75), 207 (57), 183 (31), 181 (24), 179 (20), 155 (46), 153 (70), 151 (52), 149 (26), 133 (36), 131 (30), 129 (36), 127 (28)	269 (4.13), 219 sh (3.74)	2045 (s, C=C=C=C), 1210 (s) 1020 (m), 710 (s)	0.77 (6, m), 1.15 (9, m), 1.86 (6, s), 5.66 (1, s)	100.4	169.7	158.9	119.3	29.62, 25.22, 8.72 5.13
$(CH_3)_2C{=}C{=}C{=}CHGe(CH_2CH_2CH_2CH_3)_3$ **4b**	40	309 (M^+, 1.8), 307 (2.3), 305 (2.2), 211 (100), 209 (76), 207 (57), 155 (42), 153 (62), 151 (45), 149 (22)	270 (4.38), 219 sh (3.87)	2039 (s, C=C=C=C),	0.70 (9, m), 1.15 (18, m), 1.77 (6, s), 5.60 (1, s)	101.5	169.3	158.9	119.1	27.28, 26.28, 25.26, 25.21, 13.55, 11.90
$(C_6H_5)_2C{=}C{=}C{=}CHGe(C_2H_5)_3$ **4c**	81	364 (M^+, 73), 362 (50), 360 (36), 335 (100), 333 (71), 331 (53), 307 (45), 306 (18), 305 (38), 303 (29), 279 (69), 277 (70), 275 (54), 273 (13), 203 (34)	327 (4.48), 261 sh (4.26), 253 (4.28)	2015 (s, C=C=C=C), 1025 (m), 775 (s), 700 (s)	0.5-1.3 (15, m), 6.17 (1, s), 7.25 (10, m)	111.0	168.4	165.2	139.2	129.1, 129.0, 128.7, 128.2, 128.1, 127.9, 8.96, 5.29
$(CH_3)_2C{=}C{=}C{=}CHSn(C_2H_5)_3$ **5a**	79	286 (M^+, 20), 284 (15), 261 (17), 259 (15), 257 (100), 256 (36), 255 (79), 254 (31), 253 (46), 199 (76), 197 (56), 179 (24), 149 (77), 147 (59), 145 (59)	272 (4.06), 224 sh (3.90)	2035 (s, C=C=C=C), 1200 (m), 1020 (m), 680 (s)	0.8-1.2 (15, m), 1.88 (6, s), 5.84 (1, s)	99.98	171.9	159.9	119.3	25.48, 9.83, 1.80
$(CH_3)_2C{=}C{=}C{=}CHSn(CH_2CH_2CH_2CH_3)_3$ **5b**	88	371 (M^+, 2), 369 (2), 313 (73), 311 (9), 291 (100), 289 (76)		2030 (s, C=C=C=C), 790, 670 (s)	0.75 (9, m), 1.20 (18, m), 1.84 (6, s), 5.87 (1, s)	101.0	171.4	161.9	119.0	28.98, 27.21, 24.06, 10.68, 9.98
$(C_6H_5)_2C{=}C{=}C{=}CHSn(C_2H_5)_3$ **5c**	26	410 (M^+, 0.84), 408 (0.49), 406 (0.31), 381 (10), 379 (7), 377 (3), 325 (8), 323 (5), 321 (4), 205 (21), 204 (68), 203 (100), 202 (88), 201 (15), 200 (13)	332 (4.14), 261 sh (4.09), 254 (4.09)	2015 (s, C=C=C=C), 1220 (s), 1110 (s), 760 (s), 700 (s)	1.0-1.33 (15, m), 6.16 (1, s), 7.4 (10, m)	112.0	171.2	167.9	146.7	129.4, 128.7, 128.5, 128.4, 128.1, 11.01, −0.47

[a] All isolated yields. [b] Hexane. [c] Neat, salt plates. [d] $CDCl_3$ (int TMS) except 3a in CCl_4. [e] $CDCl_3$, wideband decoupled, exept 3a and 3b in C_6D_6.



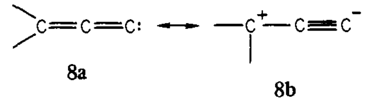
6, R = H, CH$_3$

7, R = H, CH$_3$

merization was observed with any of the group 4 functionalized tetratrienes **3**–**5**, even in the presence of Cu$^+$ known[15] to facilitate such dimerization. The sole product observed in the presence of CuOSO$_2$CF$_3$ was black tarry polymers. The reason for this difference in behavior between the hydrocarbon tetratrienes **6** and the functionalized cumulenes **5** might be due to electron transfer in the case of **5** facilitated by the metallic substituents.[16]

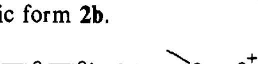
We have also previously noted[11] that alkadienylidenecarbenes **2** like alkenylidenecarbenes **8** are resonance hybrids of the neutral **2a** and zwitterionic form **2b**.

2a **2b**



8a **8b**

It is well known[10] that in numerous "insertion" reactions alkenylidenecarbenes **8** preferentially react via their zwitterionic form **8b**. Similar reaction of alkadienylidenecarbenes **2**, via their zwitterionic form **2b**, should result in terminally functionalized enynes **9**. At no time did we observe any evidence[17] for the



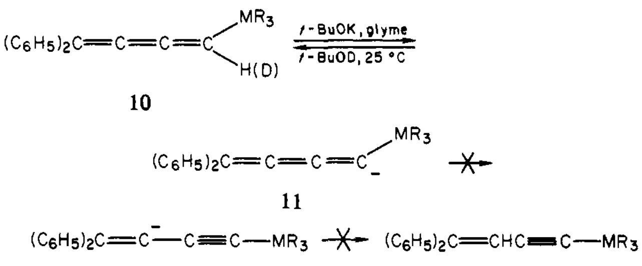
9

formation of such enzymes **9** in the insertion of carbenes **2** into group 4 hydrides. This evidence, albeit negative, strongly suggests that the zwitterionic form is less important for alkadienylidenecarbenes **2** than for alkenylidenecarbenes **8**. This may be attributable to the considerably higher energy of a vinyl cation compared to a carbenium ion.[18]

Finally, we have examined the base sensitivity and the question of isomerization of these compounds. Reaction of the silylcumulene **3c** and the germylcumulene **4a** in DME with excess *t*-BuOD and *t*-BuOK at 25 °C gave after 14 h 9.1 ± 1.2% deuterium incorporation into the reisolated starting cumulene in the case of the silyl system and 11.9 ± 1.5% in the case of the germyl substrate. In neither case was any rearranged enyne **13** observed. These data suggest the formation of the cumulenyl anion **11**, as shown in Scheme II, which under the reaction conditions maintains its integrity and does not rearrange to the vinyl anion **12**. These somewhat surprising results have interesting implications for future reactions (such as alkylation with a variety of electrophiles) for these novel functionalized cumulenes.

In conclusion, we have developed a ready, general, and simple means of synthesis of group 4 functionalized tetratrienes via insertion of alkadienylidenecarbenes **2** into the respective group 4 hydrides. The reaction affords alkyl- as well as aryl-substituted cumulenyl silanes, germanes, and stannanes. These novel cumulenes are stable, isolable, albeit air-sensitive, compounds, with the expected spectral properties. They do not undergo dimerization to [4]radialenes nor base-catalyzed isomerization to terminally substituted enynes. Further chemistry, such as cycloadditions, alkylations, etc., of these group 4 functionalized cumulenes will be the subject of future reports.

Scheme II



10 **11** **12** **13**

Experimental Section

General. Boiling points are uncorrected. Infrared spectra were recorded on a Beckmann Acculab 3 or Nicolet 6000 FT spectrophotometer. Ultraviolet spectra were recorded on a Cary 14 UV-visible spectrophotometer. ^{1}H NMR were recorded on a Varian EM-360, EM-390, or FT-80 spectrometer, and ^{13}C spectra were recorded on a FT-80 or SC-300 spectrometer. Analytical GC work was done on a Hewlett-Packard 5710A flame ionization chromatograph coupled to a Hewlett-Packard 3380A integrator. Mass spectra were recorded on a Varian MAT 112 GC–mass spectrometer.

Materials. All commercial reagents were ACS reagent grade. Solvents were purified and rigorously dried immediately prior to use. Triethylsilane and dichloromethylsilane were purchased from Petrarch and distilled prior to use. Tributylgermanium chloride was purchased from Alfa, and tri-*n*-butyltin chloride and tin tetrachloride from Aldrich.

Diisobutylmethylsilane. This silane was prepared according to literature[19] procedures from 0.75 mol of dichloromethylsilane and excess isobutyl Grignard in 83% yield, bp 152–154 °C (lit.[20] 157.8 °C (763 Torr)).

Tetraethylgermane. This germane was prepared from 150 mmol of GeCl$_4$ and excess ethyl Grignard, according to Kraus and Flood,[21] in 81% yield, bp 155–157 °C (lit.[22] 162.5–163.0 °C (760 Torr)).

Tetraethylstannane. This stannane was prepared from 0.25 mol of SnCl$_4$ and excess ethyl Grignard, similar to the preparation of the above germane, in 84% yield, bp 174–176 °C (lit.[23] 180.5–181.5 °C (768 Torr)).

Triethylgermanium Bromide. This compound was prepared according to Kraus and Flood[21] from 50 mmol of Et$_4$Ge and 50 mmol of Br$_2$ in 50 mL of ethyl bromide and immediately reduced upon workup.

Triethyltin Chloride. This chloride was prepared according to Kocheshkov[24] from 75 mmol of Et$_4$Sn and 25 mmol of SnCl$_4$ by heating for 24 h at 70 °C. The resulting chloride was used immediately and without further purification in the reduction.

Triethylgermane. This compound was prepared from 50 mmol of the above bromide by reduction with LiAlH$_4$, according to Kuivila and Beumel,[25] in 82% yield, bp 115–117 °C (lit.[21] 124.4 °C (751 Torr)).

Tri-*n*-butylgermane. Commercial *n*-Bu$_3$GeCl (21.5 mmol) was reduced[25] with LiAlH$_4$ in 91% yield to give *n*-Bu$_3$GeH, bp 61–63 °C (0.3 torr) (lit.[26] 123 °C (20 Torr)).

Triethylstannane. The above chloride (0.1 mol) was reduced[25] with LiAlH$_4$ in 71% yield to give Et$_3$SnH, bp 133–135 °C (lit.[27] 79–81 °C (92 Torr)).

Tri-*n*-butylstannane. LiAlH$_4$ reduction[25] of 0.1 mol of *n*-Bu$_3$SnCl gave in 90% yield *n*-Bu$_3$SnH, bp 68–74 °C (0.3–0.4 Torr) (lit.[27] 76–81 °C (0.7–0.9 Torr)).

α-Ethynylvinyl Triflates 1. These triflates were prepared from the appropriate precursor ketones as previously described.[12]

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General Procedure for Trapping of Alkadienylidenecarbenes with Group 4 Hydrides. 1-Triethylsilyl-4-methyl-1,2,3-pentatriene (3a). Into a 250-mL three-neck, round-bottom flask fitted with an addition funnel, magnetic stirring bar, and an argon inlet and outlet were added 1.16 g (10 mmol) of Et_3SiH and 10 mL of a 0.20 M solution of vinyl triflate **1a** (2.0 mmol) in DME along with an additional 20 mL of DME containing 0.5% w/v *t*-BuNO (as a radical trap). This solution was cooled to −50 °C using a dry ice/bis(2-ethoxyethyl)ether slush bath, and the system was purged with argon. A solution of 258 mg (2.3 mmol) of *t*-BuOK in 100 mL of DME was added dropwise over a 20–30-min period. Immediately after addition, GC analysis (6 ft × $^1/_8$ in. 10% UCW 982 on 80/100 WHP, 130 °C) showed no trace of starting triflate. A few crystals of NH_4Cl were added in order to neutralize the excess base, and the solvent and excess trap were evaporated on a Büchi rotary evaporator (or vacuum system, as necessary). The remaining sludge was extracted with four 10-mL portions of argon-flushed pentane. The pentane solution was dried over $MgSO_4$, quickly filtered, and concentrated. The dark concentrated solution was chromatographed on unactivated silica gel (25 × 1 cm column prepared with argon-flushed pentane) using argon-flushed pentane as eluent. The colorless front fraction was collected and the pentane evaporated in vacuo yielding 202 mg (52%) of **3a** as a pale yellow oil. The spectral properties of all new cumulenes are summarized in Table I. In concentrated pure form all cumulenes **3–5** appeared as pale yellow, near-colorless oils. They turned progressively dark upon standing neat at room temperature under argon, for several hours or days depending upon the particular compound. Rechromatography of these darkened samples gave back large amounts of pure compound. They may be kept for longer periods in the cold or indefinitely in solution in nonchlorinated solvents under argon.

1-(Diisobutylmethylsilyl)-4-methyl-1,2,3-pentatriene (3b). Following the above procedure, 218 mg (46%) of **3b** was isolated from reaction of 10 mmol of *i*-Bu_2MeSiH and 2.0 mmol of triflate **1a**.

1-(Diisobutylmethylsilyl)-4,4-diphenyl-1,2,3-butatriene (3c). Reaction of 2.0 mmol of vinyl triflate **1b** with 15 mmol of *i*-Bu_2MeSiH gave 390 mg (54%) of **3c**.

1-(Triethylgermyl)-4-methyl-1,2,3-pentatriene (4a). Reaction of 2.0 mmol of triflate **1a** with 6 mmol of Et_3GeH gave 401 mg (84%) of **4a**.

1-(Tri-*n*-butylgermyl)-4-methyl-1,2,3-pentatriene (4b). Reaction of 2.0 mmol of vinyl triflate **1a** with 6 mmol of *n*-Bu_3GeH gave 258 mg (40%) of **4b**.

1-(Triethylgermyl)-4,4-diphenyl-1,2,3-butatriene (4c). Reaction of 2.0 mmol of triflate **1b** and 6 mmol of Et_3GeH gave 588 mg (81%) of **4c**.

1-(Triethylstannyl)-4-methyl-1,2,3-pentatriene (5a). Reaction of 2.0 mmol of triflate **1a** and 6 mmol of Et_3SnH gave 450 mg (79%) of **5a**.

1-(Tri-*n*-butylstannyl)-4-methyl-1,2,3-pentatriene (5b). Reaction of 2.0 mmol of triflate **1a** and 6 mmol of *n*-Bu_3SnH gave 650 mg (88%) of **5b**.

1-(Triethylstannyl)-4,4-diphenyl-1,2,3-butatriene (5c). Reaction of 2.0 mmol of vinyl triflate **1b** and 6 mmol of Et_3SnH gave 213 mg (26%) of **5c**.

Attempted Cu^+-Catalyzed Dimerization of Cumulenes 3-5. A solution of 0.25 mmol of a chosen butatriene (**3b**, **3c**, **4a**, or **5a**) in 20 mL of DME was placed in a 50-mL round bottom flask, equipped with a magnetic stirrer, and cooled to −50 °C. A known solution of $CuOSO_2CF_3$[16] in DME was added to give either 10, 100, or 500 mol % Cu^+. At high concentration of Cu^+ the butatriene disappeared rapidly yielding dark polymers. At low concentration of Cu^+ the butatriene would persist until the reaction was warmed to 0 °C at which point rapid polymer formation occured. At no time with any of the cumulenes **3b**, **3c**, **4a**, or **5a** was any dimer [4]radialene observed.

Attempted *t*-BuOK-Catalyzed Isomerization of Representative Butatrienes 3–5. A solution of a chosen butatriene (**3b**, **4a**, or **5a**) in 25 mL of glyme containing 1% w/v *t*-BuNO was placed in a 50-mL three-neck, round-bottom flask fitted with a magnetic stirring bar and an argon inlet and outlet. The solution was colled to −20 °C and flushed with argon; then 0.5 mmol of *t*-BuOK in 20 mL of glyme was added. Immediately upon completion of the addition of base and at 20-min intervals thereafter, the reaction mixture was monitored by IR. After 1 h the cooling bath was removed and IR monitoring continued. No diminuition in the cumulenic IR absorption (see Table I) or appearance of any new absorptions was noted. Finally, the reaction was slowly warmed to 50 °C at which point the reaction turned dark and the cumulenic absorption slowly disappeared. Workup gave no evidence for rearranged enynes **13** but only polymers were observed.

Exchange of Cumulenic Hydrogen in *t*-BuOK/*t*-BuOD. To a solution of 0.25 mmol of butatriene **3b** or **4a** in 25 mL of DME are added 0.38 mmol of *t*-BuOK and 12.5 mmol of *t*-BuOD. The mixture was stirred at room temperature for 14 h and the butatriene reisolated. IR examination of the reisolated cumulene showed a spectrum identical with that of the starting material except for a weak absorption at 2155 cm^{-1} corresponding to the expected C–D absorption. Multiple, side-by-side analysis, by chemical ionization mass spectrometry, of the starting and reisolated cumulenes indicated a 9.1 ± 1.2% deuterium incorporation for silane **3b** and 11 ± 1.5% deuterium incorporation for germane **4a**.

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