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Regioselective Homo- and Codimerization of 1-Alkynes Leading to 2,4-Disubstituted 1-Buten-3-ynes by Catalysis of a (η^5-$C_5Me_5)_2TiCl_2$/RMgX System

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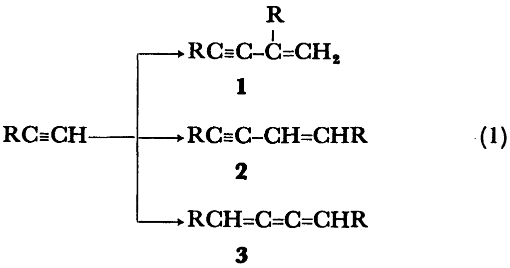
A series of 1-alkynes (RC≡CH where R=Et, *n*-Pr, *n*-Bu, *n*-C_6H_{13}, cyclohexyl, Ph, Me_3Si, Me_3SiCH_2, and Me_3SiOCH_2) was found to dimerize regioselectively (>99%) to 2,4-disubstituted 1-buten-3-ynes in 92—99% yields by catalysis of (η^5-$C_5Me_5)_2TiCl_2$/*i*-PrMgBr at 30 °C in 1—3 h. The catalyst system is also effective for the regioselective codimerization of various 1-alkynes with 1-ethynylcyclohexene or ethynylbenzene.

Linear- and cyclo-oligomerizations of 1-alkynes have been extensively studied with a variety of transition metal catalysts. Organometallic complexes of Ni,[1a)] Co,[1b)] Pd,[1c)] and Ti[1d)] are known as efficient catalysts for cyclooligomerization of alkynes converting them to substituted or unsubstituted benzenes, cyclooctatetraenes, *etc.* For linear dimerization of 1-alkynes, three different modes are possible as illustrated in Eq. 1.



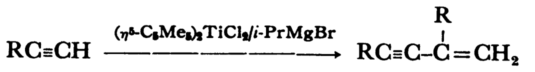
(1)

Only a few catalyst systems have been known for this type of dimerization. [Cr(O-*n*-Bu$)_4$]/$ZnEt_2$[2)] and [RhCl($PPh_3)_3$][3)] are representative catalysts for the head-to-tail dimerization of 1-alkynes to convert them to 2,4-disubstituted 1-buten-3-ynes (**1**), and some copper salts are known to be catalytically active for the head-to-head dimerization leading to 1,4-disubstituted 1-buten-3-ynes (**2**).[4)] [RuH_2(CO)($PPh_3)_3$] is the unique catalyst to convert 1-alkynes to cumulene derivatives **3**.[5)]

We wish to report herein a novel catalyst system, (η^5-$C_5Me_5)_2TiCl_2$/*i*-PrMgBr, which shows exceedingly high catalytic activities for the linear dimerization of various 1-alkynes to give the head-to-tail bound dimers **1** regioselectively. The present catalyst system is superior to the known catalysts with respect to regioselectivity, yield, reproducibility and broad applicability. Even more important is the experimental simplicity and the mild reaction conditions of our new process. It should be noted here that the formation of higher oligomers are negligible in the present system. This ambient catalyst system is also effective for the regioselective codimerization of two different 1-alkynes, which provides a variety of novel 2,4-disubstituted 1-buten-3-ynes.

Results and Discussion

Regioselective Dimerization of 1-Alkynes. In the preceding paper, we have reported the exceptionally high catalytic activity of (η^5-$C_5Me_5)_2TiCl_2$/RMgX or (η^5-$C_5Me_5)_2TiCl_2/NaC_{10}H_8$ toward the selective isomerization of 1-alkenes to (*E*)-2-alkenes.[6)] In our continuing investigations on titanocene species, we have found that "(η^5-$C_5Me_5)_2$TiH" species generated by reduction of (η^5-$C_5Me_5)_2TiCl_2$ with two equivalents of *i*-PrMgBr behaves as an efficient catalyst for the regioselective dimerization of 1-alkynes to lead to **1**. When a mixture of (η^5-$C_5Me_5)_2TiCl_2$/*i*-PrMgBr (2 mol % of (η^5-$C_5Me_5)_2TiCl_2$ based on 1-alkyne was used) and 1-butyne, 1-pentyne, 1-hexyne, or 1-octyne was stirred for 1—3 h at 30 °C in diethyl ether, the highly regioselective dimerization (>99%) occurred to give the corresponding dimers **1a**—**d** in 92—97% yields. The results are given in Table 1. The maximum turnover number for 1-hexyne was 2.0 (mol/mol min) in diethyl ether and 4.5 (mol/mol min) in THF. The corresponding reactions were examined with (η^5-$C_5Me_5)_2$-$TiCl_2/NaC_{10}H_8$ to find a significantly lower activity (turnover number was 0.24 mol/mol min in THF). Though normal and secondary alkyl-substituted acetylenes readily dimerize at ambient temperature, *t*-butylacetylene (3,3-dimethyl-1-butyne) was completely inert to both catalysts even at 60 °C and was recovered quantitatively. The present catalyst system is active also for 1-alkynes containing Me_3Si group, a leaving group useful for organic synthesis, but inactive for 1-alkynes substituted with an electron donating group such as EtO, EtS, or Et_2N. The greater reactivity of $Me_3SiC{\equiv}CH$ compared to *t*-BuC≡CH may be ascribed to the smaller cone angle and higher acidity of the former. The use of bulky η^5-C_5Me_5 ligand is essential to perform the present type dimerization. The (η^5-$C_5H_5)_2TiCl_2$/*i*-PrMgBr catalyst system with a less bulky ligand has practically no catalysis and preferred the oligomerization of 1-alkynes.



$$RC{\equiv}CH \xrightarrow{(\eta^5\text{-}C_5Me_5)_2TiCl_2/i\text{-}PrMgBr} RC{\equiv}C\text{–}\overset{R}{\overset{|}{C}}{=}CH_2 \qquad (2)$$

1a, R=Et
1b, R=*n*-Pr
1c, R=*n*-Bu
1d, R=*n*-C_6H_{13}
1e, R=Cyclohexyl
1f, R=Ph
1g, R=Me_3Si
1h, R=Me_3SiCH_2
1i, R=Me_3SiOCH_2

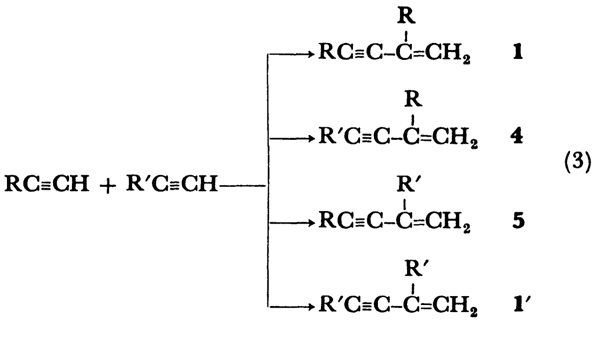
Regioselective Codimerization of 1-Alkynes. The successful regioselective dimerization of 1-alkynes prompted us to examine the codimerization between

Table 1. Homodimerization of 1-alkynes (RC≡CH) to 2,4-disubstituted 1-buten-3-ynes with $(C_5Me_5)_2TiCi_2$/*i*-PrMgBr(1:2) catalyst system[a)]

R	Products	GC yield/% (Isolated yield/%)
Et	**1a**	95 (91)
n-Pr	**1b**	97 (92)
n-Bu	**1c**	97 (91)
n-C_6H_{13}	**1d**	94 (90)
Cyclohexyl	**1e**	96 (90)
Ph	**1f**	92 (78)
Me_3Si	**1g**	95 (93)
Me_3SiCH_2	**1h**	96 (92)
Me_3SiOCH_2	**1i**	94 (90)
t-Bu		0
1-Cyclohexenyl		0
EtO		0
EtS		0
Et_2N		0

a) The reactions were carried out in diethyl ether at 30 °C for 1 h. Concentration of catalyst; 2 mol%. (Ratio of $(C_5Me_5)_2TiCl_2$/1-alkvne=1/50(mol/mol)).

two different ethynyl compounds which have normal, secondary or tertiary alkyl substituents. The following four isomers **1**, **4**, **5**, and **1′** are possible for the codimerization between RC≡CH and R′C≡CH. When the codimerization was carried out using a 1 : 1 mixture of two different normal alkyl-substituted acetylenes (R=Et and *n*-Bu), the four isomers were obtained with the



modest level of selectivities (entry 1 in Table 2). The yields of the respective isomers (**1**, **1′**, **4**, and **5**) are nearly equal. However, when the reactions of normal alkylacetylenes (RC≡CH) were conducted with second-

Table 2. Distributions and total yields of 2,4-disubstituted 1-buten-3-ynes obtained from a mixture of RC≡CH and R′C≡CH[a)]

Entry	R	R′	Reaction time/h	Distribution of the dimer/% 1	4	5	1′	Total yield/%
1	Et	*n*-Bu	1	28(**1a**)	27(**4a**)	27(**5a**)	18(**1c**)	86
2	*n*-Bu	Cyclohexyl	1	28(**1c**)	50(**4b**)	8	14(**1e**)	86
3	*n*-Bu	*t*-Bu	3	38(**1c**)	62(**4c**)	0	0	68
4	*n*-Bu	Me_3Si	1	6(**1c**)	92(**4d**)	0	2(**1g**)	92
5	Cyclohexyl	*t*-Bu	3	42(**1e**)	58(**4e**)	0	0	66
6	*n*-Bu	Me_3SiCH_2	1	31(**1d**)	43(**4f**)	7	19(**1h**)	86
7	Me_3SiCH_2	Me_3Si	1	10(**1h**)	82(**4g**)	0	8(**1g**)	96
8	Me_3SiOCH_2	*n*-Bu(1:1)	1	33(**1i**)	65(**4h**)	0	2(**1c**)	67
9	Me_3SiOCH_2	*n*-Bu(1:2)	1	15(**1i**)	83(**4h**)	0	2(**1c**)	65
10	Me_3SiOCH_2	*t*-Bu	3	48(**1i**)	52(**4i**)	0	0	63

a) Yield is expressed by (% conversion of RC≡CH+R′C≡CH)/2 and was determined by the gas chromatographic analysis. Reaction conditions; catalyst concentration, 2 mol% to the sum of RC≡CH and R′C≡CH; temperature, 30 °C in diethyl ether.

Table 3. Regioselective codimerization of ethynyl-1-cyclohexene or ethynylbenzene (R′C≡CH) with less acidic 1-alkynes (RC≡CH)[a)]

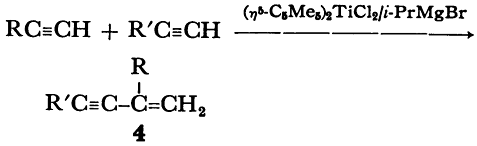
Entry	R	R′	Reaction time/h	Distribution of the dimer/% 1	4	5	1′	Total yield/%[b)]
11	*n*-Bu	1-Cyclohexenyl	1	0	99(**4j**)	0	1	91
12	Me_3SiCH_2	1-Cyclohexenyl	1	7(**1h**)	93(**4k**)	0	0	86
13	Me_3SiOCH_2	1-Cyclohexenyl	1	4(**1i**)	96(**4l**)	0	0	92
14	Me_3Si	1-Cyclohexenyl	1	21(**1g**)	79(**4m**)	0	0	80
15	Cyclohexyl	1-Cyclohexenyl	1	2(**1e**)	98(**4n**)	0	0	91
16	Ph	1-Cyclohexenyl	1	100(**1f**)	0	0	0	50
17	*t*-Bu	1-Cyclohexenyl	1	0	0	0	0	0
18	*n*-Bu	Ph	1	1(**1c**)	98(**4o**)	0	1(**1f**)	91
19	Me_3SiCH_2	Ph	1	12(**1h**)	76(**4p**)	0	12(**1f**)	89
20	Me_3SiOCH_2	Ph	1	1(**1i**)	97(**4q**)	0	2(**1f**)	93
21	Me_3Si	Ph	1	18(**1g**)	63(**4r**)	0	19(**1f**)	88
22	Cyclohexyl	Ph	1	0	93(**4s**)	0	7(**1f**)	89
23	*t*-Bu	Ph	1	0	0	0	100(**1f**)	49

a) Reactions were carried out at 30 °C in diethyl ether with 2 mol% of catalyst. b) Total yield is expressed by (sum of conversion for RC≡CH and R′C≡CH)/2.

ary or tertiary alkylacetylenes ($R'C{\equiv}CH$), the codimers were obtained with moderate regioselectivity (entries 2 and 3). The formation of **4** exceeded over that of the codimer **5** and homodimers **1** and **1′**. Similar trend was observed also in the reaction of ethynylcyclohexane with *t*-butylacetylene (entry 5) or in the reaction shown in entries 4, 6, and 7.

Thus, the more bulky alkyl groups are always introduced to the terminal position (C_4-carbon) of the 1-buten-3-ynes in preference to the internal position (C_2-carbon). In some favorable cases (entries 3, 4, 5, and 7), the formation of the dimers of the type **5** was completely suppressed. These results are reasonably interpreted by the steric effect of alkyl groups. Especially noteworthy is that the present catalyst system showed no catalysis toward the homo-dimerization of t-$BuC{\equiv}CH$ while it showed exceedingly high activity toward the codimerization of t-$BuC{\equiv}CH$ with normal or secondary alkyl-substituted acetylenes. Rather exceptional is the behavior of 3-trimethylsiloxy-1-propyne. Though the bulkiness of Me_3SiOCH_2 is nearly equal to that of *n*-Bu group and the acidity of $Me_3SiOCH_2C{\equiv}CH$ is a little higher than that of 1-hexyne as described later, the formation of **5** was completely suppressed. Since oxygen atom has a good affinity toward Ti atom, the observed enhanced regioselectivity is supposed to be the result of the interaction between the oxygen atom of $Me_3SiOCH_2C{\equiv}CH$ and the metal center.

To evaluate the electronic effect of substituent, the codimerization of ethynylcyclohexane with 1-ethynylcyclohexene or ethynylbenzene was tried (entries 15 and 22 in Table 3). Though the bulkiness of these three substituents is nearly the same, the regioisomers, 4-(1-cyclohexenyl)-2-cyclohexyl-1-buten-3-yne (**4n**) and 2-cyclohexyl-4-phenyl-1-buten-3-yne (**4s**), were formed with an extremely high selectivity. This result may be interpreted primarily by electronic effect or acidity of 1-alkynes. The $R'C{\equiv}C$ unit of the product is generally derived from the 1-alkynes of higher acidity and the $-C(R){=}CH_2$ unit is from less acidic 1-alkyne. The relative acidity strength of the 1-alkynes was estimated from the ^1H-NMR chemical shift values (Table 4) of the CH proton of 1-alkynes as $PhC{\equiv}CH > $ 1-ethynylcyclohexene $> Me_3SiC{\equiv}CH \simeq Me_3SiOCH_2C{\equiv}CH > t$-$BuC{\equiv}CH \simeq$ ethynylcyclohexane $\simeq n$-$BuC{\equiv}CH > Me_3SiCH_2C{\equiv}CH$. The CH signal appeared at lower field with increasing the acidity of 1-alkynes.[7] The ^{13}C-NMR chemical shift values also showed the similar relationship. The $C{\equiv}C$ and CH frequencies in their IR spectra are useless to estimate the relative acidity strength because the difference is too small. The reactions of 1-hexyne, 3-trimethylsiloxy-1-propyne or 3-trimethylsilyl-1-propyne with 1-ethynylcyclohexene or ethynylbenzene (entries 11—13, 18—20) also showed the highly regioselective formation of **4**. The good selectivity observed in the reaction of $Me_3SiC{\equiv}CH$ with n-$BuC{\equiv}CH$ or $Me_3SiCH_2C{\equiv}CH$ (entries 4 and 7 in Table 2) also may be interpreted by the relatively high acidity of $Me_3SiC{\equiv}CH$. However, in the reaction of 3,3-dimethyl-1-butyne with 1-ethynylcyclohexene or with ethynylbenzene, no reaction occurred. This is presumably due to the steric reasons as described later in the discussion. The structures of the resulting dimers and codimers were analyzed by the ^1H-NMR (see Experimental section) and ^{13}C-NMR (Table 5) with reference to the chemical shift values of starting 1-alkynes and related 1-alkenes.[8] In cases of $CH_2{=}C(CH_2OSiMe_3)C{\equiv}C$-$n$-Bu and $CH_2{=}C(n$-$Bu)C{\equiv}CPh$, the structures were identified after hydrogenation to $CH_3CH(CH_2OH)C_6H_{13}$ and $CH_3CH(n$-$Bu)$-CH_2CH_2Ph, respectively, by comparison with authentic samples. Thus, the present catalyst provides 1-buten-3-ynes bearing two different substituents on the C-2 and C-4 atom, most of which are not yet synthesized even in combination of conventional organic reactions.[9]



$$RC{\equiv}CH + R'C{\equiv}CH \xrightarrow{(\eta^5\text{-}C_5Me_5)_2TiCl_2/i\text{-}PrMgBr} R'C{\equiv}C\text{-}\overset{R}{\overset{|}{C}}{=}CH_2 \qquad (4)$$

4

$R'C{\equiv}CH$: bulky or acidic 1-alkyne
$RC{\equiv}CH$: less bulky or less acidic 1-alkyne

4a, $R=Et$, $R'=n$-Bu
4b, $R=n$-Bu, $R'=$cyclohexyl
4c, $R=n$-Bu, $R'=t$-Bu
4d, $R=n$-Bu, $R'=Me_3Si$
4e, $R=$cyclohexyl, $R'=t$-Bu
4f, $R=n$-C_6H_{13}, $R'=Me_3SiCH_2$
4g, $R=Me_3SiCH_2$, $R'=Me_3Si$
4h, $R=Me_3SiOCH_2$, $R'=n$-Bu
4i, $R=Me_3SiOCH_2$, $R'=t$-Bu
4j, $R=n$-Bu,
4k, $R=Me_3SiCH_2$
4l, $R=Me_3SiOCH_2$ $R'=$1-cyclohexenyl
4m, $R=Me_3Si$
4n, $R=$cyclohexyl
4o, $R=n$-Bu
4p, $R=Me_3SiCH_2$
4q, $R=Me_3SiOCH_2$ $R'=Ph$
4r, $R=Me_3Si$
4s, $R=$cyclohexyl

Table 4. ^1H- and ^{13}C-NMR chemical shift values for 1-alkynes[a)]

R in $RC{\equiv}CH$	^1H (δ) $HC{\equiv}C$-	^{13}C (δ)	
		C^1	C^2
Me_3SiCH_2	1.85	66.81	82.14
n-Bu	1.90	68.12	84.14
Cyclohexyl	2.01	67.93	88.68
t-Bu	2.05	66.64	92.65
Me_3SiOCH_2	2.34	72.93	82.08
Me_3Si	2.35	93.24	89.83
1-Cyclohexenyl	2.78	74.28	85.39
Ph	3.03	77.32	83.71

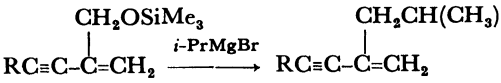
a) Measured in $CDCl_3$ at 30 °C at 100 MHz for the ^1H NMR and 22.5 MHz for the ^{13}C NMR spectra. Assignment of $RC^2{\equiv}C^1H$ was made from the non-decoupled spectra.

Table 5. ^{13}C-NMR chemical shift values (δ) for 2,4-disubstituted 1-buten-3-ynes and the deviation from the mean value (parentheses)[a)]

R	C-1	C-2	C-3	C-4	C-5	C-6	Compd[b)] (A)	Compd[b)] (B)
Et	111.8(5)	132.6(2)	80.5(2)	91.3(1)	30.9(2)	14.0(0)	2	2
n-Pr	119.5	132.2	81.3	89.8	39.8	22.4	1	1
n-Bu	120.3(14)	132.3(3)	81.4(9)	90.8(8)	37.1(3)	31.0(2)	7	4
n-C_6H_{13}	118.8(4)	132.8(2)	81.2	90.1	37.8(2)	31.5	2	1
Cyclohexyl	118.0(10)	137.8(3)	80.8(5)	94.5(4)	45.4(3)	29.6(1)	5	2
t-Bu			79.2(4)	99.2(4)	—	—	0	3
Me_3SiCH_2	118.1(17)	129.4(5)	81.0(9)	87.5(4)	28.5(2)	7.9(1)	4	2
Me_3SiOCH_2	118.9(9)	131.0(5)	83.2	88.6	64.9(3)	51.5	5	1
Me_3Si	133.5(11)	134.6(5)	95.8(28)	106.8(8)	—	—	3	3
Cyclohexenyl			87.0(21)	93.2(28)	—	—	0	5
Ph	120.7	137.7	89.2(12)	91.9(21)	—	—	1	6

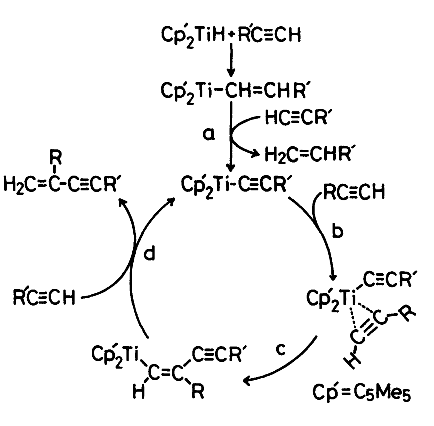
a) Numbering system follows $C^1{=}C^2(R^5)C^3{\equiv}C^4R^6$. The C-5 and C-6 express the carbons in R^5 and R^6 directly bonded to C-2 and C-4 atoms, respectively. The values were obtained by averaging the observed chemical shift values for **1a**—**i** and **4a**—**s** (deviation from the mean was shown in parentheses). b) The number of compounds used for the data collection regarding (A) C-1, C-2 and C-5 atoms and (B) C-3, C-4 and C-6 moiety.

By taking advantage of the ease of substitution of


$$\mathrm{RC{\equiv}C{-}\overset{\overset{\displaystyle CH_2OSiMe_3}{|}}{C}{=}CH_2} \xrightarrow{i\text{-PrMgBr}} \underset{\mathbf{4t}(\mathrm{R=Ph})}{\mathrm{RC{\equiv}C{-}\overset{\overset{\displaystyle CH_2CH(CH_3)_2}{|}}{C}{=}CH_2}} \qquad (5)$$

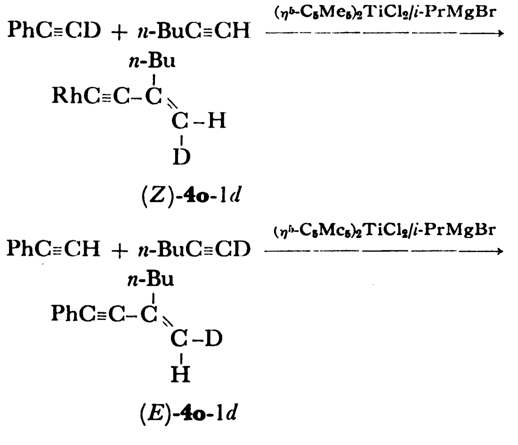
Me_3SiO group, the Me_3SiO group was transformed to *i*-Pr group by reaction with *i*-PrMgBr (Eq. 5). Similar exchange of the Me_3SiO group with an alkyl group is already known for the Ni- or Pd-catalyzed reaction of 3-trialkylsiloxy-1-butenes with PhMgX.[10)] The present sequence of reactions provides a useful route to introduce various kinds of alkyl groups into the C-2 atom of the 1-buten-3-ynes.

Reaction Pathway for the Codimerization of 1-Alkynes. A possible mechanism for the selective codimerization of 1-alkynes catalyzed by $(\eta^5\text{-}C_5Me_5)_2TiCl_2$/*i*-PrMgBr is shown in Scheme 1. Reduction of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ with *i*-PrMgBr will generate low-valent $(\eta^5\text{-}C_5Me_5)_2TiH$ species. The generation of similar species, $(\eta^5\text{-}C_5H_5)_2TiH$, has been suggested by Martin and Sato in the hydrotitanation of conjugated dienes with $(\eta^5\text{-}C_5H_5)_2TiCl_2/RMgX$[11)] and in the titanium-assisted hydromagnesiation of disubstituted acetylenes[12)] and carbonyl compounds.[13)] Hydrotitanation of alkenes with $(\eta^5\text{-}C_5H_5)_2TiH$[14)] and hydrozirconation of alkenes or alkynes with $(\eta^5\text{-}C_5H_5)_2ZrHCl$[15)] are already known. Formation of the low-valent $(\eta^5\text{-}C_5Me_5)_2Ti$ species may be ruled out because such species generally gives catalytically inactive titana-2,4-cyclopentadienes when it was reacted with 1-alkynes.[16)] The reactive species, $(\eta^5\text{-}C_5Me_5)_2TiH$, will readily react with 1-alkynes to give $(\eta^5\text{-}C_5Me_5)_2TiCH{=}CHR'$. Since $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ is known to be cleaved with 1-alkynes ($RC{\equiv}CH$) to give CH_4 and $(\eta^5\text{-}C_5H_5)_2Zr(C{\equiv}CR)_2$,[17)] it seems most likely that $(\eta^5\text{-}C_5Me_5)_2TiCH{=}CHR'$ reacts with $R'C{\equiv}CH$ to produce $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR'$ (step a). When two different 1-alkynes are present in the system, the more acidic 1-alkyne ($R'C{\equiv}CH$) will cleave the Ti–C bond in preference to the attack of a less acidic alkyne ($RC{\equiv}CH$) to result in the formation of $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR'$. Isolation of $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR$ or $(\eta^5\text{-}C_5H_5)_2TiC{\equiv}CR$ has not been achieved because of its thermal instability. In the case of $(\eta^5\text{-}C_5H_4Me)_2TiC{\equiv}CPh$, spontaneous dimerization to catalytically inactive $(\eta^5\text{-}C_5H_4Me)_4Ti_2[\mu\text{-}(1\text{-}3\text{-}\eta^2\text{-}, 2\text{-}4\text{-}\eta^2\text{-}1,4\text{-diphenylbutadiene})]$ occurs when free $PhC{\equiv}CH$ is absent in the reaction system.[18)] However, we found that when $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CPh$ was prepared *in situ* by reaction of $(\eta^5\text{-}C_5Me_5)_2TiCl$ with $LiC{\equiv}CPh$ in the presence of excess ethynylbenzene and 1-hexyne (1 : 1 mixture), the catalytic codimerization occurred successfully. The turnover number for this catalyst system (1.8 mol/mol min) is nearly equal to 2.0 mol/mol min for the $(\eta^5\text{-}C_5Me_5)_2TiCl_2$/*i*-PrMgBr system. This finding supports the above reaction pathway through $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR'$ species. Thus, the acidic 1-alkyne forms the $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR'$ at first and then insertion of less acidic 1-alkyne follows (step c) *via* an intermediate coordinated with $RC{\equiv}CH$ (step b). The subsequent Ti–C bond fission of the resulting $(\eta^5\text{-}C_5Me_5)_2TiCH{=}C(R)C{\equiv}CR'$ may be done with the



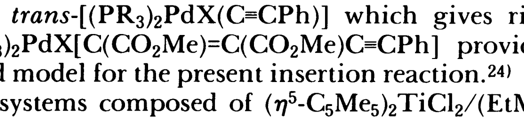
Scheme 1.

acidic R′C≡CH to release $CH_2{=}C(R)C{\equiv}CR'$ and to regenerate $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR'$ to complete the catalytic cycle. The direction of the alkynyl transfer is assumed to be controlled in the step b by steric repulsion between $\eta^5\text{-}C_5Me_5$ ligand and alkyl group of 1-alkynes. Coordination of RC≡CH in the opposite direction is sterically improbable. Insertion of RC≡CH to TiC≡CR′ bond will occur in the cis-fashion on a plane containing the Ti–C≡CR′ bond as predicted by the EH-MO calculation.[19] To verify this postulation, codimerization using PhC≡CD or *n*-BuC≡CD was examined. The 1 : 1 reaction of PhC≡CD with *n*-BuC≡CH in the presence of the catalyst gave (*Z*)-**4o**-1*d* in 98% selectivity (Eq. 6) while 1 : 1 mixture of PhC≡CH and *n*-BuC≡CD gave (*E*)-**4o**-1*d* in 97% selectivity (Eq. 7). The assignment of the structure was made with reference to the ¹H-NMR data for butadiene,[20] 1,3-pentadiene,[21] and ethenylbenzene[22] together with the NOE measurement (5—8%) in $CDCl_3$ and C_6D_6. Thus the cis-addition of less acidic 1-alkyne was verified in support of the above mechanism. Similar cis-addition of 1-alkynes is widely observed in the insertion reaction with transition metal complexes.[23] The reported insertion reaction of $MeO_2CC{\equiv}CCO_2Me$ into *trans*-$[(PR_3)_2PdX(C{\equiv}CPh)]$ which gives rise to $(PR_3)_2PdX[C(CO_2Me){=}C(CO_2Me)C{\equiv}CPh]$ provides a good model for the present insertion reaction.[24] Catalyst systems composed of $(\eta^5\text{-}C_5Me_5)_2TiCl_2/$(EtMgBr, *n*-BuMgBr, or PhMgI) also showed the activity similar to that of $(\eta^5\text{-}C_5Me_5)_2TiCl_2/i\text{-}PrMgBr$ for the codimerization of PhC≡CH and *n*-BuC≡CH, suggesting that the resulted Ti–R(R=Et, *n*-Bu, Ph) bond is cleaved by RC≡CH to generate the catalytically active $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR$ species. The isolation of $(\eta^5\text{-}C_5Me_5)_2TiC{\equiv}CR$ (R=*t*-Bu, 1-cyclohexenyl) and its stoichiometric reaction with various 1-alkynes are now in progress to get more evidence to verify the proposed mechanism.



$$PhC{\equiv}CD + n\text{-}BuC{\equiv}CH \xrightarrow{(\eta^5\text{-}C_5Me_5)_2TiCl_2/i\text{-}PrMgBr} RhC{\equiv}C{-}\overset{n\text{-}Bu}{C}{=}\underset{D}{C}{-}H \qquad (6)$$

(*Z*)-**4o**-1*d*



$$PhC{\equiv}CH + n\text{-}BuC{\equiv}CD \xrightarrow{(\eta^5\text{-}C_5Mc_5)_2TiCl_2/i\text{-}PrMgBr} PhC{\equiv}C{-}\overset{n\text{-}Bu}{C}{=}\underset{H}{C}{-}D \qquad (7)$$

(*E*)-**4o**-1*d*

Experimental

General Procedure. All operations were conducted with Schlenk technique under an argon atmosphere. 1-Butyne, 1-pentyne, 1-hexyne, 1-octyne, ethynylbenzene, and 3-oxa-1-pentyne were obtained commercially (Tokyo Kasei Co.), and 3,3-dimethyl-1-butyne,[25] ethynylcyclohexane,[26] 1-ethynylcyclohexene,[27] 3-trimethylsilyl-1-propyne,[28] *N,N*-diethylethynylamine,[29] and 3-thia-1-pentyne[30] were prepared by the reported methods. 3-Trimethylsiloxy-1-propyne was prepared from 2-propyn-1-ol and chlorotrimethylsilane. Ethynyltrimethylsilane was prepared from chlorotrimethylsilane and sodium ethynide (suspended in xylene) in DMF. All the ethynyl compounds were purified by distillation after drying over calcium hydride. $(\eta^5\text{-}C_5H_5)_2TiCl_2$[31] and $(\eta^5\text{-}C_5Me_5)_2TiCl_2$[32] were prepared referring to literatures. The GLC analyses were carried out with a Yanagimoto Model G-80 gas chromatograph using a column packed with Celite-Silicone DC-550, and the separation of products were done with a Varian-Aerograph Model 700 gas chromatograph using a column packed with DEGS. ¹H- and ¹³C-NMR spectra were recorded on a Varian XL-100 and a JEOL 90Q instruments, respectively. IR spectra were obtained on a Hitachi EPI-2 spectrometer. Mass spectra were recorded on a JEOL JMS-OISG-2 spectrometer.

Dimerization of 1-Alkynes. To a stirred suspension of dichlorobis(η^5-pentamethylcyclopentadienyl)titanum (39 mg, 0.1 mmol) in diethyl ether (1 cm³) was added a diethyl ether solution of isopropylmagnesium bromide (f=0.97, 0.21 cm³, 0.2 mmol). The color of the solution immediately turned into deep blue. After stirring the mixture for 10 min at 0 °C, 1-alkyne (5.0 mmol) was added to the resulting catalyst system over a 1 min period. The mixture was allowed to warm to 30 °C, magnetically stirred for 1—3 h, and then quenched with a small portion of 1 mol dm^{-3} aq HCl. The product was distilled and separated into the individual isomers on a preparative gas chromatograph when the separation was necessitated. Characterization of the product was made in terms of the ¹H-NMR (100 MHz), mass, IR spectra, and elemental analysis together with the ¹³C-NMR (22.5 MHz) spectrum (Table 5).

*2-Ethyl-1-hexen-3-yne (**1a**)*: ¹H NMR($CDCl_3$) δ=1.10 (3H, t, J=8.0 Hz, $C\underline{H}_3CH_2C{=}C$), 1.17 (3H, t, J=8.0 Hz, $C\underline{H}_3CH_2C{\equiv}C$), 2.16 (2H, q, J=8.0 Hz, $CH_2C{=}C$), 2.32 (2H, q, J=8.0 Hz, $CH_2C{\equiv}C$), 5.13, 5.18 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2970, 2940, 2884, 2860 (CH), 2235 (C≡C), 1613 (C=C), 1462, 1377, 1326, 1289, 1243, 894 ($C{=}CH_2$) cm^{-1}. MS (70 eV, EI) m/z (rel intensity), 108 (M^+, 1), 93 (0.7), 91 (1.1), 79 (0.9), 77 (1.7). Found: C, 88.82; H, 11.18%. Calcd for C_8H_{12}: C, 88.81; H, 11.19%.

*2-Propyl-1-hepten-3-yne (**1b**)*: ¹H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.0 Hz, $C\underline{H}_3(CH_2)_2C{=}C$), 1.00 (3H, t, J=7.0 Hz, $C\underline{H}_3(CH_2)_2C{\equiv}C$), 1.34—1.78 (4H, m, CH_2), 2.11 (2H, t, J=7.0 Hz, $-C\underline{H}_2C{=}CH_2$), 2.88 (2H, t, J=7.0 Hz, $CH_2C{\equiv}C$), 5.11, 5.20 (2H, m, $C{=}CH_2$). IR (neat) 3090, 2960, 2930, 2880, 2230, 1612, 1462, 1382, 1339, 1287, 893 cm^{-1}. MS (70 eV) m/z (rel intensity), 136 (M^+, 1), 109 (1.5), 94 (2.0), 92 (1.1), 77 (1.5). Found: C, 87.88; H, 11.81%. Calcd for $C_{10}H_{16}$: C, 88.16, H, 11.83%.

*2-Butyl-1-octen-3-yne (**1c**)*: ¹H NMR ($CDCl_3$) δ=0.91, 0.92 (6H, t, J=7.0 Hz, CH_3), 1.1—1.7 (8H, m, CH_2CH_2), 2.14 (2H, t, J=7.0 Hz, $CH_2C{=}C$), 2.32 (2H, t, J=7.0 Hz, $CH_2C{\equiv}C$), 5.12, 5.19 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2960, 2935, 2880, 2870, 2740, 1612, 1467, 1382, 1331, 1107, 892 cm^{-1}. MS (70 eV) m/z (rel intensity), 164 (M^+, 1), 122 (5.8), 107 (6.1). Found: C, 87.53; H, 12.30%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

*2-Hexyl-1-decen-3-yne (**1d**)*: ¹H NMR ($CDCl_3$) δ=0.90 (6H, t, J=6.0 Hz, CH_3), 1.1—1.7 (16H, m, $(CH_2)_4$), 2.13 (2H, t, J=7.0 Hz, $CH_2C{=}C$), 2.30 (2H, t, J=7.0 Hz, $CH_2C{\equiv}C$), 5.11, 5.19 (2H, m, $C{=}CH_2$). IR (neat) 3090, 2960, 2930, 2860, 2730, 1612, 1466, 892 cm^{-1}. MS (70 eV) m/z (rel intensity) 220 (M^+, 1), 205 (0.5), 191 (0.9). Found: C, 87.13, H, 12.86%. Calcd for $C_{16}H_{28}$: C, 87.20; H, 12.80%.

*2,4-Dicyclohexyl-1-buten-3-yne (**1e**)*: ¹H NMR ($CDCl_3$) δ=1.0—2.1 (20H, m, cyclohexyl), 1.9—2.2 (1H, m, $\overline{(CH_2)_5C}\underline{H}C{=}C$), 2.3—2.7 (1H, m, $\overline{(CH_2)_5C}\underline{H}C{\equiv}C$), 5.11, 5.17 (2H, m, $C{=}CH_2$). IR (neat) 3090, 2930, 2860, 2220, 1607, 1450, 888 cm^{-1}. MS (70 eV) m/z (rel intensity), 216 (M^+, 1), 201 (0.2), 187 (0.3), 173 (0.5). Found: C, 88.49; H, 11.31%. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18%.

*2,4-Diphenyl-1-buten-3-yne (**1f**)*: ^{1}H NMR ($CDCl_3$) $\delta=5.74$, 5.95 (2H, d, $J=8.0$ Hz, $C{=}CH_2$), 7.10—7.80 (10H, m, Ph). IR (neat) 3060, 3035, 2210, 1589, 1572, 1492, 1445, 1338, 1071, 1027, 897, 776, 760, 695 cm^{-1}. MS (70 eV) m/z (rel intensity), 204 (M^+, 1), 203 (0.7), 202 (0.6). Found: C, 93.60; H, 5.96%. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92%.

*2,4-Bis(trimethylsilyl)-1-buten-3-yne (**1g**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.15$ (9H, s, $Me_3SiC{=}C$), 0.19 (9H, s, $Me_3SiC{\equiv}C$), 5.68 (1H, d, $J=3.0$ Hz, $C{=}CH$), 6.10 (1H, d, $J=3.0$ Hz, $C{=}CH$). IR (neat) 3075, 2965, 2905, 2135, 1245, 973, 926, 840, 760, 698 cm^{-1}. MS (70 eV) m/z (rel intensity), 196 (M^+, 1), 181 (2.1), 155 (2.5). Found: C, 61.06; H, 10.25%. Calcd for $C_{10}H_{20}Si_2$: C, 61.14; H, 10.26%.

*5-Trimethylsilyl-2-trimethylsilylmethyl-1-penten-3-yne (**1h**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.03$ (9H, s, $\underline{Me}_3SiCH_2C{=}C$), 0.10 (9H, s, $\underline{Me}_3SiCH_2C{\equiv}C$), 1.57 (2H, s, $CH_2C{\equiv}C$), 1.73 (2H, m, $CH_2C{=}C$), 4.86, 5.03 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2960, 2900, 2230, 1595, 1292, 1245, 1158, 932, 850, 765, 698 cm^{-1}. MS (70 eV) m/z (rel intensity), 224 (M^+, 1), 209 (0.7), 136 (2.0). Found: C, 64.12; H, 10.75%. Calcd for $C_{12}H_{24}Si_2$: C, 64.20; H, 10.78%.

*2-Trimethylsiloxymethyl-4-trimethylsiloxy-1-penten-3-yne (**1i**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.14$ (9H, s, $\underline{Me}_3SiOCH_2C{=}C$), 0.19 (9H, s, $\underline{Me}_3SiOCH_2C{\equiv}C$), 4.11 (2H, t, $J=2.0$ Hz, $OCH_2C{=}C$), 4.41 (2H, s, $OCH_2C{\equiv}C$), 5.45, 5.55 (2H, m, $C{=}CH_2$). IR (neat) 2960, 2860, 1621, 1372, 1248, 1119, 1097, 1037, 872, 844, 756cm^{-1}. MS (70 eV) m/z (rel intensity), 256 (M^+, 1), 255 (1.1), 241 (1.9), 177 (2.4), 147 (5.6). Found: C, 56.42; H, 9.42%. Calcd for $C_{12}H_{24}O_2Si_2$: C, 56.19; H, 9.43%.

Codimerization of $RC{\equiv}CH$ with $R'C{\equiv}CH$. The procedure is essentially the same as that described for the homodimerization of 1-alkynes. For a typical example, a mixture of 1-hexyne (205 mg, 2.5 mmol) and ethynylbenzene (255 mg, 2.5 mmol) was added to the catalyst system, $(\eta^5\text{-}C_5Me_5)_2TiCl_2/i\text{-}PrMgBr$ (0.1 mmol/0.2 mmol), in diethyl ether (0.3 cm^3) at 0 °C and the mixture was stirred for a fixed time (1—3 h) at 30 °C. After the addition of 1 mol dm^{-3} aq HCl (0.3 cm^3), the organic layer was distilled to give 2-butyl-4-phenyl-1-buten-3-yne (**4o**) in 98% GC yield (90% isolated yield). This procedure was applied for the codimerization of other 1-alkynes and the separation of the isomers was made on a preparative gas chromatograph. The ^{1}H NMR, mass, and IR spectral data for the major products were given below. Elemental analysis agreed well with the calculated values.

*2-Ethyl-1-octen-3-yne (**4a**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.92$ (3H, t, $J=8.0$ Hz, CH_3), 1.08 (3H, t, $J=8.0$ Hz, CH_3), 1.20—1.70 (4H, m, CH_2CH_2), 2.16 (2H, q, $J=8.0$ Hz, $CH_2C{=}C$), 2.31 (2H, t, $J=7.2$ Hz, $CH_2C{\equiv}C$), 5.12, 5.19 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2240, 1615, 893 cm^{-1}. MS (70 eV) m/z (rel intensity) 136 (1), 121 (0.9), 107 (1.9).

*2-Butyl-1-hexen-3-yne (**5a**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.91$ (3H, t, $J=8.0$ Hz, CH_3), 1.16 (3H, t, $J=8.0$ Hz, CH_3), 1.2—1.7 (4H, m, CH_2CH_2), 2.12 (2H, t, $J=7.0$ Hz, $CH_2C{=}C$), 2.31 (2H, q, $J=8.0$ Hz, $CH_2C{\equiv}C$), 5.12, 5.19 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2240, 1615, 890 cm^{-1}. MS, m/z (rel intensity), 136, 121.

*2-Butyl-4-cyclohexyl-1-buten-3-yne (**4b**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.90$ (3H, t, $J=7.2$ Hz, CH_3), 1.1—2.0 (14H, m, CH_2CH_2 and C_6H_{11}), 2.13 (2H, t, $J=7.0$ Hz, $CH_2C{=}C$), 2.30—2.70 (1H, m, CH in C_6H_{11}), 5.12, 5.20 (2H, m, $C{=}CH_2$). IR (neat) 3090, 2225, 1610, 889 cm^{-1}. MS, m/z (rel intensity), 190 (1), 175 (0.2), 161 (1.3), 148 (1.8).

*2-Butyl-5,5-dimethyl-1-hexen-3-yne (**4c**)*: ^{1}H NMR($CDCl_3$) $\delta=0.92$ (3H, t, $J=7.1$ Hz, CH_3), 1.25 (9H, s, $C(CH_3)_3$), 1.25—1.66 (4H, m, CH_2), 2.30 (2H, t, $J=7.0$ Hz, $CH_2C{=}C$), 5.10, 5.19 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2225, 1612, 892 cm^{-1}. MS, m/z (rel intensity), 164 (1), 149 (1.2), 122 (3.1), 107 (18).

*2-Butyl-4-trimethylsilyl-1-buten-3-yne (**4d**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.18$ (9H, s, Me_3Si), 0.91 (3H, t, $J=7.0$ Hz, CH_3), 1.12—1.72 (4H, m, CH_2), 2.14 (2H, t, $J=7.0$ Hz, $CH_2C{=}C$), 5.21, 5.33 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2155, 1605 cm^{-1}. MS, m/z (rel intensity), 180 (1), 165 (4.8), 138 (2.9).

*2-Cyclohexyl-5,5-dimethyl-1-hexen-3-yne (**4e**)*: ^{1}H NMR ($CDCl_3$) $\delta=1.0$—1.5 (6H, m, CH_2), 1.26 (9H, s, $C(CH_3)_3$), 1.5—1.9 (4H, m, CH_2), 1.9—2.2 (1H, m, CH in C_6H_{11}), 5.08, 5.15 (2H, m, $C{=}CH_2$). IR (neat) 3090, 2215, 1607 cm^{-1}. MS, m/z (rel intensity), 190 (1), 175 (0.8), 161 (0.5), 147 (0.6).

*2-Hexyl-5-trimethylsilyl-1-penten-3-yne (**4f**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.12$ (9H, s, Me_3Si), 0.89 (3H, t, $J=6.3$ Hz, CH_3), 1.20—1.58 (8H, m, CH_2) 1.60 (2H, s, $CH_2C{\equiv}C$), 2.12 (2H, t, $J=7.0$ Hz, $CH_2C{=}C$), 5.07, 5.14 (2H, m, $C{=}CH_2$). IR (neat) 3095, 2230, 1612 cm^{-1}. MS, m/z (rel intensity), 222 (1), 207 (1.0), 193 (0.7), 179 (1.0).

*4-Trimethylsilyl-2-trimethylsilylmethyl-1-buten-3-yne (**4g**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.05$ (9H, s, $\underline{Me}_3SiCH_2$), 0.15 (9H, s, $Me_3SiC{\equiv}C$), 1.65 (2H, m, $SiCH_2C{=}C$), 5.01, 5.21 (2H, m, $C{=}CH_2$). IR (neat) 3100, 2150, 1595 cm^{-1}. MS, m/z (rel intensity), 210 (1), 195 (0.7), 155 (1.3).

*2-Trimethylsiloxymethyl-1-octen-3-yne (**4h**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.14$ (9H, s, Me_3Si), 0.93 (3H, t, $J=7.1$ Hz, CH_3), 2.22—2.72 (4H, m, CH_2), 2.31 (2H, t, $J=7.0$ Hz, $CH_2C{\equiv}C$), 4.09 (2H, t, $J=2.0$ Hz, $OCH_2C{=}C$), 5.34, 5.46 (2H, m, $C{=}CH_2$). IR (neat) 2235, 1620 cm^{-1}. MS, m/z (rel intensity), 210 (1), 195 (1.8), 137 (12).

*5,5-Dimethyl-2-trimethylsiloxymethyl-1-hexen-3-yne (**4i**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.12$ (9H, s, Me_3Si), 1.23 (9H, s, $(CH_3)_3C$), 4.06 (2H, t, $J=2.0$ Hz, $OCH_2C{=}C$), 5.31, 5.43 (2H, m, $C{=}CH_2$). IR (neat) 2225, 1620, 878 cm^{-1}. MS, m/z (rel intensity), 210 (1), 195 (1.4), 153 (0.3).

*2-Butyl-4-(1-cyclohexenyl)-1-buten-3-yne (**4j**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.91$ (3H, t, $J=7.2$ Hz, CH_3), 1.14—1.85 (8H, m, CH_2), 1.94—2.35 (6H, m, $CH_2C{=}C$), 5.16, 5.25 (2H, m, $C{=}CH_2$), 6.0—6.2 (1H, m, $CH{=}C$). IR (neat) 3100, 2205, 1605 cm^{-1}. MS, m/z (rel intensity), 188 (1), 173 (0.1), 159 (0.1), 146 (2.4).

*4-(1-Cyclohexenyl)-2-trimethylsilylmethyl-1-buten-3-yne (**4k**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.08$ (9H, s, Me_3Si), 1.45—1.85 (4H, m, CH_2), 1.69 (2H, m, $SiCH_2C{=}C$), 1.90—2.32 (4H, m, $CH_2C{=}C$), 4.97, 5.14 (2H, m, $C{=}CH_2$), 6.00—6.18 (1H, m, $CH{=}C$). IR (neat) 3095, 2200, 1592 cm^{-1}. MS, m/z (rel intensity), 218 (1), 203 (0.5), 190 (0.2), 175 (0.3).

*4-(1-Cyclohexenyl)-2-trimethylsiloxymethyl-1-buten-3-yne (**4l**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.8$ (9H, s, Me_3Si), 1.40—1.72 (4H, m, CH_2), 4.06 (2H, m, $OCH_2C{=}C$), 1.86—2.24 (4H, m, $CH_2C{=}C$), 5.33, 5.44 (2H, m, $C{=}CH_2$), 6.00 —6.18 (1H, m, $CH{=}C$). IR (neat) 3095, 2205, 1610 cm^{-1}. MS, m/z (rel intensity), 234 (1), 219 (0.8), 206 (0.2).

*4-(1-Cyclohexenyl)-2-trimethylsilyl-1-buten-3-yne (**4m**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.15$ (9H, s, Me_3Si), 1.44—1.80 (4H, m, CH_2), 1.96—2.38 (4H, m, $CH_2C{=}C$), 5.64 (1H, d, $J=3.0$ Hz, $CH{=}C$), 6.00 (1H, d, $J=3.0$ Hz, $CH{=}C$), 6.03—6.15 (1H, m, $CH{=}C$ in C_6H_9). IR (neat) 3065, 2180 cm^{-1}. MS, m/z (rel intensity), 204 (1), 189 (0.3), 176 (0.1), 163 (0.7).

*4-(1-Cyclohexenyl)-2-cyclohexyl-1-buten-3-yne (**4n**)*: ^{1}H NMR ($CDCl_3$) $\delta=1.0$—1.95 (14H, CH_2), 1.95—2.30 (5H, m, CH in C_6H_{11} and $CH_2C{=}C$), 5.15, 5.20 (2H, m, $C{=}CH_2$), 5.98—6.18 (1H, m, $CH{=}C$). IR (neat) 3090, 2200, 1600, 888 cm^{-1}. MS, m/z (rel intensity), 214 (1), 199 (0.3), 185 (0.5), 171 (0.4).

*2-Butyl-4-phenyl-1-buten-3-yne (**4o**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.95$ (3H, t, $J=7.0$ Hz, CH_3), 1.20—1.75 (4H, m, CH_2), 2.27 (2H, t, $J=7.5$ Hz, $CH_2C{=}C$), 5.28, 5.41 (2H, m, $C{=}CH_2$), 7.16—7.56 (5H, m, Ph). IR (neat) 2960, 2935, 2880, 1609, 1490, 1443, 897 cm^{-1}. MS, m/z (rel intensity), 184 (1), 142 (7.6), 141 (5.4), 127 (2.5).

*4-Phenyl-2-trimethylsilylmethyl-1-buten-3-yne (**4p**)*: ^{1}H NMR ($CDCl_3$) $\delta=0.11$ (9H, s, Me_3Si), 1.77 (2H, m, $SiCH_2C{=}C$), 5.08, 5.28 (2H, m, $C{=}CH_2$), 7.16—7.50 (5H, m, Ph). IR (neat) 2220, 1600, 870 cm^{-1}. MS, m/z (rel intensity), 214 (1), 199

(0.5), 159 (3.1).

4-Phenyl-2-trimethylsiloxymethyl-1-buten-3-yne (4q): ^{1}H NMR ($CDCl_3$) $\delta=0.19$ (9H, s, Me_3Si), 4.24 (2H, t, $J=2.0$ Hz, $OCH_2C=C$), 5.48, 5.54 (2H, m, $C=CH_2$), 7.18—7.56 (5H, m, Ph). IR (neat) 3080, 2218, 1613 cm^{-1}. MS, m/z (rel intensity), 230 (1), 215 (1.1), 159 (0.5), 141 (1.2).

4-Phenyl-2-trimethylsilyl-1-buten-3-yne (4r): ^{1}H NMR ($CDCl_3$) $\delta=0.21$ (9H, s, Me_3Si), 5.74 (1H, d, $J=3.5$ Hz, C=CH), 6.16 (1H, d, $J=3.5$ Hz, C=CH), 7.20—7.52(5H, m, Ph). IR (neat) 3080, 2190, 1596, 840 cm^{-1}. MS, m/z (rel intensity), 200 (1), 185 (0.6), 159 (1.0).

2-Cyclohexyl-4-phenyl-1-buten-3-yne (4s): ^{1}H NMR ($CDCl_3$) $\delta=1.1$—1.9 (10H, m, CH_2), 2.1—2.3 (1H, m, CH in C_6H_{11}), 5.27, 5.38 (2H, m, $C=CH_2$), 7.12—7.56 (5H, m, Ph). IR (neat) 1607, 892 cm^{-1}. MS, m/z (rel intensity), 210 (1), 195 (0.3), 181 (0.7), 167 (0.6).

Identification of 2-Butyl-4-phenyl-1-buten-3-yne (4o): The structure of the sample was identified with authentic samples after converting it to (3-methylheptyl)benzene by hydrogenation on Pd-charcoal. The authentic sample was prepared from the reaction of phenethylmagnesium bromide with 2-hexanone followed by hydrolysis, dehydration with *p*-toluenesulfonic acid and hydrogenation on Pd-charcoal.

(3-Methylheptyl)benzene: ^{1}H NMR ($CDCl_3$) $\delta=0.76$—1.05 (6H, m, CH_3), 1.07—1.80 (9H, m, CH_2), 2.36—2.80 (2H, m, $C\underline{H}_2Ph$), 7.00—7.42 (5H, m, Ph). IR (neat) 3025, 2940, 2925, 2880, 2860, 1604, 1455, 747, 700 cm^{-1}

Identification of 2-Trimethylsiloxymethyl-1-octen-3-yne (4h). A pure sample of the dimer (700 mg, 3.3 mmol) was treated with 0.1 mol dm^{-3} aq NaOH (1 cm^3) in 5 cm^3 methanol to give 2-hydroxymethyl-1-octen-3-yne in 83% yield which was then converted to a 1:1 mixture of 2-methyl-1-octanol and 2-methyloctanal by hydrogenation on Pd–C. The structure of these two products was identified with authentic samples in terms of the ^{1}H NMR and IR spectra, and gas chromatographic analysis. 2-Methyl-1-octanol was prepared by the literature procedure[33] and was converted to 2-methyloctanal by reaction with pyridinium chlorochromate[34] in CH_2Cl_2.

Analysis of Codimers Obtained from Monodeuterio-1-alkynes. $PhC\equiv CD$ and n-$BuC\equiv CD$ were prepared by deuteration of $PhC\equiv CMgBr$ or n-$BuC\equiv CMgBr$ with D_2O (99.5% purity) and were reacted with n-$BuC\equiv CH$ and $PhC\equiv CH$, respectively, under the same reaction conditions as described above.

(E)*-2-Butyl-4-phenyl-1-buten-3-yne-1*d *((*E*)-4o-1*d*)*: ^{1}H NMR ($CDCl_3$) $\delta=0.95$ (3H, t, CH_3), 1.21—1.74 (4H, m, CH_2), 2.28 (2H, t, $CH_2C=C$), 5.41 (1H, m, C=CHD) 7.2—7.5 (5H, m, Ph). IR (neat) 2960, 2940, 2880, 2860, 2260, 2220, 1598, 1580, 1490, 1445, 849 cm^{-1}. MS (70 eV) m/z (rel intensity), 185 (M^+).

(Z)*-2-Butyl-4-phenyl-1-buten-3-yne-1*d *((*Z*)-4o-1*d*)*: ^{1}H NMR ($CDCl_3$) $\delta=$ 0.95 (3H, t, CH_3), 1.21—1.74 (4H, m, CH_2), 2.28 (2H, t, $CH_2C=C$), 5.28 (1H, m, C=CHD) 7.1—7.4 (5H, m, Ph). IR (neat) 2960, 2940, 2880, 2860, 2280, 2240, 1598, 1583, 1490, 1445, 842 cm^{-1}. MS (70 eV) m/z (rel intensity), 185 (M^+).

Preparation of 2-(2-methylpropyl)-4-phenyl-1-buten-3-yne (4t). After treating $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ (39 mg, 0.1 mmol) with isopropylmagnesium bromide ($f=0.97$, 3.1 cm^3, 3.0 mmol) in diethyl ether (1 cm^3), an equimolar mixture of ethynylbenzene (2.5 mmol) and 3-trimethylsiloxy-1-propyne (2.5 mmol) was added to the resulting solution. The mixture was stirred at 30 °C for 3 h and then quenched with aq HCl. Fractional distillation gave **4t** in 83% yield. ^{1}H NMR ($CDCl_3$) $\delta=0.97$ (6H, d, $J=6.0$ Hz, $(C\underline{H}_3)_2CH$), 1.80—2.20 (3H, m, $(CH_3)_2C\underline{H}C\underline{H}_2$), 5.27, 5.45 (2H, m, $C=CH_2$), 7.20—7.56 (5H, m, Ph). IR (neat) 2960, 2930, 2880, 2220, 1609, 1466, 1443, 1386, 1370, 1315, 901, 758, 695 cm^{-1}. MS, m/z (rel intensity), 184 (1), 169 (1.0), 142 (2.0), 141 (1.4).

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