Aldehyde Addition and Copper-Mediated Allylation of Bicyclic Alkoxytitanacyclopentenes and -Pentadienes: New Selectivities and an Unusual Reaction

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Abstract: Bicyclic titanacyclopentenes generated in situ from 1,6-enynes and (η^2-propene)Ti(O-*i*-Pr)$_2$ (**1**) reacted with aldehydes at their alkenyl−titanium bond in the absence or presence of Ti(O-*i*-Pr)$_n$Cl$_{4-n}$ (n = 2 or 3) to give allyl alcohols such as **5**−**7** as a nearly single stereoisomer in good yields. Upon workup with DCl/D$_2$O or iodine, deuterio and iodo derivatives, **8** and **9**, were obtained. Bicyclic titanacyclopentadienes prepared analogously from 1,6- or 1,7-diynes and **1** also reacted with aldehydes in the presence of an additional equivalent of Ti(O-*i*-Pr)$_2$Cl$_2$ to afford 1,2-dialkylidenecyclopentanes or -cyclohexanes having an alcohol moiety in their side chain in good yields. In place of the simple hydrolysis, deuteriolysis or iodinolysis gave the corresponding derivatives such as **21** or **22**. Treatment of 1,6-enyne **10** with **1** in the standard way and then with a slight excess of *i*-PrMgCl at −50 °C generated a new titanium species that, upon reaction with aldehydes, afforded unexpected adducts **34** and **41**−**45** virtually as a single isomer. Copper-mediated allylation of dialkoxytitanacyclopentene such as **3** with allyl bromide proceeded at their vinyl−titanium bond to give **48** and **50**. Likewise, dialkoxytitanacyclopentadiene prepared from **29** and **1** underwent the regioselective copper-mediated monoallylation to give a 9:1 mixture of **53** and **54**. Upon workup with deuteriochloric acid, the corresponding deuterated product was obtained with a high degree of deuterium incorporation.

Introduction

Almost all of the group 4 metallabicycles utilized in organic synthesis have a bis(η^5-cyclopentadienyl)titanium or -zirconium moiety as the metal portion (Figure 1, ML$_m$ = TiCp$_2$ or ZrCp$_2$).[1] These compounds are readily available from the corresponding bis-unsaturated compounds and a low-valent metal species and undergo coupling reactions with a variety of electrophiles (El$^+$) to enable introduction of a carbon side chain and/or functional groups.[1] As the reactivities of metal complexes are often considerably affected by the nature of their ligands, the same type of metallacycles yet having ligands other than Cp may alter their behavior in the above reactions, possibly leading to development of new reactivity and selectivity.[2] Alkoxy ligands are a reasonable choice because group 4 metal alkoxides are well-known and the alkoxide group is distinctive from the η^5-cyclopentadienyl group in terms of both electronic and steric reasons. In conjunction with this discussion, a generation of new titanabicycles having alkoxy ligands (Figure 1, ML$_m$ = Ti(O-*i*-Pr)$_2$) has been recently reported.[3−5] We would like to report here the scope of their two fundamental reactions for carbon−carbon bond formation, that is, aldehyde addition[6] and allylation, emphasizing the unique feature observed for these metallacycles.

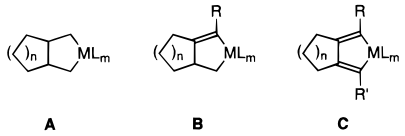

Figure 1.

Results and Discussion

Aldehyde Addition. When titanacyclopentene **3**, generated in situ from enyne **2** and (η^2-propene)Ti(O-*i*-Pr)$_2$ (**1**) in 90−97% yield determined by hydrolysis and deuteriolysis,[3a] was allowed to react with cyclohexanecarbaldehyde, allyl alcohol **5** was obtained in 7% yield as the coupling product (see eq 1). The production of **5** was quite unexpected because the corresponding Cp$_2$-zirconacyclopentenes (Figure 1, **B**, ML$_m$ = ZrCp$_2$) had been reported to react with aldehydes at their alkyl−zirconium bond, not giving the allyl alcohols such as **5**.[1b,7] Gratifyingly, the low yield of **5** was soon improved by the

(1) (a) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl*. **1987**, *26*, 723. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev*. **1988**, *88*, 1047. (c) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, p 1163. (d) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696. (e) Negishi, E.; Takahashi, T. *Acc. Chem. Res*. **1994**, *27*, 124. (f) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burkalov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (g) Sato, F.; Urabe, H. In *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996; p 23.

(2) For the use of mono(cyclopentadienyl)zirconium trichloride in place of bis(cyclopentadienyl) complexes in the diene cyclization, see: Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc*. **1989**, *111*, 6435.

(3) (a) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett*. **1995**, *36*, 4261. (b) Urabe, H.; Takeda, T.; Sato, F. *Tetrahedron Lett*. **1996**, *37*, 1253. (c) Suzuki, K.; Urabe, H.; Sato, F. *J. Am. Chem. Soc*. **1996**, *118*, 8729. (d) Urabe, H.; Suzuki, K.; Sato, F. *J. Am. Chem. Soc*. **1997**, *119*, 10014. (e) Hideura, D.; Urabe, H.; Sato, F. *Chem. Commun*. **1998**, 271.

(4) For a relevant review, see: Sato. F.; Urabe, H.; Okamoto, S. *J. Synth. Org. Chem. Jpn*. **1998**, *56*, 424.

(5) For titanacycles having bulky aryloxy ligands, see: (a) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911. (b) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc*. **1997**, *119*, 8630.

(6) A portion of this work has been communicated. Urabe, H.; Sato, F. *J. Org. Chem*. **1996**, *61*, 6756.

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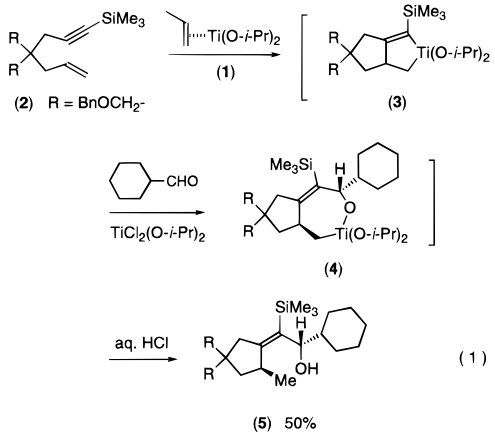
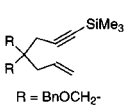
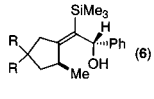
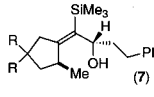
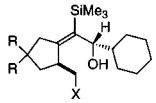
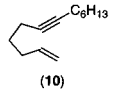
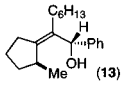


addition of an additive: if the aldehyde addition was performed in the presence of an extra equivalent of $Ti(O\text{-}i\text{-}Pr)_2Cl_2$, the desired product **5** was now obtained in 50% yield with very high regio- and stereoselectivities (eq 1 and entries 3 and 4 in Table 1). Other additives including $TiCl(O\text{-}i\text{-}Pr)_3$, $TiCl_4$, $ZnCl_2$, Me_3SiCl, and $BF_3{\cdot}OEt_2$ proved to be less effective (around or less than 30% yield of the product). Although the exact role of the externally added titanium salt is unclear at present, it may activate the aldehyde as a Lewis acid.[8] Additional results are summarized in Table 1. The reaction of titanabicycle **3** and an aromatic aldehyde required $TiCl(O\text{-}i\text{-}Pr)_3$ as the more preferable additive than $TiCl_2(O\text{-}i\text{-}Pr)_2$ in order to afford the product in good yield (entry 1). The stereochemistry of the tetra-substituted double bond of the products was determined by NOE study of ^{1}H NMR spectroscopy, and the relative stereochemistry of the hydroxy and methyl groups will be discussed later. The presence of the intermediate titanium species **4** in eq 1 was confirmed by subsequent deuteriolysis or iodinolysis to give the corresponding deuterated product **8** or the iodide **9** in good yields (entries 5 and 6).

Titanacyclopentene **11** from enyne **10** having an alkyl group rather than a trimethylsilyl group for the acetylenic substituent no longer requires the assistance of the additive to undergo the addition to aldehyde (Scheme 1). When enyne **10** was treated with **1** followed by benzaldehyde at −50 °C for 2 h, the desired product **13** was produced in 57% yield as an 85:15 mixture of diastereoisomers, from which the pure major isomer was separated in 41% yield by routine flash chromatography on silica gel. Minimization of the steric hindrance around the reacting position appears to be a critical factor for a smooth reaction in the case of the titanacyclopentenes such as **11** (as compared to **3**). To determine the 1,4-relative stereochemistry with respect to the methyl and hydroxy groups of **13**, we carried out iodinolysis of the intermediate oxatitanacycle **12** to give the corresponding iodide **14**. Ring closure of **14** with KH in THF took place to give bicyclic ether **15**. The stereochemistry of **15** was unequivocally determined by ^{1}H NMR analysis (coupling constants and NOE enhancements as depicted), which, in turn, confirmed the stereochemistry of the major isomer of **13** as depicted.

The same technique to determine the relative stereochemistry of the aforementioned silyl substituted adducts **5**−**7** (Table 1)

Table 1. Cyclization of Enynes and Subsequent Reaction with Aldehydes[a]

Entry	Enyne	Aldehyde (equiv)	Additive	Workup	Product	Yield (%)[b] [Ds[c]]
1	 R = BnOCH2- (2)	PhCHO (1.5)	Ti(O-i-Pr)3Cl	H+	 (6)	54 [>95:<5]
2	2	 (2)	Ti(O-i-Pr)2Cl2	H+	 (7)	66 [96: 4]
					 X = H (5)	
3	2	(0.6)	"	H+		(62)[d]
4	2	(2)	"	H+	H (5)	50(53-60) [single[e]]
5	2	"	"	D+	D (8)	60 [98%d]
6	2	"	"	I2	I (9)	37(58)
7	 (10)	PhCHO (1.5)	None	H+	 (13)	57 [85:15]

[a] See eq 1. [b] Isolated yields. Yields determined by ^{1}H NMR spectroscopy are shown in parentheses. [c] Diastereoselectivity. [d] Based on aldehyde. [e] Product was isolated as a single isomer.

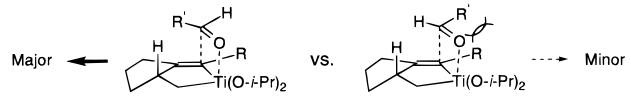
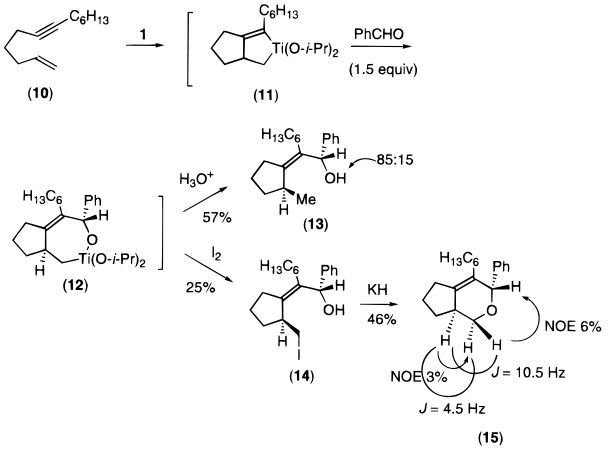


Figure 2.

Scheme 1



so far failed due to the instability of the iodinated adduct such as **9**. However, ^{1}H NMR spectra of the authentic **13** and the compounds **6** and **7** in question show the same tendency with respect to the peak positions of the methyl proton and the allylic proton α to the hydroxy group. Namely, both protons of the major isomers always display an upfield shift as shown in the experimental part. On the basis of these observations, the structures of **6** and **7** and, hence, **5** are assigned parallel to that of **13** by analogy.[9]

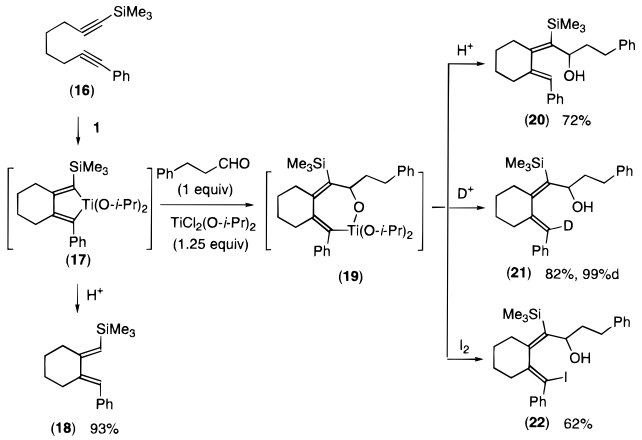
The stereochemical course of the addition would be well explained by the least hindered approach of the aldehyde to the reaction center from the convex face as illustrated above (Figure 2), where the R′ group of an aldehyde is placed so as not to suffer from the repulsion by the eclipsing R group of the

(7) Copéret, C.; Negishi, E.; Xi, Z.; Takahashi, T. *Tetrahedron Lett.* **1994**, *35*, 695.

(8) For reviews on organotitanium reagents, see: (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1986. (b) Ferreri, C.; Palumbo, G.; Caputo, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, p 139. (c) Reetz, M. T. In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: Chichester, 1994; p 195.

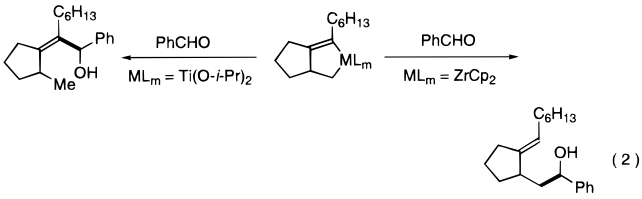
(9) Accordingly, our earlier (tentative) assignment to the stereochemistries of **5**−**7** shown in ref 6 turned out to be wrong and should be revised.

Scheme 2. Reaction of a Titanacyclopentadiene with Aldehyde



titanacycle. This rationalization is consistent with the observation that the bulkier the R group becomes (C_6H_{13} → Me_3Si), the higher is the selectivity attained in the addition (R′ = Ph, 85:15 → >95:<5).

Two characteristic features should be noted for the above reactions. The first is that the aldehyde addition proceeded selectively at the alkenyl−metal bond rather than at the alkyl−metal bond of the titanacycle, which is in marked contrast to and complementary with the aforementioned reactions of Cp_2-zirconacyclopentenes[1b,7] as shown in eq 2 (bold lines show the newly formed carbon−carbon bond).



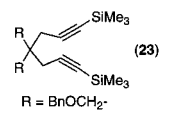
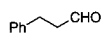
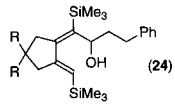
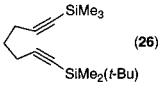
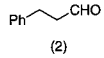
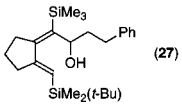
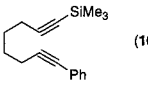
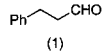
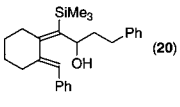
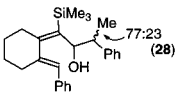
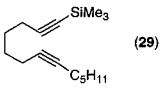
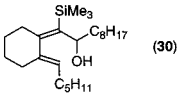
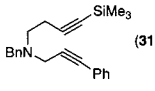
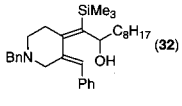
(2)

The second point is that high 1,4-diastereoselectivity of the resultant allyl alcohol, especially in the silylated series (>95:<5 by ^{1}H NMR analysis in comparison with an authentic sample), could be attained.

Addition of metallacyclopenta*dienes* to aldehydes is a related reaction to give dienyl alcohol, but its viability as a synthetic tool has not been pursued. This type of reaction with Cp_2-titanacyclopentadiene and its zirconium counterpart (Figure 1, **C**, ML_m = $TiCp_2$ or $ZrCp_2$) has not appeared. One precedent hitherto known is that a diaryloxytitanacyclopentadiene (Figure 1, **C**, ML_m = $Ti[O(2,6\text{-}Ph_2C_6H_3)]_2$) undergoes the addition to benzophenone, but the generality of the reaction has not been reported.[5] The aforementioned finding of the preferred transfer of the alkenyl−metal bond in the dialkoxytitanacyclopentenes prompted us to investigate the addition of the titanacyclo*pentadienes* to aldehydes. Titanacyclopentadiene **17** generated from the diyne **16** and **1**[3a] in >93% yield as estimated by protonolysis (to give **18**) reacted with an aldehyde in the presence of an additional equivalent of $TiCl_2(O\text{-}i\text{-}Pr)_2$ to furnish the adduct **20** in a good yield after hydrolysis (Scheme 2). Virtually no trace of another regioisomer formed, which proves that the reaction was highly regioselective. The reaction should proceed through the intermediate titanium species **19**, the presence of which was verified by its deuteriolysis and iodinolysis, to give the corresponding products **21** and **22**.

Various 1,6- and 1,7-diynes are suitable substrates for this cyclization/aldehyde addition as shown in Table 2 to give 1,2-

Table 2. Cyclization of Diynes and Subsequent Reaction with Aldehydes[a]

Entry	Diyne	Aldehyde (equiv)	Product	Yield (%)[b]
1	 R = $BnOCH_2$-	(23)  (2)	 (24)	81
2	23	 (2)	 (25)	59
3	 (26)	 (2)	 (27)	41
4	 (16)	 (1)	 (20)	72 (82)
5		(2)		80 (quant)
6	16	 (1)	 77:23 (28)	60
7	 (29)	$C_8H_{17}CHO$ (1)	 (30)	47
8	 (31)	$C_8H_{17}CHO$ (1)	 (32)	73

[a] See Scheme 2. [b] Isolated yields. Yields determined by ^{1}H NMR spectroscopy are shown in parentheses.

dialkylidenecyclopentane and -hexane frameworks. In addition, a nitrogen heterocycle could be prepared as well (entry 8). The addition of the titanacyclopentadienes to aldehydes always proceeded at the carbon bearing a silyl group. The α-charge stabilizing effect of a silyl group[10] in the transition state to increase the reactivity of the R_3SiC−Ti bond toward aldehydes would account for this regioselectivity. In the case of a diyne having two different silyl groups such as Me_3Si and (*t*-Bu)-Me_2Si (entry 3), the addition to an aldehyde took place at the carbon bearing the less hindered trimethylsilyl group to yield **27**, the regioisomer of which could not be isolated. Thus, from the synthetic point of view, the appropriate choice of acetylenic substituent may discriminate between the two acetylenic termini. In the reaction with α-phenylpropionaldehyde, moderate diastereoselectivity, approximately 3:1−4:1, was observed (entry 6).[11] Like the reaction of the aforementioned titanacyclopentenes, if an additional portion of $TiCl_2(O\text{-}i\text{-}Pr)_2$ was not added prior to the aldehyde addition, the product yields decreased by 10−30%.

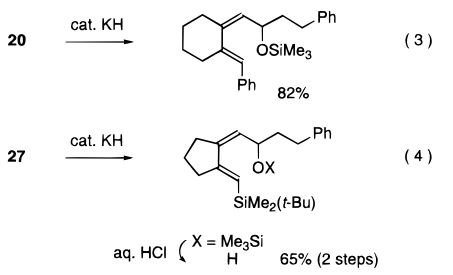
While the silylated diene moiety involved in the above products is a useful synthetic intermediate as such,[1,10,12,13] the silyl group adjacent to the hydroxy group may be selectively

(10) (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981.

(11) For the diastereoselectivity in the nucleophilic addition to chiral aldehydes, see: (a) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 111. (b) Anh, N. T. *Top. Curr. Chem.* **1980**, *88*, 145. (c) Seebach, D.; Weidmann, B.; Widler, L. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Otto Salle: Frankfurt am Main, 1983; Vol. 3, p 217.

(12) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422.

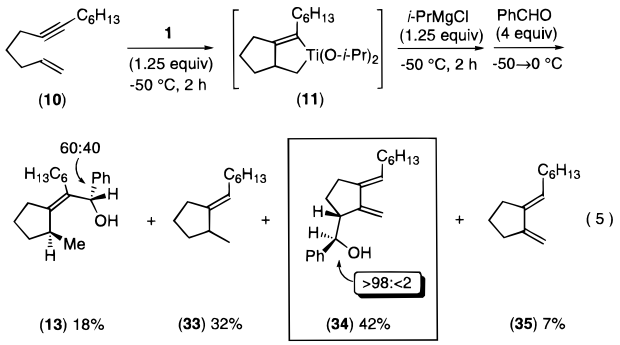
removed, if necessary, under basic conditions as exemplified in eqs 3 and 4.[14] From the synthetic point of view, this



conversion serves as a method to prepare *E,Z*-dialkylidenecyclopentanes and -hexanes, the synthesis of which is otherwise a tedious process. This desilylation may also be operative for the adducts **5**−**7**.

Unusual Coupling Reaction with Aldehydes. η^5-Cyclopentadienyl ligands once complexed to titanium and zirconium are difficult to exchange or remove. Considering this point, we thought that one important feature of dialkoxytitanacycles could be characterized by easy modification of their ligands. In an extreme case, the alkoxy ligand could be removed from the metal, which is, in other words, the reduction of the metal center. A few methods are available for this latter process. For example, the action of 2 equiv of a Grignard reagent to $Ti(IV)(OR)_4$ generates (η^2-alkene)$Ti(II)(OR)_2$,[15] as amply demonstrated in the generation of **1**.[4] A related reaction, involving the removal of a Cl ligand, is the treatment of a $Cp_2Ti(IV)Cl_2$ with 1 equiv of an appropriate Grignard reagent, giving $Cp_2Ti(III)Cl$.[16]

Under the hypothesis that a Grignard reagent would reduce the dialkoxytitanacycle as described above, we carried out the following experiment (eq 5). After the enyne **10** was treated



with **1** in the standard way, the solution of **11** was stirred with a slight excess of *i*-PrMgCl at −50 °C for an additional 2 h. To the resultant dark-brown mixture was added excess benzaldehyde at the same temperature. The reaction was warmed to an ice-bath temperature, during which the color of the solution turned light red. After aqueous workup, the normal adduct **13**, the same as the one in Scheme 1, was obtained in low yield and with inferior diastereoselectivity. However, unexpectedly, the main product in this reaction was a new adduct **34**, which was obtained virtually as a single stereoisomer and could be

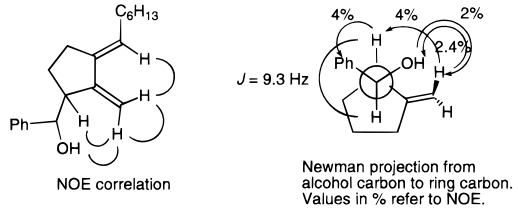
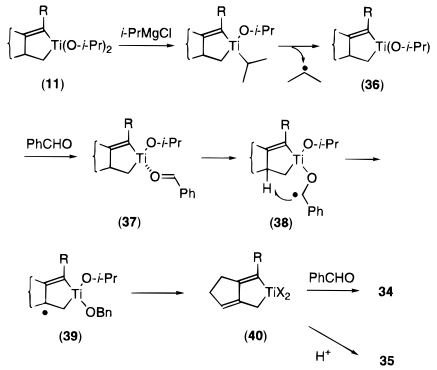


Figure 3. Structural determination of **34**.

considered as a *dehydrogenated* form of an isomer of **13**! Its structure was established by spectroscopic means and elemental analysis.[17] Moreover, the fine structure of the stereogenic centers was deduced based on consideration of the coupling constants and NOE experiments of ^{1}H NMR spectroscopy as shown in Figure 3.

The same type of product as **34** could be obtained from other combinations of enynes and aldehydes including a heteroaromatic aldehyde, aliphatic aldehydes, and an enyne having a functional group, the results of which are summarized in Table 3. In all cases, a virtually single isomer was isolated, and its stereochemistry was assigned based on the assumption that the addition took place in the same manner as the case of **34**. Synthetically, compounds of a similar structure to those in Table 3 could be prepared by the previously reported allenyne cyclization with **1** followed by the addition of aldehydes.[19] However, monosubstituted terminal allene **46** was not an acceptable substrate in this allenyne cyclization, failing to furnish the titanacycle **47** and, consequently, the corresponding adduct **34** (eq 6). Thus, the present cyclization starting from far more easily available *enynes* followed by *dehydrogenation* and trap

(17) The mechanistic rationale for this unusual reaction could be proposed as follows. The formation of the benzaldehyde adduct **34** along with the conjugated diene **35** (eq 5), the latter of which should arise from the simple protonation of the same intermediate, could assume the intermediate generation of the new titanacycle **40** in the following equation. It should be noted that the generation of **40** is triggered *by the injection of aldehyde*, because simple hydrolysis of the intermediate **36** after the treatment with *i*-PrMgCl but *before* the addition of aldehyde merely yields the ordinary cyclization product **33** shown in eq 5 in 88% yield but no trace of the conjugated diene **35**. Thus, in the possible reaction pathway from **11** to **40**, the added aldehyde plays a critical role. One-electron reduction of the aldehyde with the low-valent titanacycle **36** via **37** would generate a radical species such as **38**,[18] which abstracts the nearby hydrogen of the titanacycle to give the radical intermediate **39**. This radical intermediate collapses to give the new titanacycle **40** with hydrogen radical abstraction or radical disproportionation.



(18) Generation of α-oxy radicals by reduction of aldehydes and ketones with low-valent titanium reagents has been widely accepted as a step of the pinacol-type coupling reactions. For review, see: (a) Lenoir, D. *Synthesis* **1989**, 883. (b) Robertson, G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 563. (c) For latest reports, see: Barden, M. C.; Schwartz, J. *J. Am. Chem. Soc*. **1996**, *118*, 5484. (d) Gansäuer, A. *Synlett* **1997**, 457. (e) For other radical reactions induced by a low-valent titanium complex, see: RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc*. **1994**, *116*, 986 and references therein.

(19) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc*. **1997**, *119*, 11295.

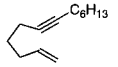
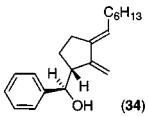
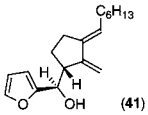
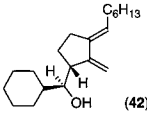
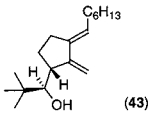
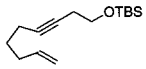
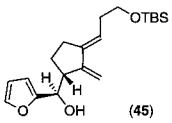
(13) (a) Luh, T.-Y.; Wong, K.-T. *Synthesis* **1993**, 349. (b) Fringuelli, F.; Taticchi, A. *Dienes in the Diels*−*Alder Reaction*; Wiley: New York, 1990.

(14) (a) Harada, K.; Urabe, H.; Sato, F. *Tetrahedron Lett*. **1995**, *36*, 3203. (b) Sato, F.; Tanaka, Y.; Sato, M. *J. Chem. Soc., Chem. Commun*. **1983**, 165.

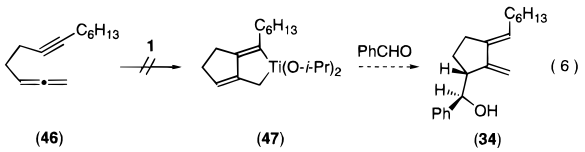
(15) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevski, D. A. *Synthesis* **1991**, 234.

(16) (a) Martin, H. A.; Jellinek, F. *J. Organomet. Chem*. **1968**, *12*, 149. (b) Martin, H. A.; Jellinek, F. *J. Organomet. Chem*. **1967**, *8*, 115.

Table 3. Cyclization of Enynes Followed by Dehydrogenation and Trap with Aldehydes[a]

Entry	Enyne	Aldehyde	Product	Yield (%)[b]
1	 (**10**)		 (**34**)	42
2	**10**		 (**41**)	43
3	**10**		 (**42**)	45
4	**10**		 (**43**)	49
5	 (**44**)		 (**45**)	37

[a] For reaction conditions, see eq 5. [b] Products were isolated as a virtually single stereoisomer. There is no evidence that other isomers were formed in more than trace amounts.



(**46**) (**47**) (**34**) (6)

with aldehydes offers a complementary method to prepare adducts that are not accessible by the allenyne cyclization.

Although the exact mechanism of the above reaction has not been necessarily elucidated yet, it denotes a new behavior of metallacycles of group 4 transition metals. The scission of the C−H bond of the titanacycle to serve the generation of reactive intermediates promoting the unexpected carbon−carbon bond formation is an interesting entry to the activation of nonfunctionalized C−H bonds with transition metal compounds, which is a current interest in organic synthesis.[20]

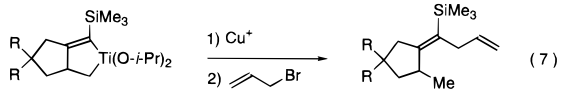
Copper-Mediated Mono-allylation. Organotitanium reagents have been less frequently utilized in substitution reactions of alkyl halides and related compounds, as they generally show diminished nucleophilicity toward these substrates as compared to the corresponding lithium and Grignard reagents.[8] Transmetalation of titanium compounds to another metallic species such as copper reagents might increase their utility. However, few attempts along this line have been made,[21,22] because the titanium reagents are generally prepared from lithium or Grignard reagents that could be transmetalated to the copper reagents in a more straightforward manner.

Table 4. Copper-Mediated Allylation of Titanacyclopentene **3** (eq 7)

entry	copper salt (equiv)	temp (°C)	period (h)	yield of **48**[a] (%)	regioselectivity
1	none	−50	1	<trace	
2	none	0	1	messy products	
3	$Li_2Cu(CN)Cl_2$ (0.05)	−50	3	24	
4	LiCu(Th)(CN)[b] (0.05)	0	0.5	30	
5	LiCu(Th)(CN) (1)	−50	3	66	
6	$Li_2Cu(CN)Cl_2$ (1)	−50	3	90 (82)	>95:<5

[a] Overall yield from enyne **2** determined by ^{1}H NMR spectroscopy. Isolated yield in parentheses. [b] Th = thienyl.

We attempted the alkylation of the aforementioned titanacyclopentenes and cyclopentadienes with allyl bromide, but these reactions failed to give the desired products, which was not unexpected based on the aforementioned precedents. To substantiate this transformation, a copper-assisted reaction of titanacyclopentene **3** was examined as shown in eq 7.



(**3**) R = $BnOCH_2$- (**48**) (7)

Some variations of reagents and conditions are summarized in Table 4. With a catalytic amount of a copper salt, the reaction did proceed to some extent at −50 °C, but the reaction stopped at low conversion (entry 3). This low conversion could not be improved by raising the reaction temperature (entry 4). However, with a stoichiometric amount of the copper, the reaction proceeded very cleanly at low temperature to give the allylation product in good yield (entry 6).[23] Of the two copper reagents investigated, $Li_2Cu(CN)Cl_2$ afforded a somewhat better yield (entries 5 and 6). Similarly, a cyclohexane derivative could be obtained as shown in entry 2, Table 5.

More importantly, a titanacyclopentadiene also undergoes the copper-mediated mono-allylation. The transmetalation of titanacyclopentadiene to copper should be carried out again in the presence of a stoichiometric amount of copper salt and at a low temperature around −50 °C. While the regioselection between the silyl and phenyl substituents shows no particular preference (entry 3, Table 5), the titanacyclopentadiene having the silyl and alkyl groups showed good selectivity as high as 9:1 (entry 4). The stereochemistries of the newly formed tri- and tetra-substituted double bonds of **53** as well as **48** have been confirmed by NOE study of ^{1}H NMR spectroscopy (see the Experimental Section). The reaction stopped at the mono-allylation stage, and another remaining carbon−titanium bond could be identified by deuteration (entry 4). In contrast to a copper-mediated bis-allylation of Cp_2-zirconacyclopentadienes reported recently,[24] the above process embodies the first *mono*-allylation of metallacyclopentadienes of group 4 transition metals, in a regioselective manner in a certain case. It is interesting to note that the carbon−carbon bond extension after the bicyclization of a diyne could be achieved in both directions

(20) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879 and references therein.

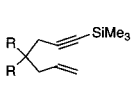
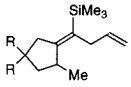
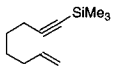
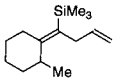
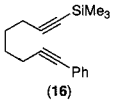
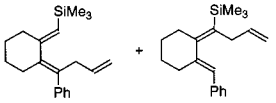
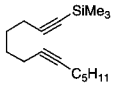
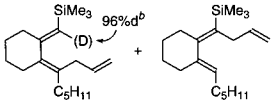
(21) Titanium/copper transmetalation is quite rare (see ref 8a, p 89) and has been only documented in the reactions of alkyltitanium reagents. Arai, M.; Lipshutz, B. H.; Nakamura, E. *Tetrahedron* **1992**, *48*, 5709.

(22) Copper-promoted reactions of group 4 transition metal intermediates have been centered on zirconium compounds. For reviews, see: (a) Wipf, P. *Synthesis* **1993**, 537. (b) Wipf, P. Jahn, H. *Tetrahedron* **1996**, *52*, 12853. (c) Lipshutz, B. H. *Acc. Chem. Res.* **1997**, *30*, 277. (d) Wipf, P.; Xu, W.; Takahashi, H.; Jahn, H.; Coish, P. D. G. *Pure Appl. Chem*. **1997**, *69*, 639. (e) Kotora, M.; Xi, Z.; Takahashi, T. *J. Synth. Org. Chem. Jpn*. **1997**, *55*, 958.

(23) Copper-mediated allylation of Cp_2-zirconacyclopentenes has been reported. Kasai, K.; Kotora, M.; Suzuki, N.; Takahashi, T. *J. Chem. Soc., Chem. Commun*. **1995**, 109.

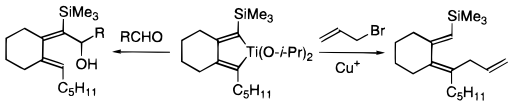
(24) Bis-allylation of Cp_2-zirconacyclopentadienes in the presence of a copper salt has been reported. (a) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Organometallics* **1994**, *13*, 4183. (b) Kotora, M.; Umeda, C.; Ishida, T.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 8355.

Table 5. Cyclization of Enynes or Diynes Followed by Copper-Mediated Alkylation with Allyl Bromide

Entry	Substrate	Period (h)[a]	Product(s) [Ratio]	Yield (%)
1	 (**2**) R = $BnOCH_2$-	3	 (**48**) [>95:<5]	82
2	 (**49**)	3	 (**50**) [>95:<5]	70
3	 (**16**)	4	 (**51**) [6:4] (**52**)	72
4	 (**29**)	4	 (**53**) [9:1] (**54**)	91

[a] This refers to the step of the copper-mediated allylation according to entry 6, Table 4. [b] Workup with 1 N DCl.

Scheme 3. Profile of the Reactions of a Dialkoxycyclopentadiene



simply by switching the electrophiles as shown in Scheme 3, making a flexible synthetic design possible.

Conclusion

The bicyclization of enynes and diynes mediated by low-valent titanium complex **1** and the subsequent, selective addition to aldehydes show new applications that are complementary to those of similar metallacycles of other group 4 transition metals. The copper-mediated allylation of titanacycles, which is a new entry to the titanium/copper bimetallic system, provides another method for the construction of a side chain. Since the necessary reagents to generate the new cyclic organotitanium intermediates are very inexpensive Ti(O-*i*-Pr)$_4$ and a Grignard reagent, the transformations described herein should offer an economical way to achieve selective transformations by taking advantage of the characteristic feature of organotitanium compounds. Further study to disclose unique reactions based on dialkoxytitanacyles is now in progress.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively. $CDCl_3$ was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as an internal standard, unless otherwise noted. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; or m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wavenumbers (cm^{-1}). All reactions were carried out under argon. Enyne **2** and diyne **23** were prepared by the following sequence: (i) mono- or dialkylation of diethyl allylmalonate or diethyl malonate with propargyl bromide (NaH, THF), (ii) reduction of the ester ($LiAlH_4$), (iii) benzylation of the diol (benzyl bromide, NaH, THF), and (iv) silylation (BuLi, Me_3SiCl, THF). Enyne **10** was prepared by Wittig methylenation of 5-dodecynal ($Ph_3PMe^+Br^-$, BuLi, Et_2O). Diyne **31** was prepared by (i) successive alkylation of benzylamine with 3-butynyl tosylate ((i-Pr)$_2$NEt, cat. NaI, DMF) and phenylpropargyl bromide (K_2CO_3, CH_3CN) and (ii) silylation (BuLi, Me_3SiCl, THF). Other enynes and diynes **16**, **26**, **29**, and **49** were prepared by alkylation of appropriate acetylenic iodides with lithiated (trimethylsilyl)acetylene in a standard manner. Similarly, **44** was prepared by alkylation of lithiated 4-[(*tert*-butyl)dimethylsiloxy]-1-butyne with 5-bromo-1-pentene.

4,4-Bis(benzyloxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (2). ^{1}H NMR δ 0.13 (s, 9 H), 2.23 (d, J = 7.7 Hz, 2 H), 2.30 (s, 2 H), 3.30−3.42 (m, 4 H), 4.49 (s, 4 H), 5.04 (br d, J = 10 Hz, 1 H), 5.08 (br d, J = 17 Hz, 1 H), 5.65−5.84 (symmetrical m, 1 H), 7.22−7.39 (m, 10 H); ^{13}C NMR δ 0.15, 23.56, 36.36, 42.22, 71.89, 73.31, 86.64, 104.33, 117.96, 127.32, 128.32, 129.22, 133.93, 138.80; IR (neat) 3075, 3040, 2970, 2900, 2870, 2175, 1640, 1500, 1480, 1450, 1360, 1245, 1200, 1100, 1020, 1000, 990, 910, 840, 750, 725, 690 cm^{-1}. Anal. Calcd for $C_{26}H_{34}O_2Si$: C, 76.80; H, 8.43. Found: C, 76.54; H, 8.46.

Confirmation of the Presence of Titanacycle 3. 1,1-Bis(benzyloxymethyl)-3-[(*E*)-(trimethylsilyl)methylene]-4-methylcyclopentane (55). ^{1}H NMR δ 0.09 (s, 9 H), 1.03 (d, J = 6.7 Hz, 3 H), 1.07 (dd, J = 10.8, 12.8 Hz, 1 H), 1.94 (dd, J = 8.3, 12.9 Hz, 1 H), 2.32 (br s, 2 H), 2.40−2.57 (m, 1 H), 3.30−3.42 (m, 4 H), 4.50 (s, 4 H), 5.23 (br s, 1 H), 7.20−7.37 (m, 10 H); ^{13}C NMR δ −0.19, 18.74, 39.24 (two carbons), 39.88, 45.80 (quaternary carbon), 73.07, 73.18 (two carbons), 74.88, 117.19, 127.29, 127.32 (two types of carbons), 127.39, 128.23 (two types of carbons), 138.91 (two types of carbons), 165.85; IR (neat) 3025, 2850, 1620, 1450, 1355, 1240, 1200, 1090, 835, 730, 690 cm^{-1}. Anal. Calcd for $C_{26}H_{36}O_2Si$: C, 76.42; H, 8.88. Found: C, 76.55; H, 8.92.

Typical Procedure for the Addition of Titanacyclopentenes to Aldehydes in the Presence of Ti(O-*i*-Pr)$_2$Cl$_2$. (*RS*)-2-[(2*RS*)-(*E*)-2-Methyl-4,4-bis(benzyloxymethyl)cyclopentylidene]-2-(trimethylsilyl)-1-cyclohexylethanol (5). To a stirred mixture of 4,4-bis(benzyloxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**2**) (50 mg, 0.123 mmol) and Ti(O-*i*-Pr)$_4$ (0.045 mL, 0.154 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.50 M in ether, 0.226 mL, 0.338 mmol) dropwise at −78 °C under argon. After stirring for 30 min, the solution was warmed to −50 °C over 30 min and kept at this temperature for 2 h. After the solution had been recooled to −78 °C, Ti(O-*i*-Pr)$_2$Cl$_2$ (1.2 M in ether, 0.128 mL, 0.154 mmol) was added, and the mixture was stirred at −78 °C for another 30 min. Cyclohexanecarbaldehyde (0.029 mL, 0.239 mmol) was then added, and the reaction mixture was stirred at the same temperature for 10 min. After the solution was rapidly allowed to warm to 0 °C and was kept at the same temperature for 30 min, the reaction was terminated by the addition of aqueous 1 N HCl. The organic layer was separated, washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to an oil, which was chromatographed on silica gel (hexanes−ether) to afford the title compound (32 mg, 50%) as a colorless oil. ^{1}H and ^{13}C NMR analyses confirmed that the product is a single isomer. There was no evidence that more than a trace amount of another diastereoisomer was present in a crude and purified product by careful ^{1}H NMR analysis. For the determination of the relative stereochemistry, see text. ^{1}H NMR δ 0.18 (s, 9 H), 0.85 (m, 2 H), 1.04 (d, J = 7 Hz, 3 H), 1.08−1.30 (m, 4 H), 1.30 (dd, J = 6, 15 Hz, 1 H), 1.43 (br d, J = 12 Hz, 1 H), 1.50−1.80 (m, 4 H), 1.80 (dd, J = 7.5, 15 Hz, 1 H), 2.13 (br d, J = 13 Hz, 1 H), 2.23 (d, J = 15 Hz, 1 H), 2.53 (d, J = 15 Hz, 1 H), 2.89 (br sextet, J = 7.2 Hz, 1 H), 3.19 (d, J = 8.5 Hz, 1 H), 3.24 (d, J = 8.5 Hz, 1 H), 3.41 (d, J = 8.5 Hz, 1 H), 3.51 (d, J = 8.5 Hz, 1 H), 4.17 (d, J = 7.7 Hz, 1 H), 4.38 (d, J = 12 Hz, 1 H), 4.50 (d, J = 12 Hz, 1 H), 4.53 (s, 2 H), 7.22−7.38 (m, 10 H); ^{13}C NMR δ 2.06, 24.61, 26.40, 26.63 (two carbons), 30.56, 31.23, 35.30, 38.78, 39.23, 42.86, 46.04 (quaternary carbon), 72.85, 73.14, 73.24, 75.15, 79.38, 127.31, 127.35, 127.39, 127.61, 128.20, 128.23, 133.97, 138.70, 138.94, 159.96; IR (neat) 3500 (OH), 3100, 3080, 3050, 2950, 2860, 1460, 1250, 1100, 840 cm^{-1}. Anal. Calcd for $C_{33}H_{48}O_3Si$: C, 76.10; H, 9.29. Found: C, 75.92; H, 9.38.

Typical Procedure for the Addition of Titanacyclopentenes to Aldehydes in the Presence of Ti(O-*i*-Pr)$_3$Cl. (*RS*)-2-[(2*RS*)-(*E*)-2-Methyl-4,4-bis(benzyloxymethyl)cyclopentylidene]-2-(trimethylsilyl)-1-phenylethanol (6). To a mixture of 4,4-bis(benzyloxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**2**) (50 mg, 0.123 mmol) and Ti(O-*i*-

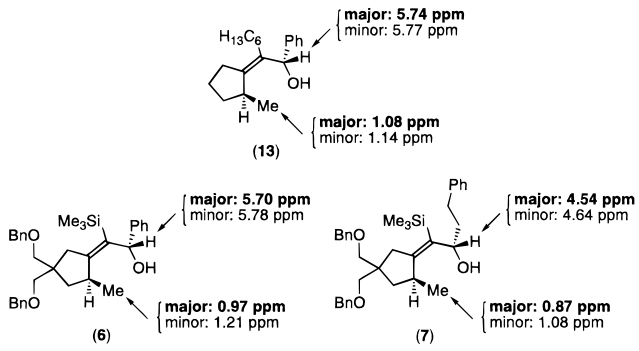
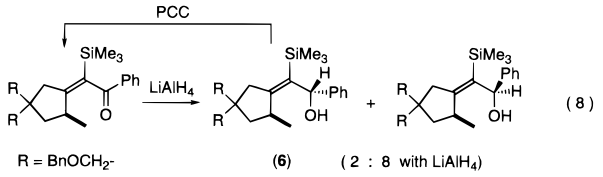


Figure 4. ^{1}H NMR spectra of authentic **13** and samples **6** and **7**. Upfield shifts are shown in boldface.

Pr)$_4$ (0.045 mL, 0.154 mmol) in 1 mL of Et$_2$O was added *i*-PrMgCl (1.50 M in ether, 0.226 mL, 0.338 mmol) dropwise at −78 °C under argon. After stirring for 30 min, the solution was warmed to −50 °C over 30 min and kept at this temperature for 2 h. After the addition of Ti(O-*i*-Pr)$_3$Cl (2 M in ether, 0.077 mL, 0.154 mmol), the mixture was stirred at −50 °C for another 30 min. Benzaldehyde (0.019 mL, 0.185 mmol) was then added, and the reaction mixture was stirred at the same temperature for 1.5 h. After the solution was allowed to warm to −40 °C over 30 min, the reaction was terminated at that temperature by the addition of aqueous 1 N HCl. The organic layer was separated, washed with aqueous NaHCO$_3$ solution, dried (Na$_2$SO$_4$), and concentrated to an oil, which was chromatographed on silica gel (hexanes−ether) to afford the title compound (34 mg, 54%) as a colorless oil. The stereochemistry of the olefinic moiety of the product was confirmed by an NOE study. ^{1}H NMR δ −0.05 (s, 9 H), 0.97 (d, J = 7 Hz, 3 H), 1.30 (dd, J = 6, 14 Hz, 1 H), 1.70 (br s, 1 H, OH), 1.95 (dd, J = 8, 14 Hz, 1 H), 2.39 (d, J = 15 Hz, 1 H), 2.61 (d, J = 15 Hz, 1 H), 2.95 (br sextet, J = 7.5 Hz, 1 H), 3.28 (d, J = 8.5 Hz, 1 H), 3.32 (d, J = 8.5 Hz, 1 H), 3.46 (d, J = 8.5 Hz, 1 H), 3.55 (d, J = 8.5 Hz, 1 H), 4.42 (d, J = 12 Hz, 1 H), 4.52 (d, J = 12 Hz, 1 H), 4.54 (d, J = 12 Hz, 1 H), 4.57 (d, J = 12 Hz, 1 H), 5.70 (br s, 1 H), 7.20−7.40 (m, 15 H). The following NOE study confirmed the assigned stereochemistry. Irradiation of the proton at δ 0.97 ppm (Me) showed 5% enhancement each at the peaks of δ 1.30 (cyclopentane CH cis to Me), 2.95 (C*H*Me), and 5.70 ppm (C*H*OH). Irradiation of the proton at δ 2.95 ppm (C*H*Me) showed 1%, 5%, and 27% enhancement at the peaks of δ 0.97 (Me), 1.95 (cyclopentane CH trans to Me), and 5.70 ppm (C*H*OH), respectively. Alternatively, irradiation of the proton at δ 5.70 ppm (C*H*OH) showed 1% and 22% enhancement at the peaks of δ 0.97 (Me) and 2.95 ppm (C*H*Me). ^{13}C NMR δ 1.21, 23.82, 35.52, 39.34, 39.51, 46.82 (quaternary carbon), 72.48, 73.25, 73.29, 74.25, 74.96, 126.09, 126.52, 127.35, 127.40, 127.44, 127.61, 127.85, 128.23, 128.27, 133.83, 138.75, 138.92, 143.83, 160.63. Peaks in the region between δ 126.09−128.27 ppm may include more than two types of carbons. IR (neat) 3580 (OH), 3100, 3075, 3050, 2960, 2930, 2900, 2860, 1620, 1500, 1460, 1370, 1250, 1100, 1030, 840, 750, 740, 700 cm^{-1}. Even after considerable effort, we could not obtain the correct elemental analysis for this particular compound due apparently to its fragile nature.

The ratio (>95:<5) of the diastereoisomers, which could not be separated by the chromatography, was determined by ^{1}H NMR spectroscopy in comparison with an authentic sample of the minor diastereoisomer (vide infra). For the determination of the relative stereochemistry, see text and Figure 4 shown above.

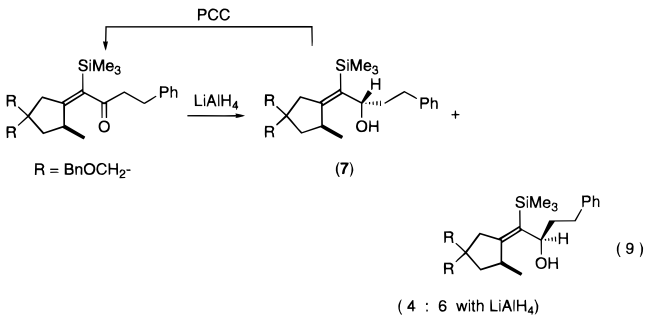
Preparation of the Minor Diastereoisomer of 6 (eq 8). Treatment of **6** with 3 equiv of PCC in CH$_2$Cl$_2$ at room temperature for 1 h afforded α-[(*E*)-2-methyl-4,4-bis(benzyloxymethyl)cyclopentylidene]-α-(trimethylsilyl)acetophenone in 41% yield. ^{1}H NMR δ 0.12 (s, 9 H), 0.88 (d, J = 8 Hz, 3 H), 1.26 (dd, J = 7, 14 Hz, 1 H), 1.80 (dd, J = 8, 14 Hz, 1 H), 2.41 (d, J = 15 Hz, 1 H), 2.52 (br sextet, J = 7 Hz, 1 H), 2.64 (d, J = 15 Hz, 1 H), 3.30 (d, J = 8.5 Hz, 1 H), 3.36 (d, J = 8.5 Hz, 1 H), 3.44 (d, J = 8.5 Hz, 1 H), 3.52 (d, J = 8.5 Hz, 1 H), 4.52 (s, 4 H), 7.20−7.35 (m, 10 H), 7.40 (t, J = 8 Hz, 2 H), 7.52 (t, J = 8 Hz, 1 H), 7.86 (d, J = 8 Hz, 2 H). This ketone was given back to a 2:8 mixture of **6** and its diastereoisomer in a quantitative yield via reduction with LiAlH$_4$ (1 equiv) in ether at room temperature for 20 min. ^{1}H NMR δ −0.09 (s, 9 H), 1.21 (d, J = 7 Hz, 3 H), 1.32 (dd, J = 6, 14 Hz, 1 H), 1.68 (br s, 1 H, OH), 1.95 (dd, J = 8, 14 Hz, 1 H), 2.35 (d, J = 15 Hz, 1 H), 2.59 (d, J = 15 Hz, 1 H), 3.00 (br sextet, J = 7 Hz, 1 H), 3.29 (d, J = 8.5 Hz, 1 H), 3.37 (d, J = 8.5 Hz, 1 H), 3.46 (d, J = 8.5 Hz, 1 H), 3.57 (d, J = 8.5 Hz, 1 H), 4.47 (d, J = 13 Hz, 1 H), 4.55 (s, 2 H), 4.58 (d, J = 13 Hz, 1 H), 5.78 (br s, 1 H), 7.20−7.40 (m, 15 H).



(*RS*)-1-[(2*RS*)-(*E*)-2-Methyl-4,4-bis(benzyloxymethyl)cyclopentylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (7). ^{1}H NMR δ 0.18 (s, 9 H), 0.87 (d, J = 7 Hz, 3 H), 1.22 (dd, J = 6, 14 Hz, 1 H), 1.30 (br s, 1 H, OH), 1.55 (m, 1 H), 1.85 (dd, J = 8.5, 14 Hz, 1 H), 2.05 (m, 1 H), 2.18 (d, J = 15 Hz, 1 H), 2.47 (d, J = 15 Hz, 1 H), 2.64 (m, 1 H), 2.78 (br sextet, J = 7.5 Hz, 1 H), 2.86 (m, 1 H), 3.19 (d, J = 8.5 Hz, 1 H), 3.24 (d, J = 8.5 Hz, 1 H), 3.40 (d, J = 8.5 Hz, 1 H), 3.50 (d, J = 8.5 Hz, 1 H), 4.37 (d, J = 12 Hz, 1 H), 4.49 (d, J = 12 Hz, 1 H), 4.52 (s, 2 H), 4.54 (d, J = 10 Hz, 1 H), 7.15−7.35 (m, 15 H). Decoupling study showed that the proton at δ 2.05 ppm (PhCH$_2$C*H*$_2$) is vicinal (or geminal) to the protons at δ 1.55 (PhCH$_2$C*H*$_2$), 2.64 (PhCH$_2$), 2.86 (PhCH$_2$), and 4.54 (C*H*OH) ppm. ^{13}C NMR δ 2.06, 23.46, 33.10, 35.54, 38.84, 39.27, 39.49, 46.50 (quaternary carbon), 72.47, 73.17, 73.25, 74.10, 75.04, 125.76, 127.35, 127.55, 128.20, 128.25, 128.35, 128.55, 135.75, 138.80, 138.94, 142.21, 158.40. Peaks in the region between δ 125.76 and 128.55 ppm may include more than two types of carbons. IR (neat) 3600 (OH), 3100, 3080, 3040, 2950, 2860, 1950, 1880, 1810, 1720, 1610, 1500, 1460, 1370, 1250, 1210, 1100, 1030, 920, 840, 750, 700 cm^{-1}. Anal. Calcd for C$_{35}$H$_{46}$O$_3$Si: C, 77.44; H, 8.54. Found: C, 77.67; H, 8.54.

The ratio (96:4) of the diastereoisomers, which could not be separated by the chromatography, was determined by ^{1}H NMR spectroscopy in comparison with an authentic sample of the minor diastereoisomer (vide infra). For the determination of the relative stereochemistry, see text and Figure 4 shown above.

Preparation of the Minor Diastereoisomer of 7 (eq 9). Treatment of **7** with 3 equiv of PCC in CH$_2$Cl$_2$ at room temperature for 1 h afforded 1-[(*E*)-2-methyl-4,4-bis(benzyloxymethyl)cyclopentylidene]-1-(trimethylsilyl)-4-phenyl-2-butanone in 51% yield. ^{1}H NMR δ 0.11 (s, 9 H), 0.96 (d, J = 7 Hz, 3 H), 1.25 (dd, J = 7, 14 Hz, 1 H), 1.81 (dd, J = 8, 14 Hz, 1 H), 2.26 (d, J = 15 Hz, 1 H), 2.41 (d, J = 15 Hz, 1 H), 2.53 (br sextet, J = 7 Hz, 1 H), 2.68 (m, 2 H), 2.87 (q, J = 8 Hz, 2 H), 3.19 (d, J = 8.5 Hz, 1 H), 3.26 (d, J = 8.5 Hz, 1 H), 3.40 (d, J = 8.5 Hz, 1 H), 3.48 (d, J = 8.5 Hz, 1 H), 4.45 (d, J = 8 Hz, 1 H), 4.48 (d, J = 8 Hz, 1 H), 4.50 (s, 2 H), 7.15−7.35 (m, 15 H); IR (neat) 3080, 3040, 2960, 2940, 2860, 1680, 1610, 1460, 1250, 1100, 840, 750, 700 cm^{-1}. This ketone was given back to a 4:6 mixture of **7** and its diastereoisomer in a quantitative yield via reduction with LiAlH$_4$ (1 equiv) in ether at room temperature for 20 min. ^{1}H NMR δ (characteristic peaks are shown) 0.21 (s, 9 H), 1.08 (d, J = 7 Hz, 3 H), 4.64 (t, J = 8 Hz, 1 H).



(*RS*)-2-[(2*RS*)-(*E*)-2-(Deuteriomethyl)-4,4-bis(benzyloxymethyl)-cyclopentylidene]-2-(trimethylsilyl)-1-cyclohexylethanol (8). This showed the same ^{1}H NMR spectrum as that of the nondeuterated

compound except that the peaks at δ 1.03 ppm (br d, $J = 6.7$ Hz, 2 H) and 2.88 ppm (br quintet, $J = 7$ Hz, 1 H) were observed in place of those at 1.04 ppm (d, $J = 7$ Hz, 3 H) and 2.89 ppm (br sextet, $J = 7.2$ Hz, 1 H). Deuterium incorporation was determined to be >98%.

Typical Procedure for the Iodinolysis of the Oxatitanacycle such as 4. (*RS*)-2-[(2*RS*)-(*E*)-2-(Iodomethyl)-4,4-bis(benzyloxymethyl)-cyclopentylidene]-2-(trimethylsilyl)-1-cyclohexylethanol (9). The same reaction was carried out with 4,4-bis(benzyloxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**2**) (40 mg, 0.0984 mmol), Ti(O-*i*-Pr)$_4$ (0.036 mL, 0.123 mmol), *i*-PrMgCl (1.44 M in ether, 0.188 mL, 0.271 mmol), Ti(O-*i*-Pr)$_2$Cl$_2$ (1.25 M in ether, 0.098 mL, 0.123 mmol), and cyclohexanecarbaldehyde (0.024 mL, 0.197 mmol). In place of the aqueous workup, the solution was cooled to −78 °C, and I_2 (55 mg, 0.216 mmol) in 0.4 mL of THF was rapidly added. The solution was warmed to 0 °C and stirred at this temperature for 10 min. The reaction was terminated by the addition of 1 N HCl. The organic layer was separated and washed successively with aqueous $NaHCO_3$ solution and $Na_2S_2O_3$ solution, dried (Na_2SO_4), and concentrated to an oil, ^{1}H NMR analysis of which showed the formation of the title compound in 58% yield. Purification on preparative TLC afforded a pure sample (23 mg, 37%) as an oil, which was rather unstable and suddenly decomposed completely. ^{1}H NMR δ 0.16 (s, 9 H), 0.85 (m, 2 H), 0.89 (dd, $J = 7$, 15 Hz, 1 H), 1.1−1.32 (m, 4 H), 1.44 (br d, $J = 12$ Hz, 1 H), 1.50−1.80 (m, 4 H), 1.81 (dd, $J = 7.5$, 15 Hz, 1 H), 2.08 (br d, $J = 14$ Hz, 1 H), 2.34 (d, $J = 15$ Hz, 1 H), 2.55 (d, $J = 15$ Hz, 1 H), 3.10 (d, $J = 8$ Hz, 1 H), 3.16 (m, 1 H), 3.18 (d, $J = 8.5$ Hz, 1 H), 3.23 (d, $J = 8.5$ Hz, 1 H), 3.34 (dd, $J = 2$, 8 Hz, 1 H), 3.44 (d, $J = 8.5$ Hz, 1 H), 3.48 (d, $J = 8.5$ Hz, 1 H), 4.07 (d, $J = 7.7$ Hz, 1 H), 4.37 (d, $J = 12$ Hz, 1 H), 4.49 (d, $J = 12$ Hz, 1 H), 4.54 (s, 2 H), 7.23−7.39 (m, 10 H); IR (neat) 3400 (OH), 3040, 1460, 1250, 1100, 740, 700 cm^{-1}.

1-Tridecen-6-yne (10). ^{1}H NMR δ 0.88 (t, $J = 7$ Hz, 3 H), 1.18−1.62 (m, 13 H), 2.13 (m, 6 H), 4.96 (d, $J = 10$ Hz, 1 H), 5.02 (d, $J = 17$ Hz, 1 H), 5.80 (ddt, $J = 10$, 17, 7 Hz, 1 H); ^{13}C NMR δ 14.35, 18.49, 19.06, 22.90, 28.67, 28.87, 29.45, 31.71, 33.15, 80.16, 81.02, 115.38, 138.66; IR (neat) 3080, 2930, 2860, 1640, 1460, 1440, 1335, 990, 915 cm^{-1}. Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.72; H, 12.16.

(*RS*)-2-[(2*SR*)-(*Z*)-2-Methyl-1-cyclopentylidene]-1-phenyl-1-octanol (13). ^{1}H NMR δ 0.89 (t, $J = 7$ Hz, 3 H), 1.08 (d, $J = 7$ Hz, 3 H), 1.04−1.35 (m, 8 H), 1.58 (br s, 1 H, OH), 1.72 (m, 5 H), 1.95 (dt, $J = 4$, 12 Hz, 1 H), 2.26 (dd, $J = 8$, 17 Hz, 1 H), 2.39 (ddd, $J = 4$, 9, 17 Hz, 1 H), 3.00 (quintet, $J = 7$ Hz, 1H), 5.74 (s, 1 H), 7.20−7.43 (m, 5 H); ^{13}C NMR δ 13.90, 21.93, 22.42, 22.99, 29.28 (two carbons), 29.53, 29.87, 31.37, 34.70, 35.65, 73.91, 126.14, 126.77, 128.06, 131.86, 142.94, 147.98; IR (neat) 3360 (OH), 3090, 3065, 3030, 2960, 2925, 2860, 1495, 1450, 1375, 1020, 1000, 740, 700 cm^{-1} for an 85:15 mixture of the diastereoisomers. Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.98; H, 10.47 for an 85:15 mixture of the diastereoisomers.

(Minor) Diastereoisomer of 13. Characteristic peaks of the ^{1}H NMR spectrum are shown: δ 1.14 (d, $J = 7$ Hz, 3 H), 3.04 (m, 1 H), 5.77 (s, 1 H).

(*RS*)-2-[(2*SR*)-(*Z*)-2-(Iodomethyl)-1-cyclopentylidene]-1-phenyl-1-octanol (14). ^{1}H NMR δ 0.90 (t, $J = 7$ Hz, 3 H), 1.04−1.36 (m, 8 H), 1.58 (br s, 1 H, OH), 1.77 (m, 4 H), 1.96 (m, 2 H), 2.32 (dd, $J = 8$, 16 Hz, 1 H), 2.43 (m, 1 H), 3.05 (dd, $J = 10.5$, 12.6 Hz, 1 H), 3.21−3.31 (m, 2 H), 5.60 (s, 1 H), 7.23−7.40 (m, 5 H).

(3*RS*,6*SR*)-2-Hexyl-3-phenyl-4-oxa-1-bicyclo[4.3.0]nonene (15). ^{1}H NMR δ 0.83 (t, $J = 7$ Hz, 3 H), 1.10−1.35 (m, 9 H), 1.62 (m, 2 H), 1.86 (m, 3 H), 2.35 (distorted t, $J = 7$ Hz, 2 H), 2.62 (m, 1 H), 3.23 (t, $J = 10.5$ Hz, 1 H), 4.24 (dd, $J = 4.5$, 10.5 Hz, 1 H), 4.91 (q, $J = 2$ Hz, 1 H), 7.22−7.35 (m, 5 H). Decoupling of the proton at δ 2.62 ppm (bridgehead H) changed the following peaks: δ 3.23 ppm (t, $J = 10.5$ Hz, 1 H, *endo*-CH_2O) → (distorted m); δ 4.24 ppm (dd, $J = 4.5$, 10.5 Hz, 1 H, *exo*-CH_2O) → (d, $J = 10.5$ Hz); δ 4.91 ppm (q, $J = 2$ Hz, 1 H, CHPh) → (br s). The following NOE study confirmed the assigned stereochemistry. Irradiation of the peak at δ 2.62 ppm (bridgehead H) showed a 3% enhancement to the proton at δ 4.24 ppm (*exo*-CH_2O). Irradiation of the peak at δ 3.23 ppm (*endo*-CH_2O) showed 32% and 6% enhancement to the protons at δ 4.24 ppm (*exo*-CH_2O) and δ 4.91 ppm (CHPh). Irradiation of the peak at δ 4.24 ppm (*exo*-CH_2O) showed a 27% enhancement to the proton at δ 3.23 ppm (*endo*-CH_2O), but no enhancement to the proton at δ 4.91 ppm (CHPh). ^{13}C NMR δ 13.92, 22.39, 23.68, 27.55, 28.18, 29.09, 29.50, 29.59, 31.45, 40.33, 70.19, 79.43, 127.86, 128.37, 128.40, 129.35, 137.94, 141.77; IR (neat) 3070, 3025, 2960, 2930, 2860, 1455, 1105, 1065, 700 cm^{-1}.

1-Phenyl-8-(trimethylsilyl)-1,7-octadiyne (16). ^{1}H NMR δ 0.15 (s, 9 H), 1.70 (m, 4 H), 2.29 (distorted t, $J = 7$ Hz, 2 H), 2.45 (distorted t, $J = 7$ Hz, 2 H), 7.27 (m, 3 H), 7.39 (m, 2 H); ^{13}C NMR δ 0.17, 18.97, 19.46, 27.78, 27.82, 80.91, 84.76, 89.80, 107.05, 124.01, 127.52, 128.17, 131.55; IR (neat) 3080, 3040, 2960, 2860, 2180, 1500, 1250, 840, 760, 690 cm^{-1}. Anal. Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.71. Found: C, 80.15; H, 8.70.

Verification of the Presence of Titanacycle 17 by Hydrolysis. 1-[(*E*)-Benzylidene]-2-[(*E*)-(trimethylsilyl)methylene]cyclohexane (18). ^{1}H NMR δ 0.16 (s, 9 H), 1.61 (br quintet, $J = 6$ Hz, 2 H), 1.70 (br quintet, $J = 6$ Hz, 2 H), 2.44 (t, $J = 6$ Hz, 2 H), 2.55 (t, $J = 6$ Hz, 2 H), 5.57 (s, 1 H), 6.56 (s, 1 H), 7.18−7.35 (m, 5 H); ^{13}C NMR δ 0.17, 26.16, 26.76, 29.96, 34.46, 123.28, 123.38, 126.20, 127.96, 129.31, 138.05, 146.07, 159.86; IR (neat) 3090, 3070, 3040, 2960, 2940, 2860, 1600, 1500, 1450, 1250, 930, 920, 850, 770, 700 cm^{-1}.

Typical Procedure for the Addition of Titanacyclopentadienes to Aldehydes. 1-[(*E*)-2-[(*E*)-Benzylidene]cyclohexylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (20). To a stirred mixture of 1-phenyl-8-(trimethylsilyl)-1,7-octadiyne (**16**) (30 mg, 0.118 mmol) and Ti(O-*i*-Pr)$_4$ (0.043 mL, 0.148 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.44 M in ether, 0.225 mL, 0.325 mmol) dropwise at −78 °C under argon. After stirring for 30 min, the solution was warmed to −50 °C over 30 min and kept at this temperature for 4 h. After the solution had been recooled to −78 °C, Ti(O-*i*-Pr)$_2$Cl$_2$ (1.33 M in ether, 0.111 mL, 0.148 mmol) was added, and the mixture was stirred at −78 °C for another 30 min. 3-Phenylpropanal (0.016 mL, 0.118 mmol) was added, and the solution was rapidly allowed to warm to 0 °C with stirring. After the mixture was allowed to stand in a refrigerator (2−3 °C) overnight, the reaction was terminated by the addition of aqueous 1 N HCl at 0 °C. The organic layer was separated and washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to an oil, which was chromatographed on silica gel (hexanes−ether) to afford the title compound (33 mg, 72%) as a colorless oil. ^{1}H NMR δ 0.30 (s, 9 H), 1.51 (br s, 1 H, OH), 1.68 (m, 4 H), 1.84 (m, 1 H), 2.06 (m, 1 H), 2.47 (br m, 4 H), 2.60 (ddd, $J = 6.6$, 9.8, 13.5 Hz, 1 H), 2.75 (m, 1 H), 4.85 (dd, $J = 5.1$, 8.6 Hz, 1 H), 6.17 (s, 1 H), 7.20−7.40 (m, 10 H). The following NOE study confirmed the stereochemical assignments. Irradiation of the proton at δ 4.85 ppm (C*H*OH) showed a 7% enhancement to that at δ 6.17 ppm (vinylic H). Alternatively, irradiation of the proton at δ 6.17 ppm (vinylic H) showed a 7% enhancement to that at δ 4.85 ppm (C*H*OH). ^{13}C NMR δ 2.52, 28.00, 28.63, 31.65, 33.06, 37.48, 39.55, 74.64, 124.75, 125.67, 126.36, 128.11, 128.33 (may involve two types of carbons), 128.93, 135.91, 137.38, 142.12, 144.33, 155.70; IR (neat) 3460 (OH), 3080, 3040, 2950, 2860, 1605, 1580, 1500, 1460, 1450, 1250, 1040, 860, 840, 740, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{34}OSi$: C, 79.94; H, 8.77. Found: C, 80.14; H, 8.84. Further structural confirmation was made by the selective removal of the vinylic silyl group (vide infra).

Desilylation of the Vinylic Trimethylsilyl Group of 20 (eq 3). 2-[(*E*)-Benzylidene]-1-[(*Z*)-2-(trimethylsilyloxy)-4-phenylbutylidene]-cyclohexane. Treatment of **20** with a catalytic amount of KH in THF at room temperature for 10 min[14] afforded the title compound (82%) after purification on silica gel (hexanes−ether). ^{1}H NMR δ 0.08 (s, 9 H), 1.45−2.00 (m, 5 H), 2.10−2.40 (m, 3 H), 2.52−2.80 (m, 4 H), 4.59 (dt, $J = 5$, 9 Hz, 1 H), 5.29 (d, $J = 9$ Hz, 1 H), 6.11 (s, 1 H), 7.00−7.40 (m, 10 H). Protons at δ 4.59 ppm (C*H*OSiMe$_3$) and at δ 5.29 ppm (C=C*H*CH(OSiMe$_3$)) proved to be vicinal by a decoupling experiment. The following NOE study further confirmed the stereochemical assignments. Irradiation of the proton at δ 4.59 ppm (C*H*OSiMe$_3$) showed a 9% enhancement to that at δ 6.11 ppm (C=C*H*Ph). Alternatively, irradiation of the proton at δ 6.11 ppm (C=C*H*Ph) showed 10% enhancement each to that at δ 4.59 ppm (C*H*OSiMe$_3$) and that at δ 7.12 ppm (*o*-PhH) but no enhancement to that at δ 5.29 ppm (C=C*H*CH(OSiMe$_3$)).

1-[(*E*)-2-[(*E*)-Deuterio(phenyl)methylene]cyclohexylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (21). The ^{1}H NMR spectrum was

virtually the same as that of the nondeuterated compound except that the peak at δ 6.11 ppm (vinylic H) disappeared (99% deuterium incorporation). The ^{13}C NMR spectrum was virtually the same as that of the nondeuterated compound except that the peak at δ 124.75 ppm (C═*C*Ph) was not observed under the experimental conditions.

Typical Procedure for the Iodinolysis of the Intermediate Oxatitanacycle such as 19. 1-[(*E*)-2-[(*Z*)-Iodo(phenyl)methylene]-cyclohexylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (22). The above reaction was repeated. In place of the aqueous workup (1 N HCl), the solution was cooled to −78 °C and I_2 (120 mg, 0.472 mmol) in 0.3 mL of THF was rapidly added under vigorous stirring. The solution was rapidly warmed to 0 °C and stirred at this temperature for 30 min. Additional ether (1 mL) was added to make the reaction mixture fluid. After stirring for another 20 min, the reaction was terminated by the addition of 1 N HCl at 0 °C. The organic layer was separated, washed successively with aqueous $NaHCO_3$ solution and $Na_2S_2O_3$ solution, dried (Na_2SO_4), and concentrated to an oil, purification of which by silica gel chromatography (hexanes−ether) afforded the title compound (38 mg, 62%) as an oil. ^{1}H NMR δ 0.29 (s, 9 H), 1.26 (br s, 1 H, OH), 1.35−1.65 (m, 2 H), 1.73 (m, 1 H), 1.90−2.10 (m, 3 H), 2.22 (dt, J = 4.6, 11.5 Hz, 1 H), 2.40 (m, 1 H), 2.60 (br d, J = 11 Hz, 1 H), 2.76 (m, 2 H), 2.94 (ddd, J = 4.5, 8.5, 11.5 Hz, 1 H), 4.61 (dd, J = 1.7, 10.5 Hz, 1 H), 7.12−7.36 (m, 10 H); ^{13}C NMR δ 2.24, 29.45 (two carbons), 33.87, 36.47, 36.60, 38.05, 75.89, 92.77, 125.71, 127.70, 128.24, 128.37, 128.69, 128.77, 134.63, 142.36, 143.34, 152.39, 156.78; IR (neat) 3500 (OH), 3080, 3040, 2940, 2860, 1600, 1500, 1450, 1250, 1040, 850, 750, 700 cm^{-1}. A structural confirmation was made by the following iodine/lithium exchange reaction with *t*-BuLi. Treatment of the iodide **22** with 3.5 equiv of *t*-BuLi (1.7 M solution in pentane) in ether at −78 °C → −25 °C afforded the dehalogenated product **20** in 96% yield. Its spectroscopic properties and mobility on TLC were identical with those of an authentic sample given above.

4,4-Bis(benzyloxymethyl)-1,7-bis(trimethylsilyl)-1,6-heptadiyne (23). ^{1}H NMR δ 0.12 (s, 18 H), 2.44 (s, 4 H), 3.49 (s, 4 H), 4.51 (s, 4 H), 7.20−7.40 (m, 10 H); ^{13}C NMR δ 0.15, 23.61, 42.31 (quaternary carbon), 71.57, 73.49, 86.85, 103.89, 127.37 (two types of carbons), 128.26, 138.73; IR (neat) 3080, 3040, 2960, 2910, 2860, 2180, 1460, 1370, 1250, 1100, 1040, 850, 760, 740, 700 cm^{-1}. Anal. Calcd for $C_{29}H_{40}O_2Si_2$: C, 73.05; H, 8.46. Found: C, 72.94; H, 8.62.

1-[(*E*)-2-[(*E*)-(Trimethylsilyl)methylene]-4,4-bis(benzyloxymethyl)cyclopentylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (24). ^{1}H NMR δ 0.18 (s, 9 H), 0.24 (s, 9 H), 1.60 (br s, 1 H, OH), 1.80 (m, 1 H), 2.11 (m, 1 H), 2.28 (dd, J = 1.6, 15 Hz, 1 H), 2.29 (d, J = 15 Hz, 1 H), 2.41 (dd, J = 1.6, 15 Hz, 1 H), 2.49 (d, J = 15 Hz, 1 H), 2.66 (m, 1 H), 2.88 (m, 1 H), 3.35 (d, J = 8 Hz, 1 H), 3.36 (d, J = 8 Hz, 1 H), 3.39 (d, J = 8 Hz, 1 H), 3.43 (d, J = 8 Hz, 1 H), 4.49 (d, J = 13 Hz, 1 H), 4.54 (s, 2 H), 4.56 (d, J = 13 Hz, 1 H), 4.96 (dd, J = 1.5, 9.6 Hz, 1 H), 5.41 (t, J = 1.6 Hz, 1 H), 7.2−7.4 (m, 15 H); ^{13}C NMR δ −0.28, 1.98, 32.69, 38.48, 39.20, 39.50, 44.23 (quaternary carbon), 73.14, 73.18, 73.30, 73.70, 74.67, 125.75, 127.37, 127.42, 127.49, 128.14, 128.22, 128.36, 128.40, 138.71 (two peaks), 141.57, 142.26, 151.43, 155.64. Peaks in the region between δ 127.37 and 128.40 ppm may include more than two types of carbons. IR (neat) 3570 (OH), 3100, 3080, 3040, 2950, 2860, 1600, 1500, 1460, 1370, 1250, 1100, 850, 750, 700 cm^{-1}. Anal. Calcd for $C_{38}H_{52}O_3Si_2$: C, 74.46; H, 8.55. Found: C, 74.49; H, 8.41.

2-[(*E*)-2-[(*E*)-(Trimethylsilyl)methylene]-4,4-bis(benzyloxymethyl)cyclopentylidene]-2-(trimethylsilyl)-1-cyclohexylethanol (25). ^{1}H NMR δ 0.13 (s, 9 H), 0.20 (s, 9 H), 0.8−1.8 (m, 11 H), 2.07 (br d, J = 13 Hz, 1 H), 2.24 (d, J = 15 Hz, 1 H), 2.31 (d, J = 15 Hz, 1 H), 2.32 (d, J = 15 Hz, 1 H), 2.38 (d, J = 15 Hz, 1 H), 3.35 (s, 2 H), 3.35 (d, J = 8.5 Hz, 1 H), 3.37 (d, J = 8.5 Hz, 1 H), 4.45 (d, J = 12 Hz, 2 H), 4.51 (d, J = 12 Hz, 2 H), 4.72 (d, J = 7.7 Hz, 1 H), 5.64 (s, 1 H), 7.22−7.35 (m, 10 H). The following NOE study confirmed the assigned stereochemistry. Irradiation of the proton at δ 4.72 ppm (C*H*OH) showed a 20% enhancement at the peak of δ 5.64 ppm (vinylic H). ^{13}C NMR δ −0.26, 1.89, 26.09, 26.25, 26.62, 30.09, 30.41, 38.39, 39.63, 43.17, 44.15 (quaternary carbon), 73.19, 73.23, 73.54, 73.64, 78.26, 127.38, 127.44, 127.50, 128.24, 138.73, 138.76, 139.21, 154.43, 155.34; IR (neat) 3500 (OH), 3040, 2940, 2850, 1600, 1460, 1360, 1240, 1100, 840, 740, 700 cm^{-1}. Anal. Calcd for $C_{36}H_{54}O_3Si_2$: C, 73.16; H, 9.21. Found: C, 73.20; H, 9.38.

1-(*tert*-Butyldimethylsilyl)-7-(trimethylsilyl)-1,6-heptadiyne (26). ^{1}H NMR δ 0.08 (s, 6 H), 0.14 (s, 9 H), 0.92 (s, 9 H), 1.73 (quintet, J = 7.7 Hz, 2 H), 2.35 (t, J = 7.7 Hz, 4 H); ^{13}C NMR δ −4.45, 0.13, 16.50, 18.99 (two carbons), 26.09, 27.78, 83.22, 85.09, 106.30, 106.81; IR (neat) 2960, 2940, 2860, 2180, 1250, 840, 780 cm^{-1}. Anal. Calcd for $C_{16}H_{30}Si_2$: C, 68.98; H, 10.85. Found: C, 68.63; H, 10.78.

1-[(*E*)-2-[(*E*)-(*tert*-Butyldimethylsilyl)methylene]cyclopentylidene]-1-(trimethylsilyl)-4-phenyl-2-butanol (27). ^{1}H NMR δ 0.12 (s, 3 H), 0.14 (s, 3 H), 0.24 (s, 9 H), 0.95 (s, 9 H), 1.64 (br s, 1 H, OH), 1.62−1.80 (m, 2 H), 1.80 (m, 1 H), 2.11 (m, 1 H), 2.30−2.55 (m, 4 H), 2.65 (dt, J = 5, 12 Hz, 1 H), 2.93 (dt, J = 5, 12 Hz, 1 H), 5.05 (br d, J = 9.5 Hz, 1 H), 5.46 (t, J = 2 Hz, 1 H), 7.15−7.32 (m, 5 H); ^{13}C NMR δ −4.66, −4.44, 2.17, 17.23, 23.36, 26.59, 32.85 (two carbons), 33.94, 39.29, 74.82, 124.58, 125.72, 128.29, 128.38, 140.44, 142.38, 153.25, 157.80; IR (neat) 3500 (OH), 3080, 3040, 2960, 2860, 1600, 1500, 1470, 1250, 1040, 840, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{42}OSi_2$: C, 72.40; H, 10.21. Found: C, 72.48; H, 10.32. The assigned structure was verified by the selective desilylation of the trimethylsilyl group with a catalytic amount of a base (vide infra).

Desilylation of the Trimethylsilyl Group of 27 (eq 4). 1-[(*E*)-2-[(*E*)-(*tert*-Butyldimethylsilyl)methylene]cyclopentylidene]-4-phenyl-2-butanol. Treatment of **27** with a catalytic amount of KH in THF at room temperature for 10 min[14] afforded the silyl ether, which was dissolved in ether and aqueous 1 N HCl. This heterogeneous mixture was stirred vigorously at room temperature for 45 min to afford the title compound (65%) after purification on silica gel (hexanes−ether). ^{1}H NMR δ 0.09 (s, 6 H), 0.90 (s, 9 H), 1.58 (br s, 1 H, OH), 1.69 (quintet, J = 7.5 Hz, 2 H), 1.89 (m, 2 H), 2.36 (dt, J = 1.5, 7.5 Hz, 2 H), 2.44 (dt, J = 2, 7.5 Hz, 2 H), 2.70 (ddd, J = 7, 8, 14 Hz, 1 H), 2.81 (ddd, J = 7, 12, 14 Hz, 1 H), 4.75 (dt, J = 5, 7 Hz, 1 H), 5.50 (d, J = 7.6 Hz, 1 H), 5.73 (t, J = 1.5 Hz, 1 H), 7.15−7.34 (m, 5 H).

1-[(*E*)-2-[(*E*)-Benzylidene]cyclohexylidene]-3-phenyl-1-(trimethylsilyl)-2-butanol (28). **Major Isomer**. ^{1}H NMR δ 0.33 (s, 9 H), 1.34 (d, J = 7 Hz, 1 H), 1.47 (br s, 1 H, OH), 1.3−1.72 (m, 4 H), 2.00 (m, 1 H), 2.50 (m, 3 H), 3.02 (dt, J = 9, 7 Hz, 1 H), 4.94 (d, J = 9 Hz, 1 H), 6.00 (br s, 1 H), 7.09−7.40 (m, 10 H); IR (neat) 3580 (OH), 3480 (OH), 3080, 3060, 3025, 2960, 2925, 2855, 1600, 1580, 1490, 1450, 1250, 1005, 990, 850, 840, 760, 735, 700 cm^{-1} for a 2:1 mixture of the diastereoisomers. Anal. Calcd for $C_{26}H_{34}OSi$: C, 79.94; H, 8.77. Found: C, 79.98; H, 8.93 for a 2:1 mixture of the diastereoisomers.

Minor Isomer. Characteristic peaks of the ^{1}H NMR spectrum are shown: δ 0.37 (s, 9 H), 1.16 (d, J = 7 Hz, 3 H), 6.34 (s, 1 H).

1-(Trimethylsilyl)-1,7-tridecadiyne (29). ^{1}H NMR δ 0.14 (s, 9 H), 0.88 (t, J = 7 Hz, 3 H), 1.31 (m, 4 H), 1.46 (quintet, J = 7 Hz, 2 H), 1.58 (m, 4 H), 2.14 (m, 4 H), 2.24 (t, J = 7 Hz, 2 H); ^{13}C NMR δ 0.15, 13.97, 18.30, 18.72, 19.43, 22.21, 27.75, 28.21, 28.83, 31.08, 79.58, 80.60, 84.52, 107.20; IR (neat) 2940, 2860, 2180, 1460, 1250, 1050, 850, 760 cm^{-1}. Anal. Calcd for $C_{16}H_{28}Si$: C, 77.34; H, 11.36. Found: C, 76.92; H, 11.38.

1-[(*E*)-2-[(*E*)-Hexylidene]cyclohexylidene]-1-(trimethylsilyl)-2-decanol (30). ^{1}H NMR δ 0.21 (s, 9 H), 0.85 (t, J = 7 Hz, 3 H), 0.87 (t, J = 7 Hz, 3 H), 1.20−1.55 (m, 20 H), 1.55−1.75 (m, 5 H), 2.03 (q, J = 7 Hz, 2 H), 2.20 (br m, 2 H), 2.33 (br m, 2 H), 4.61 (dd, J = 4.8, 7.9 Hz, 1 H), 5.04 (t, J = 7 Hz, 1 H). The following NOE study confirmed the assigned stereochemistry. Irradiation of the proton at δ 4.61 ppm (C*H*OH) showed a 7% enhancement to that at δ 5.04 ppm (vinylic H). Alternatively, irradiation of the proton at δ 5.04 ppm (vinylic H) showed a 6% enhancement to that at δ 4.61 ppm (C*H*OH). ^{13}C NMR δ 2.51, 14.04, 22.56, 22.67, 26.71, 27.30, 28.05, 28.92, 29.29, 29.63, 29.68 (may involve more than two carbons), 29.71, 30.90, 31.60, 31.90, 37.65, 37.85, 75.28, 124.89, 134.82, 141.41, 155.96; IR (neat) 3450 (OH), 2920, 2850, 1450, 1240, 840 cm^{-1}. Anal. Calcd for $C_{25}H_{48}OSi$: C, 76.46; H, 12.32. Found: C, 76.06; H, 12.33.

***N*-Benzyl-*N*-(3-phenylpropargyl)-*N*-[4-(trimethylsilyl)-3-butynyl]-amine (31)**. ^{1}H NMR δ 0.15 (s, 9 H), 2.48 (t, J = 7.7 Hz, 2 H), 2.85 (t, J = 7 Hz, 2 H), 3.56 (s, 2 H). 3.74 (s, 2 H), 7.22−7.51 (m, 10 H); ^{13}C NMR δ 0.11, 19.38, 42.42, 52.42, 57.92, 84.44, 85.40, 85.54, 105.51, 123.32, 127.11, 127.99, 128.26 (two types of carbons), 129.00, 131.74, 138.76; IR (neat) 3080, 3040, 2970, 2850, 2200, 1690, 1500,

1460, 1340, 1260, 1130, 1040, 850, 760, 700 cm^{-1}. Anal. Calcd for $C_{23}H_{27}NSi$: N, 4.05. Found: N, 3.72.

***N*-Benzyl-3-[(*E*)-benzylidene)]-4-[(*E*)-1-(trimethylsilyl)-2-hydroxydecylidene]piperidine (32)**. ^1H NMR δ 0.26 (s, 9 H), 0.86 (t, $J = 7$ Hz, 3 H), 1.23 (br m, 10 H), 1.44 (br s, 1 H, OH), 1.52 (m, 2 H), 1.70 (br m, 2 H), 2.57 (br m, 2 H), 2.70 (br m, 2 H), 3.25 (br m, 2 H), 3.50 (s, 2 H), 4.82 (dd, $J = 5.1$, 6.9 Hz, 1 H), 6.31 (s, 1 H), 7.10 (d, $J = 7.5$ Hz, 2 H), 7.15−7.30 (m, 8 H). Irradiation of the proton at δ 4.82 ppm (C*H*OH) showed a 9% NOE enhancement to that at δ 6.31 ppm (vinylic H), which confirmed the stereochemistry. ^{13}C NMR δ 2.61, 14.06, 22.66, 26.67, 29.25, 29.59 (two carbons), 31.84, 35.79, 37.67, 55.11, 55.73, 61.99, 74.89, 126.66, 127.03, 127.33, 128.10 (two types of carbons), 128.93, 129.21, 136.71, 137.91, 138.19, 138.72, 151.73; IR (neat) 3450 (OH), 3080, 3040, 2950, 2860, 1480, 1260, 850, 740, 705 cm^{-1}. Anal. Calcd for $C_{32}H_{47}ONSi$: N, 2.86. Found: N, 2.50.

1-[(*E*)-Heptylidene]-2-methylcyclopentane (33). ^1H NMR δ 0.88 (t, $J = 7$ Hz, 3 H), 1.04 (d, $J = 7$ Hz, 3 H), 1.05−1.40 (m, 9 H), 1.52 (m, 1 H), 1.70 (m, 1 H), 1.84 (m, 1 H), 1.95 (br q, $J = 7$ Hz, 2 H), 2.13−2.37, (m, 3 H), 5.11 (tt, $J = 2.1$, 7 Hz, 1 H).

(*RS*)-[(*SR*)-3-[(*E*)-Heptylidene]-2-methylenecyclopentyl](phenyl)methanol (34). ^1H NMR δ 0.89 (t, $J = 7$ Hz, 3 H), 1.24−1.48 (m, 8 H), 1.48−1.64 (m, 2 H), 2.06 (q, $J = 7.1$ Hz, 2 H), 2.31 (m, 2 H), 2.40 (br s, 1 H, OH), 2.82 (t-like m, 1 H), 4.32 (d, $J = 9.2$ Hz, 1 H), 5.05 (s, 1 H), 5.43 (s, 1 H), 5.94 (tt, $J = 2.6$, 7.6 Hz, 1 H), 7.22−7.40 (m, 5 H). The following NOE study confirmed the assigned stereochemistry. Irradiation of the peak at δ 5.43 ppm (*endo*-C=C*H*$_2$) showed 31% and 13% enhancement to the protons at δ 5.05 (*exo*-C=C*H*$_2$) and δ 5.94 ppm (C=C*H*C_6H_{13}). Irradiation of the peak at δ 5.05 ppm (*exo*-C=C*H*$_2$) showed 2.4%, 4%, 31%, and −3% enhancement to the protons at δ 2.40 (OH), δ 2.82 C*H*CH(OH)), δ 5.43 (*endo*-C=C*H*$_2$), and δ 5.94 ppm (C=C*H*C_6H_{13}). Irradiation of the peak at δ 5.94 ppm (C=C*H*C_6H_{13}) showed 2%, −1.4%, and 6% enhancement to the protons at δ 2.06 (allylic CH_2 of C_6H_{13}), δ 5.05 (*exo*-C=C*H*$_2$), and δ 5.43 ppm (*endo*-C=C*H*$_2$). Irradiation of the peak at δ 2.40 ppm (OH) showed 6.5% and 2% enhancement to the protons at δ 4.32 (C*H*(OH)) and δ 5.05 ppm (*exo*-C=C*H*$_2$). Irradiation of the peak at δ 2.82 ppm (C*H*CH-(OH)) showed 2% and 4% enhancement to the protons at δ 5.05 (*exo*-C=C*H*$_2$) and δ 7.35 ppm (*o*-Ph). ^{13}C NMR δ 13.99, 22.53, 26.26, 27.43, 29.03, 29.14, 29.60, 31.68, 53.67, 74.93, 101.14, 122.78, 127.19, 127.77, 128.39, 139.04, 142.66, 151.09; IR (neat) 3400 (OH), 3070, 3030, 2960, 2920, 2860, 1620, 1495, 1455, 1380, 1190, 1040, 1020, 885, 760, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.41; H, 10.14.

1-[(*E*)-Heptylidene]-2-methylenecyclopentane (35). Characteristic peaks of the ^1H NMR spectrum: δ 4.76 (s, 1 H), 5.21 (s, 1 H), 5.86 (tt, $J = 2.5$, 7.5 Hz, 1 H).

(*RS*)-[(*SR*)-3-[(*E*)-Heptylidene]-2-methylenecyclopentyl](2-furyl)methanol (41). ^1H NMR δ 0.88 (t, $J = 7$ Hz, 3 H), 1.17−1.44 (m, 8 H), 1.51 (m, 1 H), 1.73 (m, 1 H), 2.06 (q, $J = 7.4$ Hz, 2 H), 2.32 (d, $J = 3.7$ Hz, 1 H, OH), 2.32 (m, 2 H), 3.05 (t-like m, 1 H), 4.44 (dd, $J = 3.7$, 8.9 Hz, 1 H), 4.97 (s, 1 H), 5.42 (s, 1 H), 5.92 (tt, $J = 2.7$, 7.4 Hz, 1 H), 6.28 (d, $J = 3.2$ Hz, 1 H), 6.37 (dd, $J = 2.1$, 3.2 Hz, 1 H), 7.40 (dd, $J = 0.8$, 2.1 Hz, 1 H); ^{13}C NMR δ 13.99, 22.53, 26.38, 27.48, 29.03, 29.14, 29.60, 31.67, 50.74, 68.65, 104.39, 107.44, 110.16, 122.76, 138.95, 142.22, 150.16, 155.06; IR (neat) 3420 (OH), 3120, 3080, 2960, 2920, 2860, 1620, 1505, 1460, 1380, 1150, 1040, 1010, 885, 810, 735 cm^{-1}. Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.78; H, 9.62.

(*RS*)-[(*RS*)-3-[(*E*)-Heptylidene]-2-methylenecyclopentyl](cyclohexyl)methanol (42). ^1H NMR δ 0.88 (t, $J = 7$ Hz, 3 H), 1.10−1.85 (m, 19 H), 1.68 (d, $J = 3.5$ Hz, 1 H, OH), 2.05 (q, $J = 7.2$ Hz, 2 H), 2.34 (t-like m, 2 H), 2.65 (t-like m, 1 H), 3.14 (dt, $J = 8.6$, 3.5 Hz, 1 H), 4.91 (s, 1 H), 5.36 (s, 1 H), 5.87 (tt, $J = 2.5$, 7.6 Hz, 1 H); ^{13}C NMR δ 13.98, 22.53, 25.66, 26.28, 26.48, 26.68, 26.74, 27.71, 29.03, 29.17, 29.57, 31.00, 31.68, 40.55, 48.58, 75.78, 103.51, 122.08, 139.57, 151.42; IR (neat) 3480 (OH), 3080, 2920, 2855, 1620, 1450, 1380, 1260, 1100, 985, 890 cm^{-1}. Anal. Calcd for $C_{20}H_{34}O$: C, 82.70; H, 11.80. Found: C, 82.76; H, 11.96.

Typical Procedure for the Cyclization and Dehydrogenation of Enynes Followed by the Addition to Aldehydes. (*RS*)-1-[(*SR*)-3-[(*E*)-Heptylidene]-2-methylenecyclopentyl]-2,2-dimethyl-1-propanol (43). To a mixture of 1-tridecen-6-yne (**10**) (20 mg, 0.112 mmol) and Ti(O-*i*-Pr)$_4$ (0.041 mL, 0.140 mmol) in 1.5 mL of Et_2O was added *i*-PrMgCl (1.66 M in ether, 0.186 mL, 0.308 mmol) dropwise at −78 °C under argon. After stirring for 30 min, the solution was warmed to −50 °C over 30 min and kept at this temperature for 2 h. After another portion of *i*-PrMgCl (1.66 M in ether, 0.084 mL, 0.140 mmol) was added at the same temperature, the dark-brown mixture was further stirred at −50 °C for 2 h. Pivalaldehyde (0.049 mL, 0.448 mmol) was then added, and the light-brown reaction mixture was stirred at −50 °C for 5 min and was rapidly allowed to warm to 0 °C. After the solution was stirred at 0 °C for an additional 30 min, the reaction was terminated by the addition of aqueous 1 N HCl. The organic layer was separated, washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to an oil, which was chromatographed on silica gel (hexanes−ether) to afford the title compound (14.5 mg, 49%) as a colorless oil. ^1H NMR δ 0.89 (t, $J = 6.8$ Hz, 3 H), 0.95 (s, 9 H), 1.24−1.43 (m, 8 H), 1.69 (m, 1 H), 1.82 (m, 1 H), 1.88 (d, $J = 3.7$ Hz, 1 H, OH), 2.05 (q, $J = 7.3$ Hz, 2 H), 2.36 (m, 2 H), 2.75 (br t, $J = 7.0$ Hz, 2 H), 3.00 (dd, $J = 3.7$, 7.0 Hz, 1 H), 4.81 (s, 1 H), 5.47 (s, 1 H), 5.88 (tt, $J = 2.5$, 7.3 Hz, 1 H); ^{13}C NMR δ 13.97, 22.52, 26.11, 27.54, 29.03, 29.14, 29.66, 30.53, 31.67, 35.90 (quaternary carbon), 47.64, 78.21, 105.20, 122.31, 139.25, 150.91; IR (neat) 3560 (OH), 3080, 2960, 2925, 2870, 2860, 1620, 1480, 1460, 1395, 1360, 1285, 1235, 1080, 1010, 880 cm^{-1}. Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20. Found: C, 81.57; H, 12.24.

9-[(*tert*-Butyl)dimethylsiloxy]-1-nonen-6-yne (44). ^1H NMR δ 0.06 (s, 6 H), 0.89 (s, 9 H), 1.56 (quintet, $J = 7$ Hz, 2 H), 2.15 (m, 4 H), 2.37 (tt, $J = 2.3$, 7.2 Hz, 2 H), 3.69 (t, $J = 7.5$ Hz, 2 H), 4.97 (d, $J = 11$ Hz, 1 H), 5.03 (d, $J = 17$ Hz, 1 H), 5.89 (ddt, $J = 11$, 17, 7.5 Hz, 1 H); ^{13}C NMR δ −5.42, 18.06, 18.24 (quaternary carbon), 23.08, 25.80, 28.06, 32.71, 62.36, 77.22, 81.01, 115.01, 138.16; IR (neat) 3080, 2925, 2860, 1640, 1470, 1460, 1255, 1105, 915, 840, 775 cm^{-1}. Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.01; H, 10.90.

(*RS*)-[(*SR*)-3-[(*E*)-3-[(*tert*-Butyl)dimethylsiloxy]propylidene]-2-methylenecyclopentyl](2-furyl)methanol (45). ^1H NMR δ 0.06 (s, 6 H), 0.90 (s, 9 H), 1.51 (m, 1 H), 1.74 (dq, $J = 13$, 7.6 Hz, 1 H), 2.26−2.40 (m, 5 H), 3.06 (t-like m, 1 H), 3.66 (t, $J = 7$ Hz, 2 H), 4.44 (dd, $J = 3.6$, 8.8 Hz, 1 H), 5.00 (s, 1 H), 5.43 (s, 1 H), 5.92 (tt, $J = 2.7$, 7.6 Hz, 1 H), 6.28 (d, $J = 3.2$ Hz, 1 H), 6.34 (dd, $J = 1.8$, 3.2 Hz, 1 H), 7.40 (dd, $J = 0.8$, 1.8 Hz, 1 H); ^{13}C NMR δ −5.43, 18.24 (quaternary carbon), 25.82, 26.34, 27.61, 33.34, 50.67, 62.45, 68.66, 104.96, 107.45, 110.16, 118.45, 140.84, 142.23, 149.93, 155.00; IR (neat) 3420 (OH), 2960, 2930, 2890, 2860, 1620, 1500, 1470, 1460, 1380, 1360, 1255, 1150, 1100, 1010, 940, 920, 840, 810, 780, 735 cm^{-1}. Anal. Calcd for $C_{20}H_{32}O_3Si$: C, 68.92; H, 9.25. Found: C, 68.60; H, 8.97.

Typical Procedure for the Copper-Mediated Allylation of Titanabicycles. 1,1-Bis(benzyloxymethyl)-3-[(*E*)-1-(trimethylsilyl)-3-butenylidene]-4-methylcyclopentane (48). To a stirred mixture of 4,4-bis(benzyloxymethyl)-1-(trimethylsilyl)-6-hepten-1-yne (**2**) (30 mg, 0.074 mmol) and Ti(O-*i*-Pr)$_4$ (0.027 mL, 0.092 mmol) in 1 mL of Et_2O was added *i*-PrMgCl (1.60 M in ether, 0.127 mL, 0.203 mmol) dropwise at −78 °C under argon. After stirring for 30 min, the solution was warmed to −50 °C over 30 min and kept at this temperature for 2 h. Then a THF solution of $Li_2Cu(CN)Cl_2$ (0.5 M in THF, 0.148 mL, 0.074 mmol) was added, followed 10 min later by allyl bromide (2 M solution in hexane, 0.044 mL, 0.089 mmol) at the same temperature. After the heterogeneous mixture was stirred at −50 °C for 3 h, the reaction was terminated by the addition of aqueous 1 N HCl. The organic layer was separated, washed with aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated to an oil, ^1H NMR analysis of which showed the nearly quantitative formation of the title compound and less than 5% each of the (possible) regioisomer and the bis-protonated **55**. Purification on silica gel (hexanes−ether) afforded the title compound (27 mg, 82%) of the same composition as above as a colorless oil. ^1H NMR δ 0.08 (s, 9 H), 1.03 (d, $J = 7.5$ Hz, 3 H), 1.25 (dd, $J = 6$, 14 Hz, 1 H), 1.84 (dd, $J = 8$, 14 Hz, 1 H), 2.22 (d, $J = 15$ Hz, 1 H), 2.46 (d, $J = 15$ Hz, 1 H), 2.75 (m, 1 H), 2.79 (dd, $J = 5.5$, 15 Hz, 1 H), 2.93 (dd, $J = 5.5$, 15 Hz, 1 H), 3.18 (d, $J = 8$ Hz, 1 H), 3.26 (d, $J = 8$ Hz, 1 H), 3.40 (d, $J = 8$ Hz, 1 H), 3.54 (d, $J = 8$ Hz, 1 H), 4.40 (d, $J = 12$ Hz, 1 H), 4.50 (d, $J = 12$ Hz, 1 H), 4.54 (s, 2 H), 4.90 (d, $J = 18$ Hz, 1 H), 4.92 (d, $J = 9.5$ Hz, 1 H), 5.77 (ddt, $J = 9.5$, 18, 5.5 Hz, 1 H), 7.22−7.36

(m, 10 H). Decoupling of the proton at δ 5.77 ppm (C*H*═CH_2) changes the following peaks: δ 2.79 ppm (dd, J = 5.5, 15 Hz, 1 H, bis-allylic H) → (d, J = 15 Hz); δ 2.93 ppm (dd, J = 5.5, 15 Hz, 1 H, bis-allylic H) → (d, J = 15 Hz); δ 4.90 ppm (d, J = 18 Hz, 1 H, CH═C*H*$_2$) and δ 4.92 ppm (d, J = 9.5 Hz, 1 H, CH═C*H*$_2$) → δ 4.91 ppm (br s). The following NOE study confirmed the assigned stereochemistry. Irradiation of the peak at δ 1.03 ppm (cyclopentyl Me) showed a 9% enhancement to the proton at δ 2.75 ppm (C*H*Me). Irradiation of the peak at δ 2.93 ppm (bis-allylic H) showed 2% and 5% enhancement to the protons at δ 1.03 (cyclopentyl Me) and δ 5.77 ppm (C*H*═CH_2). ^{13}C NMR δ 0.18, 22.79, 35.11, 35.89, 38.80, 39.45, 47.01 (quaternary carbon), 72.43, 73.19, 73.23, 75.06, 114.23, 127.26, 127.34, 127.48, 128.17, 128.22, 138.41, 138.75, 138.83, 139.04, 159.16. The peaks in the region between δ 127.26 and 128.22 ppm may contain two types of aromatic carbons. IR (neat) 3070, 3030, 2955, 2920, 2895, 2860, 1635, 1620, 1495, 1455, 1360, 1250, 1100, 1030, 910, 850, 840, 735, 700 cm^{-1}. Anal. Calcd for $C_{29}H_{40}O_2Si$: C, 77.62; H, 8.99. Found: C, 77.62; H, 9.10.

The Possible Minor Regioisomer. A characteristic peak of the ^{1}H NMR spectrum: δ 5.01 (br q, J = 1.5 Hz, 1 H).

1-(Trimethylsilyl)-7-octen-1-yne (49). ^{1}H NMR δ 0.13 (s, 9 H), 1.50 (m, 4 H), 2.06 (q, J = 7 Hz, 2 H), 2.23 (t, J = 7 Hz, 2 H), 4.95 (d, J = 9 Hz, 1 H), 5.01 (d, J = 17 Hz, 1 H), 5.80 (ddt, J = 9, 17, 7 Hz, 1 H); ^{13}C NMR δ 0.17, 19.71, 28.01, 28.05, 33.17, 84.44, 107.44, 114.50, 138.61; IR (neat) 3080, 2960, 2940, 2860, 2175, 1640, 1430, 1250, 990, 915, 840, 760, 700, 640 cm^{-1}. Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.13; H, 11.14.

1-Methyl-2-[(*E*)-1-(trimethylsilyl)-3-butenylidene]cyclohexane (50). ^{1}H NMR δ 0.10 (s, 9 H), 1.04 (d, J = 7.5 Hz, 3 H), 1.24 (m, 1 H), 1.40−1.65 (m, 4 H), 1.79 (br d, J = 12 Hz, 1 H), 2.17 (dt, J = 5, 13 Hz, 1 H), 2.39 (br d, J = 13 Hz, 1 H), 2.75−2.95 (m, 3 H), 4.93 (dt, J = 11, 2 Hz, 1 H), 4.94 (dt, J = 16.7, 2 Hz, 1 H), 5.81 (m, 1 H); IR (neat) 3080, 2960, 2920, 2860, 1635, 1600, 1450, 1250, 990, 910, 855, 835, 760, 685 cm^{-1}. Anal. Calcd for $C_{14}H_{26}Si$: C, 75.59; H, 11.78. Found: C, 75.22; H, 11.81.

A 6:4 Mixture of 2-[(*E*)-(Trimethylsilyl)methylene]-1-[(*E*)-1-phenyl-3-butenylidene]cyclohexane (51) and 2-[(*E*)-Benzylidene]-1-[(*E*)-1-(trimethylsilyl)-3-butenylidene]cyclohexane (52). ^{1}H NMR δ 0.17 (s, 9 H, **51**), 0.19 (s, 9 H, **52**), 1.50−1.75 (m, 4 H, **51** + **52**), 2.10 (t, J = 6 Hz, 2 H, **51**), 2.36 (t, J = 6 Hz, 2 H, **51**), 2.43 (m, 4 H, **52**), 3.04 (dt, J = 6, 2 Hz, 2 H, **52**), 3.20 (d, J = 7 Hz, 2 H, **51**), 4.85 (d, J = 11 Hz, 1 H, **51**), 4.85 (d, J = 17 Hz, 1 H, **51**), 4.95 (d, J = 17 Hz, 1 H, **52**), 4.98 (d, J = 9 Hz, 1 H, **52**), 5.38 (s, 1 H, **51**), 5.65 (m, 1 H, **51**), 5.87 (m, 1 H, **52**), 6.28 (s, 1 H, **52**), 7.10−7.35 (m, 5 H, **51** + **52**); IR (neat) 3080, 2955, 2925, 2855, 1600, 1440, 1250, 910, 850, 840, 700 cm^{-1} for a 6:4 mixture of **51** and **52**. Anal. Calcd for $C_{20}H_{28}Si$: C, 81.01; H, 9.52. Found: C, 81.07; H, 9.75 for a 6:4 mixture of **51** and **52**.

1-[(*Z*)-1-Nonen-4,4-ylidene]-2-[(*E*)−(trimethylsilyl)methylene]cyclohexane (53). ^{1}H NMR δ 0.09 (s, 9 H), 0.87 (t, J = 7 Hz, 3 H), 1.28 (br m, 6 H), 1.62 (br m, 4 H), 2.00 (t, J = 7.5 Hz, 2 H), 2.22 (m, 4 H), 2.87 (d, J = 6.6 Hz, 2 H), 4.95 (d, J = 10.5 Hz, 1 H), 4.97 (d, J = 17 Hz, 1 H), 5.13 (s, 1 H), 5.75 (ddt, J = 10.5, 17, 7 Hz, 1 H). The following NOE study confirmed the assigned stereochemistry. Irradiation of the peak at δ 2.87 ppm (bis-allylic CH_2) showed a 4% enhancement to the proton at δ 5.13 ppm (C═C*H*SiMe_3). ^{13}C NMR δ 0.34, 14.07, 22.61, 28.05, 28.67, 28.80, 30.62, 32.06, 32.14, 36.51, 37.73, 114.70, 123.11, 128.57, 138.51, 140.86, 159.36; IR (neat) 3080, 2960, 2925, 2855, 1635, 1600, 1440, 1250, 910, 855 cm^{-1}. Anal. Calcd for $C_{19}H_{34}Si$: C, 78.54; H, 11.79. Found: C, 78.32; H, 11.95.

1-[(*Z*)-1-Nonen-4,4-ylidene]-2-[(*E*)-(trimethylsilyl)(deuterio)methylene]cyclohexane (**53-*d*$_1$**). The ^{1}H NMR peak at δ 5.13 ppm (s, 1 H) of **53** almost completely disappeared.

1-[(*E*)-Hexylidene]-2-[(*E*)-1-(trimethylsilyl)-3-butenylidene]cyclohexane (54). A characteristic peak of the ^{1}H NMR spectrum: δ 2.93 (dt, J = 5.4, 2 Hz, 2 H).

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