Regio- and Stereoselective Synthesis of the 1,3-Cyclohexadiene Nucleus by [2 + 2 + 2] Cycloaddition Reactions Catalyzed by Titanium Aryloxide Compounds

Eric S. Johnson, Gary J. Balaich, and Ian P. Rothwell*

Contribution from the Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, Indiana 47907-1393

Received February 18, 1997[⊗]

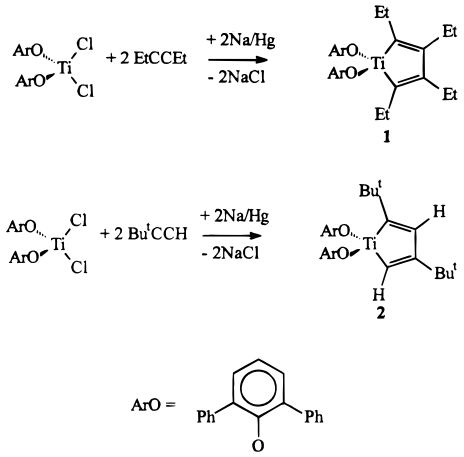
Abstract: A variety of titanium aryloxide reagents catalyze the cross coupling of two alkyne units with 1 equiv of olefin to produce the 1,3-cyclohexadiene nucleus. Catalysts include isolated titanacyclopentadiene or titanacyclopentane complexes. The reaction proceeds via attack of the olefin upon a titanacyclopentadiene compound initially formed by coupling of two alkyne units. The reaction is limited to bulky alkyne substrates that undergo slow catalytic cyclotrimerization via competing attack of a third alkyne upon the titanacyclopentadiene ring. The organic products isolated are typically the result of an isomerization within the initially produced 1,3-cyclohexadiene nucleus. Mechanistic studies show that these isomerization processes occur via sequential, metal-mediated 1,5-hydrogen shifts upon a single face of the six-membered ring, exclusively leading to a *cis*-stereochemistry within the final products. In the reactions of the diynes R−C≡C$(CH_2)_4$C≡C−R (R = Et, $SiMe_3$), coupling with ethylene and α-olefins produces a variety of substituted hexalins. A combination of NMR spectroscopy, photochemistry, and molecular mechanics calculations has been applied to determine the stereochemistry and ground state conformations adopted by the product 1,3-cyclohexadienes and hexalins. The primary and secondary photoproducts obtained from some of these 1,3-cyclohexadiene compounds have been characterized.

Introduction

The 1,3-cyclohexadiene nucleus has a rich and diverse reaction chemistry.[1] Two important areas of study are the utilization of 1,3-cyclohexadienes in Diels−Alder condensations[2] and in photochemical ring opening to produce a variety of primary and secondary photoproducts.[3] The study of the photochemistry of substituted 1,3-cyclohexadienes gains importance from their direct relevance to photoinduced transformations in the vitamin D field.[4] The stereochemical outcome of the photochemical and thermal interconversions of 1,3-cyclohexadienes and acyclic trienes was an important component in the development of the Woodward−Hoffman rules.[5]

Existing routes to the 1,3-cyclohexadiene nucleus include isomerization of 1,4-cyclohexadienes generated by Birch reduction[6] and a limited number of other methods.[7] Of direct relevance to the work described here is the pioneering studies of Volhardt et al. on the cobalt-mediated [2 + 2 + 2] cycloaddition of 2 equiv of alkyne with an olefin.[8] This is conceptually the simplest and potentially the most powerful method for the synthesis of 1,3-cyclohexadienes. We report here our understanding of a titanium aryloxide catalyst system

Scheme 1



which produces 1,3-cyclohexadienes with a high degree of regio- and stereoselectivity. Some aspects of this work have been communicated.[9]

Results and Discussions

Synthesis of 1,3-Cyclohexadienes. Previously, we have shown that the titanacyclopentadiene compounds **1** and **2** can be obtained in high yield by sodium amalgam reduction of the dichloride $[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$ ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide) in the presence of 3-hexyne or Bu^{t}C≡CH (Scheme 1).[10] In the presence of excess reagent alkyne, **1** and **2** will slowly produce hexaethylbenzene and 1,3,5-tri-*tert*-butylbenzene under ambient conditions (Scheme 1). In contrast, small terminal alkynes exothermically yield copious amounts of 1,2,4- and 1,3,5-trisubstituted benzene upon addition to **1** or

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) Okamura, W. H.; De Lera, A. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, **1991**; Vol 5, Chapter 6.2.

(2) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; John Wiley: New York, 1990.

(3) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

(4) Dauben, W. G.; Kellog, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendshuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 197.

(5) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

(6) *Organic Reactions*; Paquette, L. A., Ed.; John Wiley: New York, 1992; Vol. 42, pp 1−334.

(7) Mironov, V. A.; Federovich, A. D.; Akhrem, A. A. *Russ. Chem. Rev.* **1983**, *52*, 61.

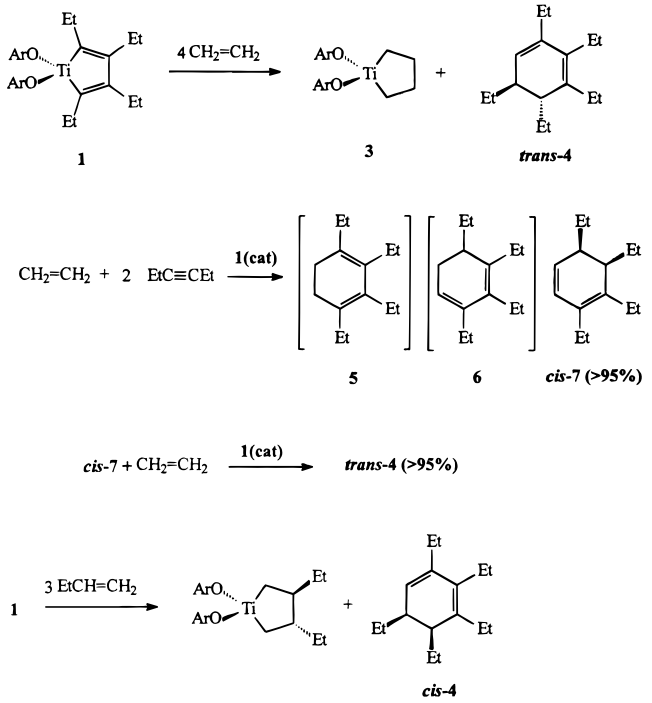
(8) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(9) Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581.

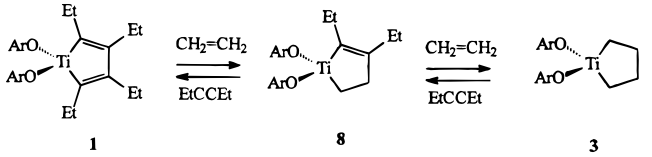
(10) Hill, J. E.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

S0002-7863(97)00516-7 CCC: $14.00

Scheme 2



Scheme 3



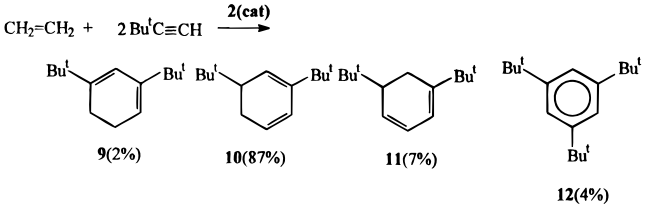
2.[10] We have also shown that compound **1** reacts with ethylene to produce a thermally stable titanacyclopentane **3** as the organometallic product (Scheme 2).[11] Surprisingly, we discovered that the organic byproduct was a pentaethyl-1,3-cyclohexadiene (**4**) whose stereochemistry is now known to be exclusively *trans*. When ethylene is added to a mixture of **1** and excess 3-hexyne, catalytic formation of *cis*-1,2,5,6-tetraethyl-1,3-cyclohexadiene (***cis*-7**) occurs (Scheme 2). Upon exhaustion of all of the 3-hexyne, the titanium system then catalyzes the cross coupling of ***cis*-7** with a further equivalent of ethylene to produce ***trans*-4** (Scheme 2). We have carried out a separate study of the regio- and stereochemistry of the cross coupling of olefins with 1,3-cyclohexadienes catalyzed by titanium aryloxides and these results have been communicated[12] and full details will be reported elsewhere. In the presence of excess 3-hexyne, compound **1** reacts with 1-butene to exclusively produce *cis*-1,2,3,4,5-pentaethyl-1,3-cyclohexadiene (***cis*-4**, Scheme 2).

The addition of **1** to hydrocarbon solutions containing an excess of both 3-hexyne and ethylene can generate three organotitanium species: titanacyclopentadiene **1**; titanacyclopentane **3**; as yet unisolated titanacyclopent-2-ene **8** (Scheme 3). Analysis of the ^{1}H NMR spectrum of a mixture of **1**, 3-hexyne, and ethylene in C_6D_6 reveals the majority of the titanium to be present as **1**. The selective formation of 1,3-cyclohexadiene, therefore, originates in the stability of **1** over **3** and **8** within the reaction media coupled with a faster reaction

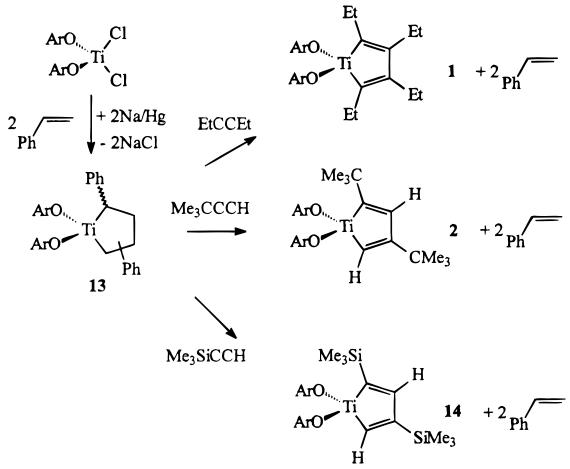
(11) (a) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. In press. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15.

(12) Waratuke, S. A.; Johnson, E. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun*. **1996**, 2617.

Scheme 4



Scheme 5



of **1** with ethylene versus 3-hexyne (leading to cyclotrimerization). These gross features control the selectivity of formation of 1,3-cyclohexadienes below, although more intimate mechanistic details will be discussed later in the paper. Another important property of this catalytic system is the extensive isomerization observed leading to a 1,3-cyclohexadiene regiochemistry not directly predicted on the basis of alkyne/olefin structure. The product regio- and stereochemistry can be rationalized on the basis of either kinetically and/or thermodynamically controlled 1,5-hydrogen shifts mediated by the titanium metal center (see mechanistic section below). In the formation of ***cis*-7** from 3-hexyne/ethylene, two sequential 1,5-hydrogen shifts within metal bound **5** and **6** (Scheme 2) are envisaged.

The 2,4-di-*tert*-butyltitanacyclopentadiene complex **2** reacts with ethylene in the presence of excess Bu^{t}C≡CH to produce the 1,3-cyclohexadienes **9**, **10** (major component) and **11** (Scheme 4) along with small amounts of 1,3,5-tri-*tert*-butylbenzene **12**. Separation and purification of the components of this reaction mixture is hampered by facile dehydrogenation (aromatization) on prolonged exposure to air and on silica TLC plates.

We have extensively investigated the products obtained by the catalytic [2 + 2 + 2] cycloaddition of styrene with a variety of alkynes. These reactions can be carried out either by addition of styrene to isolated titanacyclopentadienes **1** or **2** in the presence of alkyne or, alternatively, by utilization of the diphenyltitanacyclopentane **13**[11a] as the catalyst precursor (Scheme 5). This compound reacts with 3-hexyne, Bu^{t}C≡CH, or Me$_3$SiC≡CH to initially produce titanacyclopentadienes **1**, **2**, and **14** quantitatively (^{1}H NMR) along with 2 equiv of styrene (Scheme 5). Use of either of these two catalyst precursors leads to the phenyl-substituted 1,3-cyclohexadienes shown (Scheme 6, Table 1). Utilization of either Bu^{t}C≡CH or Me$_3$SiC≡CH generates a series of 1,3,5-tris-substituted-1,3-cyclohexadienes. In the Bu^t-substituted compounds, the product ratio of **18**/**19** is kinetically controlled by the reaction conditions (Table 2), whereas for the trimethylsilyl compounds, kinetically produced

Scheme 6

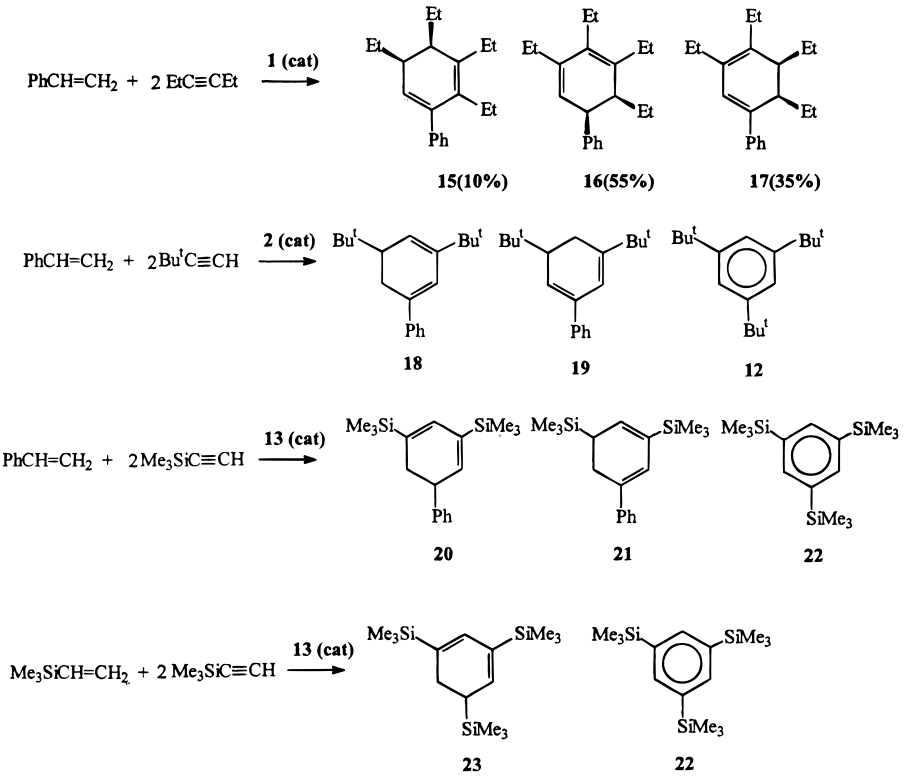


Table 1. Product Yields and Distributions[a]

[olefin] (equiv per Ti)	[alkyne] (equiv per Ti)	yield %[c]	product distribution[d]
$PhCH{=}CH_2$; 1.9 M (40)	EtC≡CEt; 3.1 M (65)	54	**15** (13), **16** (35), **17** (53)
$PhCH{=}CH_2$; 1.9 M (40)	*t*-BuC≡CH; 1.4 M (28)	24	**18** (66), **19** (28), **12** (6)
$PhCH{=}CH_2$; 1.9 M (40)	$Me_3SiC{\equiv}CH$; 2.7 M (55)	52	**20** (57), **21** (25), **22** (18)
$Me_3SiCH{=}CH2$; 2.1 M (45)	$Me_3SiC{\equiv}CH$; 2.8 M[e] (60)	51	**23** (61), **22** (39)
$PhCH{=}CH_2$; 3.7 M (78)	$Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$; 1.0 M (20)	42[b]	**36** (>95)

[a] Catalyst used **13**, 0.048 M; solvent C_6D_6; alkyne and olefin mixed with **13** and maintained at 25 °C unless otherwise stated. [b] 105 °C. [c] Isolated yield of product mixture based upon alkyne reagent. [d] GC analysis. [e] Alkyne added slowly over 3 days.

Table 2. Effect of Initial 3,3-Dimethylbutyne/Styrene Concentration on the Product Distribution[a]

reagents (M)		product distribution (%)		
		18	**19**	**12**
[t-Bu—≡—H]	$[PhCH{=}CH_2]$			
2.90	1.45	47	34	19
2.90	2.90	62	30	8
2.90	4.35	74	20	6
1.45	1.45	48	45	7
1.45	1.45[b]	75[b]	20[b]	5

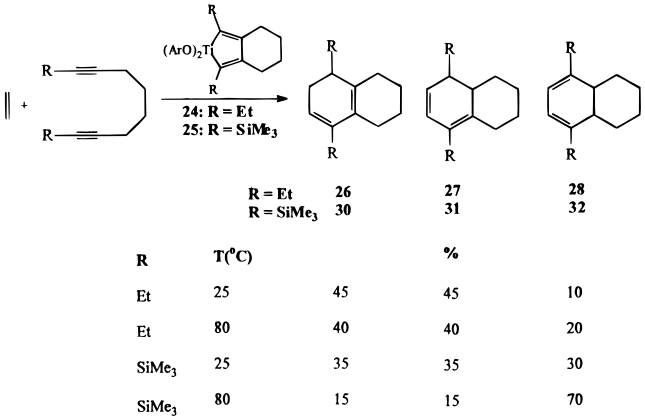
[a] [**2**] = 0.072 M; solvent C_6D_6. [b] Styrene-d_8; T = 25 °C.

20 can subsequently be isomerized thermally by the reaction mixture to produce **21** as the dominant product. These observations are of mechanistic significance (*vide infra*).

The coupling of vinyltrimethylsilane with $Me_3SiC{\equiv}CH$ can be achieved using **13** as the catalyst precursor. In this case, only a single 1,3-cyclohexadiene product (**23**) is generated, although large amounts of 1,3,5-tris(trimethylsilyl)benzene (**22**) are also produced (Scheme 6, Table 1). To minimize cyclotrimerization, the alkyne was added in small batches over a three day period to a mixture of **13**/vinyltrimethylsilane.

Utilizing 3,9-dodecadiyne or 1,8-bis(trimethylsilyl)-1,7-octadiyne as the alkyne component allows the synthesis of the

Scheme 7

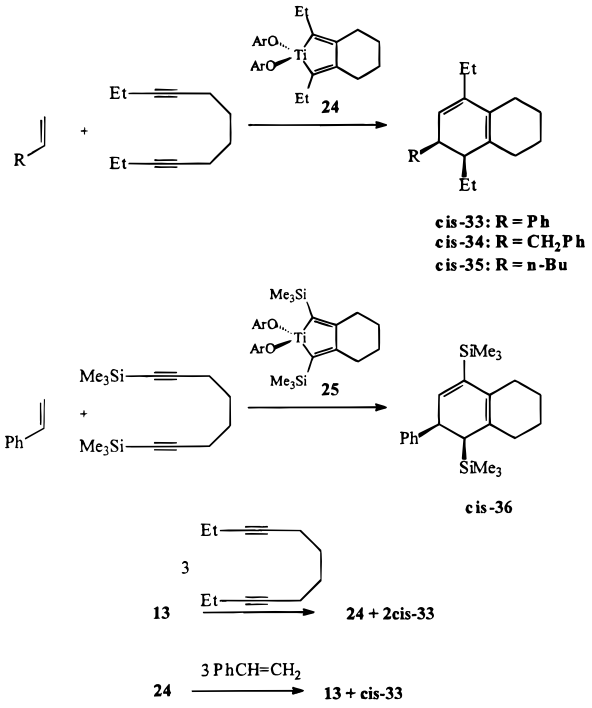


hexalin nucleus from entirely acyclic precursors.[13] In these reactions the intermediate titanacyclopentadienes **24** and **25** (Scheme 7)[14] are observed in C_6D_6 solution. Although ethylene generates the product mixture shown (Scheme 7), the [2 + 2 + 2] cyclization of α-olefins $RCH{=}CH_2$ (R = Ph, Bu^n, and CH_2Ph) with 3,9-dodecadiyne leads almost exclusively to a series of *cis*-1,2,4-trisubstituted-1,2,5,6,7,8-hexahydronaphtha-

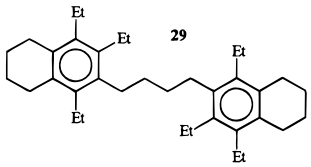
(13) Hillard, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058.

(14) Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1994**, *13*, 4117.

Scheme 8



lenes (Scheme 8). These reactions are complicated, however, by the formation of significant quantities of the 3,9-dodecadiyne trimerization product **29**.[13]



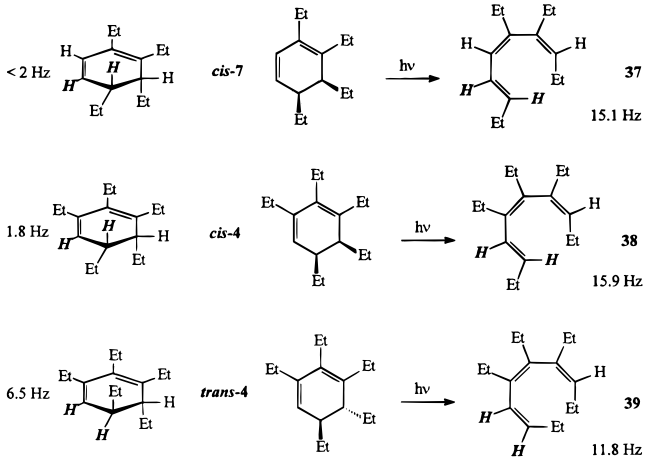
The titanacyclopentane compound **13** has been shown to react with 3 equiv of 3,9-dodecadiyne to stoichiometrically (^{1}H NMR) produce **24** and 2 equiv of **cis-33** (Scheme 8). Addition of excess styrene to **24** then regenerates **13** along with an additional 1 equiv of **cis-33**.

One of the cleanest [2 + 2 + 2] cycloaddition reactions we have identified is the reaction of styrene with 1,8-bis(trimethylsilyl)-1,7-octadiyne[15] catalyzed by **25** (Scheme 8, Table 1). Although much slower than the corresponding reactions with 3,9-dodecadiyne (presumable a steric consequence), this reaction produces a single hexalin product (***cis*-36**) with no contaminating cyclotrimerization products.

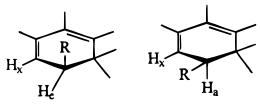
Product 1,3-Cyclohexadiene Stereochemistry. A thorough understanding of the stereochemistry of these 1,3-cyclohexadiene products is not only of synthetic importance but is also crucial to any comprehension of the mechanism of their formation and/or isomerization by the titanium aryloxide catalysts. The conformational ground state structure of 1,3-cyclohexadiene and its substituted derivatives has been extensively studied by a variety of methods, and we have utilized three particular techniques in this study.

Routine ^{1}H NMR methods have been successfully applied to the determination of the ground state conformations adopted by 5- and 5,6-substituted-1,3-cyclohexadienes.[16,17] Analysis of

Scheme 9



$^3J(H_5-H_6)$ coupling constants within the saturated unit will typically indicate whether substituents occupy pseudoaxial or pseudoequatorial sites. A powerful, complementary analysis of the $^3J(H_4-H_{5/6})$ coupling constants by Knowles et al. is of significance to this work.[18] A detailed analysis of chorismate in a variety of solvents demonstrates the magnitude of this parameter can be successfully used to determine the predominant ground state conformational structure.



The photochemistry of 1,3-cyclohexadienes has been extremely well documented. The conrotatory photochemical ring opening of a 1,3-cyclohexadiene to produce a hexatriene backbone as the primary photoproduct is typically followed by secondary photoreactions producing a variety of cyclic and acyclic products.[4,19] Detailed studies have shown that the position of substituents in the triene primary photoproduct are controlled by the "principal of least motion" (PLM); pseudoaxial groups occupy the Z-sites in the terminal methylene groups.[20]

More recently molecular mechanics methods have been brought to bear on the problem of ground state structures of 1,3-cyclohexadienes and in particular for the conformational analysis of partially hydrogenated polycyclic aromatic hydrocarbons.[16]

The series of ethyl derivatives **4** and **7** (Scheme 2) have complex patterns in the aliphatic region of the ^{1}H NMR spectrum, precluding analysis of the $^3J(H_5-H_6)$ coupling constants to indicate the absolute stereochemistry. The $^3J(H_4-H_5)$ parameter is, however, highly informative. A low value of <2 Hz in both ***cis*-4** and ***cis*-7** indicates that H_5 occupies a pseudoaxial site in these compounds, whereas the larger, 6.5 Hz coupling in ***trans*-4** is consistent with a pseudoequatorial site for H_5 in this compound (Scheme 9).[18] Steric considerations argue that the ethyl groups at C-6 will occupy a pseudoaxial

(15) (a) Birkofer, L.; Hansel, E.; Steigel, A. *Chem. Ber.* **1982**, *115*, 2574. (b) Brandsma, L.; Verkryijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981, p 57.

(16) *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH Publishers, Inc.: New York, 1989.

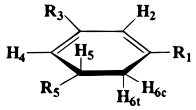
(17) (a) Lightner, D. A.; Bouman, T. D.; Gawronski, J. K.; Gawronska, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314. (b) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1988**, *53*, 4909.

(18) Copley, S. D.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5008.

(19) Woning, J.; Lijten, F. A.; Laarhoven, W. H. *J. Org. Chem.* **1991**, *56*, 2427 and references therein.

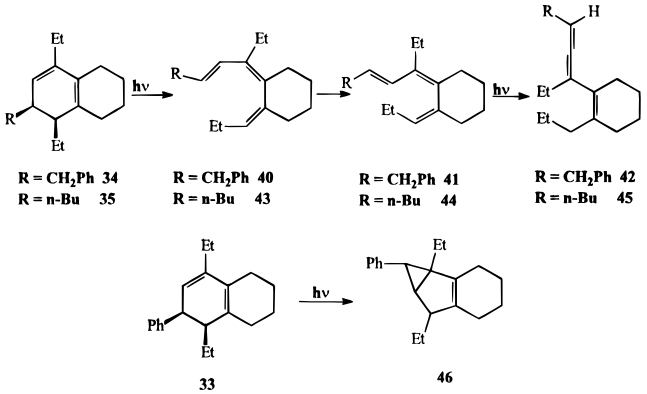
(20) (a) Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767. (b) Courtot, P.; Rumin, R.; Salaun, J. Y. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 192. (c) Lamberts, J. J. M.; Laarhoven, *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 131. (d) Spangler, C. W.; Hennis, R. P. *J. Chem. Soc., Chem. Commun.* **1972**, 24.

Table 3. Selected Coupling Constants (hertz) for 1,3,5-Trisubstituted-1,3-Cyclohexadienes



	R_1	R_3	R_5	$^2J(H_{6c}-H_{6t})$	$^3J(H_5-H_{6t})$	$^3J(H_5-H_{6c})$	$^3J(H_4-H_5)$
18	Ph	Bu^t	Bu^t	16.3	13.2	8.7	3.5
19	Bu^t	Ph	Bu^t	15.0	14.8	7.0	<2
20	$SiMe_3$	$SiMe_3$	Ph	16.5	14.8	8.1	3.2
21	Ph	$SiMe_3$	$SiMe_3$	16.3	9.8	4.0	5.6
23	$SiMe_3$	$SiMe_3$	$SiMe_3$	16.5	9.5	4.0	5.6

Scheme 10

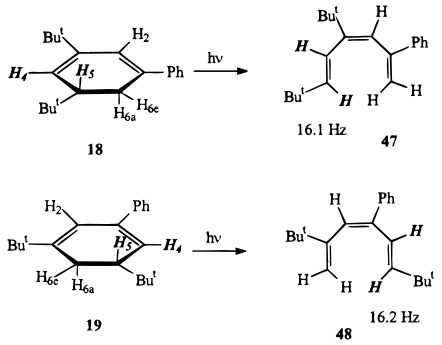


site in all three compounds to minimize interactions with the ethyl substituent at C-1. This argument is strongly supported by molecular mechanics calculations on the compound 1,2,3,5,6-pentamethyl-1,3-cyclohexadiene where, in both the *cis*- and *trans*-isomers, a preference of a pseudoaxial substituent at C-6 was calculated (see the Supporting Information). The above arguments, therefore, lead to the stereochemistry assigned to these three molecules (shown in Scheme 9). We have also carried out the photolysis of these three products. The magnitude of the relevant vicinal coupling constants in the product trienes **37**−**39** (Scheme 9) confirms the ground state conformational position of the substituents at C5.

Directly analogous arguments, when applied to the three hexalin compounds **33**−**35** (Scheme 8), show the product stereochemistry to be *cis*. Molecular mechanics calculations on the model compound 1,2,4-trimethylhexalin (see the Supporting Information) show the substituent at C1 is pseudoaxial, while ^{1}H NMR data and photochemical studies of **34** and **35** show the substituent at C-2 is pseudoequatorial (Scheme 10). Extended photolysis of trienes **41** and **44** (Scheme 10) was found to lead to the allene compounds **42** and **45** as the major secondary photoproducts. In contrast photolysis of the 2-phenyl derivative, **33** did not produce significant quantities of a triene. Instead, the major photoproduct appears to be a bicyclo[3.1.0]-hexene, whose stereochemistry we have not assigned. The stereochemical outcome of the photochemical conversion of phenyl-substituted 1,3-cyclohexadienes to bicyclo[3.1.0]hexenes has been reported.[20]

The situation with the five 1,3,5-tris-substituted-1,3-cyclohexadienes is more straightforward. In this case, the resolution and analysis of ^3J coupling constants reveals the 5-substituent in **18**−**20** to be predominantly pseudoequatorial in solution (Table 3). This data is consistent with reported studies of 5-*tert*-butyl-1,3-cyclohexadiene.[16,17a] It is interesting to note that the values of the coupling constants indicate that the $SiMe_3$ substituents in **21** and **23**[17b] imply that significant amounts of the pseudoaxial conformer are present. The predominance of

Scheme 11



a pseudoequatorial conformer for **18** and **19** is confirmed by their photochemical conversion to **47** and **48** (Scheme 11).

Mechanistic Considerations. The formation of 1,3-cyclohexadienes studied here has some mechanistic similarities to the [2 + 2 + 2] cyclotrimerization of alkynes.[10] In this latter case, a long-standing mechanistic dilemma has been the exact nature of intermediate organometallic species. The addition of ethylene to a titanacyclopentadiene may lead (via an olefin adduct) to the concerted formation of the two new carbon−carbon bonds or else proceed in a stepwise fashion via a titanacycloheptatriene (Scheme 12). The concerted pathway has many similarities with the ubiquitous Diels−Alder reaction. Three observations argue strongly against a stepwise pathway for these reactions. First, the facile insertion of olefins into the Ti−C bonds of neutral species $[(ArO)_2TiR_2]$[21] (R = alkyl, aryl, or part of a metallacyclic ring) has not been observed. Although the expansion of titanacyclopent-3-ene rings upon addition of ethylene and α-olefins occurs readily, it proceeds via coupling of the olefin with a diene double bond.[22] Second, seven-membered titanacyclic rings undergo β-hydrogen abstraction/elimination processes (whether concerted or stepwise) at a much faster rate than five-membered analogues.[11a,22] In a number of cases this would lead to the formation of 1,3,5-trienes, which we have synthesized by photochemical experiments but do not detect in the [2 + 2 + 2] cycloaddition reaction mixtures. Finally, we have no evidence in our previous work on titanium aryloxides for the facile reductive/elimination (coupling) of adjacent Ti−C bonds in $[(ArO)_2TiR_2]$ species.

The kinetics of formation of the hexalin ***cis*-36** by reaction of styrene with 1,8-bis(trimethylsilyl)-1,7-octadiyne were investigated. This reaction was chosen for study because only a single isomer is produced with no cyclotrimerization side reaction. The kinetics were carried out by adding titanacyclopentane **13** to a mixture of styrene (excess) and 1,8-bis-

(21) (a) Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, *6*, 2019. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (c) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 15.

(22) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656.

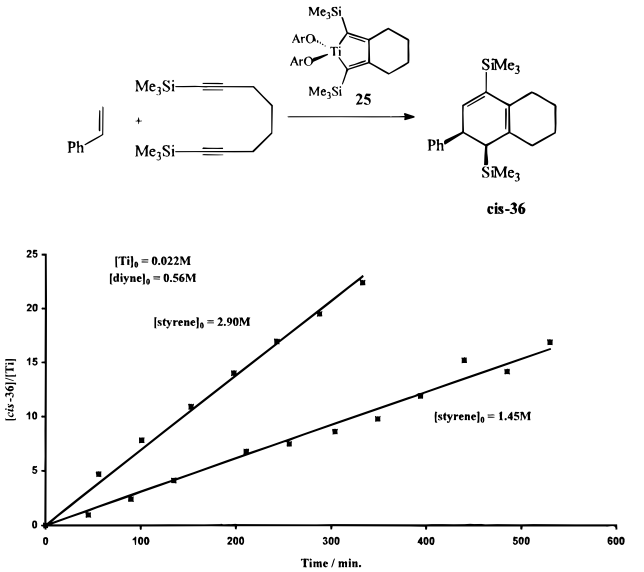
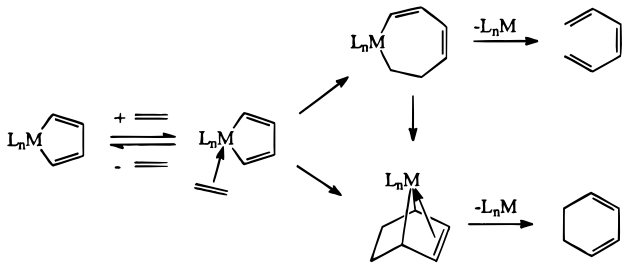


Figure 1. Plot showing the appearance of ***cis*-36** (equivalents per Ti) at 105 °C during the [2 + 2 + 2] cycloaddition of 1,8-bis-(trimethylsilyl)-1,7-octadiene with styrene.

Scheme 12

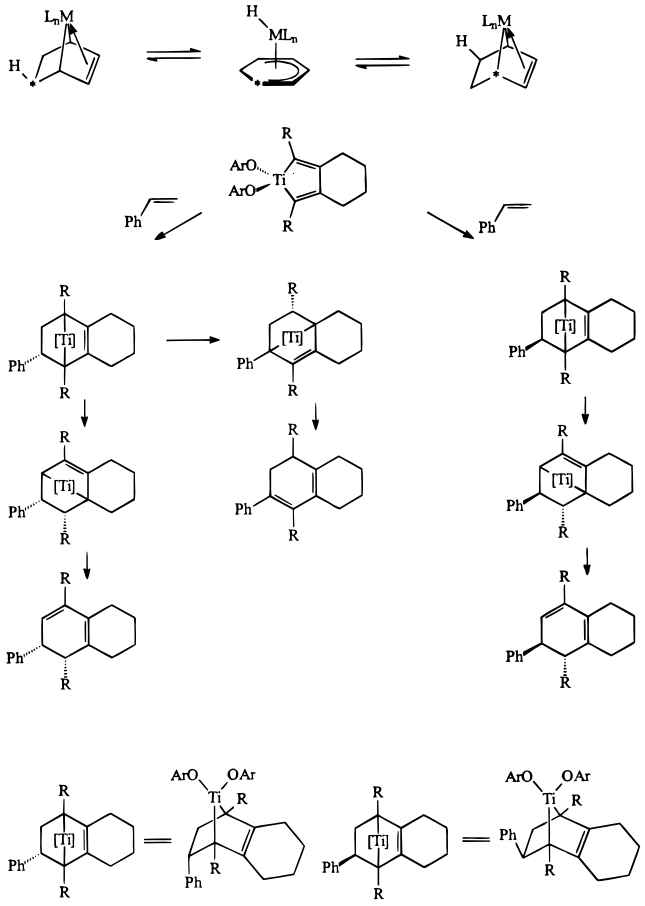


(trimethylsilyl)-1,7-octadiyne in C_6D_6 solvent. Analysis of the initial reaction mixture by ^{1}H NMR spectroscopy reveals the clean conversion of **13** into **25** (Scheme 8). The solutions were then heated at 105 °C, and the reaction was monitored at various time intervals by ^{1}H NMR. The reactions were found to demonstrate a zero-order dependence on [diyne] and a first-order dependence on both [styrene] and [Ti]. In Figure 1 is shown a plot of the appearance of ***cis*-36** utilizing 25 equiv of diyne per Ti and 65 or 130 equiv of styrene. Under the conditions shown, the product ***cis*-36** is produced at rates of 1.9(1) and 4.1(2) equiv Ti^{-1} h^{-1}, respectively.

The kinetic results as well as the product regio- and stereochemistry can be accounted for by a mechanistic pathway in which rate-determining attack of olefin on the titanacyclopentadiene produces a metal-bound 1,3-cyclohexadiene. On the basis of related studies of the structure and bonding within the niobium and tantalum species $[(ArO)_3M(\eta^4\text{-}C_6H_8)]$ and $[(ArO)_2M(Cl)(\eta^4\text{-}C_6H_8)]$[23] as well as related group 4 metal 1,3-diene species,[24] a titananorbornene bonding picture appears reasonable for this molecule (Scheme 12). Direct dissociation of 1,3-cyclohexadiene, releasing the extremely high-energy fragment $[Ti(OAr)_2]$, is doubtful. Instead, displacement of the product by alkyne or olefin present in solution will lead to regeneration of the titanacyclopentadiene, titanacyclopentene and titanacyclopentane equilibrium mixture (Scheme 3).

The isomerization process occurs within the titananorbornadiene complex via intermediate cyclohexadienyl hydride com-

Scheme 13



pounds leading to an overall 1,5-hydrogen shift (Scheme 13).[25,26] During the formation of ***cis*-7** (Scheme 2) and many other products, two sequential 1,5-hydrogen shifts are necessary. The mediating metal center remaining bound to a single face of the cyclohexadiene nucleus will lead exclusively to the observed *cis*-stereochemistry. An indiscriminate isomerization process would lead to the thermodynamically more stable *trans*-isomer.

In the reaction of 3,9-dodecadiyne and 1,8-bis(trimethylsilyl)-1,7-octadiyne with α-olefins (Scheme 8), the initially formed titananorbornene may exist as either an *exo*- or *endo*-stereoisomer. On the basis of steric arguments, the *endo*-isomer (alkyl *trans* to the titanium metal center) is preferred. The stereochemistry of the isolated products could only originate via a metal-mediated 1,5-shift within the *endo*-isomer; the *exo*-isomer can only produce the *trans*-stereoisomer (Scheme 13). Furthermore, the *endo*-isomer also has available an alternative hydrogen for migration (Scheme 13). This pathway would lead to a regiochemistry that is not observed, indicating that the metal center is highly selective at abstracting and migrating a hydrogen from the methylene group.

We have also applied molecular mechanics methods to determine the relative stabilities of all regio- and stereoisomers of the model compounds pentamethyl-1,3-cyclohexadiene and 1,2,4-trimethylhexalins (see the Supporting Information).[27] These results show that the *cis*-products observed are slightly more stable than the isomers initially expected on the basis of

(23) (a) Visciglio, V. M.; Nguyen, M. T.; Clark, J. R.; Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 3490. (b) Visciglio, V. M.; Nguyen, M. T.; Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1996**, *15*, 551.

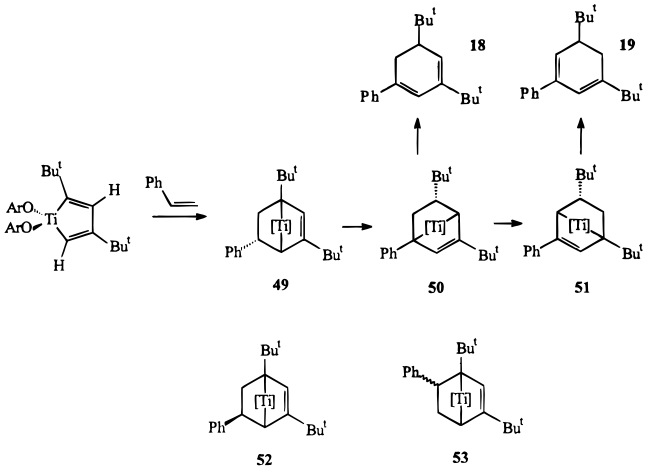
(24) Diamond, G. M.; Green, M. L. H.; Walker, N. M.; Howard, J. A. K.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2641.

(25) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. (b) Karel, K. J.; Brookhart, M.; Aumann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2695.

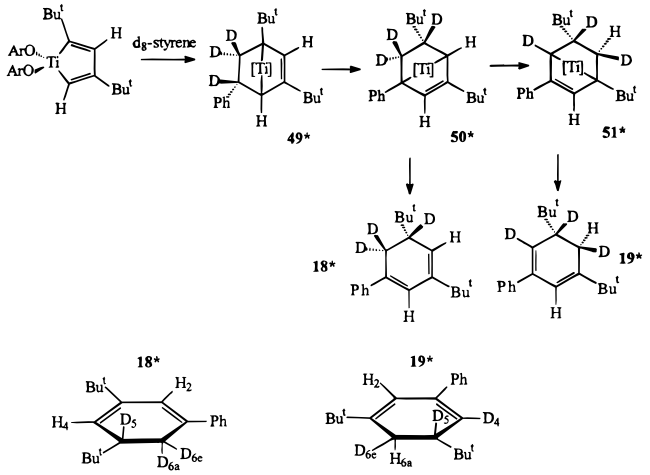
(26) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

(27) Dilworth, J. R.; Hanich J.; Krestel M. *J. Organomet. Chem*. **1986**, *315*, 9.

Scheme 14



Scheme 15



the olefin/alkyne structure. The analysis also shows that the corresponding *trans*-isomers are much more stable. The lack of observation of *trans*-products indicates that the isomerization process is being controlled by the titanium reagent. The only *trans*-isomer obtained, ***trans*-4** (Scheme 2), is obtained via a different pathway involving coupling of a preformed 1,3-cyclohexadiene (***cis*-4**) with ethylene.[12]

Support for this mechanism of formation and isomerization is obtained by a detailed study of the formation of the isomeric products **18** and **19**. When the reaction conditions are varied, the product ratio can be varied. In this case, increasing the concentration of reagent alkene and/or alkyne boosts the proportion of **18** over **19** (Table 2). This indicates that once titananorbornene **49** is generated (Scheme 14), rapid isomerization to **50** occurs. The subsequent rates of isomerization to **51** and displacement of **18** by olefin and/or alkyne are comparable. The observed products can only be generated via the *endo*-isomer **49**, in which the phenyl substituent is oriented away from the metal coordination sphere. Neither the *exo*-isomer **52** nor the alternative regioisomer **53** can lead to the observed products. Further mechanistic insight is given by reacting $Bu^tC{\equiv}CH$ with styrene-d_8 in the presence of **2**. In this case, a higher proportion of the isomer **18*** (Table 2) indicates that a primary kinetic isotope effect is present for the isomerization. Analysis of the ^1H NMR spectra of these labeled compounds shows that the two deuterium atoms migrating to form **19*** do so on the same face of the 1,3-cyclohexadiene ring, i.e., they are mutually *cis*, consistent with the proposed mechanism. This is concluded by the observation that in **19*** the proton at H_6 occupies a pseudoaxial site, i.e., *cis* to the *tert*-butyl substituent (Scheme 15, Figure 2).

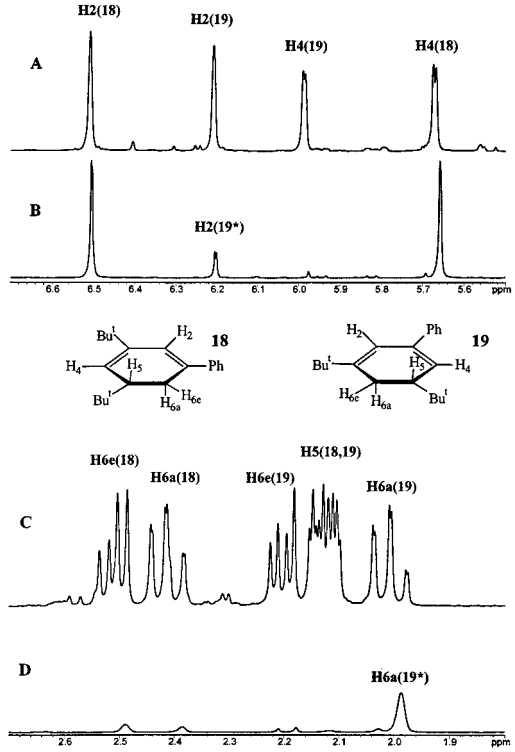


Figure 2. ^1H NMR spectra (500 MHz, C_6D_6) of the olefinic and aliphatic protons in the mixtures of **18**/**19** (A and C) and **18***/**19*** (B and D) produced by the [2 + 2 + 2] cycloaddition of 3,3-dimethylbutyne with styrene and styrene-d_8, respectively.

A constant product ratio following formation of **18** and **19** indicates that the *tert*-butyl-1,3-cyclohexadiene products do not revisit the titanium metal center following formation. In contrast, the trimethylsilyl-substituted compound **20** can be isomerized to **21** following completion of the [2 + 2 + 2] cycloaddition process. It is interesting to note that excess alkyne in the reaction mixture inhibits the isomerization while excess styrene leads to slow conversion. We interpret this as indicating that very stable titanacyclopentadiene **14** does not allow the product cyclohexadiene to recoordinate, whereas the titanacyclopentane **13** is known to undergo facile fragmentation and exchange of styrene for olefinic reagents in solution.

Experimental Section

All reactions were carried out under N_2 or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by Standard Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N_2. The synthesis of compounds **1**, **2**,[10] **3**, **13**,[11a] and $[Ti(OC_6H_3Ph_2\text{-}2,6)_2Cl_2]$[27] have been previously reported. The compound 3,9-dodecadiyne was purchased from Lancaster Synthesis, Inc., and dried over 4 Å molecular sieves. All other reagents were purchased from Aldrich Chemical Company and dried with 4 Å molecular sieves prior to use. ^1H and ^{13}C NMR spectra were recorded using Varian Associates 200 or 500 MHz spectrometers and a General Electric QE-300-MHz spectrometer. Gas chromatographic analyses were performed with a Hewlett Packard model 5890 Series II gas chromatograph using a capillary column (HP-1, cross-linked silicone gum; 25 m × 0.2 mm × 0.33 μm film thickness) with a flame ionization detector. TLC separations were performed with Kieselgel 60 F_{254} 25 Folien 20 cm × 20 cm, 2 mm thickness, preparative scale TLC plates. Mass spectral data was acquired through Purdue in-house facilities. Molecular mechanics calculations were performed with MacroModel V4.5[28] (MM3*) with full conformational searching. Due to the similarity of

the experimental procedures only representative examples are given. Full experimental details are present in the Supporting Information.

Synthesis of *cis*-1,2,5,6-Tetraethyl-1,3-cyclohexadiene (*cis*-7). A sample of $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(C_4Et_4)]$ (**1**, 0.1 g, 0.14 mmol) was dissolved in 3-hexyne (3 mL, 26 mmol), and the reaction mixture was stirred rapidly under one atmosphere of ethylene for 2 h. Excess 3-hexyne and ethylene were removed under vacuum, and the ***cis*-7** (1.25 g, 6.5 mmol, 50%) was isolated by preparative TLC. HRMS: calcd for $C_{14}H_{24}$ 192.1878, found 192.1878. ^{1}H NMR (C_6D_6, 30 °C): δ 5.77 (dd, $^3J_{H-H}$ = 9.5 Hz, $^4J_{H-H}$ = 2.9 Hz, 1H, CHC*H*CEt); 5.43 (br dd, $^3J_{H-H}$ < 2 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, CHC*H*CHEt); 0.8−2.5 (m, 22H, C*H*$_2$Me, CH$_2$*Me*, C*H*Et). ^{13}C NMR (C_6D_6, 30 °C): δ 139.8, 131.4 (C1, C2); 129.8, 128.6 (C3, C4); 42.1, 41.4 (C5, C6); 26.4, 24.4, 24.1, 19.3 (*C*H$_2$CH$_3$); 15.8, 14.5, 13.0, 12.4 (*C*H$_2$*C*H$_3$). Photolysis of ***cis*-7** in pentane produced (*Z*,*Z*,*E*)-4,5-diethyl-3,5,7-decatriene (**37**). ^{1}H NMR (C_6D_6, 30 °C): δ 5.33 (tt, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 1.3 Hz, 1H, CH$_2$C*H*CEt); 6.02 (d, $^3J_{H-H}$ = 10.7 Hz, 1H, CEtC*H*CH); 6.28 (dd, *trans*-$^3J_{H-H}$ = 15.1 Hz, ^4J = 1.4 Hz, 1H, CHC*H*CHEt); 5.65 (dt, $^3J_{H-H}$ = 6.6 Hz, 1H, CH$_2$C*H*CH); 0.5−2.8 (m, 20H, *C*H$_2$Me, CH$_2$*Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 142.2, 140.5 (C4, C5); 134.8, 129.9, 128.6, 126.3 (C3, C6, C7, C8); 29.7, 29.6, 26.4, 22.9 (*C*H$_2$Me); 13.0, 13.1, 14.2, 14.5 (CH$_2$*Me*).

Characterization of *trans*-1,2,3,5,6-Pentaethyl-1,3-cyclohexadiene (*trans*-4) and Photoproduct (39). HRMS: calcd for $C_{16}H_{28}$ 220.2191, found 220.2191. ^{1}H NMR (C_6D_6, 30 °C): δ 5.44 (br d, $^3J_{H-H}$ = 6.5 Hz, $^4J_{H-H}$ = 1.0 Hz, 1H, CEtC*H*CHEt); 0.85−2.45 (m, 27H, C*H*$_2$Me, CH$_2$*Me*, C*H*Et); ^{13}C NMR C_6D_6: 138.4, 138.0, 131.0 (C1−3); 122.9 (C-4); 44.2, 38.1 (C5, C6); 26.4, 26.1, 25.8, 24.2, 20.5 (*C*H$_2$CH$_3$); 15.6, 14.3, 13.9, 12.6, 12.3 (CH$_2$*C*H$_3$). Photolysis of ***trans*-4** in pentane produced (*Z*,*Z*,*Z*)-4,5,6-triethyl-3,5,7-decatriene (**39**). ^{1}H NMR (C_6D_6, 30 °C): δ 6.05 (d, *cis*-$^3J_{H-H}$ = 11.8 Hz, 1H, CEtC*H*CH); 5.23 (m, 2H, CH$_2$C*H*CEt, CH$_2$C*H*CH); 0.8−2.5 (m, 25H, C*H*$_2$Me, CH$_2$*Me*).

Characterization of *cis*-1,2,3,5,6-Pentaethyl-1,3-cyclohexadiene (*cis*-4) and Photoproducts. ^{1}H NMR (C_6D_6, 30 °C): δ 5.22 (m, $^3J_{H-H}$ = 1.8 Hz, 1H, CEtC*H*CEtH); 0.9−2.6 (m, 27H, *C*H$_2$Me, CH$_2$*Me*, C*H*Et). ^{13}C NMR (C_6D_6, 30 °C): δ 142,0, 139.6, 133.0 (C1−3); 125.2 (C4); 41.9, 41.7 (C5, C6); 27.3, 25.9, 24.6, 20.7, 19.1 (*C*H$_2$Me); 16.0, 15.7, 14.2, 13.3, 12.5 (CH$_2$*Me*). Photolysis of ***cis*-4** in pentane produced (*Z*,*Z*,*E*)-4,5,6-triethyl-3,5,8-decatriene (**38**). ^{1}H NMR (C_6D_6, 30 °C): δ 5.33 (tt, $^3J_{H-H}$ = 7.1 Hz, $^3J_{H-H}$ = 1.3 Hz, 1H, CH$_2$C*H*CEt); 6.43 (dt, *trans*-$^3J_{H-H}$ = 15.9 Hz, $^4J_{H-H}$ = 1.5 Hz, 1H, CH(Et)C*H*CEt); 5.68 (dt, $^3J_{H-H}$ = 6.5 Hz, 1H, CH$_2$C*H*CH); 0.9−2.8 (m, 25H, C*H*$_2$Me, CH$_2$*Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 140.9, 138.8, 135.2 (C4−6); 130.0, 129.7, 128.9 (C3, C7, C8); 30.1, 26.8, 24.7, 23.0, 23.1 (*C*H$_2$Me). A secondary photoproduct (*Z*)-5,7-diethyl-3,4,6-decatriene was observed upon extended irradiation. ^{1}H NMR (C_6D_6, 30 °C): δ 5.15 (tt, $^3J_{H-H}$ = 6.4 Hz, $^5J_{H-H}$ = 3.3 Hz, 1H, CH$_2$C*H*C); 0.5−2.8 (m, 22H, C*H*$_2$Me, *C*H$_2$-CH$_2$*Me*). ^{13}C NMR C_6D_6: 201.7 (C4); 92.6 (C3); 107.4 (C5); 137.0, 134.5 (C7, C8); 36.0, 26.5, 25.0, 24.4, 23.5, 22.8 (*C*H$_2$).

Characterization of Products from [2 + 2 + 2] Cycloaddition of 3,3-Dimethyl-1-butyne with Ethylene. Spectroscopic data for 2,6-di-*tert*-butyl-1,3-cyclohexadiene **10**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.61 (m, $^4J_{H-H}$ = 1.2 Hz, 1H, CH(But)C*H*CBut); 6.08 (dq, $^3J_{H-H}$ = 9.8 Hz, 1H, CHC*H*CBu^t); 5.82 (dt, $^4J_{H-H}$ = 1.2 Hz, $^3J_{H-H}$ = 4.1 Hz, 1H, CH$_2$C*H*CH); 1.9−2.8 (m, 3H, CBu^t(*H*)CH$_2$); 1.08 (s, 9H, CC(C*H*$_3$)$_3$); 0.88 (s, 9H, CHC(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 44.4 (C5); 34.4 (C*C*(CH$_3$)$_3$); 33.4 (CH*C*(CH$_3$)$_3$); 29.3 (CC(*C*H$_3$)$_3$); 27.7 (CHC(*C*H$_3$)$_3$); 24.5 (C6); 127.5, 125.4, 121.5, 119.3 (C1−4). MS(EI) of **10**: 192 (M$^+$, 0.8%), 134 (2.2), 120 (0.8), 119 (12.2), 105 (1.7), 91 (3.1), 79 (1.1), 77 (1.3), 58 (2.6), 57 (100). MS(EI) of **11**: 192 (M$^+$, 0.7%), 134 (0.8), 119 (4.3), 105 (1.4), 91 (2.1), 79 (0.9), 77 (1.1), 58 (2.2), 57 (100). MS(EI) of **9**: 192 (M$^+$, 1.3%), 119 (9.9), 105 (1.5), 91 (3.2), 79 (1.1), 77 (1.3), 58 (1.6), 57 (100).

Characterization of Products from [2 + 2 + 2] Cycloaddition of 3-Hexyne with Styrene. Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.85; H, 10.62. Attempts to separate the reaction mixture by chromatographic methods led to extensive aromatization. ^{1}H NMR of the reaction mixture (C_6D_6, 30 °C): δ 7.0−7.5 (aromatics, all three isomers); 0.5−2.9 (aliphatic and Et group protons of all three isomers); 3.81 (C*H*Ph of **16**); 5.67 (br s, olefinic proton of **16**); 5.71 (br s, olefinic ring proton of **15**); 6.09 (s, olefinic proton of **17**). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 40.6, 42.6 (C5, C6 of **15**); 45.5, 47.2 (C5, C6 of **16**); 38.8, 43.1 (C5, C6 of **17**). GC/MS analysis of the reaction mixture yielded: MS(EI) of **15** 268 (M$^+$, 32%), 239 (93), 211 (100), 195 (8), 183 (38), 165 (12), 155 (30), 105 (17), 91 (11), 77 (8); MS(EI) of **16** 268 (M$^+$, 29%), 239 (81), 211 (100), 195 (5), 183 (42), 165 (12), 155 (38), 105 (8), 91 (13), 77 (7); MS(EI) of **17** 268 (M$^+$, 22%), 239 (100), 211 (59), 195 (4), 183 (26), 165 (10), 155 (26), 105 (15), 91 (50), 77 (11).

The reaction can also be catalyzed by **13**. See Table 1.

Characterization of Products from [2 + 2 + 2] Cycloaddition of 3,3-Dimethyl-1-butyne with Styrene. Spectroscopic data for **18**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.56 (m, $^4J_{H-H}$ = 1.4 Hz, 1H, CBu^{t}C*H*CPh); 5.72 (dd, $^3J_{H-H}$ = 3.5 Hz, 1H, CBu^{t}C*H*CH(Bu^t)); 2.51 (dd, $^2J_{H-H}$ = 16.3 Hz, $^3J_{H-H}$ = 8.7 Hz, 1H, CPhC*H*$_e$(H$_a$)CH(Bu^t)); 2.42 (m, $^3J_{H-H}$ = 13.2 Hz, $^4J_{H-H}$ = 1.7 Hz, 1H, CPhCH$_e$(*H*$_a$)CH(Bu^t)); 7.0−7.6 (m, 5H, Ph); 1.14 (s, 9H, CC(C*H*$_3$)$_3$); 0.91 (s, 9H, CHC(C*H*$_3$)$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 146.1 (C1); 122.2 (C2); 138.0 (C3); 119.2 (C4); 45.0 (C5); 28.0 (C6); 34.6 (C*C*(CH$_3$)$_3$); 33.8 (CH*C*(CH$_3$)$_3$); 29.6 (CC(*C*H$_3$)$_3$); 27.8 (CHC(*C*H$_3$)$_3$; 143.0 (ipso); 129.2, 127.6, 126.1 (C*Ph*) MS(CI): 269 ((M + H)$^+$, 100.0%), 211 (2.3), 210 (1.5). Photolysis of **18** in pentane produced (*Z*,*E*)-7,7-dimethyl-2-phenyl-4-*tert*-butyl-1,3,5-octatriene (**47**). ^{1}H NMR (C_6D_6, 30 °C): δ 6.31 (br s, 1H, CPhC*H*); 5.75 (d, *trans*-$^3J_{H-H}$ = 16.1 Hz, 1H, CH(Bu^t)C*H*); 5.51 (d, 1H, CHC*H*(Bu^t)); 5.47 (m, 1H) 5.24 (t, 1H) (*gem*-^2J = 1.6 Hz, C*H*(*H*)CPh); 7.0−7.7 (m, 5H, aromatics); 1.14 (s, 9H, CC(C*H*$_3$)$_3$); 0.81 (s, 9H, CHC(C*H*$_3$)$_3$. Spectroscopic data for **19**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.26 (m, $^4J_{H-H}$ = 1.6 Hz, 1H, CBu^{t}C*H*); 6.04 (m, 1H, CH(Bu^t)C*H*); 2.20 (dd, $^2J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 7.0 Hz, CBu^{t}C*H*$_e$(H$_a$)); 2.01 (m, $^3J_{H-H}$ = 15.0 Hz, CBu^{t}C*H*$_a$(H$_e$)); 2.1−2.2 (m, 1H, CH$_2$CH(Bu^t)); 7.0−7.6 (m, 5H, aromatics); 1.10 (s, 9H, CC(C*H*$_3$)$_3$); 0.93 (s, 9H, CHC(C*H*$_3$)$_3$. ^{13}C NMR (C_6D_6, 30 °C): δ 138.5 (C1); 118.0 (C2); 150.9 (C3); 124.2 (C4); 46.6 (C5); 25.4 (C6); 36.2 (C*C*(CH$_3$)$_3$); 33.4 (CH*C*(CH$_3$)$_3$); 29.1 (CC(*C*H$_3$)$_3$); 27.9 (CHC(*C*H$_3$)$_3$); 142.7 (ipso); 129.2, 127.5, 126.7 (Ph). MS(CI): 277 ((M + H$^+$), 100.0%), 218 (1.9), 217 (3.2), 276 (11.6). Photolysis of **18** in pentane produced (*Z*,*E*)-7,7-dimethyl-4-phenyl-2-*tert*-butyl-1,3,5-octatriene (**48**). ^{1}H NMR (C_6D_6, 30 °C): δ 6.37 (br s, 1H, CBu^{t}C*H*CPh); 6.46 (d, *trans*-$^3J_{H-H}$ = 16.2 Hz, 1H, CPhC*H*CH(Bu^t)); 5.56 (d, H, C*H*(Bu^t)CH), 4.88 (d, 1H), 4.69 (t, 1H) (*gem*-$^2J_{H-H}$ = 1.5 Hz, (*H*(*H*)CBu^t); 7.0−7.7 (m, 5H, aromatics); 0.99, 0.80 (s, 18H, CC(C*H*$_2$)$_3$).

Reaction of 3,3-dimethyl-1-butyne with styrene-d_8 produced **18*** and **19***. Spectroscopic data for **18***. ^{1}H NMR (C_6D_6, 30 °C): δ 6.53 (d, $^4J_{H-H}$ = 1.4 Hz, 1H, (CPhC*H*); 5.69 (d, 1H, CD(Bu^t)C*H*); 1.14 (s, 9H, CC(C*H*$_3$)$_3$); 0.90 (s, 9H, CDC(C*H*$_3$)$_3$. ^{13}C NMR (C_6D_6, 30 °C): δ 146.1 (C1); 122.1 (C2); 137.8 (C3); 119.1 (C4); 44.2 (t, C5); 28.0 (C6); 34.6 (C*C*(CH$_3$)$_3$); 33.7 (CD*C*(CH$_3$)$_3$); 29.6 (CC*C*(CH$_3$)$_3$); 27.8 (CDC(*C*H$_3$)$_3$). MS(CI): 277 {(M + H)$^+$, 100.0%}, 218 (1.9), 217 (3.2), 276 (11.6). Spectroscopic data for **19***. ^{1}H NMR (C_6D_6, 30 °C): δ 6.22 (d, $^4J_{H-H}$ = 2.3 Hz, 1H, C*H*); 2.02 (s, 1H, CD(*H*)); 1.10 (s, 9H, CC(C*H*$_3$)$_3$; 0.93 (s, 9H, CDC(C*H*$_3$)$_3$. ^{13}C NMR (C_6D_6, 30 °C): δ 121.5 (C2); 150.0 (C3); 36.1 (C*C*(CH$_3$)$_3$); 33.3 (CD*C*(CH$_3$)$_3$); 29.1 (CC(*C*H$_3$)$_3$); 27.9 (CDC(*C*H$_3$)$_3$); 142.5 (ipso). MS(CI): 277 ((M + H)$^+$, 100.00%), 276 (15.7), 218 (1.3).

The reaction can also be catalyzed by **13**. See Table 1.

Characterization of Products from [2 + 2 + 2] Cycloaddition of Trimethylsilylacetylene with Styrene. Anal. Calcd for $C_{28}H_{28}Si_2$: C, 71.92; H, 9.39. Found: C, 71.45; H, 9.71. The slow isomerization of **20** to **21** was observed by ^{1}H NMR upon thermolysis of the reaction mixture at 95 °C. Attempts at separation by TLC was frustrated by extensive aromatization. Spectroscopic data for **20**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.59 (m, $^3J_{H-H}$ = 3.2 Hz, 1H, C(H)PhC*H*); 6.27 (d, $^4J_{H-H}$ = 1.0 Hz, 1H, CSiMe$_3$C*H*CSiMe$_3$); 3.40 (ddd, $^3J_{H-H}$ = 14.8 Hz, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.9 Hz, 1H, C*H*Ph); 2.43 (dd, $^2J_{H-H}$ = 16.5 Hz, 1H, C*H*$_e$H$_a$); 2.28 (m, $^4J_{H-H}$ = 2.3 Hz, 1H, C*H*$_a$H$_e$); 7.0−7.6 (m, 5H, aromatics); 0.167, 0.098 (s, 18H, CSi*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 134.1 (C2); 141.0 (C4); 41.5 (C5); 34.1 (C6); −1.10, −1.20 (CSi-(*C*H$_3$)$_3$). Spectroscopic data for **21**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.47 (d, $^4J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 2.3 Hz, 1H, CPhC*H*); 6.23 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CHSiMe$_3$C*H*); 2.85 (ddd, $^2J_{H-H}$ = 16.3 Hz, $^3J_{H-H}$ = 9.9 Hz, C*H*$_a$H$_e$); 2.53 (dd, $^3J_{H-H}$ = 4.0 Hz, 1H, C*H*$_e$H$_a$); 1.74 (ddd, 1H,

(28) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caulfield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

C*H*SiMe$_3$); 7.0−7.6 (m, 5H, aromatics); 0.195 (s, 9H, CSi*Me*$_3$); 0.00 (s, 9H, CHSi*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 137.1 (C1); 139.6 (C2); 124.3 (C4); 28.2 (C5); 26.8 (C6); −0.90 (CSi(*C*H$_3$)$_3$); −1.45 (CHSi(*C*H$_3$)$_3$).

The reaction can also be catalyzed by **13**. See Table 1.

Characterization of 1,3,5-Tris(trimethylsilyl)-1,3-cyclohexadiene (23). The ^{1}H NMR spectrum of **23** obtained was essentially identical to that previously reported.[17b] ^{1}H NMR (C_6D_6, 30 °C): δ 2.44 (ddd, $^2J_{H-H}$ = 16.5 Hz, $^3J_{H-H}$ = 9.5 Hz, $^4J_{H-H}$ = 2.5 Hz, 1H, C*H*$_a$(H$_e$)); 2.24 (dd, $^3J_{H-H}$ = 4.0 Hz, 1H, C*H*$_e$(H$_a$)); 1.62(ddd, $^3J_{H-H}$ = 5.6 Hz, 1H, C*H*(SiMe$_3$)); 6.25 (d, 1H, CSiMe$_3$(H)C*H*); 6.34 (d, 1H CSiMe$_3$C*H*CSiMe$_3$); 0.03(s, 9H, CHSi*Me*$_3$); 0.14, 0.12 (s, 18H, CSi*Me*$_3$).

Characterization of Products from [2 + 2 + 2] Cycloaddition of 3,9-Dodecadiyne with Ethylene. Spectroscopic data for **26**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.36 (br m, 1H, C*H*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 40.8 (C4), 13.0, 14.3 (*Me*). Spectroscopic data for **27**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.55 (dd, $^3J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 2.9 Hz, 1H, CH(Et)C*H*); 5.82 (dd, 1H, CEtC*H*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 39.5, 44.5 (C4, C10), 12.8, 14.7 (*Me*). Spectroscopic data for **28**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.74 (m, $^4J_{H-H}$ = 2.4 Hz, 1H, C*H*). ^{13}C NMR (C_6D_6, 30 °C): δ 128.7 (C2, C3); 128.2 (C1, C4); 42.6 (C9, C10); 28.7, 27.3 (*C*H$_2$Me, C5, C8); 24.0 (C6, C7); 10.9 (*Me*). Spectroscopic data for **29**. ^{1}H NMR (C_6D_6, 30 °C): δ 1.12 (m, 18H, *Me*); 1.65 (m, 12H, C*H*$_2$); 2.61 (m, 24H, C*H*$_2$). ^{13}C NMR (C_6D_6, 30 °C): δ 138.2, 138.0, 137.4, 135.8, 135.7, 133.2, 31.6, 30.3, 29.4, 27.6, 23.9, 22.7, 22.3, 22.2, 19.0, 16.5, 15.1, 14.7.

Characterization of Products from [2 + 2 + 2] Cycloaddition of 1,8-Bis(trimethylsilyl)-1,7-octadiyne with Ethylene. Analysis by GC/MS showed three components with M$^+$ ions of 278, each with a base peak of 73 (SiMe$_3^+$). Spectroscopic data for **30**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.97 (dd, J = 6.9 Hz, J = 3.0 Hz, 1H, C*H*); 0.05 (s, 9H), 0.22 (s, 9H, Si*Me*$_3$). Spectroscopic data for **31**. ^{1}H NMR C_6D_6: 5.65 (dd, $^3J_{H-H}$ = 9.5 Hz, $^3J_{H-H}$ = 4.8 Hz, 1H, C*H*SiMe$_3$*H*); 6.06 (dd, $^4J_{H-H}$ = 2.4 Hz, 1H, CSiMe$_3$C*H*); 0.02, (s, 9H), 0.17 (s, 9H, Si*Me*$_3$). Spectroscopic data for **32**. ^{1}H NMR (C_6D_6, 30 °C): δ 5.57 (m, AA′XX′, $^4J_{H-H}$ = 2.6 Hz, 2H, C*H*); 2.24 (m, 2H, C*H*); 1.6−2.1 (br m, 8H, CH$_2$); 0.11 (s, 18H, Si*Me*$_3$). ^{13}C NMR C_6D_6: 125.4 (C1, C4); 123.7 (C2, C3); 36.6 (C9, C10); 32.1 (C5, C8); 24.3 (C6, C7); 0.00 (Si*Me*$_3$).

The reaction can also be catalyzed by **13**. See Table 1.

Characterization of *cis*-2-Phenyl-1,4-diethyl-1,2,5,6,7,8-hexahydronaphthalene (*cis*-33). Anal. Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 89.98; H, 10.19. HRMS: calcd for $C_{20}H_{26}$ 266.2035, found 266.2032. ^{1}H NMR (C_6D_6, 30 °C): δ 0.71 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, CCH$_2$(C*H*$_3$)); 1.08 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, CHCH$_2$C*H*$_3$); 3.98 (m, 1H, C*H*Ph); 5.70 (br s, 1H; C*H*); 0.8−2.5 (m, 18H, C*H*$_2$Me, C*H*$_2$). ^{13}C NMR (C_6D_6, 30 °C): δ 13.1, 13.9, (*C*H$_3$); 19.7, 31.3 (*C*H$_2$CH$_3$); 23.4, 23.9, 25.5, 25.6 (C5−8); 46.2 (C1); 47.6 (C2). MS(EI): 266 (M$^+$, 23.0), 264 (59.8), 249 (12.4), 238 (10.5), 237 (100.0), 235 (41.1), 221 (10.5), 209 (25.3), 195 (13.3), 191 (10.2), 179 (25.4), 178 (18.0), 167 (38.8), 165 (22.6), 115 (11.7), 105 (14.9), 91 (42.8), 77 (14.2). MS(CI): 275 ((M + H)$^+$, 100.0%), 274 (28.4), 273 (18.1), 272 (14.6). Use of styrene-d_8 in the above procedure produces ***cis*-33***. ^{1}H NMR (C_6D_6, 30 °C): δ 0.71 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, CCH$_2$C*H*$_3$); 1.08 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, CDCH$_2$C*H*$_3$); 0.8−2.5 (m, 18H, C*H*$_2$Me, C*H*$_2$). ^{13}C NMR (C_6D_6, 30 °C): δ 13.5, 14.2 (*C*H$_3$); 19.9, 31.5 (CH$_3$*C*H$_2$); 23.7, 24.2, 25.7, 25.8 (C5−8) 45.6 (t, $^1J_{D-C}$ = 19.2 Hz, C-1); 47.1 (t, $^1J_{D-C}$ = 19.5 Hz, C-2). MS(EI): 274 (M$^+$, 55.8), 246 (16.9), 245 (100.0), 217 (19.4), 176 (16.3), 175 (24.0), 98 (11.1), 97 (12.6). MS(CI): 275 ((M + H)$^+$, 100.0%), 274 (28.4), 273 (18.1), 272 (14.6). The photolysis of ***cis*-33** in pentane produced a product assigned as 2,5-diethyl-3-phenyltricyclo[4.4.0.0^{2,4}] deca-1(6)-ene (**46**). ^{1}H NMR (C_6D_6, 30 °C): δ 7.0−7.6 (m, 5H, aromatics); 0.6−3.0 (m, 21H, C*H*$_2$Me, C*H*$_2$CH$_2$*Me*, C*H*). ^{13}C NMR (C_6D_6, 30 °C): δ 12.9, 14.3 (CH$_2$*Me*); 19.8, 23.8, 23.9, 24.2, 24.8, 25.1 (*C*H$_2$Me,C7−10); 29.5 (C-3); 36.3 (C-4); 126.2, 128.7, 129.5, 137.5 (*Ph*); 140.5, 140.7 (C1, C6).

Characterization of *cis*-2-Benzyl-1,4-diethyl-1,2,5,6,7,8-hexahydronaphthalene (*cis*-34). ^{1}H NMR (C_6D_6, 30 °C): δ 5.24 (br s, 1H, C*H*); 6.9−7.4 (m, 5H, aromatics); 0.7−3.1 (m, 20H, C*H*$_2$Me, C*H*$_2$ CH$_2$*Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 13.6, 14.1 (*C*H$_3$); 19.7, 31.7 (*C*H$_2$CH$_3$); 37.8 (PhCH$_2$); 23.8, 24.2, 25.7, 25.9 (C5, C6, C7, C8); 40.8 (C1); 44.2 (C2). The photolysis of ***cis*-34** in pentane initially produced triene **40**. ^{1}H NMR (C_6D_6, 30 °C): δ 3.38 (d, $^3J_{H-H}$ = 6.7 Hz, 2H, PhC*H*$_2$); 5.81 (dt, *trans*-$^3J_{H-H}$ = 15.8 Hz, 1H, PhCH$_2$C*H*); 6.53 (dt, 1H, CHC*H*); 5.2−5.3 (m, 1H, CH$_3$CH$_2$C*H*); 6.9−7.4 (m, 5H, aromatics); 0.7−3.1 (m, 20H, C*H*$_2$Me, C*H*$_2$CH$_2$Me). Continued photolysis produced allene **42**. ^{1}H NMR (C_6D_6, 30 °C): δ 3.32 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, PhC*H*$_2$); 5.31 (tt, *trans*-$^3J_{H-H}$ = 3.3 Hz, PhCH$_2$C*H*); 1.07 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, CCH$_2$C*H*$_3$); 0.93 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); 7.0−7.4 (m, 5H, aromatics); 0.6−2.8 (m, 22H, C*H*$_2$-Me, C*H*$_2$, CH$_2$*Me*). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 202.1, 91.0, 109.0. MS(EI): 280 (M$^+$, 5.4%), 189 (53.7), 161 (12.7), 119 (14.8), 105 (13.8), 91 (100). MS(CI): 281 ((M + H)$^+$, 100.0%), 280 (17.6), 279 (39.4), 189 (10.9).

Characterization of *cis*-2-*n*-Butyl-1,4-diethyl-1,2,5,6,7,8-hexahydronaphthalene (*cis*-35). ^{1}H NMR (C_6D_6, 30 °C): δ 5.22 (br s, 1H, C*H*); 0.8−1.2 (overlapping triplets, 9H, C*H*$_3$); 1.2−2.3 (m, 18H, C*H*$_2$C*H*). ^{13}C NMR (C_6D_6, 30 °C): δ 13.7, 14.2, 14.8 (*Me*); 23.8, 24.2 (C6, C7); 25.7, 25.9 (C5, C8); 30.7, 19.4 (*C*H$_2$CH$_3$); 23.8, 31.6, 31.9 (*C*H$_2$C*H*$_2$C*H*$_2$); 39.0, 44.5 (C1, C2). The primary photoproduct of ***cis*-35** in pentane is triene **43**. HRMS: calcd. for $C_{18}H_{30}$ 246.2348, found 246.2351. ^{1}H NMR (C_6D_6, 30 °C): δ 5.28 (td, 1H, CH$_3$CH$_2$C*H*); 6.49 (dt, $^3J_{H-H}$ = 15.8 Hz, 1H, CH$_2$CHC*H*); 5.71 (dt, $^3J_{H-H}$ = 7.0 Hz, 1H, CH$_2$C*H*CH); 0.7−2.9 (m, 19H, C*H*$_2$Me, C*H*$_2$, CH$_2$*Me*). ^{13}C NMR (C_6D_6, 30 °C): 14.6, 14.8, 15.1 (*C*H$_3$); 127.0, 130.9, 128.7 (*C*H═); 132.2, 137.4, 140.3 (*C*═). MS(EI): 246 (M$^+$, 32.2%), 217 (43.4), 190 (13.2), 189 (93.2), 162 (12.6), 161 (100.0), 14 (29.7), 145 (10.1), 133 (45.0), 131 (19.0), 119 (60.4), 117 (17.5), 77 (14.6), 67 (12.8), 57 (24.9), 55 (29.2). Continued photolysis produced allene **45**. HRMS: calcd for $C_{18}H_{30}$ 246.2348, found 246.2351. ^{1}H NMR (C_6D_6, 30 °C): δ 5.18 (tt, $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 3.2 Hz, CH); 0.8−2.5 (m, 29H, C*H*$_2$Me, C*H*$_2$, C*H*$_2$Me). Selected ^{13}C NMR (C_6D_6, 30 °C): δ 201.5, 91.3, 108.3. 130.0, 133.1. MS(EI): 246 (M$^+$, 37.8%), 217 (52.8), 203 (18.8), 190 (14.6), 189 (100.0), 176 (15.1), 175 (14.0), 162 (12.8), 161 (97.5), 147 (40.7), 145 (11.3), 133 (45.7), 131 (19.7), 119 (66.7), 117 (22.3), 115 (11.5), 105 (38.9), 93 (15.8), 91 (69.1), 81 (12.8), 79 (26.0), 77 (20.6), 67 (18.8), 57 (29.5), 55 (41.8), 53 (11.9).

Characterization of *cis*-2-Phenyl-1,4-bis(trimethylsilyl)-1,2,5,6,7,8-hexahydronaphthalene (*cis*-36). ^{1}H NMR (C_6D_6, 30 °C): δ 5.87 (d, $^3J_{H-H}$ = 5.1 Hz, 1H, CH); 2.98 (d, $^3J_{H-H}$ = 5.04, 1H, C*H*SiMe$_3$); 2.41 (t, 1H, C*H*Ph); 7.0−7.5 (m, 5H, aromatics); 0.142 (s, 9H, CSi*Me*$_3$); −0.018 (s, 9H, C*H*SiMe$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 0.2, 1.2 (Si*Me*$_3$); 24.1, 24.4, 31.8, 32.3 (C5−8); 37.6 (C1); 39.3 (C2); 123.3 (C3); 126.1, 126.7, 127.1, 130.4 (Ph); 124.8, 135.2, 144.2 (C4, C9, C10). MS(EI): 354 (M$^+$, 1.4%), 281 (15.7), 73 (100.0). MS(CI): 355 ((M + H)$^+$ 44.4%), 354 (41.6), 353 (52.7), 337 (22.0); 323 (19.3), 282 (21.1); 28 (100.0), 265 (39.8).

Acknowledgment. I.P.R. thanks the National Science Foundation (Grant CHE-9321906) for research support.

Supporting Information Available: Figures of calculated energies and full experimental procedures (7 pages). See any current masthead page for ordering and Internet access instructions.

JA970516R