Cyclization/Hydrosilylation of Functionalized 1,6-Diynes Catalyzed by Cationic Platinum Complexes Containing Bidentate Nitrogen Ligands

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A 1:1 mixture of the platinum dimethyl diimine complex [PhN═C(Me)C(Me)═NPh]$PtMe_2$ (**4a**) and $B(C_6F_5)_3$ catalyzed the cyclization/hydrosilylation of dimethyl dipropargylmalonate (**1**) and $HSiEt_3$ to form 1,1-dicarbomethoxy-3-methylene-4-(triethylsilylmethylene)cyclopentane (**3**) in 82% isolated yield with 26:1 Z:E selectivity. Platinum-catalyzed diyne cyclization/hydrosilylation tolerated a range of functional groups including esters, sulfones, acetals, silyl ethers, amides, and hindered ketones. Diynes that possessed propargylic substitution underwent facile cyclization/hydrosilylation to form silylated 1,2-dialkylidene cyclopentanes as mixtures of regioisomers. Diynes that possessed an electron-deficient internal alkyne underwent cyclization/hydrosilylation in moderate yield to form products resulting from silyl transfer to the less substituted alkyne. The silylated 1,2-dialkylidenecyclopentanes formed via diyne cyclization/hydrosilylation underwent a range of transformations including protodesilylation, Z/E isomerization, and [4 + 2] cycloaddition with dieneophiles.

Introduction

The cyclization/addition of dienes,[1−4] enynes,[5,6] and tetraenes[7] employing H−X or X−X′ [X, X′ = SiR_3, SnR_3, BR_2] as the stoichiometric reductant are synthetically useful transformations that form both a C−C bond and one or more C−X bonds. Cyclization/hydrosilylation processes are of particular interest because of the ready availability of silanes and the reactivity of the silylated carbocycles formed in these transformations.[8] Examples of catalytic cyclization/hydrosilylation include the ytterocene-catalyzed cyclization/hydrosilylation of both dienes[2] and enynes[5] and the rhodium-catalyzed cyclization/hydrosilylation of 1,6-enynes.[6] In addition, both cationic palladium phenanthroline[3] and optically active palladium pyridine-oxazoline[4] complexes catalyze the cyclization/hydrosilylation of functionalized dienes to form silylated carbocycles in good yield with good stereoselectivity (Scheme 1).

Nonconjugated diynes undergo transition metal catalyzed cyclization/addition in the presence of hydrostannanes,[9] stannylsilanes,[10] borylsilanes,[11] borylstannanes,[12] and hydrogen equivalents[13] to form substituted 1,2-dialkylidenecycloalkanes. In contrast, the cyclization/hydrosilylation of diynes, particularly 1,6-diynes, remains problematic. Although Ni(0) complexes catalyze the cyclization/hydrosilylation of 1,7-diynes to form silylated (*Z*)-1,2-dialkylidenecyclohexanes, these catalysts do not cyclize 1,6-diynes.[14] Rhodium phosphine complexes catalyze the cyclization/hydrosilylation of 1,6-diynes to form predominantly (*E*)-1,2-dialkylidenecyclopentanes but these protocols suffer from limited substrate scope and low yield.[15] Similarly, rhodium carbonyl complexes catalyze the cyclization/hydrosilylation of 1,6-diynes but form primarily disilylated mono alkylidenecyclopentanes and silylbicyclization products.[16] The absence of a selective and general catalyst system for the cyclization/hydrosilylation of 1,6-diynes is unfortunate as the silylated 1,2-

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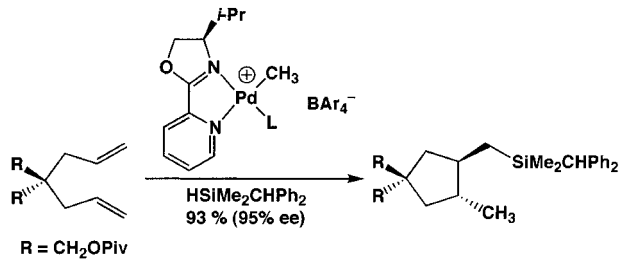
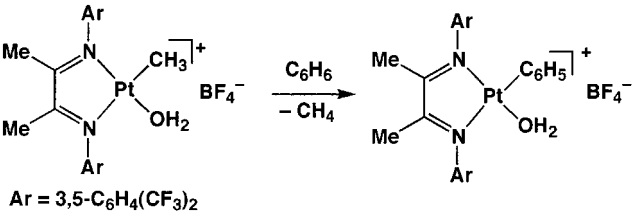
Scheme 1



Scheme 2



dialkylidenecyclopentanes formed in these processes are useful synthetic intermediates.

Cationic platinum complexes activate C−H bonds under mild conditions.[17−20] For example, [(TMEDA)Pt(Me)-C_5F_5N]$^+BF_4^-$ [TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine] reacts with benzene at 85 °C to form the platinum phenyl complex [(TMEDA)Pt(Ph)C_5F_5N]$^+BF_4^-$ with release of methane.[18] Similarly, the cationic platinum diimine aquo complex [(N-N)Pt(Me)OH_2]$^+BF_4^-$ [N-N = ArN═C(Me)C(Me)═NAr, Ar = 3,5-$(CF_3)_3C_6H_3$] reacts with benzene at room temperature to form [(N-N)Pt(Ph)-OH_2]$^+BF_4^-$ and methane (Scheme 2).[19] Of particular significance, the cationic 2,2-bipyrimidyl complex [(bipyr)-Pt(Me)L]$^+BF_4^-$ catalyzes the oxidation of methane in concentrated sulfuric acid under oxygen to form methyl sulfate in 72% yield.[20]

The cationic platinum complexes that activate C−H bonds are structurally and electronically similar to the cationic palladium complexes that catalyze the cyclization/hydrosilylation of functionalized dienes.[3,4] Because of this, we considered that cationic platinum complexes that contain bidentate nitrogen ligands might catalyze cyclization/hydrosilylation. Although these platinum complexes showed no activity toward dienes, they were active catalysts for the cyclization/hydrosilylation of functionalized 1,6-diynes. Here we report a full account of our study of the platinum-catalyzed cyclization/hydrosilylation of functionalized 1,6-diynes to form silylated 1,2-alkylidenecyclopentanes in good yield with high *Z*-selectivity.[21]

Results and Discussion

Platinum Phenanthroline Catalysts. Platinum phenanthroline complexes were first targeted as cyclization/hydrosilylation catalysts on account of the high activity of the corresponding palladium phenanthroline complexes with respect to diene cyclization/hydrosilylation.[4] A solution of dimethyl dipropargylmalonate (**1**), $HSiEt_3$ (1.5 equiv), naphthalene (internal standard), and a catalytic 1:1 mixture of (phen)$PtMe_2$ (**2a**) and $B(C_6F_5)_3$ (5 mol %) in toluene was heated at 110 °C and monitored periodically by GC analysis.[22] The relative concentration of **1** decreased steadily to ∼10% after 75 min and then disappeared completely after 2.5 h to form 1,1-dicarbomethoxy-3-methylene-4-(triethylsilylmethylene)cyclopentane (**3**) in 95% yield (GC) as a 20:1 mixture of Z:E isomers along with traces of disilylated products (Figure 1). Evaporation of solvent and flash chromatography of the residue on neutral alumina gave **3** in 74% yield as an 18:1 mixture of Z:E isomers (Scheme 3).[23]

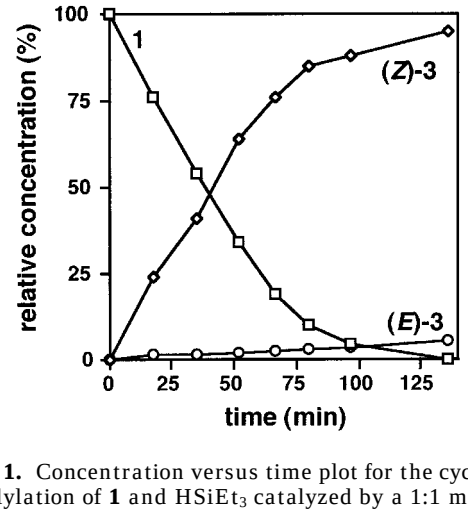
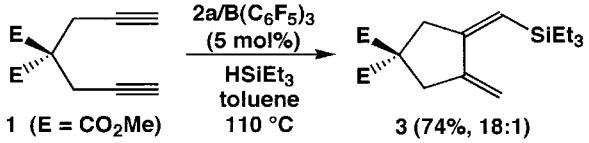


Figure 1. Concentration versus time plot for the cyclization/hydrosilylation of **1** and $HSiEt_3$ catalyzed by a 1:1 mixture of (phen)$PtMe_2$ (**2a**) and $B(C_6F_5)_3$ in toluene at 110 °C to form **3**.

Scheme 3



The cationic palladium catalyst employed in diene cyclization/hydrosilylation was most efficiently generated in situ via halide abstraction from (phen)Pd(Me)Cl with $NaBAr_4$ [Ar = 3,5-$C_6H_3(CF_3)_2$].[3,4] However, a 1:1 mixture of (phen)Pt(Me)Cl (**2b**) and $NaBAr_4$ was less effective for diyne cyclization/hydrosilylation than was the **2a**/$B(C_6F_5)_3$ mixture. For example, cyclization/hydrosilylation of **1** and $HSiEt_3$ catalyzed by a 1:1 mixture of **2b** and $NaBAr_4$ at 110 °C for 2 h formed **3** as a ∼6:1 mixture of Z:E isomers. Evaporation of solvent followed by chromatography of the residue on neutral alumina gave **3** in 83% yield as a 6:1 mixture of Z:E isomers (Scheme 4). Surprisingly, silica gel chromatography of crude **3** generated via cyclization/hydrosilylation of **1** catalyzed by **2b**/$NaBAr_4$ led to Z/E isomerization and isolation of (*E*)-**3** in 73% yield with ≥96% isomeric purity (Scheme 4). Although the mechanism of this isomerization remains unknown, silica gel, **2b**, and $NaBAr_4$ were all required for Z/E isomerization.

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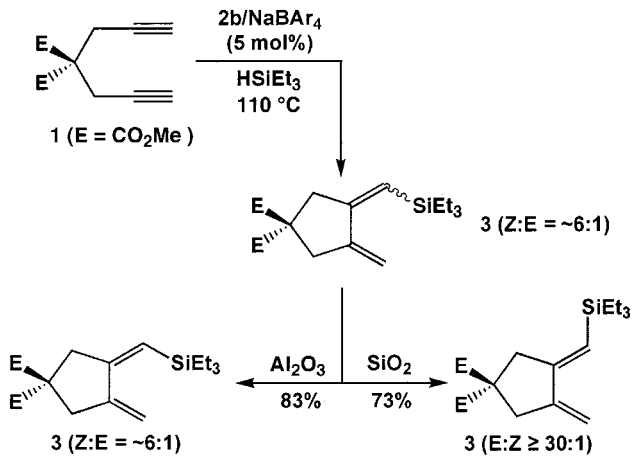
(23) Chromatography on silica gel gave diminished yields but did not lead to Z/E isomerization.

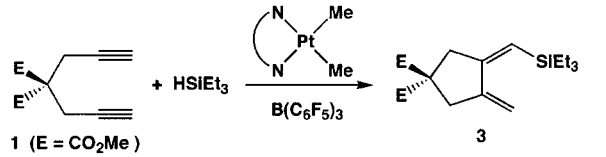
Scheme 4

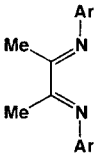
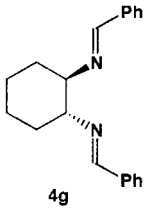
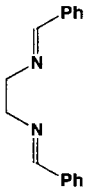


Platinum Diimine Catalysts. The cyclization/hydrosilylation of **1** and $HSiEt_3$ catalyzed by **2a**/$B(C_6F_5)_3$ gave **3** in good yield with good Z:E-selectivity but required rather forcing conditions (110 °C, 3 h). In an effort to identify a more active diyne cyclization/hydrosilylation catalyst, we turned our attention to cationic platinum diimine complexes. These diimine complexes proved to be both more active and more stereoselective than the platinum phenanthroline complexes. For example, reaction of **1** and $HSiEt_3$ catalyzed by a 1:1 mixture of [PhN=C(Me)C(Me)=NPh]$PtMe_2$ (**4a**) and $B(C_6F_5)_3$ was complete after 10 min at 110 °C or after 85 min at 70 °C to form (*Z*)-**3** in 95% yield (GC) with ≥30:1 stereoselectivity (Table 1, entries 1 and 2).[24] Dialkylidenecyclopentane (*Z*)-**3** was isolated in 82% yield as a 26:1 mixture of stereoisomers from the former reaction (Table 2, entry 1).

Cationic group 10 diimine complexes are active catalysts for the polymerization of ethylene and α-olefins.[25] The utility of these complexes stems in part from the ease with which the steric and electronic parameters of the complex can be tuned by varying the N-aryl groups. In an effort to probe the effect of the steric and electronic nature of the catalyst on diyne cyclization/hydrosilylation, the platinum diimine complexes [ArN=C(Me)C(Me)=NAr]$PtMe_2$ [Ar = 4-C_6H_4OMe (**4b**), 4-$C_6H_4CH_3$ (**4c**), 2,6-$C_6H_3(CH_3)_2$ (**4d**), 4-$C_6H_4CF_3$ (**4e**), 3,5-$C_6H_3(CF_3)_2$ (**4f**)] were employed as precatalysts in the cyclization/hydrosilylation of **1** and $HSiEt_3$ (Table 1, entries 3−7). The rate of cyclization/hydrosilylation appeared to decrease slightly with both the increasing electron density and increasing steric bulk of the diimine ligand, although the effects were nominal (Table 1). Likewise, the Z:E selectivity of cyclization/hydrosilylation did not vary appreciably with the steric and electronic nature of the diimine ligand (Table 1). In addition to complexes **4a**−**f**, the platinum bis(benzylidene) complexes **4g** and **4h** also catalyzed the cyclization/hydrosilylation of **1** and $HSiEt_3$ (Table 1, entries 8 and 9).

Table 1. Cyclization/Hydrosilylation of 1 Catalyzed by a 1:1 Mixture of Platinum Dimethyl Precatalyst and $B(C_6F_5)_3$ in Toluene



entry	N–N	temp (°C)	time (min)	yield (%)[a]	Z:E[b]
1	 4a (Ar = C_6H_5)	110	10	95	≥30:1
2		70	85	98	≥30:1
3	4b (Ar = 4-C_6H_4OMe)	70	300	91	20:1
4	4c (Ar = 4-C_6H_4Me)	70	88	97	26:1
5	4d (Ar = 2,6-$C_6H_3Me_2$)	70	118	99	29:1
6	4e (Ar = 4-$C_6H_4CF_3$)	70	43	88	≥30:1
7	4f [Ar = 3,5-$C_6H_3(CF_3)_2$]	70	98	87	23:1
8	 4g	70	88	93	11:1
9	 4h	70	178	84	13:1

[a] Product yield determined by GC analysis versus internal standard. [b] Z:E ratio determined by ^1H NMR analysis of the crude reaction mixture.

Substrate Scope. The scope of platinum-catalyzed diyne cyclization/hydrosilylation was probed as a function of silane and diyne employing platinum diimine catalyst **4a**. A number of tertiary silanes reacted with diene **1** in the presence of **4a**/$B(C_6F_5)_3$ to give the corresponding 1,2-dialkylidenecyclopentanes **5**−**8** in ∼70% yield with >20:1 Z:E selectivity (Table 2, entries 2−5). The rate of the cyclization/hydrosilylation of **1** decreased with the increasing steric bulk of the silane and reaction of **1** with $HSi(i\text{-}Pr)_3$ was ∼10 times slower than the reaction of **1** with $HSiEt_3$ (Table 1, entries 1 and 5). Phenylsilanes such as dimethylphenylsilane were largely ineffective in platinum-catalyzed diyne cyclization/hydrosilylation. This limitation precluded oxidation of the silylated 1,2-dialkylidenecyclopentanes formed via cyclization/hydrosilylation.[8] Platinum-catalyzed diyne cyclization/hydrosilylation tolerated a number of functional groups including pivaloate esters (**9**), benzyl (**10**) and silyl ethers (**11**), acetals (**12**), aromatic groups (**13**), sulfones (**14**), amides (**15**), and hindered ketones (**16**) to form dienes **17**−**24** in 65−86% yield with ≥25:1 Z:E selectivity (Table 2, entries 6−13).

(24) The Z:E ratio of the silylated 1,2-dialkylidenecyclopentanes was determined by integration of the downfield triethylsilylmethylene vinyl resonance of the E isomer at δ ∼6.0 relative to the internal methylene vinyl proton of the Z isomer at δ ∼5.3 in the ^1H NMR spectrum. ^1H NMR spectroscopy provided more reproducible Z:E ratios than did GC analysis for dienes with high isomeric purity (Z:E ≥ 20:1). We estimate ≤ 3% of the minor isomer (≥30:1) as the detection limit via ^1H NMR analysis.

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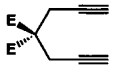
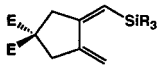
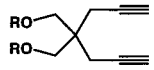
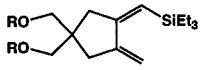
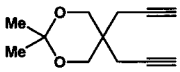
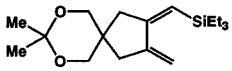
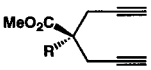
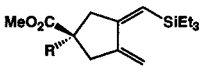
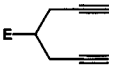
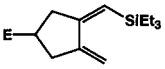
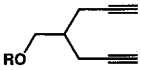
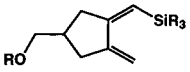
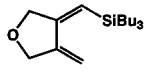
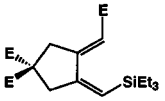
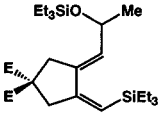
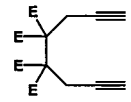
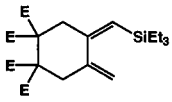
Table 2. Cyclization/Hydrosilylation of Functionalized Diynes Catalyzed by a 1:1 Mixture of 4a and $B(C_6F_5)_3$ in Toluene at 110 °C

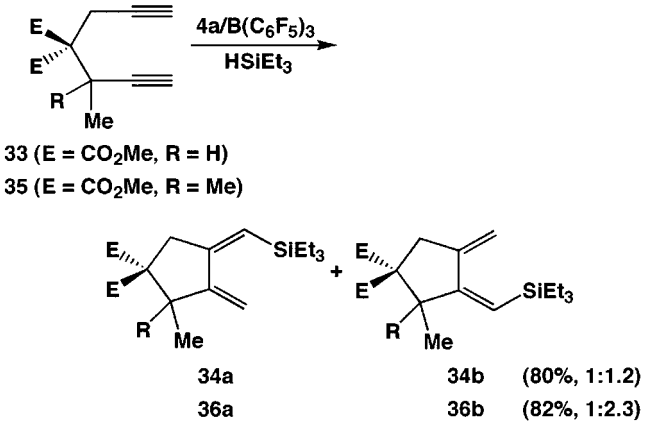
entry	diyne	silane	time (min)	carbocycle	yield (%)[a]	Z:E[b]
						
1	1 (E = CO_2Me)	$HSiEt_3$	10	3	82	26:1
2		$HSiMe_2t$-Bu	20	5	73	21:1
3		$HSiMe_2Bn$	15	6	74	≥30:1
4		$HSi(n\text{-}Bu)_3$	30	7	69	20:1
5		$HSi(i\text{-}Pr)_3$	100	8	70	23:1
						
6	9 (R = Piv)	$HSiEt_3$	12	17	76	29:1
7	10 (R = Bn)		10	18	86	≥30:1
8	11 (R = TBDMS)		15	19	80[d]	29:1
9	 12		15	 20	77	26:1
						
10	13 (R = Ph)		10	21	84	25:1
11	14 (R = SO_2Me)		15	22	74	29:1
12	15 (R = $CONMe_2$)		10	23	80	≥30:1
13	16 (R = COMe)		30[c]	24	65	29:1
						
14	25 (E = CO_2Me)		26	26	72	≥30:1
						
15	27 (R = Piv)	$HSiBu_3$	15[c]	29	78	12:1
16	28 (R = TBDMS)	$HSiEt_3$	15	30 (R = CH_2OH)[e]	58	≥30:1
17	 31	$HSiBu_3$	60	 32	36	21:1
18	 37 (E = CO_2Me)	$HSiEt_3$	15	 38	43	≥30:1
19	 39 (E = CO_2Me)	$HSiEt_3$	50	 40	56	9:1
20	 41 (E = CO_2Et)		10	 42	77	28:1

[a] Yields refer to isolated material of ≥95% purity. [b] Z:E ratio determined by ^1H NMR analysis of the crude reaction mixture. [c] Silane added slowly as a 10% solution in toluene. [d] Product isolated as the Diels−Alder adduct of 4-phenyl-[1,2,4]triazole-3,5-dione. [e] Product isolated as the corresponding alcohol after treatment with TBAF.

Many transition metal mediated or catalyzed cyclization processes are facilitated by gem dialkyl groups on the substrate backbone (Thorpe−Ingold effect).[26] However, 4,4-disubstitution of the diyne was not required for efficient platinum-catalyzed cyclization/hydrosilylation. For example, reaction of 4-carbomethoxy-1,6-heptadiyne (**25**) with $HSiEt_3$ catalyzed by **4a**/$B(C_6F_5)_3$ formed cyclopentane **26** in good yield with good selectivity (Table 2, entry 14). Likewise, diynes that possessed a single trimethylacetoxymethyl (**27**) or *tert*-butyldimethylsiloxymethyl (**28**) group at the 4-position underwent cyclization/hydrosilylation to form carbocycles **29** and **30**, respectively (Table 2, entries 15 and 16). In comparison, platinum-catalyzed cyclization/hydrosilylation of dipro-

(26) (a) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 1037. (b) DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505. (c) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

Scheme 5



pargyl ether (**31**) required 1 h at 110 °C and formed the heterocyclic diene **32** in only 36% yield (Table 2, entry 17).

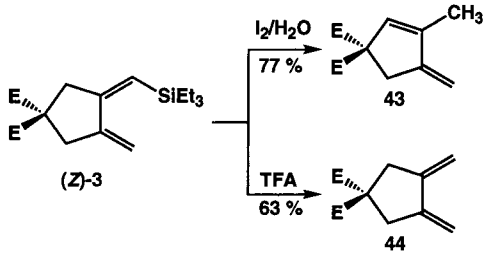
Diynes that possessed propargylic substitution underwent platinum-catalyzed cyclization/hydrosilylation to form mixtures of regioisomeric silylated dialkylidenecyclopentanes with predominant transfer of the silyl group to the more hindered, more electron-rich alkyne. For example, reaction of diyne **33**, which possessed a single propargylic methyl group, and $HSiEt_3$ catalyzed by **4a**/$B(C_6F_5)_3$ formed a 1:1.2 mixture of isomeric dienes **34a** and **34b** in 80% combined yield (Scheme 5). Similarly, cyclization/hydrosilylation of diyne **35**, which possessed *gem*-dimethyl propargylic substitution, formed a 1:2.3 mixture of isomeric dienes **36a** and **36b** in 82% combined yield (Scheme 5).

Attempted cyclization/hydrosilylation of diynes that possessed one or more electron-rich internal alkynes such as 4,4-dicarbomethoxy-1,6-octadiyne or 5,5-dicarbomethoxy-1,6-nonadiyne led to formation of intractable mixtures of products. In comparison, diynes that possessed a single electron-deficient internal alkyne underwent cyclization/hydrosilylation in moderate yield to form products resulting from silyl transfer to the terminal alkyne. For example, reaction of diyne **37**, which possessed a terminal carbomethoxy group, with $HSiEt_3$ catalyzed by **4a**/$B(C_6F_5)_3$ led to the isolation of diene **38** in 43% yield as a single isomer (Table 2, entry 18). In comparison, Pt-catalyzed reaction of diyne **39**, which possessed a terminal acetyl group, and $HSiEt_3$ led to cyclization/hydrosilylation coupled with hydrosilylation of the terminal acetyl group to form disilylated diene **40** in 56% isolated yield (Table 2, entry 19).

Mixtures of **4a** and $B(C_6F_5)_3$ also catalyzed the cyclization/hydrosilylation of 1,7-diyne **41** to form 1,2-dialkylidenecyclohexane **42** in good yield with high Z-selectivity (Table 2, entry 20). Although attempts to apply platinum-catalyzed cyclization/hydrosilylation to the synthesis of additional silylated 1,2-dialkylidenecyclohexanes were unsuccessful, the cyclization/hydrosilylation of 1,7-diynes is efficiently catalyzed by Ni(0) complexes.[14]

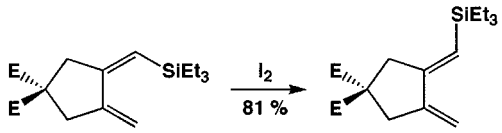
Reactivity of Silylated 1,2-Dialkylidene Cycloalkanes. Although generally unreactive toward nucleophilic substitution, vinyl silanes undergo electrophilic

Scheme 6

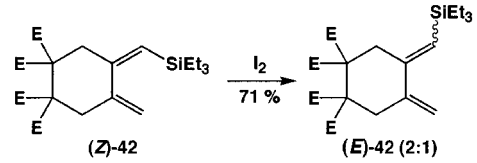


substitution.[27] The proton represents the simplest electrophile that reacts with vinylsilanes and protodesilylation of (*Z*)-**3** was therefore investigated. To this end, treatment of (*Z*)-**3** with a mixture of iodine and water in benzene led to protodesilylation/isomerization with formation of 3,3-dicarbomethoxy-1-methyl-5-methylenecyclopentene (**43**) in 77% yield (Scheme 6).[28] Alternatively, treatment of (*Z*)-**3** with trifluoroacetic acid in CH_2Cl_2 led to protodesilylation without isomerization to form the desired 1,1-dicarbomethoxy-3,4-dimethylenecyclopentane (**44**) in 63% isolated yield (Scheme 6).[29]

Molecular models suggest that silylated dialkylidene cyclopentane (*Z*)-**3** is significantly less stable than the isomeric (*E*)-**3** as a result of unfavorable steric interaction between the silyl group and the proximal vinyl hydrogen atom. In accord with this analysis, diene (*Z*)-**3** isomerized readily to (*E*)-**3**. For example, treatment of (*Z*)-**3** (Z:E = 24:1) with a catalytic amount of iodine[30] (25 mol %, 13 mM) in benzene at room temperature for 2 h formed an equilibrium ≥30:1 mixture of (*E*)-**3**:(*Z*)-**3**.[31] Diene (*E*)-**3** was isolated in 81% yield (E:Z = 20:1) from the corresponding preparative scale reaction (eq 1).[32] Steric in-



(1)



(2)

teraction between the silyl group and the proximal vinylic hydrogen of dialkylidene cyclohexane (*Z*)-**42** is less pronounced than in (*Z*)-**3** as a result of the increased flexibility of the cyclohexyl ring relative to the cyclopentyl ring, and as a result, iodine-catalyzed isomerization of

(27) (a) Luh, T.-Y.; Liu, S.-T. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Chapter 30, pp 1793−1868. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983; Chapter 7.4, pp 81−89. (c) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, D. W., Eds.; Pergamon Press: Oxford, New York, 1979; Vol. 3, Chapter 13.7.6, pp 625−634.

(28) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, *33*, 2825.

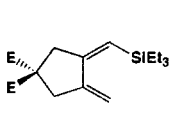
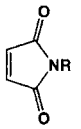
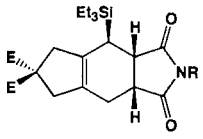
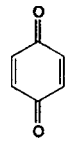
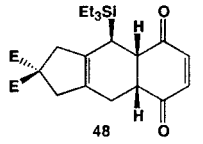
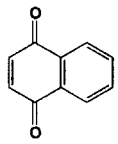
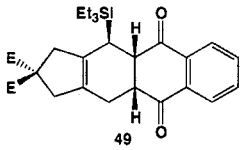
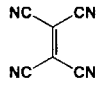
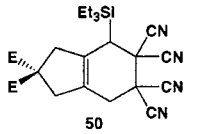
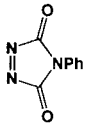
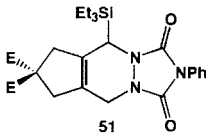
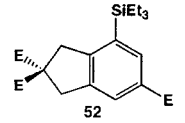
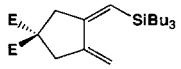
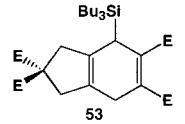
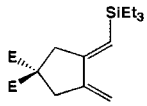
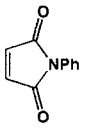
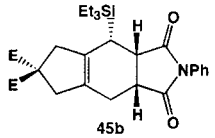
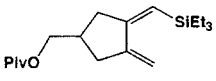
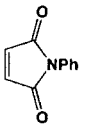
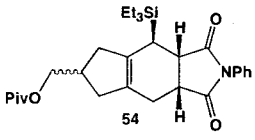
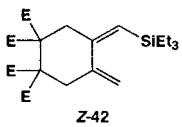
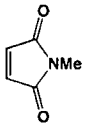
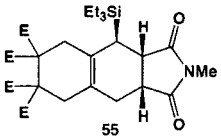
(29) Eaton, B.; King, J. A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359.

(30) Jain, N. F.; Cirillo, P. F.; Schaus, J. V.; Panek, J. S. *Tetrahedron Lett.* **1995**, *36*, 8723.

(31) Continued exposure of the mixtures led to no detectable change in the Z:E ratio.

(32) Attempts to increase the E:Z ratio by employing longer reaction times led to the formation of undesired isomers.

Table 3. Diels−Alder [4 + 2] Cycloaddition of Silylated 1,2-Dialkylidene Cyclopentanes in Toluene

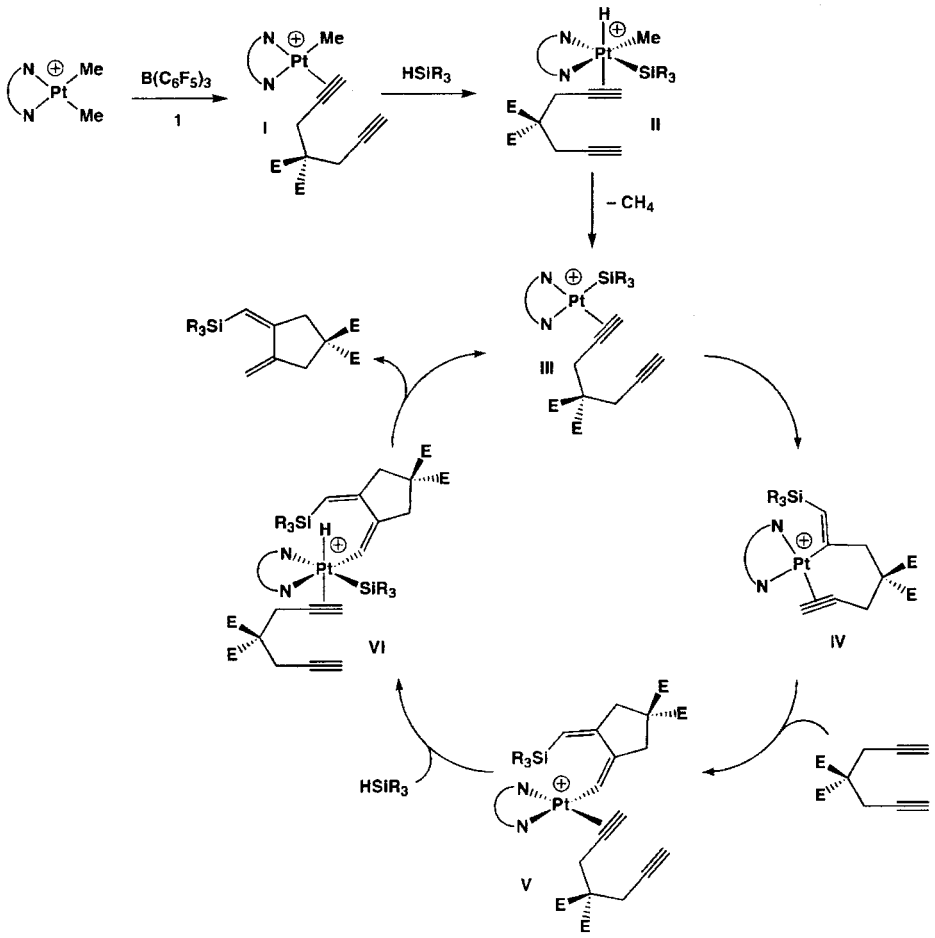
entry	diene	dieneophile	temp (°C)	time (h)	product	yield (%)[a]	isomer ratio[b]
1	 *Z*-3	 R = Ph	80	20	 45a	quant	≥30:1
2		R = *t*-Bu	110	12	46	78	≥30:1
3		R = Me	110	12	47	94	16:1
4			110	12	 48	96	≥30:1
5			110	12	 49	89	≥30:1
6			110	12	 50	85	—
7			25	0.5	 51	73	—
8			130	24	 52	54	20:1
9	 *Z*-7		110	24	 53	73	—
10	 *E*-3	 NPh	50	9	 45b	51	18:1
11	 29	 NPh	110	15	 54	61	2:1
12	 *Z*-42	 NMe	110	48	 55	67	5:1

[a] Yields refer to isolated material of ≥95% purity. [b] Isomer ratio determined by GC analysis of the purified reaction mixture.

(*Z*)-**42** was less efficient than was isomerization of (*Z*)-**3**. For example, treatment of (*Z*)-**42** (Z:E = 10:1) with a catalytic amount of iodine (25 mol %, 26 mM) at room temperature for 6 h formed an equilibrium 4.5:1 mixture of (*E*)-**42**:(*Z*)-**42**.[31] Diene (*E*)-**42** was isolated in 71% yield as a 2:1 mixture of E:Z isomers form the corresponding preparative scale reaction (eq 2).[32]

The silylated 1,2-dialkylidenecyclopentanes formed via platinum-catalyzed cyclization/hydrosilylation are active substrates for [4 + 2] cycloaddition with dieneophiles to form polycyclic compounds (Table 3). For example, diene (*Z*)-**3** reacted with maleimides and quinones to form polycycles **45a** and **46**−**49** in good yield with high endo-selectivity (Table 3, entries 1−5). Diene (*Z*)-**3** also reacted with tetracyanoethylene, 4-phenyl-[1,2,4]triazole-3,5-dione, and methyl propiolate to form adducts **50**−**52**, respectively (Table 3, entries 6−8), while diene (*Z*)-**7** reacted with dimethyl acetylenedicarboxylate to form

Scheme 7



cyclohexadiene **53** (Table 3, entry 9). Dienes (*E*)-**3**, **29**, and (*Z*)-**42** also reacted with maleimides to form the cycloaddition products **45b**, **54**, and **55**, respectively, in moderate yield (Table, entries 10−12). Noteworthy is that the allylic silyl group renders these Diels−Alder adducts potentially reactive both toward both electrophiles[33] and toward oxidation.[8]

Mechanistic Considerations. In the presence of CO or ethylene, $B(C_6F_5)_3$ abstracts a methyl group from the platinum dipyridine complex (N-N)$PtMe_2$ (N-N = 4,4′-di-*tert*-butyl-2,2′-bipyridine) within minutes at −78 °C to form complexes of the form $[(N\text{-}N)Pt(Me)L]^+[MeB(C_6F_5)_3]^-$ [L = CO, $H_2C{=}CH_2$].[34] In a similar manner, reaction of $B(C_6F_5)_3$ with **2a** or **4a** in the presence of diyne **1** could form the four-coordinate cationic platinum alkyne complex **I** (Scheme 7). The cationic platinum(II) diimine complex $Pt[MeO(CH_2)_3N{=}C(Me)C(Me){=}N(CH_2)_3OMe](Me)]^+[BAr_4]^-$ [Ar = 3,5-$C_6H_3(CF_3)_2$] reacts rapidly with triethylsilane at −30 °C via Si−H oxidative addition to form the octahedral platinum (IV) silyl hydride complex $\{Pt[MeO(CH_2)_3N{=}C(Me)C(Me){=}N(CH_2)_3OMe](Me)(SiEt_3)(H)]\}^+[BAr_4]^-$.[35] Likewise, oxidative addition of silane to intermediate **I** could form the six-coordinate platinum silyl hydride intermediate **II** (Scheme 7). The six-coordinate platinum(IV) alkyl hydride complex (TMEDA)$Pt(Cl)_2(Me)(H)$ decomposes readily at −30 °C via C−H reductive elimination to form (TMEDA)$PtCl_2$ with release of methane.[18,36] Similarly, C−H reductive elimination from methyl hydride species **II** would form the four-coordinate platinum silyl alkyne complex **III**. Insertion of the coordinated alkyne into the Pt−Si bond of **III** could form platinum alkenyl alkyne complex **IV**, which could undergo intramolecular carbometalation to form the platinum dienyl species **V**. Oxidative addition of silane to **V** would form the six-coordinate platinum dienyl hydride species **VI** that could decompose via C−H reductive elimination to release the diene and regenerate the platinum silyl species **III** (Scheme 7).

In summary, a 1:1 mixture of the cationic platinum diimine complex **4a** and $B(C_6F_5)_3$ catalyzed the cyclization/hydrosilylation of 1,6-diynes to form silylated 1,2-dialkylidenecyclopentanes in good yield with high *Z*-selectivity. The procedure tolerated a number of functional groups and a range of substitution. The 1,2-dialkylidenecyclopentanes formed via cyclization/hydrosilylation underwent a range of transformations including [4 + 2] cycloaddition with dieneophiles.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained at 400 MHz for ^1H and at

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(34) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

(35) Fang, X.; Scott, B. L.; Watkins, J. G.; Kubas, G. J. *Organometallics* **2000**, *19*, 4193.

(36) Platinum(IV) alkyl hydride complexes that cannot generate an open coordination site are stable toward reductive elimination. (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (b) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684.

100 MHz for ^{13}C in $CDCl_3$ unless otherwise specified. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Toluene, benzene (Aldrich, anhydrous), and silanes (Aldrich) were used as received; CH_2Cl_2 was distilled from CaH_2 under nitrogen. The synthesis of diynes, ligands, and platinum complexes is included in Supporting Information. The stereochemistry of compounds (*Z*)-**3**, (*E*)-**3**, **38**, **42**, **45a** and **45b** were established by NOE and/or combined COSY/NOESY analysis (see Supporting Information).

Synthesis of Silylated 1,2-Dialkylidenecycloalkanes. (*Z*)-1,1-Dicarbomethoxy-3-methylene-4-triethylsilylmethylenecyclopentane [(*Z*)-3]. Toluene (20 mL) and $HSiEt_3$ (150 μL, 1.0 mmol) were added sequentially to a mixture of **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.023 mmol), and **1** (105 mg, 0.50 mmol) at 0 °C. The resulting orange solution was heated at 110 °C for 10 min, cooled to room temperature, and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 24:1) gave (*Z*)-**3** (128 mg, 82%) as a faintly pink oil. ^1H NMR: δ 5.41 (t, J = 1.9 Hz, 1 H), 5.31 (t, J = 2.0 Hz, 1 H), 5.00 (t, J = 1.6 Hz, 1 H), 3.70 (s, 6 H), 3.07 (d, J = 1.87 Hz, 2 H), 3.03 (t, J = 1.9 Hz, 2 H), 0.89 (t, J = 7.9 Hz, 9 H), 0.64 (q, J = 7.9 Hz, 6 H). IR (neat, cm^{-1}): 2954, 2912, 2876, 1754, 1745, 1738, 1731, 1681, 1651, 1455, 1434, 1257, 1201, 1164, 1073, 1015. $^{13}C\{^1H\}$ NMR: δ 171.1, 153.4, 146.0, 119.9, 109.2, 56.3, 52.1, 44.8, 41.2, 6.9, 3.5. Anal. Calcd (found) for $C_{17}H_{28}SiO_4$: C, 62.93 (62.79); H, 8.70 (8.68).

The procedure used to synthesize (*Z*)-**3** was applied to the synthesis of the remaining silylated 1,2-dialkylidenecycloalkanes unless noted otherwise. Yields, reaction conditions, and isomeric ratios are given in Table 2. All carbocycles were isolated as colorless oils unless noted otherwise.

(*E*)-1,1-Dicarbomethoxy-3-methylene-4-triethylsilylmethylenecyclopentane [(*E*)-3]. Toluene (20 mL) and $HSiEt_3$ (150 μL, 1.0 mmol) were added sequentially to a mixture of (phen)Pt(Me)Cl (**2b**) (9 mg, 0.023 mmol), $NaBAr_4$ (12 mg, 0.023 mmol), and **1** (105 mg, 0.50 mmol) at 0 °C. The resulting orange solution was heated at 110 °C for 2 h, cooled to room temperature, concentrated, and absorbed onto silica gel for 30 min at room temperature. Chromatography (SiO_2; hexanes−EtOAc = 24:1) gave (*E*)-**3** (134 mg, 83%) as a faintly pink oil. ^1H NMR: δ 5.97 (t, J = 2.4 Hz, 1 H), 5.40 (t, J = 2.4 Hz, 1 H), 4.94 (t, J = 2.0 Hz, 1 H), 3.73 (s, 6 H), 3.04 (d, J = 2.2 Hz, 2 H), 3.03 (t, J = 2.1 Hz, 2 H), 0.95 (t, J = 8.0 Hz, 9 H), 0.65 (q, J = 8.0 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 171.9, 162.7, 145.9, 116.6, 105.7, 57.9, 53.0, 41.5, 40.7, 7.7, 4.3. HRMS calcd (found) for $C_{17}H_{29}SiO_4$ (MH^+): 325.1835 (325.1830).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-dimethyl-*tert*-butylsilylmethylenecyclopentane (5). ^1H NMR: δ 5.51 (br s, 1 H), 5.31 (t, J = 1.9 Hz, 1 H), 5.02 (s, 1 H), 3.70 (s, 6 H), 3.08 (d, J = 1.8 Hz, 2 H), 3.02 (br s, 1 H), 0.87 (s, 9 H), 0.08 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 171.1, 153.3, 144.2, 120.4, 110.1, 56.1, 52.1, 44.7, 41.4, 25.6, 16.4, −5.9. Anal. Calcd (found) for $C_{17}H_{29}SiO_4$: C, 62.92 (62.79); H, 8.70 (8.79).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-dimethylbenzylsilylmethylenecyclopentane (6). ^1H NMR: δ 7.25−6.95 (m, 5 H), 5.49 (s, 1 H), 5.29 (s, 1 H), 5.08 (s, 1 H), 3.71 (s, 6 H), 3.06 (m, 4 H), 2.20 (s, 2 H), 0.90 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 171.9, 154.2, 145.3, 140.2, 128.5, 128.3, 124.2, 122.2, 111.2, 57.1, 53.0, 45.5, 42.3, 26.0, −2.1. Anal. Calcd (found) for $C_{20}H_{26}SiO_4$: C, 67.01 (67.12); H, 7.31 (7.10).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-tributylsilylmethylenecyclopentane (7). ^1H NMR: δ 5.42 (t, J = 1.8 Hz, 1 H), 5.30 (t, J = 2.2 Hz, 1 H), 5.00 (t, J = 2.0 Hz, 1 H), 3.70 (s, 6 H), 3.06 (d, J = 1.8 Hz, 2 H), 3.03 (t, J = 2.1 Hz, 2 H), 1.35−1.15 (m, 12 H), 0.85 (t, J = 6.8 Hz, 9 H), 0.61 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 172.0, 153.8, 145.5, 121.8, 110.2, 57.2, 52.9, 45.8, 42.2, 26.9, 26.5, 14.0, 13.1. Anal. Calcd (found) for $C_{23}H_{40}SiO_4$: C, 67.60 (67.24); H, 9.87 (9.73).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-triisopropylsilylmethylenecyclopentane (8). ^1H NMR: δ 5.39 (t, J = 2.0 Hz, 1 H), 5.34 (t, J = 2.0 Hz, 1 H), 4.91 (s, 1 H), 3.67 (s, 6 H), 3.08 (d, J = 2.0 Hz, 2 H), 3.02 (m, 2 H), 1.17−1.08 (m, 3 H), 1.10 (d, J = 7.2 Hz, 18 H). $^{13}C\{^1H\}$ NMR: δ 172.0, 154.7, 145.6, 119.3, 109.5, 57.0, 53.0, 46.4, 42.2, 19.2, 12.7. IR (neat, cm^{-1}): 2944, 2889, 1737, 1253. Anal. Calcd (found) for $C_{20}H_{34}O_4Si$: H, 9.35 (9.24); C, 65.53 (65.46).

(*Z*)-1,1-Bis(trimethylacetoxymethyl)-3-methylene-4-triethylsilylmethylenecyclopentane (17). ^1H NMR: δ 5.38 (s, 1 H), 5.32 (br s, 1 H), 4.97 (br s, 1 H), 3.94 (s, 4 H), 2.45 (d, J = 1.7 Hz, 2 H), 2.40 (br s, 2 H), 1.18 (s, 18 H), 0.90 (t, J = 7.9 Hz, 9 H), 0.63 (q, J = 7.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 178.5, 155.9, 146.7, 121.1, 110.6, 66.5, 44.4, 42.9, 40.6, 39.2, 27.4, 7.9, 4.5. Anal. Calcd (found) for $C_{25}H_{44}SiO_4$: C, 68.76 (69.17); H, 10.16 (10.39).

(*Z*)-4,4-Dibenzyloxymethyl-1,6-heptadiyne-3-methylene-4-triethylsilyl methylenecyclopentane (18). ^1H NMR: δ 7.29 (m, 10 H), 5.33 (t, J = 1.7 Hz, 1 H), 5.27 (br s, 1 H), 4.91 (br s, 1 H), 4.49 (s, 4 H), 3.37 (s, 4 H), 2.44 (br s, 1 H), 2.44 (d, J = 1.9 Hz, 2 H), 2.40 (t, J = 1.7 Hz, 2 H), 0.90 (t, J = 7.83 Hz, 9 H), 0.62 (q, J = 7.8 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 157.9, 148.2, 139.1, 128.5, 127.6, 119.7, 109.7, 73.4, 73.2, 44.9, 44.5, 40.7, 8.0, 4.6. Anal. Calcd (found) for $C_{29}H_{40}SiO_2$: C, 77.62 (77.35); H, 8.99 (8.84).

3-Methylene-4-(triethylsilylmethylene)-1,1-bis(*tert*-butyldimethylsilyloxymethyl)cyclopentane (19) and the Diels−Alder Adduct with 4-Phenyl-[1,2,4]triazole-3,5-dione (19a). A solution of **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.023 mmol), $HSiEt_3$ (150 μL, 0.90 mmol), and **11** (190 mg, 0.50 mmol) in toluene (20 mL) was heated at 110 °C for 15 min to form **19** as a 29:1 mixture of Z:E isomers. The resulting solution was cooled to 0 °C, treated with 4-phenyl-[1,2,4]triazole-3,5-dione (90 mg, 0.51 mmol), stirred at room temperature for 30 min, and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 50:1 → 12:1) gave **19a** (270 mg, 80%) as a white solid, mp 93−95 °C. ^1H NMR: δ 7.53−7.51 (m, 2 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 1 H), 4.35 (s, 1 H), 4.18 (br d, J = 15.6 Hz, 1 H), 3.95 (br d, J = 15.6 Hz, 1 H), 3.44−3.59 (m, 4 H), 2.43 (br d, J = 15.6 Hz, 1 H), 2.17 (s, 2 H), 2.12 (t, J = 16.4 Hz, 1 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.57−0.75 (m, 6 H), 0.05 (s, 6 H), 0.03 (s, 6 H). $^{13}C\{^1H\}$ NMR: δ 154.3, 149.3, 131.8, 131.7, 129.3, 128.1, 125.5, 124.1, 66.0, 65.6, 49.6, 46.8, 46.7, 39.7, 38.7, 26.1, 18.5, 7.3, 3.1, −5.3. IR (neat, cm^{-1}): 2953, 2929, 2880, 2855, 1775, 1720, 1713, 1415, 1254. Anal. Calcd (found) for $C_{35}H_{61}N_3O_4Si$: H, 9.15 (9.38); C, 62.54 (62.59); N, 6.25 (6.28).

(*Z*)-(8,8-Dimethyl-3-methylene-7,9-dioxa-spiro[4.5]dec-2-ylidenemethyl)-triethylsilane (20). ^1H NMR: δ 5.38 (s, 1 H), 5.31 (s, 1 H), 4.96 (s, 1 H), 3.60 (s, 4 H), 2.41 (d, J = 1.6 Hz, 2 H), 2.39 (s, 2 H), 1.40 (s, 6 H), 0.90 (t, J = 8.0 Hz, 9 H), 0.60−0.66 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 156.6, 147.2, 120.6, 110.2, 98.0, 68.4, 45.6, 41.5, 38.2, 24.2, 23.8, 7.8, 4.5. IR (neat, cm^{-1}): 2990, 2950, 2871, 1454. Anal. Calcd (found) for $C_{18}H_{32}O_2Si$: H, 10.45 (10.42); C, 70.07 (69.83).

(*Z*)-1-Carbomethoxy-3-methylene-1-phenyl-4-tributylsilylmethylenecyclopentane (21). ^1H NMR: δ 7.20−7.34 (m, 5 H), 5.51 (s, 1 H), 5.34 (s, 1 H), 5.05 (s, 1 H), 3.60 (s, 3 H), 3.45 (dd, J = 1.3, 15.2 Hz, 1 H), 3.42 (td, J = 1.6, 13.9 Hz, 1 H), 1.20−1.33 (m, 12 H), 0.86 (t, J = 7.0 Hz, 9 H), 0.60−0.64 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 174.7, 154.1, 145.1, 141.5, 127.7, 126.3, 125.9, 120.5, 109.0, 54.1, 51.7, 47.8, 44.1, 26.0, 25.6, 25.5, 13.2, 12.2. IR (neat, cm^{-1}): 3030, 2954, 2920, 1733, 1463, 1446. Anal. Calcd (found) for $C_{27}H_{42}O_2Si$: H, 9.92 (10.32); C, 76.60 (76.21).

(*Z*)-1-Carbomethoxy-1-methanesulfonyl-3-methylene-4-triethylsilylmethylenecyclopentane (22). ^1H NMR: δ 5.49 (t, J = 2.0 Hz, 1 H), 5.38 (t, J = 2.0 Hz, 1 H), 3.79 (s, 2 H), 3.24 (dq, J = 2.8, 16.0 Hz, 2 H), 3.22 (d, J = 2.4 Hz, 2 H), 3.02 (s, 3 H), 0.90 (t, J = 6.8 Hz, 9 H), 0.61−0.67 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 169.3, 152.0, 143.7, 122.6, 111.2, 73.8, 53.9, 42.6, 38.7, 38.4, 7.7, 4.3. Anal. Calcd (found) for $C_{16}H_{28}O_4SSi$: H, 8.19 (8.45); C, 55.78 (56.01).

(*Z*)-1-Carbomethoxy-1-dimethylcarbamoyl-3-methylene-4-triethylsilylmethylenecyclopentane (23). ^1H NMR: δ 5.35 (s, 1 H), 5.26 (t, J = 2.0 Hz, 1 H), 4.95 (s, 1 H), 3.69 (s, 3 H), 3.15 (td, J = 2.0, 15.6 Hz, 1 H), 3.09 (dq, J = 2.0, 16.8 Hz,

2 H), 2.94 (d, J = 16.4 Hz, 2 H), 2.92 (s, 3H), 2.82 (s, 3 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.58−0.64 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 174.1, 170.1, 154.9, 146.1, 119.9, 109.6, 56.1, 52.9, 46.0, 43.0, 37.0, 7.8, 4.7, 4.4. Anal. Calcd (found) for $C_{18}H_{31}NO_3Si$: H, 9.26 (9.58); C, 64.05 (63.94); N, 4.15 (4.38).

(*Z*)-1-Acetyl-1-carbomethoxy-3-methylene-4-triethylsilylmethylenecyclopentane (24). A solution $HSiEt_3$ (150 μL, 0.90 mmol) in toluene (9 mL) was added over 30 min to a solution of **16** (100 mg, 0.52 mmol), **4a** (12 mg, 0.025 mmol), and $B(C_6F_5)_3$ (12 mmol, 0.023 mmol) in toluene (10 mL) at 110 °C. The resulting solution was cooled to room temperature and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 24:1) gave **24** (104 mg, 65%). ^1H NMR: δ 5.42 (t, J = 2.0 Hz, 1 H), 5.30 (t, J = 2.0 Hz, 1 H), 5.00 (s, 1 H), 3,71 (s, 3 H), 3.01 (dd, J = 1.6, 16.4 Hz, 1 H), 2.99 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 2.97 (d, J = 2.4 Hz, 1 H), 2.96 (d, J = 2.4 Hz, 1 H), 2.16 (s, 3 H), 0.89 (t, J = 8.0 Hz, 6 H), 0.63 (q, J = 7.2 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 203.4, 172.8, 154.4, 145.7, 120.9, 112.1, 63.4, 52.9, 44.4, 40.7, 26.5, 7.7, 4.4. IR (neat, cm^{-1}): 2953, 2910, 2896, 1738, 1713. HRMS calcd (found) for $C_{17}H_{28}O_3Si$ (M^+): 308.1808 (308.1812).

4-Carbomethoxy-1-methylene-2-triethylsilylmethylenecyclopentane (26). ^1H NMR (300 MHz): δ 5.39 (s, 1 H), 5.30 (s, 1 H), 4.97 (s, 1 H), 3.96 (s, 1 H), 2.90−2.87 (m, 5 H), 0.91 (t, J = 8.2 Hz, 9 H), 0.66 (q, J = 8.0 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz): δ 174.8, 155.5, 146.5, 118.8, 108.5, 51.0, 41.0, 40.3, 37.3, 6.9, 3.5. Anal. Calcd (found) for $C_{15}H_{26}O_2Si$: H, 9.84 (9.93); C, 67.61 (67.54).

4-(Trimethylacetoxy)methyl-1-methylene-2-triethylsilylmethylenecyclopentane (29). A solution $HSiBu_3$ (200 mL, 0.78 mmol) in toluene (9 mL) was added over 30 min to a solution of **27** (100 mg, 0.49 mmol), **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mmol, 0.023 mmol) in toluene (10 mL) at 110 °C. The resulting solution was cooled to room temperature and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−ether = 100:1 → 50:1) gave **6** (155 mg, 78%). ^1H NMR: δ 5.39 (s, 1 H), 5.29 (s, 1 H), 4.96 (s, 1 H), 3.96 (d, J = 6.4 Hz, 2 H), 2.54−2.64 (m, 2 H), 2.35−2.20 (m, 3 H), 1.23−1.33 (m, 9 H), 1.19 (s, 9 H), 0.86 (t, J = 6.8 Hz, 9 H), 0.62−0.66 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 178.6, 157.0, 148.1, 120.5, 109.4, 67.4, 41.8, 39.0, 38.1, 35.7, 27.4, 26.9, 26.5, 14.0, 13.2. IR (neat, cm^{-1}): 2955, 1736, 1731, 1155. Anal. Calcd (found) for $C_{25}H_{46}O_2Si$: H, 11.40 (11.38); C, 73.83 (73.79).

4-Hydroxymethyl-1-methylene-2-triethylsilylmethylenecyclopentane (30). A solution of triethylsilane (150 μL, 0.90 mmol), **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.023 mmol), and **28** (100 mg, 0.42 mmol) in toluene (20 mL) was generated at room temperature, heated at 110 °C for 15 min, cooled to room temperature, and concentrated. The resulting oily residue was treated with TBAF (1 M in THF, 1.5 mL), stirred at room temperature for 10 min, and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 5:1 → 3:1) gave **30** (58 mg, 58%). ^1H NMR: δ 5.38 (t, J = 2.0 Hz, 1 H), 5.30 (s, 1 H), 4.96 (s, 1 H), 3.52 (d, J = 6.0 Hz, 2 H), 2.56−2.67 (m, 2 H), 2.16−2.33 (m, 3 H), 1.56 (s, 1 H), 0.92 (s, t, J = 7.6 Hz, 9 H), 0.62−0.68 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 158.0, 148.5, 119.3, 109.2, 66.5, 41.7, 38.9, 37.8, 7.9, 4.5. Anal. Calcd (found) for $C_{14}H_{26}OSi$: H, 10.99 (11.08); C, 70.52 (70.67).

3-Methylene-4-triethylsilylmethylenetetrahydrofuran (32). ^1H NMR: δ 5.47 (t, J = 1.8 Hz, 1 H), 5.45 (t, J = 2.0 Hz, 1 H), 5.05 (t, J = 2.0 Hz, 1 H), 4.48 (t, J = 2.4 Hz, 2 H), 4.43 (d, J = 2.0 Hz, 2 H), 1.23−1.36 (m, 12 H), 0.88 (t, J = 6.8 Hz, 9 H), 0.67−0.71 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 153.1, 145.1, 118.6, 107.3, 76.3, 74.2, 26.9, 26.4, 14.0, 12.9. Anal. Calcd (found) for $C_{18}H_{34}OSi$: H, 11.63 (11.74); C, 73.40 (73.17).

Cyclization/Hydrosilylation of 4,4-Dicarbomethoxy-3-methyl-1,6-heptadiyne (33). A solution of **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.023 mmol), triethylsilane (150 μL, 0.90 mmol), and **33** (110 mg, 0.495 mmol) in toluene (20 mL) was generated at room temperature, heated at 110 °C for 16 min, cooled to room temperature, and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 50:1 → 25:1) gave a 1:1.2 mixture of (*Z*)-1,1-dicarbomethoxy-2-methyl-4-methylene-3-(triethylsilylmethylene)cyclopentane (**34a**) and (*Z*)-1,1-dicarbomethoxy-2-methyl-3-methylene-4-(triethylsilylmethylene)cyclopentane (**34b**) (135 mg, 0.40 mmol, 80%). Anal. Calcd (found) for $C_{18}H_{30}O_4Si$: H, 8.93 (8.90); C, 63.87 (63.82).

For 34a: ^1H NMR: δ 5.33 (t, J = 2.4 Hz, 1 H), 5.31 (d, J = 2.0 Hz, 1 H), 4.97 (t, J = 2.0 Hz, 1 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 3.25 (dq, J = 2.0 Hz, 6.4 Hz, 1 H), 3.19 (td, J = 2.0, 16.0 Hz, 1 H), 3.77 (td, J = 2.0, 16.4 Hz, 1 H), 1.05 (d, J = 6.8 Hz, 3 H), 0.91 (t, J = 7.6 Hz, 9 H), 0.64 (q, J = 7.6 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 172.1, 170.8, 151.3, 145.3, 118.7, 109.8, 61.2, 52.2, 43.6, 39.7, 16.4, 7.7, 4.2.

For 34b: ^1H NMR: δ 5.38 (t, J = 2.0 Hz, 1 H), 5.33 (d, J = 2.0 Hz, 1 H), 4.92 (d, J = 2.0 Hz, 1 H), 3.69 (s, 3 H), 3.66 (s, 3 H), 3.29 (tq, J = 2.0, 7.2 Hz, 1 H), 2.23 (dd, J = 2.0, 16.8 Hz, 1 H), 2.82 (dd, J = 2.0, 16.8 Hz, 1 H), 0.90 (t, J = 8.0 Hz, 9 H), 0.63 (q, J = 8.0 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 172.0, 170.7, 160.1, 154.1, 120.2, 108.8, 60.9, 52.7, 48.4, 45.7, 15.7, 7.7, 4.7.

Cyclization/Hydrosilylation of 4,4-Dicarbomethoxy-3,3-dimethyl-1,6-heptadiyne (35). A solution of **4a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.023 mmol), $HSiEt_3$ (150 μL, 0.90 mmol), and **35** (110 mg, 0.470 mmol) in toluene (20 mL) was generated at room temperature, heated at 110 °C for 15 min, cooled to room temperature, and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 40:1 → 20:1) gave a 1:2.3 mixture of (*Z*)-1,1-dicarbomethoxy-2,2-dimethyl-4-methylene-3-triethylsilylmethylenecyclopentane (**36a**) and (*Z*)-1,1-dicarbomethoxy-2,2-dimethyl-3-methylene-4-triethylsilylmethylenecyclopentane (**36b**) (135 mg, 0.383 mmol, 82%). IR (neat, cm^{-1}): 2951, 2909, 2873, 1735, 1253. Anal. Calcd (found) for $C_{19}H_{32}O_4Si$: H, 9.15 (9.07); C, 64.73 (64.61).

For 36a: ^1H NMR: δ 5.37 (t, J = 2.4 Hz, 1 H), 5.21 (s, 1 H), 4.99 (t, J = 2.4 Hz, 1 H), 3.64 (s, 6 H), 2.95 (t, J = 2.4 Hz, 2 H), 1.11 (s, 6 H), 0.89 (t, J = 8.0 Hz, 9 H), 0.61−0.67 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 171.4, 165.4, 145.4, 115.2, 110.0, 64.7, 52.2, 51.1, 38.3, 25.1, 7.8, 4.5.

For 36b: ^1H NMR: δ 5.38 (t, J = 2.4 Hz, 1 H), 5.26 (s, 1 H), 4.84 (s, 1 H), 3.65 (s, 6 H), 3.01 (d, J = 2.0 Hz, 6 H), 1.15 (s, 6 H), 0.88 (t, J = 8.0 Hz, 9 H), 0.59−0.67 (m, 6 H). $^{13}C\{^1H\}$ NMR: δ 171.3, 156.8, 154.2, 120.2, 106.5, 64.1, 52.1, 49.2, 42.1, 24.6, 7.8, 4.5.

Methyl[4,4-Dicarbomethoxy-2-(triethylsilylmethylene)-cyclopentylidene] Acetate (38). ^1H NMR (300 MHz): δ 6.19 (t, J = 2.4 Hz, 1 H), 5.81 (s, 1 H), 3.82 (s, 3 H), 3.80 (s, 6 H), 3.64 (d, J = 2.4 Hz, 2 H), 3.16 (d, J = 1.8 Hz, 2 H), 0.99 (t, J = 7.8 Hz, 9 H), 0.75 (q, J = 7.8 Hz, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz): δ 170.8, 166.1, 155.4, 154.0, 126.6, 112.4, 56.3, 52.1, 50.6, 44.6, 39.6, 6.77, 3.59. IR (neat, cm^{-1}): 2954, 2910, 2874, 1738, 1705. Anal. Calcd (found) for $C_{19}H_{30}O_6Si$: C, 59.66 (59.58); H, 7.90 (7.88).

1,1-Dicarbomethoxy-3-(triethylsilylmethylene)-4-[2-(triethylsilyloxy)propylidene]cyclopentane (40). ^1H NMR: δ 5.80 (td, J = 2.4, 8.0 Hz, 1 H), 5.30 (m, 1 H), 4.41 (qd, J = 2.4, 8.0 Hz, 1 H), 3.69 (s, 3 H), 3.68 (s, 3 H), 1.21 (d, J = 2.4 Hz, 3 H), 0.91 (t, J = 8.0 Hz, 9 H), 0.87 (t, J = 8.0 Hz, 9 H), 0.63 (q, J = 8.0 Hz, 6 H), 0.54 (q, J = 8.0 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 172.1, 172.0, 155.2, 134.9, 131.2, 119.3, 67.5, 57.5, 53.1, 45.7, 37.8, 24.3, 7.9, 7.1, 5.1, 4.9. IR (neat, cm^{-1}): 2953, 2909, 2875, 1739, 1457, 1434, 1418, 1249, 1200, 1162, 1077, 1014. HRMS calcd (found) for $C_{25}H_{46}O_5Si_2$ (M^+): 482.2884 (482.2891).

(*Z*)-1,1,2,2-Tetracarboethoxy-4-methylene-5-(triethylsilylmethylene)cyclohexane [(*Z*)-42]. ^1H NMR: δ 5.35 (s, 1 H), 5.14 (t, J = 2.1 Hz, 1 H), 4.94 (t, J = 2.2 Hz, 1 H), 4.31 (q, J = 7.0 Hz, 4 H), 4.28 (q, J = 7.0 Hz, 4 H), 3.23 (br s, 2 H), 3.09 (br s, 2 H), 1.37 (t, J = 7.0 Hz, 6 H), 1.36 (t, J = 7.0 Hz, 6 H), 1.01 (t, J = 7.7 Hz, 9 H), 0.68 (q, J = 7.7 Hz, 6 H). $^{13}C\{^1H\}$ NMR: δ 168.6, 168.5, 151.7, 143.1, 124.0, 113.0, 60.8, 60.7, 60.6, 58.4, 42.7, 38.1, 13.0, 6.7, 4.0. Anal. Calcd (found) for $C_{26}H_{42}SiO_8$: C, 61.15 (61.05); H, 8.29 (8.37).

Reactions of Silylated 1,2-Dialkylidenecycloalkanes. Isomerization of (*Z*)-3. A solution of (*Z*)-**3** (166 mg, 0.51 mmol, >95% *Z*) and I_2 (2 mg, 8 × 10^{-3} mmol) in benzene (5 mL) was stirred at 75 °C for 4 h and concentrated under

vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 25:1) gave (*E*)-**3** (134 mg, 81%, 95% *E*).

Isomerization of (*Z*)-42. A solution (*Z*)-**42** (72 mg, 0.14 mmol) and iodine (12 mg, 0.047 mmol) in benzene (1.5 mL) was stirred at room temperature for 6.5 h, quenched with 10% aqueous sodium thiosulfate (5 mL), and extracted with ethyl acetate (2 × 100 mL). The combined organic fractions were washed with sodium thiosulfate solution (2 × 75 mL), dried ($MgSO_4$), and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 30:1 → 3:1) gave **42** (51 mg, 71%) as a 2:1 mixture of E:Z isomers.

For (*E*)-42: ^{1}H NMR: δ 5.68 (s, 1 H), 5.21 (s, 1 H), 5.15 (d, J = 1.6 Hz, 1 H), 5.00 (d, J = 2.0 Hz, 1 H), 4.80 (d, J = 2.0 Hz, 1 H), 4.73 (d, J = 1.2 Hz, 1 H), 4.11−4.24 (m, 8 H), 3.70 (m, 1 H), 2.95−3.14 (m, 2 H), 2.61−2.85 (m, 1 H), 1.21−1.29 (m, 12 H), 0.85−1.00 (m, 9 H), 0.69−0.78 (m, 3 H), 0.51−0.62 (m, 3 H). ^{13}C{^{1}H} NMR. δ 169.7, 151.8, 145.8, 134.0, 125.2, 123.2, 114.2, 113.0, 62.3, 62.1, 61.9, 58.8, 39.3, 38.2, 37.4, 35.4, 15.5, 14.2, 8.1, 7.9, 5.2, 4.8, 4.4.

3,3-Dicarbomethoxy-1-methyl-5-methylenecyclopentene (43).[37] A solution of (*Z*)-**3** (120 mg, 0.37 mmol), iodine (11 mg), and water (0.1 mL) in benzene (3 mL) was stirred at 80 °C for 6 h and concentrated under vacuum. Chromatography of the residue (Al_2O_3; hexanes−EtOAc = 25:1) gave **43** (60 mg, 77%). ^{1}H NMR: δ 5.89 (s, 1 H), 4.91−4.88 (m, 2 H), 3.71 (s, 6 H), 3.16 (t, J = 2.0 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 171.6, 151.3, 144.7, 131.3, 104.1, 63.7, 53.2, 38.3, 12.9.

1,1-Dicarbomethoxy-3,4-dimethylenecyclopentane (44).[38] A solution of (*Z*)-**3** (108 mg, 0.33 mmol) and trifluoroacetic acid (60 μL, 0.77 mmol) in CH_2Cl_2 (1 mL) was stirred at 0 °C for 35 min, quenched with Na_2CO_3 (5 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 25:1) gave **44** (44 mg, 63%). ^{1}H NMR: δ 5.37 (t, J = 2.0 Hz, 2 H), 4.94 (t, J = 1.6 Hz, 2 H), 3.71 (s, 6 H), 3.02 (d, J = 2.0 Hz, 2 H), 3.01 (d, J = 1 6 Hz, 2 H). ^{13}C{^{1}H} NMR. δ 172.0, 144.7, 106.0, 57.9, 53.2, 41.5.

Diels−Alder Adduct of (*Z*)-3 and *N*-Phenylmaleimide (45a). A solution of (*Z*)-**3** (88 mg, 0.27 mmol) and *N*-phenylmaleimide (50 mg, 0.29 mmol) in toluene (4 mL) was stirred at 80 °C for 20 h and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 10:1 → 3:1) gave **45a** (138 mg, 102%) as a viscous colorless oil. ^{1}H NMR: δ 7.39 (t, J = 7.6 Hz, 2 H), 7.31 (t, J = 10.8 Hz, 1 H), 7.19 (d, J = 7.6 Hz, 2 H), 3.68 (s, 3 H), 3.60 (s, 3 H), 3.28 (dt, J = 1.6, 8.4 Hz, 1 H), 3.17 (dd, J = 1.6, 8.4 Hz, 1 H), 3.02 (br d, J = 14 Hz, 1 H), 2.97 (br d, J = 12 Hz, 1 H), 2.93 (br d, J = 12 Hz, 1 H), 2.89 (br d, J = 12 Hz, 1 H), 2.85 (br d, J = 15 Hz, 1 H), 2.59 (br d, J = 15 Hz, 1 H), 2.54 (s, 1 H), 2.30−2.34 (m, 1 H), 0.97 (t, J = 7.6 Hz, 9 H), 0.61 (q, J = 7.6 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 180.0, 179.4, 172.6, 172.3, 134.3, 132.4, 129.2, 128.7, 127.8, 126.7, 58.2, 53.0, 44.8, 44.0, 40.8, 40.1, 25.0, 24.8, 7.6, 3.5. IR (neat, cm^{-1}): 2953, 2911, 2876, 1737, 1730, 1712, 1598, 1257, 1197. HRMS calcd (found) for $C_{27}H_{35}NO_6Si$ (M^+): 497.2234 (497.2220).

The procedure used to synthesize **45a** was applied to the synthesis of the remaining Diels−Alder adducts, except where noted. Yields, reaction conditions, and isomer ratios are given in Table 3. All Diels−Alder adducts were isolated as colorless oils unless noted otherwise.

Diels−Alder Adduct of (*E*)-3 and *N*-Phenylmaleimide (45b). ^{1}H NMR: δ 7.41−7.45 (m, 2 H), 7.34−7.36 (m, 1 H), 7.19−7.21 (m, 2 H), 3.72 (s, 3 H), 3.65 (s, 3 H), 3.34 (dd, J = 6.0, 8.0 Hz, 1 H), 3.25 (dt, J = 4.0, 8.6 Hz, 1 H), 2.99−3.09 (m, 4 H), 2.60 (br d, J = 15.8 Hz, 1 H), 2.36 (br dd, J = 8.4, 16.4 Hz, 1 H), 1.99 (m, 4 H), 0.97 (t, J = 8.0 Hz, 9 H), 0.54−0.83 (m, 6 H). ^{13}C{^{1}H} NMR: δ 179.3, 178.3, 172.3, 135.3, 129.5, 128.9, 126.9, 58.7, 53.2, 44.3, 43.2, 41.5, 25.2, 23.6, 8.2, 4.8. IR (neat, cm^{-1}): 2951, 2362, 2433, 1734, 1709, 1498, 1381, 1262, 1195, 1168, 1070. HRMS calcd (found) for $C_{27}H_{35}NO_6Si$ (M^+): 497.2234 (497.2229).

Diels−Alder Adduct of (*Z*)-3 and *N-tert*-Butylmaleimide (46). ^{1}H NMR: δ 3.69 (s, 3 H), 3.66 (s, 3 H), 2.93−2.99 (m, 3 H), 2.82−2.86 (m, 3 H), 2.42−2.46 (m, 1 H), 2.21−2.31 (m, 2 H), 1.49 (s, 9 H), 1.20−1.35 (m, 12 H), 0.87 (t, 7.0 Hz, 9 H), 0.52−0.56 (m, 6 H). ^{13}C{^{1}H} NMR: δ 181.9, 172.7, 134.2, 127.6, 58.0, 52.9, 44.9, 43.9, 40.8, 40.0, 28.4, 27.1, 26.1, 25.5, 25.0, 13.9, 12.2. IR (neat, cm^{-1}): 2985, 1740, 1447, 1373, 1241, 1098, 1047, 938, 787. HRMS calcd (found) for $C_{27}H_{35}NO_6Si$: 561.3486 (561.3483).

Diels−Alder Adduct of (*Z*)-3 and *N*-Methylmaleimide (47). White solid, mp 105−106 °C. ^{1}H NMR: δ 3.68 (s, 3 H), 3.65 (s, 3 H), 3.11 (td, J = 1.6, 8.8 Hz, 1 H), 3.00 (d, J = 8.8 Hz, 1 H), 2.95 (m, 1 H), 2.92 (s, 3 H), 2.78−2.85 (m, 2 H), 2.46−2.51 (m, 2 H), 2.36 (s, 1 H), 2.24−2.30 (m, 1 H), 0.96 (t, J = 8.0 Hz, 9 H), 0.59 (q, J = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 181.2, 180.6, 172.8, 172.4, 134.0, 127.6, 58.2, 53.1, 44.7, 43.8, 40.6, 39.9, 25.7, 24.7, 24.6, 7.7, 3.6. IR (neat, cm^{-1}): 2953, 2876, 1775, 1735, 1700, 1434, 1383, 1336, 1262, 1198, 1157, 1122, 1071, 1042, 994, 730. Anal. Calcd (found) for $C_{22}H_{33}NO_6Si$: C, 60.66 (60.74); H 7.64 (7.73); N 3.22 (3.18).

Diels−Alder Adduct of (*Z*)-3 and Benzoquinone (48). Yellow solid. ^{1}H NMR: δ 6.64 (s, J = 10.8 Hz, 1 H), 6.56 (d, J = 10.4 Hz, 1 H), 3.14−3.17 (m, 2 H), 3.08−3.14 (m, 1 H), 2.84−2.93 (m, 2 H), 2.74−2.78 (m, 1 H), 2.57 (s, 1 H), 2.22−2.24 (m, 1 H), 1.97−2.04 (m, 1 H), 0.93 (t, J = 8.0 Hz, 1 H), 0.58 (q, J = 8.0 Hz, 6 H). ^{13}C {^{1}H} NMR: δ 201.9, 198.6, 172.9, 172.5, 140.2, 138.2, 133.4, 125.9, 58.1, 53.2, 48.7, 47.6, 44.4, 43.4, 27.1, 21.7, 7.8, 4.1. IR (neat, cm^{-1}): 1733, 1653, 1638, 1264, 1079, 1044, 877. Anal. Calcd (found) for $C_{23}H_{32}O_6Si$: C, 63.86 (63.80); H, 7.46 (7.57).

Diels−Alder Adduct of (*Z*)-3 and Naphthylquinone (49). ^{1}H NMR: δ 8.00−8.05 (m, 1 H), 7.95−7.99 (m, 1 H), 7.69−7.74 (m, 2 H), 3.70 (s, 3 H), 3.69 (s, 3 H), 3.31−3.36 (m, 2 H), 3.12−3.16 (m, 1 H), 2.94−2.98 (m, 1 H), 2.76−2.85 (m, 3 H), 2.25−2.30 (m, 1 H), 1.96−1.99 (m, 1 H), 0.94 (dd, J = 7.6, 8.4 Hz, 9 H), 0.59−0.65 (m, 6 H). ^{13}C {^{1}H} NMR: δ 199.6, 197.1, 172.9, 172.5, 134.8, 134.6, 133.6, 133.2, 127.6, 125.9, 58.1, 53.1, 48.2, 47.9, 44.5, 43.4, 27.0, 22.1, 7.9, 4.2. IR (neat, cm^{-1}): 2952, 2874, 2362, 2343, 1735, 1690, 1539, 1436, 1252, 1200, 1160, 1116, 1069. HRMS calcd (found) for $C_{27}H_{34}O_6Si$: 482.2125 (482.2122).

Diels−Alder Adduct of (*Z*)-3 and Tetracyanoethylene (50). Yellow solid, mp 137−139 °C. ^{1}H NMR: δ 3.74 (s, 3 H), 3.73 (s, 3 H), 2.92−3.16 (m, 6 H), 2.58−2.59 (m, 1 H), 1.06 (t, J = 8.0 Hz, 9 H), 0.92 (m, 3 H), 0.77−0.86 (m, 3 H). ^{13}C{^{1}H} NMR: δ 171.5, 171.3, 131.6, 125.2, 112.7, 111.8, 111.4, 110.5, 57.9, 53.7, 53.6, 43.5, 43.3, 42.1, 40.4, 32.8, 32.1, 7.9, 3.8. IR (neat, cm^{-1}): 1735, 1654, 1437, 1268, 1203. HRMS calcd (found) for $C_{23}H_{29}N_4O_4Si$ (MH^+): 453.1958 (453.1963).

Diels−Alder Adduct of (*Z*)-3 and 4-Phenyl-[1,2,4]triazole-3,5-dione (51). A solution of **1** (100 mg, 0.48 mmol), **2a** (12 mg, 0.025 mmol), $B(C_6F_5)_3$ (12 mg, 0.025 mmol), and $HSiEt_3$ (150 μL, 0.93 mmol) in toluene (20 mL) was heated at 110 °C for 2 h. The resulting solution of (*Z*)-**3** was cooled to 0 °C, treated with 4-phenyl-[1,2,4]triazole-3,5-dione (100 mg, 0.57 mmol), warmed to room temperature over 1 h, and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 3:1) gave **51** (178 mg, 73%) as a white solid, mp 45−47 °C. ^{1}H NMR (300 MHz): δ 7.50−7.30 (m, 5 H), 4.39 (br s, 1 H), 4.24 (d, J = 15.3 Hz, 1 H), 4.00 (d, J = 14.7 Hz, 1 H), 3.22 (d, J = 15.5 Hz, 1 H), 3.08 (br s, 2 H), 3.03 (d, J = 15.3, 1 H), 0.95 (t, J = 7.8 Hz, 9 H), 0.66 (q, J = 7.8 Hz, 3 H), 0.62 (q, J = 7.8 Hz, 3 H). ^{13}C{^{1}H} NMR (75 MHz): δ 171.8, 171.6, 154.1, 149.2, 131.5, 131.0, 129.2, 128.1, 125.4, 123.3, 58.6, 53.3, 53.2, 46.2, 46.1, 42.3, 42.3, 41.0, 7.2, 2.9. Anal. Calcd (found) for $C_{25}H_{33}N_3SiO_6$; H, 6.66 (6.79); C, 60.10 (59.74); N, 8.41 (8.22).

Diels−Alder Adduct of (*Z*)-3 and Methyl Propiolate (52). A solution of methyl propiolate (200 μL, 2.2 mmol), *Z*-**3** (49 mg, 0.15 mmol) and benzoquinone (≤1 mg) was heated at 130 °C for 24 h and concentrated under vacuum. Chromatography of the residue (SiO_2; hexanes−EtOAc = 35:1 → 4:1) gave **52** (31 mg, 51%). ^{1}H NMR: δ 7.95 (d, J = 1.2 Hz, 1 H), 7.82 (d, J = 1.2 Hz, 1 H), 3.87 (s, 3 H), 3.72 (s, 6 H), 3.59 (s, 2 H), 3.57 (s, 2 H), 0.89−0.94 (m, 9 H), 0.83−0.87 (m, 6 H). ^{13}C {^{1}H}

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NMR: δ 172.0, 167.8, 151.4, 139.9, 135.6, 133.6, 128.2, 126.4, 60.9, 53.3, 52.3, 42.1, 40.1, 7.7, 3.6. IR (neat, cm^{-1}): 2954, 2875, 1737, 1721, 1434, 1389, 1284, 1247, 1201, 1160, 1050, 1003. Anal. Calcd (found) for $C_{22}H_{30}O_6Si$: C, 62.04 (62.10); H, 7.44 (7.47).

Diels−Alder Adduct of (*Z*)-7 and Dimethyl Acetylenedicarboxylate (53). Pale yellow oil. ^1H NMR (300 MHz): δ 3.72 (br s, 6 H), 3.71 (br s, 6 H), 3.10−2.80 (m, 7 H), 1.35−1.10 (m, 12 H), 0.85 (t, J = 6.9 Hz, 9 H), 0.50 (m, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz): δ 172.6, 172.5, 169.0, 168.7, 138.1, 132.5, 130.5, 125.9, 58.9, 53.1, 52.3, 52.2, 43.7, 43.0, 32.2, 29.6, 27.0, 26.0, 13.9, 11.8. Anal. Calcd (found) for $C_{29}H_{46}SiO_8$; H, 8.42 (8.55); C, 63.24 (63.06).

Diels−Alder Adduct of (*Z*)-29 and *N*-Phenylmaleimide (54). Mixture (2:1) of diastereomers. ^1H NMR (major diastereomer): δ 7.40−7.44 (m, 2 H), 7.31−7.36 (m, 1 H), 7.18−7.24 (m, 2 H), 3.93 (d, J = 7.2 Hz, 2 H), 3.28−3.33 (m, 3 H), 3.18 (d, J = 1.2 Hz, 1 H), 2.47−2.62 (m, 6 H), 1.17 (s, 3 H), 1.17 (s, 3 H), 1.16 (s, 3 H), 0.98 (m, 9 H), 0.59−0.66 (m, 6 H). $^{13}C\{^1H\}$ NMR (major diastereomer): δ 180.4, 179.9, 135.5, 132.5, 129.4, 129.3, 128.8, 126.6, 67.9, 41.1, 40.4, 40.3, 39.3, 35.8, 27.5, 25.5, 7.7, 3.8. IR (neat, cm^{-1}): 2955, 2909, 2875, 1773, 1711, 1598, 1499, 1480, 1457, 1382, 1284, 1157, 1016, 691. HRMS calcd (found) for $C_{29}H_{41}NO_4Si$ (M^+): 495.2805 (495.2998).

Diels−Alder Adduct of (*Z*)-42 and *N*-Methylmaleimide (55). Mixture (5:1) of diastereomers. ^1H NMR (major diastereomer): δ 4.01−4.18 (m, 8 H), 2.89−3.06 (m, 6 H), 2.19−2.35 (m, 2 H), 1.16−2.22 (m, 12 H), 0.95 (t, J = 8.0 Hz, 9 H), 0.57 (q, J = 8.0 Hz, 6 H). $^{13}C\{^1H\}$ NMR (major diastereomer): δ 181.3, 180.5, 134.5, 123.8, 61.9, 61.8, 57.2, 41.3, 40.7, 37.4, 36.6, 29.7, 29.3, 25.5, 14.1, 14.0, 8.2, 7.8, 5.0, 3.9. IR (neat, cm^{-1}): 3458, 2957, 2905, 2875, 1772, 1733, 1437, 1385, 1366, 912, 863, 609. HRMS calcd (found) for $C_{31}H_{48}NO_{10}Si$ (MH^+): 622.3048 (622.3045).

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for new diynes and platinum complexes, and determination of regio- and stereochemistry of compounds (*Z*)-**3**, (*E*)-**3**, **38**, **42**, **45a** and **45b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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