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Synthesis of Carbobicyclic Compounds via Palladium−Catalyzed Cyclization/Hydrosilylation: Evidence for Reversible Silylpalladation

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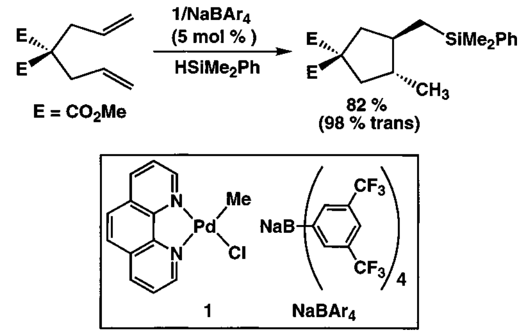
Cyclization/hydrosilylation of substituted 1-vinyl-1-(3-butenyl)cycloalkanes catalyzed by a 1:1 mixture of (phen)Pd(Me)Cl (**1**) and $NaBAr_4$ [phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$] formed silylated spirocycles in high yield with excellent regio and diastereoselectivity. Cyclization/hydrosilylation of substituted 3-(3-butenyl)cycloalkenes or 2,3-diallyl-5,6-dimethyl-1,4-hydroquinone diacetate (**16**) formed silylated fused bicyclic complexes in good yield. Reaction of substituted 1,6,11-nonatrienes with silane catalyzed by **1**/$NaBAr_4$ led to cascade cyclization with hydrosilylation. This latter procedure was employed in the synthesis of silylated bicyclopentanes and a linear triquinane.

Introduction

Many naturally occurring molecules possess a polycyclic core, typically heavily substituted and highly oxygenated, and often containing one or more five-membered rings.[1] As a result, considerable effort has been directed toward the development of efficient methods for the synthesis of polycyclic organic compounds.[2] We recently reported several related procedures for the synthesis of silylated five- and six-membered carbocycles via the palladium-catalyzed cyclization/hydrosilylation of functionalized 1,6- and 1,7-dienes, respectively.[3−10] For example, reaction of dimethyl diallylmalonate and dimethylphenylsilane catalyzed by a 1:1 mixture of (phen)-Pd(Me)Cl (**1**) and $NaBAr_4$ [phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$] formed the corresponding silylated cyclopentane in 82% yield with high trans selectivity (Scheme 1).[6] The high activity and good selectivity displayed in the formation of silylated carbocycles suggested that this protocol might also be applicable in the synthesis of carbobicyclic compounds. Here we report the synthesis of spiro-, fused, and tethered bicyclic compounds via palladium-catalyzed cyclization/hydrosilylation.

Results and Discussion

Scheme 1



Cyclization/Hydrosilylation of Dienes. The synthesis of monocyclic compounds via palladium-catalyzed cyclization/hydrosilylation revealed several substitution patterns which could potentially be exploited in the synthesis of bicyclic compounds.[6] For example, cyclization/hydrosilylation tolerated substitution at the allylic positions of the diene, which suggested that 1-vinyl-1-(3-butenyl) carbocycles would also undergo cyclization/hydrosilylation to form functionalized spirocyclic derivatives. To this end, cyclization/hydrosilylation of vinyl cyclobutyl (**2**), cyclopentyl (**3**), and cyclohexyl derivatives (**4**) gave the corresponding silylated spirocyclic compounds **5**−**10** in good yield and with excellent regio- and diastereoselectivity (Table 1, entries 1−6). We have previously established the regiochemistry of cyclization/hydrosilylation as that resulting from transfer of the silane to the less hindered olefin along with trans stereochemistry about the newly formed C−C bond.[2,5] Because dimethylbenzylsilyl[11] and pentamethylsiloxy[9] derivatives can be oxidized in high yield under mild conditions,[12] spirocycles **6**, **8**, and **10** are direct precursors to spirocyclic alcohols.

Palladium-catalyzed cyclization/hydrosilylation also tolerated substitution at the terminal olefinic position,[6] which pointed to the feasibility of forming fused bicyclic

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[1] (a) Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467. (b) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141.

[2] (a) Paquette L. A. *Top. Curr. Chem.* **1979**, *79*, 41. (b) Sannigrahi, M. *Tetrahedron* **1999**, *55*, 9007.

[3] Widenhoefer, R. A.; DeCarli, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 3805.

[4] Stengone, C. N.; Widenhoefer, R. A. *Tetrahedron Lett.* **1999**, *40*, 1451.

[5] Perch, N. S.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **1999**, *121*, 6960.

[6] Widenhoefer, R. A.; Stengone, C. N. *J. Org. Chem.* **1999**, *64*, 8681.

[7] Perch, N. S.; Pei, T.; Widenhoefer, R. A. *J. Org. Chem.* **2000**, *65*, 3836.

[8] Widenhoefer, R. A.; Vadehra, A. *Tetrahedron Lett.* **1999**, *40*, 8499.

[9] Pei, T.; Widenhoefer, R. A. *Org. Lett.* **2000**, *2*, 1469.

[10] Pei, T.; Widenhoefer, R. A. *Tetrahedron Lett.* **2000**, *41*, 7597.

[11] Mirura, K.; Hondo, T.; Nakagawa, T.; Takahashi, T.; Hosomi, A. *Org. Lett.* **2000**, *2*, 385.

[12] Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599.

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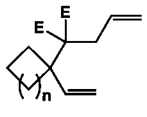
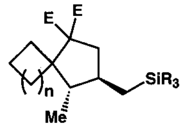
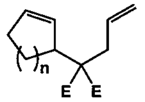
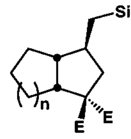
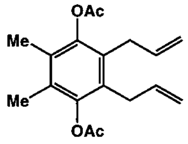
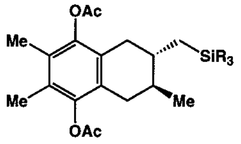
Table 1. Cyclization/Hydrosilylation of Dienes Catalyzed by a 1:1 Mixture of 1 and $NaBAr_4$ in DCE at Room Temperature Where E = CO_2Me

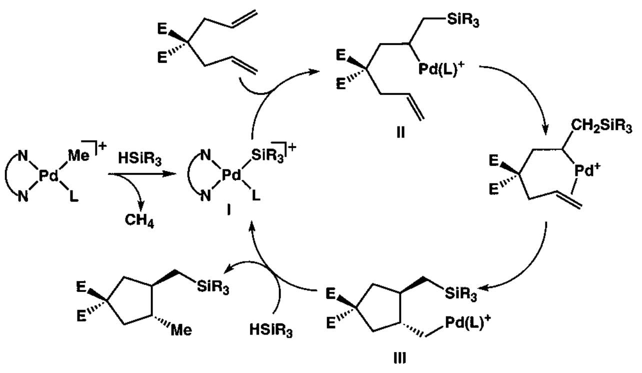
entry	diene	silane	catalyst load (%)	time (min)	carbocycle	yield (%)[a]	dr[b]
							
1	2 (n = 1)	$HSiEt_3$	5	5	5	98	>50:1
2		$HSiMe_2Bn$	5	30	6	83	>50:1
3	3 (n = 2)	$HSiEt_3$	5	30	7	98	>50:1
4		$HSiMe_2Bn$	5	90	8	95	>50:1
5	4 (n = 3)	$HSiEt_3$	5	60	9	94	>50:1
6		$HSiMe_2OTMS$	5	40	10	92	>50:1
							
7	11 (n = 1)	$HSiEt_3$	5	20	12	71	43:1
8		$HSiMe_2Bn$	10	120	13	71	39:1
9	14 (n = 2)	$HSiMe_2Ph$	5	120	15	69	33:1[c]
							
10	16	$HSiEt_3$	5	30	17	64	6:1
11			10	20		99	8:1
12		$HSiMe_2Ph$	10	60	18	93	12:1
13		$HSiMe_2Bn$	10	15	19	40	20:1

[a] Yield refers to isolated material of >95% purity. [b] Diastereomeric ratio determined by GC analysis of the crude reaction mixture. [c] Isolated material contained 6% of the silylated uncyclized isomer.

ring systems from the cyclization/hydrosilylation of 3-(3-butenyl)cycloalkenes. For example, reaction of dimethyl allyl(3-cyclopentenyl)malonate (**11**) with $HSiEt_3$ or $HSiMe_2Bn$ catalyzed by **1**/$NaBAr_4$ gave the corresponding bicyclo[3.3.0]octanes **12** or **13**, respectively, in good yield and with excellent regio- and diastereoselectivity (Table 1, entries 7 and 8). Similarly, cyclization/hydrosilylation of the allylcyclohexenyl derivative **14** formed bicyclo[4.3.0]nonane **15** in 69% yield with good diastereoselectivity (33:1) (Table 1, entry 9). Noteworthy was the selective formation of three contiguous stereocenters on the more substituted cyclopentane ring of compounds **12**, **13**, and **15**. Cyclization/hydrosilylation of 2,3-diallyl-5,6-dimethyl-1,4-hydroquinone diacetate (**16**) led to the isolation of the silylated tetrahydronaphthalene derivatives **17**–**19** (Table 1, entries 10–13) in good yield with good diastereoselectivity.

Mechanistic Insights. We have previously proposed a mechanism for palladium-catalyzed cyclization/hydrosilylation initiated by β-migratory insertion of an olefin into the Pd–Si bond of the palladium silyl intermediate **I** to form palladium alkyl intermediate **II** (Scheme 2).[6] Coordination and insertion of the pendant olefin of **II** into the Pd–C bond could then form the palladium methylcyclopentyl intermediate **III** which could react with silane to release the silylated carbocycle and regenerate **I**. Both the formation of **I** from reaction of cationic palladium alkyl complexes with silane and the insertion of unfunctionalized olefins into the Pd–Si bond of **I** have been established.[13] The proposed mechanism also accounts for many of our experimental observations. In particular, the transfer of the silane to the less hindered olefin of dienes **2**–**4**, **11**, and **14** is consistent with a mechanism initiated by silylpalladation rather than hydropalladation.

Scheme 2



Brookhart has reported that unfunctionalized alkenes such as 1-hexene undergo rapid and reversible β-migratory insertion into the Pd–Si bond of **I**.[13] In contrast, the reversibility of silylpalladation in palladium-catalyzed cyclization/hydrosilylation has not been established and we have previously considered that coordination of the

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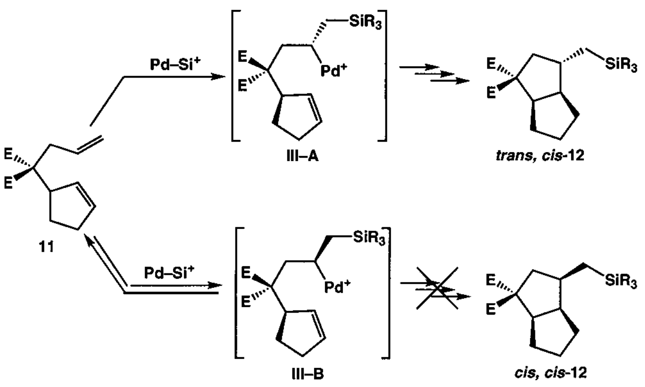
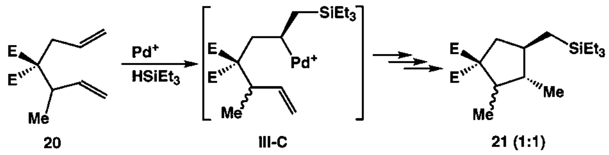
[13] LaPoint, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

Scheme 3



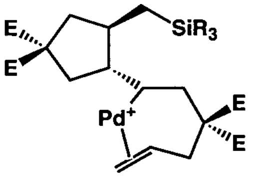
Scheme 4



pendant olefin of palladium alkyl complex **II** may render silylpalladation irreversible by filling the coordination site required for β-silyl elimination.[7] However, the exclusive ($>$97%) formation of the trans,cis diastereomer of **12** (*trans,cis*-**12**) (or the formation of *trans,cis*-**13** or *trans,cis*-**15**) in the cyclization/hydrosilylation of **11** strongly suggests that silylpalladation is reversible under these conditions. Silylpalladation of the unhindered olefin of **11** could form two diastereomeric palladium alkyl intermediates, **III-A** and **III-B** (Scheme 3). Of these two, only **III-A** can cyclize to form *trans,cis*-**12**.[14] The failure to observe *cis,cis*-**12** in the cyclization of **11** indicates that intermediate **III-B** is either not formed under reaction conditions or once formed, undergoes β-silyl elimination to regenerate **11** and **I**.[15]

We have previously observed that cyclization/hydrosilylation of 4,4-dicarbomethoxy-3-methyl-1,6-heptadiene (**20**) forms 1,1-dicarbomethoxy-2,3-dimethyl-4-triethylsilylmethylcyclopentene (**21**) as a 1:1 mixture of the diastereomers (Scheme 4).[6] This observation is consistent with the initial, nonselective silylpalladation of the less hindered olefin of **20** and formation of palladium alkyl intermediate **III-C** as a 1:1 mixture of diastereomers (Scheme 4). Therefore, it appears unlikely that intermediate **III-A** is formed selectively in the cyclization/hydrosilylation of **11** and strongly suggests that silylpalladation of **11** by **I** is rapid and reversible. Furthermore, the failure to observe significant amounts ($<$2%) of dimethyl 2-cyclopentenyl-3-(triethylsilyl)butylmalonate (resulting from hydrosilylation of **11** without cyclization) indicates that β-silyl elimination from **III-B** is fast relative to reaction of **III-B** with free silane.[16]

Cascade Cyclization/Hydrosilylation of Trienes. The fused- and spirobicyclic compounds shown in Table 1 were synthesized by closing a ring on an existing monocyclic ring system. A more desirable approach to the synthesis of bicyclic compounds would be through multiple cyclization of a suitably designed triene. Specifically, if the initially formed palladium cyclopentylmethyl intermediate **III** could be trapped by a tethered olefin prior to silylative cleavage, a bicyclic compound would be formed (Scheme 2). To this end, reaction of 1,6-11-undecatriene **22** with HSiEt$_3$ or HSiMe$_2$Bn catalyzed by **1**/NaBAr$_4$ led to formation of the tethered bicyclic derivatives **23** or **24**, respectively, in $>$80% isolated yield as a single diastereomer by ^{1}H and ^{13}C NMR analysis (Table 2, entries 1 and 2). Noteworthy was the formation of four contiguous stereocenters with high stereoselectivity in these transformations. The absence of any silylated monocyclized products in the conversion of **22** to either **23** or **24** indicates that β-migratory insertion of the pendant olefin of intermediate **III-D** is significantly faster than reaction of **III-D** with free silane.



III–D

Reaction of tetrapivolate **25** with silane catalyzed by **1**/NaBAr$_4$ led to the isolation of a 10:1 mixture of silylated bicyclopentane **26** along with the corresponding monocyclized isomer (Table 2, entry 3). Cascade cyclization/hydrosilylation tolerated the presence of allylic gem dimethyl groups, and triene **27** cyclized to form bicyclopentane **28** with excellent regio and diastereoselectivity (Table 2, entry 4). In contrast, palladium-catalyzed reaction of triene **29**, which possessed substitution at one of the terminal olefinic carbon atoms, with HSiEt$_3$ led to formation of a 2:1 mixture of the desired silylated bicyclopentane **30** along with the monocyclized/silylated product (Table 2, entry 5). Palladium-catalyzed cascade cyclization/hydrosilylation was also employed in the synthesis of a fused tricyclic system. For example, reaction of 3,5-bis(3-butenyl)cyclopentane **31** with HSiEt$_3$ catalyzed by **1**/NaBAr$_4$ led to the isolation of a silylated linear triquinane **32** in 74% yield as a 20:1 mixture of isomers (Table 2, entry 6).[17] The selective conversion of **31** to **32** also presumably requires reversible silylpalladation to achieve high selectivity.

The radical-mediated or transition metal-catalyzed cascade cyclization of polyolefins and polyenynes has been an area of considerable interest.[18] The majority of transition-metal-catalyzed procedures are initiated by oxidative addition of an (sp^2)C−X (X = Br, I, OTf) bond to Pd(0).[19,20] Alternative pathways for initiation of cascade cyclization include the hydro-,[21] silyl-,[22] or carbometala-

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[14] Cyclization of **III-B** would be disfavored because it would lead either to a highly strained trans-fused bicyclo[3.3.0]octane ring structure or to a cis arrangement of the triethylsilyl and methylene group about the newly formed C−C bond (the origin of the stereoselectivity of ring closure is not understood).

[15] This requires both β-silyl elimination and olefin dissociation.

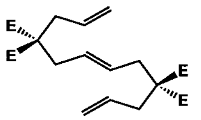
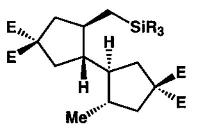
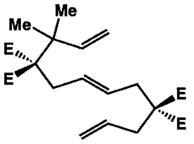
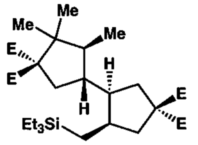
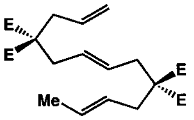
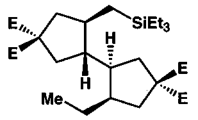
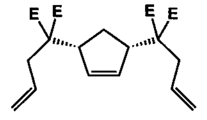
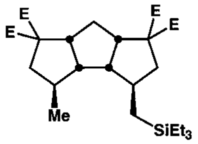
[16] The conversion of **11** to **12** or **13** and also the conversion of **14** to **15** and **31** to **32** may be a special cases, and we cannot conclude that all cyclization/hydrosilylation occurs via reversible silylpalladation. Nevertheless, these experiments establish reversible silylpalladation as a viable pathway in palladium-catalyzed diene cyclization/hydrosilylation.

[17] Attempts to extend the cascade cyclization/hydrosilylation to the cyclization of tetraenes led to the formation of inseparable mixtures of di- and tricyclized isomers.

[18] Malacria, M. *Chem. Rev.* **1996**, *96*, 289.

[19] Negishi, E.; Coperet, C.; Ma, S.; Liou, S. Y.; Lium F. *Chem. Rev.* **1996**, *96*, 365.

Table 2. Cascade Cyclization/Hydrosilyation of Trienes Catalyzed by a 1:1 Mixture of 1 and NaBAr$_4$ (10 mol %) in DCE at Room Temperature

entry	triene	silane	time	carbocycle	yield (%)[a]	isomer ratio[b]
1	 **22** (E = CO_2Me)	$HSiEt_3$	20 min	 **23**	81	>25:1
2		$HSiMe_2Bn$	1 h	**24**	85	>25:1
3	**25** (E = CH_2OPv)	$HSiEt_3$	4 h	**26**	71	10:1[c]
4	 **27** (E = CO_2Me)	$HSiEt_3$	2 h	 **28**	76	>25:1
5	 **29** (E = CO_2Me)	$HSiEt_3$	12 h	 **30**	84	2:1[c]
6	 **31** (E = CO_2Me)	$HSiEt_3$	6 h[d]	 **32**	74	20:1

[a] Yield refers to isolated material of >95% purity. [b] Isomer ratio determined by GC analysis of the isolated material. [c] Minor isomer was the monocyclization/hydrosilylation product. [d] Reaction run at 40 °C.

tion[23] of an alkyne. The palladium-catalyzed cascade cyclization/hydrosilylation reactions reported here are unusual as these transformations are initiated by silylpalladation of an unactivated olefin. Previous examples of cascade cyclization initiated by olefin metalation are limited to the titanium-catalyzed cascade carboalumination of dienes and trienes[24] and the yttrium-catalyzed cascade cyclization/hydrosilylation of trienes.[25] However, due to the extreme Lewis acidity of both the organoaluminum reagent and group IV catalyst in the former case and the yttrocene catalyst in the latter case, these procedures are restricted primarily to the cyclization of unfunctionalized substrates.

Conclusions

Several types of spiro- and fused bicyclic ring systems were constructed via palladium-catalyzed cyclization/hydrosilylation of carbocyclic dienes. Similarly, several silylated bicyclopentanes and a linear triquinane derivative were formed via the palladium-catalyzed cascade cyclization/hydrosilylation of functionalized trienes. The selective conversion of **11** to **12** or **13** and also the selective conversion of **14** to **15** and **31** to **32** was consistent with a mechanism initiated by rapid and reversible silylpalladation.

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 100 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Flash chromatography was performed employing 200−400 mesh silica gel (EM). Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). Methylene chloride and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Triethylsilane (Aldrich), benzyldimethylsilane (Petrarch), and pentamethyldisiloxane (Gelest) were used as received. Precatalysts (phen)PdMeCl[26] (**1**) and NaBAr$_4$[27] were prepared employing known

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[20] (a) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (b) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454. (c) Wu, G.; Lamaty, F.; Negishi, E. *J. Org. Chem.* **1989**, *54*, 2507. (d) Ashimori, A.; Overman, L. E. *J. Org. Chem.* **1992**, *57*, 4571. (e) Sugihara, T.; Coperet, C.; Owczarczyk, Z.; Harring, L. S.; Negishi, E. *J. Am. Chem. Soc.* **1994**, *116*, 7923. (f) Burns, B.; Grigg, R.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakun, T. *Tetrahedron Lett.* **1989**, *30*, 1135. (g) Zhang, Y.; Wu, G.; Agnel, G.; Negishi, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 8590. (h) Meyer, F. E.; Parsons, P. J.; de Meijere, A. *J. Org. Chem.* **1991**, *56*, 6487. (i) Overman, L. E.; Ableman, M. M.; Kucera, D. J.; Tran, V. D.; Ricca, D. J. *Pure Appl. Chem.* **1992**, *64*, 1813.

[21] (a) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421. (b) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 701. (c) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1992**, *114*, 791. (d) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255.

[22] Ojima, I.; McCullagh, J. V.; Shay, W. R. *J. Organomet. Chem.* **1996**, *521*, 421.

[23] Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104.

[24] (a) Kondakov, D. Y.; Wang, S.; Negishi, E. *Tetrahedron Lett.* **1996**, *37*, 3803. (b) Negishi, E.; Jensen, M. D.; Kondakov, D. Y.; Wang, S.; *J. Am. Chem. Soc.* **1994**, *116*, 8404.

[25] Molander, G. A.; Retsch, W. H. *J. Org. Chem.* **1998**, *63*, 5507.

[26] De Delice, V.; Albano, B. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem.* **1991**, *403*, 269.

[27] Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

procedures. The synthesis of the dienes and trienes employed in this study are described in the Supporting Information.

General Procedure for Cyclization/Hydrosilylation. Silane (1.5 mmol) was added via syringe to a solution of (phen)-PdMeCl (**1**) (9 mg, 0.027 mmol), NaBAr$_4$ (30 mg, 0.034 mmol), and diene (0.50 mmol) or triene (0.25 mmol) in 5 mL DCE at 0 °C, warmed to room temperature (or 40 °C in the case of **30**), and stirred for the time indicated in Tables 1 and 2. The solvent was evaporated and the residue was chromatographed on silica gel to give the silylated carbocycles as colorless oils.

The stereochemistry of the silylated carbocycles was assigned based on the previously established trans selectivity of cyclization/hydrosilylation. In addition, the stereochemistry of the diquinane **12** and linear triquinane **32** were unambiguously determined through combined COSY and NOE analysis (see Supporting Information).

Dimethyl 7-Triethylsilylmethyl-8-methyl-spiro[3.4]-octane-5,5-dicarboxlate (5). ^{1}H NMR: δ 3.77 (s, 3 H), 3.66 (s, 3 H), 2.69 (dd, J = 9.2, 14.0 Hz, 1 H), 2.50−2.56 (m, 1 H), 1.97−2.04 (m, 1 H), 1.84−1.90 (m, 1 H), 1.59−1.78 (m, 4 H), 1.50 (dd, J = 8.4, 14.0 Hz, 1 H), 1.35−1.43 (m, 1 H), 1.11 (d, J = 6.8 Hz, 3 H), 0.91 (t, J = 8.0 Hz, 9 H), 0.81 (dd, J = 2.0, 14.4 Hz, 1 H), 0.50 (q, J = 8.0 Hz, 6 H), 0.26 (dd, J = 11.6, 14.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.7, 171.9, 65.9, 53.2, 52.4, 52.2, 51.1, 40.0, 37.8, 28.4, 25.3, 16.3, 16.0, 12,5, 7.6, 4.0. Anal. Calcd (found) for $C_{20}H_{36}O_4Si$: H, 9.84 (9.76); C, 65.17 (65.08).

Dimethyl 7-Benzyldimethylsilylmethyl-8-methyl-spiro-[3.4]octane-5,5-dicarboxylate (6). ^{1}H NMR: δ 7.20 (t, J = 7.6 Hz, 2 H), 7.06 (t, J = 7.6 Hz, 1 H), 6.98 (d, J = 7.2 Hz, 2 H), 3.76 (s, 3 H), 3.70 (s, 3 H), 2.71 (dd, J = 8.8, 13.6 Hz, 1 H), 2.56 (td, J = 8.8, 11.2 Hz, 1 H), 2.08 (s, 2 H), 1.98−2.05 (m, 1 H), 1.58−1.89 (m, 6 H), 1.49 (dd, J = 8.8, 13.6 Hz), 1.34−1.44 (m, 1 H), 1.58−1.89 (m, 6 H), 1.49 (dd, J = 8.8, 13.6 Hz), 1.34−1.44 (m, 1 H), 1.09 (d, J = 6.8 Hz, 3 H), 0.84 (dd, J = 2.4, 14.8 Hz, 1 H), 0.28 (dd, J = 11.6, 14.8 Hz, 1 H), −0.01 (s, 3 H), −0.02 (s, 3 H). ^{13}C{^{1}H} NMR: δ 172.6, 171.9, 140.4, 128.3, 124.1, 65.9, 53.1, 52.6, 52.3, 50.8, 40.0, 37.7, 28.2, 26.3, 25.3, 19.9, 16.0, 12.4, −2.3, −2.6. IR (neat, cm^{-1}): 3023, 2951, 2894, 1737, 1730, 1493, 1453. Anal. Calcd (found) for $C_{21}H_{40}O_5Si_2$: H, 8.51 (8.76); C, 68.62 (68.53).

Dimethyl 3-(Triethylsilylmethyl)-4-methyl-spiro[4.4]-nonane-1,1-dicarboxylate (7). ^{1}H NMR: δ 3.70 (s, 3 H), 3.63 (s, 3 H), 2.17 (dd, J = 6.8, 13.6 Hz, 1 H), 2.13 (d, J = 15.6 Hz, 1 H), 2.02 (dd, J = 11.6, 13.6 Hz, 1 H), 1.53−1.65 (m, 6 H), 1.30−1.43 (m, 3 H), 1.19 (dd, J = 3.6, 12.4 Hz, 1 H), 1.13 (d, J = 6.8 Hz, 3 H), 1.06 (td, J = 3.6, 12.8 Hz, 1 H), 0.92 (t, J = 8.0 Hz, 9 H), 0.49 (q, J = 8.0 Hz, 6 H), 0.46−0.53 (m, 1 H). ^{13}C{^{1}H} NMR: δ 171.9, 171.7, 69.9, 52.1, 50.8, 49.6, 41.4, 40.6, 36.6, 27.3, 25.6, 24.0, 22.5, 19.4, 17.0, 7.6, 4.0. IR (neat, cm^{-1}): 2950, 2874, 1732, 1432, 1242, 756, 721. Anal. Calcd (found) for $C_{22}H_{40}O_4Si$: H, 10.16 (9.99); C, 66.62 (66.58).

Dimethyl 3-Benzyldimethylsilylmethyl-4-methyl-spiro-[4.4]nonane-1,1-dicarboxylate (8). ^{1}H NMR: δ 7.20 (t, J = 7.2 Hz, 2 H), 7.06 (t, J = 7.2 Hz, 1 H), 6.98 (d, J = 8.0 Hz, 2 H), 3.69 (s, 3 H), 3.67 (s, 3 H), 2.68 (dd, J = 10.0, 14.4 Hz, 1 H), 2.06−2.15 (m, 1 H), 2.08 (s, 2 H), 1.95 (qd, J = 6.8, 10.4 Hz, 1 H), 1.68 (dd, J = 7.2, 10.4 Hz, 1 H), 1.43−1.67 (m, 7 H), 1.21−1.26 (m, 1 H), 0.85 (d, J = 7.2 Hz, 3 H), 0.82 (dd, J = 2.4, 14.8 Hz, 1 H), 0.38 (dd, J = 12.0, 14.8 Hz, 1 H), −0.01 (s, 3 H), −0.02 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.2, 172.0, 140.4, 128.3, 124.1, 67.3, 57.9, 52.4, 52.2, 40.7, 38.4, 34.8, 30.1, 26.7, 26.3, 20.6, 13.0, −2.3, −2.6. IR (neat, cm^{-1}): 3023, 2950, 2871, 1731, 1492, 1451, 1432, 1247, 1206. Anal. Calcd (found) for $C_{24}H_{36}O_4$-Si: H, 8.71 (8.79); C, 69.19 (68.83).

Dimethyl 3-Triethylsilylmethyl-4-methyl-spiro[4.5]-decane-1,1-dicarboxylate (9). ^{1}H NMR: δ 3.70 (s, 3 H), 3.64 (s, 3 H), 2.17 (dd, J = 6.8, 13.2 Hz, 1 H), 2.13 (d, J = 15.6 Hz, 1 H), 2.02 (dd, J = 11.6, 13.6 Hz, 1 H), 1.53−1.69 (m, 6 H), 1.31−1.43 (m, 3 H), 1.19 (dd, J = 3.6, 12.4 Hz, 1 H), 1.12 (d, J = 6.8 Hz, 3 H), 1.07 (td, J = 3.2, 12.8 Hz, 1 H), 0.92 (t, J = 8.0 Hz, 9 H), 0.85−0.89 (overlapping region, 1 H), 0.50 (q, J = 8.0 Hz, 6 H), 0.44−0.50 (overlapping region, 1 H). ^{13}C{^{1}H} NMR: δ 171.9, 171.7, 69.7, 52.1, 50.8, 49.6, 41.4, 40.6, 36.6, 27.3, 25.6, 23.9, 22.5, 19.4, 17.0, 7.6, 4.0. IR (neat, cm^{-1}): 2949, 2874, 1733, 1432, 1242, 1207. Anal. Calcd (found) for $C_{22}H_{40}O_4$-Si: H, 10.16 (9.99); C, 66.62 (66.58).

Dimethyl 3-[Dimethyl(trimethylsiloxy)silyl]methyl-4-methyl-spiro[4.5] decane-1,1-dicarboxylate (10). ^{1}H NMR: δ 3.71 (s, 3 H), 3.65 (s, 3 H), 2.21 (dd, J = 7.2, 13.6 Hz, 1 H), 2.23 (d, J = 11.6, 13.6 Hz, 1 H), 2.06 (dd, J = 11.6, 13.6 Hz, 1 H), 1.54−1.76 (m, 6 H), 1.29−1.43 (m, 3 H), 1.18 (dd, J = 3.6, 12.4 Hz, 1 H), 1.13 (d, J = 7.2 Hz, 3 H), 1.07 (td, J = 7.2, 12.8 Hz, 1 H), 0.89 (dd, J = 4.4, 14.8 Hz, 1 H), 0.5 (dd, J = 10.4, 14.8 Hz, 1 H), 0.60 (s, 9 H), 0.47 (s, 6 H). ^{13}C{^{1}H} NMR: δ 171.9, 171.7, 69.6, 52.1, 49.9, 49.8, 40.9, 40.6, 36.5, 27.4, 26.5, 25.6, 24.0, 22.5, 17.0, 2.1, 1.4, 1.3. IR (neat, cm^{-1}): 2951, 2859, 1730, 1451, 1433, 1252, 1056. Anal. Calcd (found) for $C_{21}H_{40}O_2$-Si_2: H, 9.40 (9.61); C, 58.83 (58.57).

Dimethyl 3-Triethylsilylmethyl-hexahydropentalene-1,1-dicarboxylate (12). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.72 (s, 3 H), 3.68 (s, 3 H), 3.24 (q, J = 8.8 Hz, 1 H), 2.70 (dd, J = 6.9, 13.4 Hz, 1 H), 2.11 (dq, J = 4.1, 8.8 Hz, 1 H), 1.74−1.83 (m, 2 H), 1.62−1.69 (m, 2 H), 1.50−1.55 (m, 1 H), 1.51 (dd, J = 9.6, 13.0 Hz, 1 H), 1.32−1.38 (m, 1 H), 1.16−1.21 (m, 1 H), 0.93 (t, J = 8.1 Hz, 9 H), 0.76 (dd, J = 4.1, 14.6 Hz, 1 H), 0.54 (dq, J = 1.3, 7.8 Hz, 6 H), 0.35 (dd, J = 9.9, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.7, 172.2, 63.1, 54.9, 52.7, 52.2, 49.9, 44.5, 42.1, 30.9, 29.74, 26.9, 16.9, 7.7, 4.0. Anal. Calcd (found) for $C_{19}H_{34}O_4Si$: C, 64.36 (64.44); H, 9.67 (9.78).

Dimethyl 3-Dimethylbenzylsilylmethyl-hexahydropentalene-1,1-dicarboxylate (13). ^{1}H NMR: δ 7.20 (t, J = 7.2 Hz, 2 H), 7.06 (t, J = 7.2 Hz, 1 H), 6.99 (d, J = 7.2 Hz, 2 H), 3.70 (s, 3 H), 3.69 (s, 3 H), 3.23 (q, J = 8.8 Hz, 1 H), 2.69 (dd, J = 6.8, 13.2 Hz, 1 H), 2.09 (s, 2 H), 2.06−2.14 (overlapping region, 1 H), 1.64−1.85 (m, 4 H), 1.46−1.56 (m, 2 H), 1.27−1.35 (m, 4 H), 1.14−1.22 (m, 1 H), 0.76 (dd, J = 4.8, 14.4 Hz, 1 H), 0.37 (dd, J = 10.0, 14.4 Hz, 1 H), 0.00 (s, 3 H), −0.01 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.7, 172.1, 140.4, 128.4, 124.1, 54.6, 49.9, 44.3, 42.0, 31.0, 29.7, 26.9, 26.3, 20.6, −2.5, −2.7. IR (neat, cm^{-1}): 3023, 2951, 2867, 1737, 1731, 1493, 1453, 1434. Anal. Calcd (found) for $C_{22}H_{32}O_4Si$: H, 8.30 (8.20); C, 68.00 (68.18).

5,8-Diacetoxy-2-triethylsilylmethyl-3,6,7-trimethyl-1,4-dihydronaphthalene (17). ^{1}H NMR: δ 2.3−2.6 (m, 2 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.78 (s, 6 H), 1.22 (m, 4 H), 0.76 (d, J = 6.0 Hz, 3 H), 0.69 (t, J = 8.0 Hz, 9 H), 0.29 (q, J = 8.0 Hz, 6 H), 0.19−0.00 (m, 1 H). One Et_3SiCH_2 proton obscured. ^{13}C-{^{1}H} NMR: δ 169.3, 145.3, 127.9, 127.2, 35.5, 32.6, 20.9, 20.8, 20.1, 15.9, 13.2, 7.9, 7.8, 7.7, 4.5, 3.6, 3.5. IR (CCl_4, cm^{-1}): 3053, 2408, 2350, 1755, 1714, 1681, 1650, 1556, 1538, 1504, 1265, 1200, 1077, 896, 738, 705. Anal. Calcd (found) for $C_{24}H_{38}SiO_4$: H, 9.17 (9.28); C, 69.04 (68.80).

5,8-Diacetoxy-3,6,7-trimethyl-2-dimethylphenylsilyl-methyl-1,4-dihydronaphthalene (18). ^{1}H NMR: δ 7.53−7.51 (m, 2 H), 7.36−7.26 (m, 3 H), 2.80−2.60 (m, 2 H), 2.33 (s, 6 H), 2.15 (d, J = 3.6 Hz, 3 H), 2.02 (s, 6 H), 1.54−1.51 (m, 4 H), 0.91−0.86 (m, 1 H), 0.32 (s, 3 H), 0.30 (s, 3 H), 0.25−0.24 (m, 1 H). ^{13}C{^{1}H} NMR: δ 169.0, 144.7, 139.5, 133.4, 133.3, 128.7, 127.7, 127.6, 127.5, 126.6, 57.8, 34.0, 20.3, 20.2, 20.1, 20.0, 19.5, 18.0, 13.0, 12.6, −2.3, −3.4. IR (neat, cm^{-1}): 3054, 2956, 2408, 2350, 1757, 1556, 1427, 1369, 1265, 1247, 1198, 1112, 1079, 1013, 894, 834, 738, 703. Anal. Calcd (found) for $C_{26}H_{34}SiO_4$: H, 7.81 (8.17); C, 71.19 (71.37).

5,8-Diacetoxy-3,6,7-trimethyl-2-dimethylbenzylsilyl-methyl-1,4-dihydronaphthalene (19). ^{1}H NMR: δ 7.20−6.96 (m, 5 H), 2.85−2.45 (m, 2 H), 2.31 (s, 3 H), 2.28 (s, 3 H), 2.08 (s, 2 H), 2.02 (s, 6 H), 1.62−1.39 (m, 2 H), 1.30−1.21 (m, 2 H), 0.95 (d, J = 6.4 Hz, 3 H), 0.40−0.30 (m, 1 H), 0.00 (s, 3 H), −0.02 (s, 3 H). One $BnMe_2SiCH_2$ proton partially obscured. ^{13}C{^{1}H} NMR: δ 170.1, 170.0, 146.0, 141.3, 141.2, 129.3, 129.2, 128.5, 128.1, 128.0, 125.1, 125.0, 36.5, 35.2, 33.2, 27.4, 23.4, 21.59, 21.55, 20.7, 20.4, 15.1, 14.0, −1.0, −1.6. Anal. Calcd (found) for $C_{27}H_{36}SiO_4$: H, 8.02 (8.29); C, 71.64 (71.89).

Tetramethyl 2-Triethylsilylmethyl-2′-methyl-bicyclopentyl-4,4,4′,4′-tetracarboxylate (23). ^{1}H NMR: δ 3.65−3.67 (s, 12 H), 2.50−2.54 (m, 2 H), 2.44 (dd, J = 6.4, 12.6 Hz, 2 H), 2.13−2.22 (m, 2 H), 1.48−1.87 (m, 7 H), 0.86−0.92 (m, 12 H), 0.48 (q, J = 8.0 Hz, 6 H), 0.19 (dd, J = 10.8, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.6, 173.5, 58.3, 58.2, 53.1, 48.1, 45.8, 43.2, 39.8, 38.1, 34.4, 33.7, 17.5, 14.9, 7.8, 4.2. IR (neat, cm^{-1}): 3732, 3646, 3626, 2952, 2874, 1734, 1653, 1558, 1457, 1253, 1196, 1164, 1144, 1104, 1016, 960, 861, 759, 727. Anal. Calcd (found) for $C_{26}H_{44}O_8Si$: C, 60.91 (60.43); H, 8.65 (8.64).

Tetramethyl 2-Benzyldimethylsilylmethyl-2′-methylbicyclopentyl-4,4,4′,4′-tetracarboxylate (24). ^{1}H NMR: δ 7.15 (m, 2 H), 7.00−7.05 (m, 1 H), 6.95−6.98 (m, 2 H), 3.68−3.70 (s, 12 H), 2.54 (d, *J* = 6.4 Hz, 1 H), 2.45−2.51 (m, 1 H), 2.23 (dd, *J* = 6.8 Hz, 13.4 Hz, 1 H), 2.16 (dd, *J* = 6.8 Hz, 13.4 Hz, 1 H), 2.07 (s, 2 H), 1.79−1.91 (m, 2 H), 1.54−1.72 (m, 6 H), 0.92 (d, *J* = 5.6 Hz, 3 H), 0.84−0.86 (m, 1 H), 0.25 (dd, *J* = 10.4, 14.6 Hz, 1 H), −0.03 (s, 3 H), −0.04 (s, 3 H). ^{13}C{^{1}H} NMR: δ 173.5, 173.4, 140.3, 128.5, 128.4, 124.2, 58.2, 58.1, 52.9, 45.7, 43.1,4 3.0, 39.7, 38.0, 34.3, 33.7, 26.3, 18.6, 17.5, −2.3, −2.5. IR (neat, cm^{-1}): 2977, 2935, 2869, 2804, 1737, 1683, 1653, 1636, 1559, 1457, 1490, 1444, 1382, 1350, 1297, 1254, 1120, 1076, 1043, 1024, 934, 845, 794. Anal. Calcd (found) for $C_{29}H_{43}O_8Si$: C, 63.71 (63.65); H, 7.74 (8.09).

2-Triethylsilylmethyl-2′-methyl-4,4,4′,4′-tetrakis(trimethylacetoxymethyl) Bicyclopentane (26). ^{1}H NMR: δ 3.85−4.07 (s, 8 H), 2.06 (d, *J* = 5.6 Hz, 1 H), 1.77 (dd, *J* = 6.8, 12.8 Hz, 2 H), 1.56−1.71 (m, 2 H), 1.40−1.53 (m, 4 H), 1.18−1.20 (s, 34 H), 0.88−1.07 (m, 12 H), 0.53 (q, *J* = 8.0 Hz, 6 H), 0.50 (q, *J* = 8.0 Hz, 6 H), 0.19 (dd, *J* = 11.6 Hz, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 178.8, 68.8, 68.6, 41.5, 40.8, 39.3, 39.1, 37.4, 35.5, 34.5, 32.0, 31.4, 27.5, 17.7, 16.4, 15.2, 15.0, 7.8, 4.2. IR (neat, cm^{-1}): 3691, 3630, 3584, 2957, 1733, 1654, 1480, 1459, 1397, 1364, 1282, 1146, 1034. HRMS (EI) calcd (found) for $C_{40}H_{71}O_8Si$ ($M^+ - C_2H_5$): 707.4918 (707.4951).

Tetramethyl 2′-Triethylsilylmethyl-2,3,3-trimethyl-bicyclopentane-4,4,4′,4′-tetracarboxylate (28). ^{1}H NMR: δ 3.64−3.69 (s, 12 H), 2.43−2.55 (m, 2 H), 2.06−2.19 (m, 2 H), 1.81−1.91 (m, 2 H), 1.45−1.71 (m, 4 H), 1.17 (s, 3 H), 0.89 (t, *J* = 7.8 Hz, 9 H), 0.78 (d, *J* = 6.8 Hz, 3 H), 0.76 (d, *J* = 2.4 Hz, 3 H), 0.70 (s, 3 H), 0.48 (q, *J* = 8.0 Hz, 6 H), 0.21 (dd, *J* = 6.0, 11.4 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.7, 173.5, 172.7, 171.9, 66.7, 58.3, 52.9, 52.3, 48.9, 48.1, 45.6, 43.2, 41.5, 39.3, 34.1, 31.9, 22.1, 19.4, 14.8, 12.3, 7.8, 4.1. IR (neat, cm^{-1}): 2952, 2904, 2875, 1654, 1636, 1559, 1458, 1426, 1261, 1197, 1166, 1094, 1048, 1016, 958. Anal. Calcd (found) for $C_{28}H_{48}O_8Si$: C, 62.25 (62.19); H, 8.95 (8.91).

Cyclization/Hydrosilylation of 4,4,9,9-Tetracarbomethoxy-1,6,11-tridecatriene (29). Triethylsilane (1.5 mmol) was added via syringe to a solution of (phen)PdMeCl (**1**) (9 mg, 0.027 mmol), $NaBAr_4$ (30 mg, 0.034 mmol), and triene **29** (135 mg, 0.33 mmol) in 5 mL of DCE at 0 °C, warmed to room temperature, and stirred for 12 h. Solvent was evaporated, and the residue was chromatographed (SiO_2; hexanes−EtOAc = 12:1) to give a 2:1 mixture of tetramethyl 2′-ethyl-2-triethylsilylmethyl-bicyclopentyl-4,4,4′,4′-tetracarboxylate (**30**) and 1,1-dicarbomethoxy-4-(5,5-carbomethoxy-(*E*)-2-heptenyl)-3-(triethylsilylmethyl)cyclopentane (**33**) (145 mg, 84%). The mixture was analyzed by IR spectroscopy and elemental analysis and then rechromatographed to give samples of pure **30** (39 mg, 23%) and **33** (24 mg, 14%) which were analyzed by NMR spectroscopy. IR (neat, cm^{-1}): 3695, 3634, 2952, 2874, 1734, 1459, 1437, 1252, 1196, 1165, 1017. Anal. Calcd (found) for $C_{27}H_{46}O_8Si$: C, 61.57 (61.36); H, 8.80 (8.93).

For 30. ^{1}H NMR: δ 3.66−3.69 (s, 12 H) 2.53−2.58 (m, 1 H), 2.48 (dd, *J* = 7.0, 13.4 Hz, 1 H), 2.23 (dd, *J* = 6.0, 13.6 Hz, 1 H), 2.17 (dd, *J* = 7.4, 13.0 Hz, 1 H), 1.71−1.89 (m, 5 H), 1.48−1.67 (m, 3 H), 1.38−1.43 (m, 1 H), 1.23−1.31 (m, 1 H), 0.99−1.15 (m, 1 H), 0.79−0.92 (m, 12 H), 0.47−0.53 (m, 6 H), 0.20 (dd, *J* = 10.8, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 173.6, 173.5, 58.2, 58.1. 53.0, 48.3, 44.8, 44.0, 43.1, 40.4, 39.7, 34.9, 33.9, 25.9, 14.9, 12.6, 7.9, 4.1.

For 33. ^{1}H NMR: δ 5.00 (m, 2 H), 3.65 (m, 12 H), 2.97 (d, *J* = 17.6 Hz, 1 H), 2.82 (d, *J* = 17.2 Hz, 1 H), 2.60−2.40 (m, 3 H), 2.20 (m, 1 H), 1.92−1.53 (m, 4 H), 1.33−1.15 (m, 3 H), 1.10 (m, 2 H), 0.90 (t, *J* = 8.0 Hz, 9 H), 0.80 (d, *J* = 6.4 Hz, 3 H), 0.49 (q, *J* = 8.0 Hz, 6 H), 0.36 (dd, *J* = 10.8, 14.8 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 172.4, 172.2, 148.7, 114.4, 58.4, 57.8, 52.9, 52.5, 42.5, 39.4, 37.1, 32.7, 32.5, 26.5, 23.1, 15.5, 14.0, 12.4, 7.6, 7.0, 6.5, 4.1.

Tetramethyl 4-Triethylsilylmethyl-3-methyl-octahydro cyclopenta[α]pentalene-1,1,6,6-tetracarboxylate (32). ^{1}H NMR (600 MHz): δ 3.71 (s, 3 H), 3.65 (s, 3 H), 3.23−3.35 (m, 2 H), 2.78 (dd, *J* = 7.8, 14.0 Hz, 1 H), 2.76 (dd, *J* = 7.5, 13.8 Hz, 1 H), 2.37 (q, *J* = 8.7 Hz, 1 H), 2.31 (q, *J* = 8.7 Hz, 1 H), 2.12−2.24 (m, 2 H), 1.65 (dd, *J* = 7.8, 13.7 Hz, 1 H), 1.58 (dd, *J* = 9.0, 13.3 Hz, 1 H), 1.50 (td, *J* = 6.8, 13.0 Hz, 1 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 0.94 (t, *J* = 8.0 Hz, 9 H), 0.82 (q, *J* = 12.1 Hz, 1 H), 0.77 (dd, *J* = 3.1, 14.9 Hz, 1 H), 0.54 (q, *J* = 8.0 Hz, 6 H), 0.37 (dd, *J* = 11.2, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 133.4, 173.3, 171.6, 171.4, 62.0, 61.3, 56.5, 53.5, 52.8, 52.2, 51.9, 44.4, 43.5, 36.2, 34.0, 31.2, 21.7, 19.1, 7.6, 4.0. Anal. Calcd (found) for $C_{27}H_{44}O_8Si$: C, 61.80 (61.59); H, 8.45 (8.64).

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for relevant compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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