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Regio- and Stereoselectivity of Ene Reactions: The Dimerization of Bicyclic 1,3-Fused 2-(Trimethylsilyl)cycloprop-1-enes

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Cycloalkenes proceed through bromination, dehydrobromination and dibromocarbene addition reactions to give tribromocyclopropanes **10** and **11**. The treatment of tribromocyclopropanes **10** and **11** with 3 equiv. of methyllithium in diethyl ether at –78 °C followed by treatment with trimethylsilyl chloride produce 8-(trimethylsilyl)bicyclo[5.1.0]oct-1(8)-ene (**4**) and 9-(trimethylsilyl)bicyclo[6.1.0]non-1(9)-ene (**5**). Both **4** and **5** undergo ene dimerization via the same steric isomer and an *endo* transition state to generate the stable adducts **6** and **7**, respectively, as the sole isomers. Compound **6**, containing an unstable bicyclo[5.1.0]oct-1(8)-enyl group and produced in high yields, has been reported to be an unstable species. Both of the ene dimers, (trimethylsilyl)cyclopropenes **6** and **7**, can be converted into cyclopropenes **8** and **9** by treatment with a fluoride salt followed by protonation.

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Introduction

Although the first derivative of cyclopropane was obtained as early as 1881,[1] cyclopropenes continue to fascinate both theoretical and experimental chemists because of their unique structures, high degree of ring strain and the difficulties associated with their synthesis.[2] Cyclopropenes are usually unstable as a result of their high ring-strain energy and isomerize, dimerize and/or react with other reagents to form a variety of products.[3,4] Therefore, it is very important to develop methods to control the reactions of cyclopropenes, to generate high yields of a single product and to synthesize versatile, stable cyclopropenes to expand their applications.

When cyclopropenes undergo ene dimerization, the intermediate *exo* and *endo* transition states generate different stereoadducts.[4] Asymmetric cyclopropenes usually undergo ene reactions to form several regio- and stereodimers.[4,5] Therefore, control of the regio- and stereochemistry of ene reactions of cyclopropenes is an important issue in the synthesis of functionalized 3-cyclopropylcyclopropenes. The regio- and stereochemistry of ene reactions of several substituted cyclopropenes have been reported. When cyclopropenes contain a trimethylsilyl group, such as 1-chloro-3-(trimethylsilyl)cyclopropene,[6] 1,2-bis(trimethylsilyl)cyclopropene[7] or 1-phenyl-2-(trimethylsilyl)cyclopropene,[8] they undergo ene reactions to give high yields of ene dimers. Bicyclic 1,3-fused cyclopropenes, bicyclo[*n*.1.0]-alk-1(*n*+3)-enes, are unstable compounds when $n < 6$.[9] Although the synthesis and chemistry of 1,3-fused bicyclic cyclopropenes are well known,[9,10] only three cyclopropenes, bicyclo[4.1.0]hept-1(7)-ene (**1**), 8-chlorobicycloct[5.1.0]oct-1(8)-ene (**2**) and bicyclo[5.1.0]oct-1(8)-ene (**3**), are reported to undergo ene reactions to give ene dimers (Figure 1). Compound **1** undergoes an ene reaction to give an unstable ene dimer ($n = 4$) which then dimerizes through [2+2] cyclization and/or a coupling reaction to give tetramers. The regio- and stereochemistry of this ene reaction have been confirmed by single-crystal X-ray analysis of the tetramers formed from [2+2] dimerization of an ene dimer.[11] The regiochemistry of the ene reactions of compound **2** ($n = 5$) was assigned based on NMR spectroscopic data, but the stereochemistry of these reactions remains unknown.[12] Both of the ene dimers were unstable ($n = 5$) and isomerized or treated with oxygen at room temperature. Based on ^{1}H NMR and mass spectra, Billups and co-worker reported that compound **3** ($n = 5$) underwent ene dimerization and trimerzation, but the regio- and stereochemistry were not clear.[11]

We wish to report herein that two bicyclic 1,3-fused 2-(trimethylsilyl)cycloprop-1-enes, 8-(trimethylsilyl)bicyclo-[5.1.0]oct-1(8)-ene ($n = 5$) (**4**) and 9-(trimethylsilyl)bicyclo[6.1.0]non-1(9)-ene ($n = 6$) (**5**) undergo ene reactions to form stable 1,3-fused cyclopropenes, (*n*+3)-trimethylsilyl-(*n*+2)-[(*n*+3)-(trimethylsilyl)bicyclo[*n*.1.0]alkyl]bicyclo-[*n*.1.0]alk-1(*n*+3)-enes [$n = 5$ (**6**) and 6 (**7**)] as the sole products. The regio- and stereochemistry of these ene reactions have been confirmed by single-crystal X-ray analysis of (tri-

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methylsilyl)cyclopropenes **6** and **7** and these two (trimethylsilyl)cyclopropenes can be converted into cyclopropenes **8** and **9**.

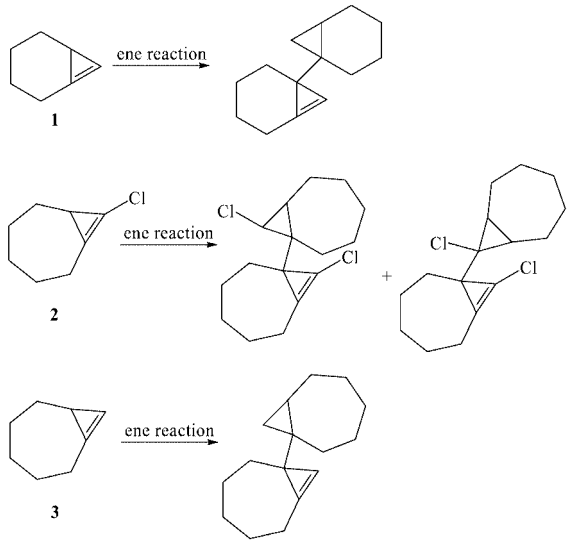
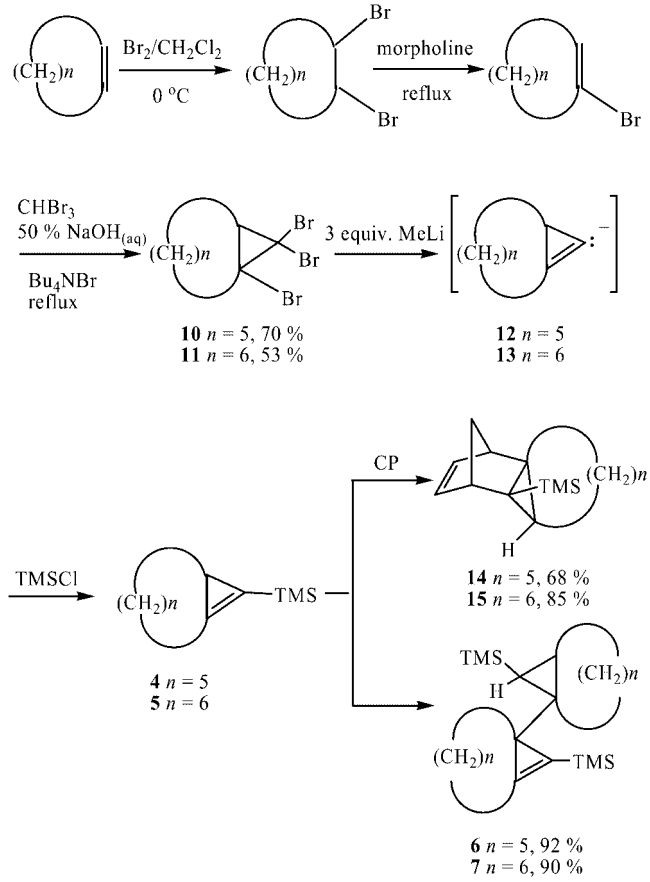


Figure 1. Ene dimerizations of bicyclo[4.1.0]hept-1(7)-ene (**1**), 8-chlorobicyclo[5.1.0]oct-1(8)-ene (**2**), and bicyclo[5.1.0]oct-1(8)-ene (**3**).

Results and Discussion

We previously reported an easier synthesis of the 2-substituted bicyclic 1,3-fused cyclopropenes, 8-substituted bicyclo[5.1.0]oct-1(8)-ene, using 1,8,8-tribromobicyclo[5.1.0]-octane (**10**).[13] Compound **10** was generated from cycloheptene. The cycloalkene reacted by bromination, dehydrobromination and dibromocarbene addition to give tribromocyclopropane **10** (Scheme 1). Treatment of tribromocyclopropane **10** with 3 equiv. of methyllithium in diethyl ether at –78 °C generated cyclopropenyl anion **12**, which was treated with trimethylsilyl chloride to produce **4**.[13] Cyclopropene **4** was trapped with cyclopentadiene to give the corresponding [4+2] cycloadduct **14**.[13] The higher analogue, compound **5**, was synthesized by the same procedure and also trapped with cyclopentadiene (Scheme 1).



Scheme 1.

After compound **4** had been synthesized and purified at low temperature, it was kept neat at room temperature for 1 day and a sole stable product **6** (Scheme 1) was isolated in 92% yield. According to spectral analysis (MS: *m/z* = 360; ^{13}C NMR: δ = 145.4 and 114.4 ppm; IR: $\tilde{\nu}$ = 1772 cm^{-1}), compound **6**, with a dimeric mass and a cyclopropenyl group, is an ene dimer of **4**.

In principle, four regioisomers, two 1,3- and two 1,2-fused cyclopropenes, can be generated when compounds **4** and **5** undergo ene dimerizaton (Figure 2).

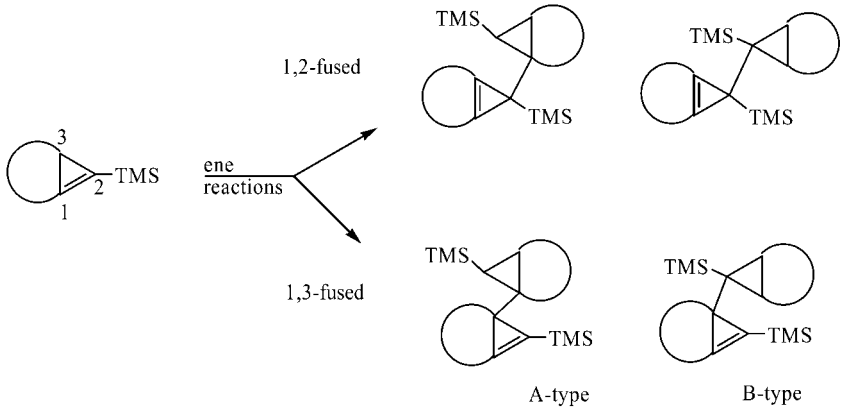


Figure 2. Regiochemistry of ene dimerization reactions of **4** and **5**.

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Furthermore, theoretical calculations have shown that the heats of formation of the bicyclic 1,3-fused cyclopropenes, 8-trimethylbicyclo[5.1.0]oct-1(8)-ene (**4**) (1.9 kcal/mol) and 9-(trimethylsilyl)bicyclo[6.1.0]non-1(9)-ene (**5**) (–5.6 kcal/mol), are lower than those of the bicyclic 1,2-fused cyclopropenes, 1-trimethylbicyclo[5.1.0]oct-1(7)-ene (5.8 kcal/mol) and 9-(trimethylsilyl)bicyclo[6.1.0]non-1(8)-ene (–1.4 kcal/mol).[14] These results suggest that only compound **4** can form 1,3-fused ene dimers when they undergo ene dimerization reactions. There are four stereoisomers, *RR exo*, *RR endo*, *SR exo* and *SR endo* adducts, that can be produced for each dimerization reaction (Figure 3).

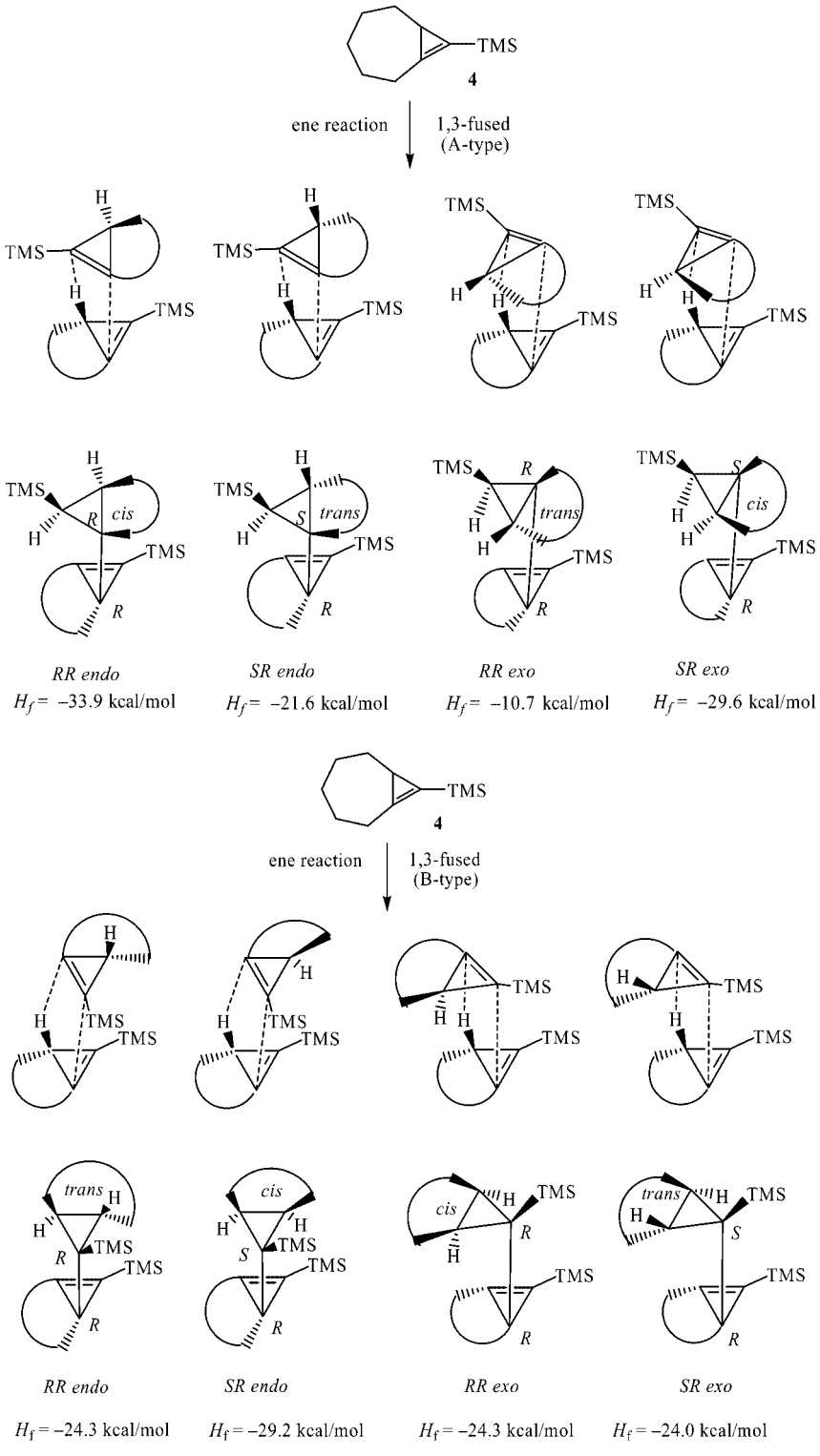

Figure 3. Transition states of ene dimerization reactions of **4** in the formation of the 1,3-fused bicyclic cyclopropenes and the heats of formation of these adducts.

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According to the PM3 theoretical calculations, the heats of formation of the 1,3-fused ene dimers of compound **4**, type-A *RR endo*, *SR endo*, *RR exo*, *SR exo* and type-B *RR endo*, *SR endo*, *RR exo*, *SR exo*, are –33.9, –21.6, –10.7, –29.6 and –24.3, –29.2, –24.3, –24.0 kcal/mol, respectively.[14] Based on these results, compound **6** may be a type-A *RR endo* adduct. Although compound **6** contains a 1,3-fused bicyclo[5.1.0]oct-1(8)-enyl group, which is reported to be an unstable species, it is stable at room temperature and its structure was determined by single-crystal X-ray analysis (Figure 4). Thus, compound **6** is formed from the same steric compound **4** via an *endo* transition state. Compound **4** dimerizes within one day at room temperature, but the 7-substituted derivative **6** is stable as a result of the bulky group that protects the active cyclopropenyl site.

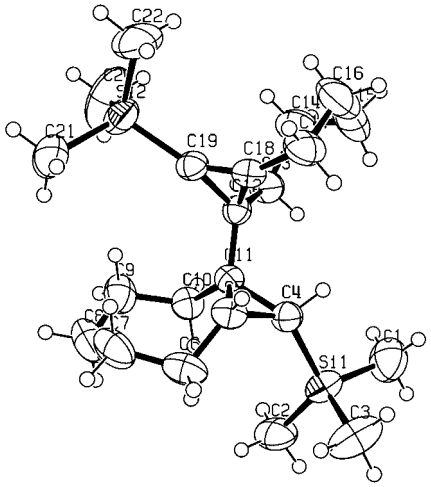


Figure 4. The X-ray crystal structure of **6**.

The higher analogue, compound **5**, was also synthesized and isolated at room temperature and was then stirred at 50 °C for two weeks: product **7** was isolated as the sole stable product in 90% yield. According to its spectra (MS: m/z = 388; ^{13}C NMR: δ = 145.9 and 118.1 ppm; IR: $\tilde{\nu}$ = 1758 cm^{-1}), compound **7**, with a dimeric mass and cyclopropenyl group, is an ene dimer of **5**. The structure of **7** was determined by single-crystal X-ray analysis (Figure 5). Compound **7** was also formed from the same steric isomer of **5** via an *endo* transition state.

Treatment of ene dimers **6** and **7** with a fluoride salt generated the cyclopropenyl anions **16** and **17**, which reacted further with water to produce (n+2)-[(n+3)-(trimethylsilyl)-bicyclo[n.1.0]alkyl]bicyclo[n.1.0]alk-1(n+3)-enes [n = 5 (**8**) and 6 (**9**)] (Scheme 2). The selectivity of the desilylation reaction of the ene dimers is based on the stability of the carbanion. Because a carbanion at an sp^2 carbon atom is more stable than at an sp^3 carbon atom, F$^-$ only reacts with the trimethylsilyl group of the cyclopropenyl moiety to generate sp^2 carbanions **16** and **17**.

In summary, the trimethylsilyl group has been used to control the cyclopropene ene dimerization reaction via the same steric isomer and an *endo* transition state to generate

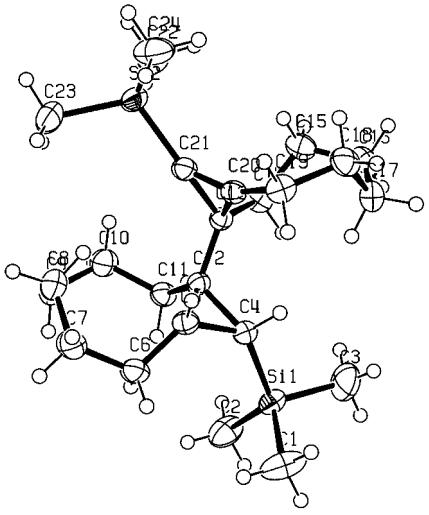
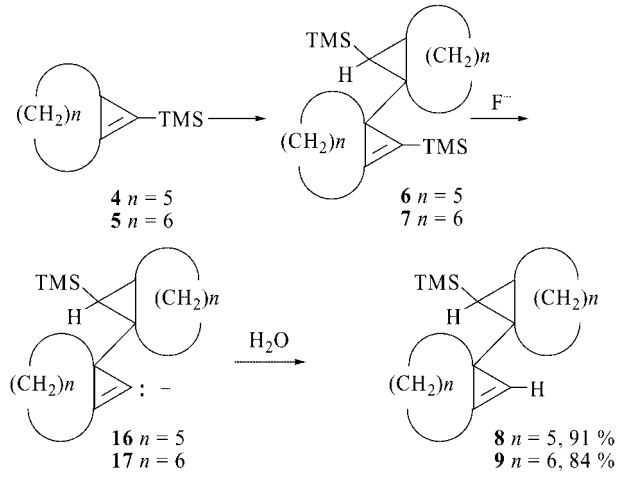


Figure 5. The X-ray crystal structure of **7**.



Scheme 2.

stable sole adducts in which one of the two adducts contains an unstable bicyclo[5.1.0]oct-1(8)-enyl group. Both of the ene dimers, (trimethylsilyl)cyclopropenes **6** and **7**, can be converted into cyclopropenes **8** and **9** by treatment with a fluoride salt and subsequent protonation gives **8** and **9**.

Experimental Section

General: All solvents were dried using standard methods. Deuteriated solvents were used to collect ^{1}H and ^{13}C NMR spectra. HRMS data were obtained with a JEOL JEM-200CX instrument. Infrared spectra were obtained with a Perkin–Elmer 1600 instrument. X-ray data for compounds were recorded with a Kappa CCD diffractometer. Calculations were performed with the HyperChem Molecular Modeling System for Windows, Version 6.03 (geometry optimization, semi-empirical, PM3). Silica gel for column chromatography (70–230 mesh) and flash chromatography (230 mesh) was obtained from E. Merck. Purity of solvents: reagent grade.

1,8,8-Tribromobicyclo[5.1.0]octane (10): 1-Bromocycloheptene was synthesized from cycloheptanol, essentially by the procedure re-

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ported by Halton′s group but with minor modifications.[15] A suspension of 1-bromocycloheptene (10.0 g, 57.1 mmol) and bromoform (15 mL), 50% sodium hydroxide (15 mL) and tetra-*n*-butylammonium bromide (0.1 g) were placed in a 100 mL flask. The mixture was stirred for 24 h at room temperature and dichloromethane (25 mL) and water (30 mL) were then added. The water layer was extracted with dichloromethane (3 × 25 mL). The combined organic phases were washed with water and brine and dried with anhydrous magnesium sulfate. Filtration and distillation gave **10** as a yellow liquid (81 °C, 1.5 Torr, 13.9 g, 70%). All spectroscopic data for compound **10** are in agreement with literature values.[13]

1,9,9-Tribromobicyclo[6.1.0]nonane (11): A modification of a previously reported procedure was used.[16] A mixture of 1-bromocyclononene (18.9 g, 100 mmol) and bromoform (26 mL), 50% sodium hydroxide (26 mL) and tetra-*n*-butylammonium bromide (0.1 g) were placed in a 100 mL flask. The mixture was stirred under reflux for 12 h and dichloromethane (25 mL) and water (30 mL) were then added. The aqueous phase was extracted with dichloromethane (3 × 25 mL). The combined organic phases were washed with water and brine and dried with anhydrous magnesium sulfate. Filtration and distillation gave compound **11** as a yellow liquid (70 °C, 0.2 Torr, 19.0 g, 53%). IR (neat): $\tilde{\nu}$ = 2924, 2854, 1461, 1445, 1139, 899, 833, 773, 719, 563 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.31–2.18 (m, 1 H, CH), 2.14–2.03 (dq, ^1J = 4, 14 Hz, 1 H, CH_2), 1.86–1.50 (m, 9 H, CH_2), 1.39–1.14 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.6 (C), 43.7 (CH), 41.5 (C), 35.1 (CH_2), 28.2 (CH_2), 27.2 (CH_2), 27.1 (CH_2), 25.8 (CH_2), 25.5 (CH_2) ppm. MS: *m*/*z* (%) = 364 (0.2) $[M + 6]^+$, 358 (0.2) $[M]^+$, 119 (100). HRMS: calcd. for $C_9H_{13}Br_3$ 357.8567; found 357.8570. $C_9H_{13}Br_3$ (360.91): calcd. C 29.95, H 3.63; found C 30.05, H 3.63.

Trapping of 8-(Trimethylsilyl)bicyclo[5.1.0]oct-1(8)-ene (4) with Cyclopentadiene: Methyllithium (6.1 mL, 1.5 M) in diethyl ether was added to a solution of compound **10** (1.06 g, 3.05 mmol) in dry diethyl ether (5 mL) at –78 °C over 30 min and trimethylsilyl chloride (0.58 mL, 4.58 mmol) was then added. The mixture was stirred for 1 h and cyclopentadiene (10 mL) was added. The mixture was then warmed to –40 °C and stirred for 6 h. Water was added and mixture was extracted with diethyl ether (3 × 25 mL). The ether phase was dried, concentrated and the residue purified by chromatography to give **14** as a yellow liquid (0.51 g, 68%). All spectroscopic data for compound **14** are in agreement with literature values.[13]

Trapping of 9-(Trimethylsilyl)bicyclo[6.1.0]non-1(9)-ene (5) with Cyclopentadiene: Methyllithium (100.0 mL, 1.5 M) in diethyl ether was added to a solution of compound **11** (18.0 g, 50 mmol) in dry diethyl ether (100.0 mL) at –78 °C over 1 h and trimethylsilyl chloride (9.6 mL, 75 mmol) was then added. The mixture was stirred for 1 h and cyclopentadiene (30 mL) was added. The mixture was then warmed to room temperature and stirred for 12 h. Water was added and the mixture was extracted with diethyl ether (3 × 25 mL). The ether phase was dried, concentrated and the residue purified by chromatography to give **15** as a yellow liquid (11.07 g, 85%). Compound **15**: IR (neat): $\tilde{\nu}$ = 3056, 2953, 2917, 2856, 1644, 1565, 1449, 1246, 886, 843, 738 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.87–5.83 (dd, ^1J = 3, 6 Hz, 1 H, CH), 5.67–5.64 (dd, ^1J = 3, 6 Hz, 1 H, CH), 2.74–2.70 (m, 1 H, CH), 2.62–2.58 (m, 1 H, CH), 1.87–1.79 (dt, ^1J = 4, 14 Hz, 1 H, CH_2), 1.74–1.64 (m, 2 H, CH_2, CH), 1.61–1.39 (m, 6 H, CH_2), 1.35–1.15 (m, 5 H, CH_2), 0.44–0.36 (d, ^1J = 11 Hz, 1 H, CH), 0.10 (s, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.2 (CH), 130.8 (CH), 59.4 (CH_2), 48.3 (CH), 46.8 (CH), 37.7 (CH), 34.2 (C), 29.9 (CH_2), 28.9 (CH_2), 28.1 (CH_2), 26.7 (CH_2), 26.5 (CH_2), 25.9 (CH_2), 14.6 (C), 0.9 (CH_3) ppm. MS: *m*/*z* (%) = 260 (34) $[M]^+$. HRMS: calcd. for $C_{17}H_{28}Si$ 260.1960; found 260.1956. $C_{17}H_{28}Si$ (260.49): calcd. C 78.38, H 10.83; found C 78.25, H 10.14.

Compound 5: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.77–2.69 (m, 1 H, CH_2), 2.43–2.30 (m, 1 H, CH_2), 1.95–1.82 (m, 1 H, CH_2), 1.73–1.03 (m, 10 H, CH_2, CH), 0.15 (s, 9 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4 (C), 110.3 (C), 33.4 (CH_2), 30.1 (CH_2), 28.4 (CH_2), 26.0 (CH_2), 25.6 (CH_2), 20.6 (CH_2), 18.4 (CH), –0.8 (CH_3) ppm.

8-(Trimethylsilyl)-1-[8-(trimethylsilyl)bicyclo[5.1.0]octan-1-yl]bicyclo[5.1.0]oct-7-ene (6): Methyllithium (58 mL, 1.5 M) in diethyl ether was added to a solution of 1,8,8-tribromobicyclo[5.1.0]octane (**10**)[15] (10.0 g, 28.82 mmol) in dry diethyl ether (20.0 mL) at –78 °C over 30 min and trimethylsilyl chloride (5.5 mL, 43.23 mmol) was then added. The mixture was stirred for 1 h and then warmed to room temperature and stirred for 8 h. Water was added and the solution was extracted with diethyl ether (3 × 25 mL). The ether phase was dried, concentrated and purified by chromatography (hexanes) to give 8-(trimethylsilyl)bicyclo-[5.1.0]oct-1(8)-ene (**4**). Compound **4** was degassed and kept at room temperature. After 1 d, the mixture was purified by chromatography (hexanes) and recrystallization to give compound **6** as a white solid (4.8 g, 92%). M.p. 53–54 °C. IR (neat): $\tilde{\nu}$ = 2958, 2916, 2848, 1772, 1461, 1444, 1414, 1245, 1049, 989, 835, 757, 627 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.78–2.73 (m, 1 H, CH_2), 2.32–2.22 (dt, ^1J = 6, 18 Hz, 2 H, CH_2), 1.97–1.89 (m, 2 H, CH_2), 1.86–1.70 (m, 5 H, CH_2), 1.65–1.60 (m, 2 H, CH_2, CH), 1.25–1.16 (m, 1 H, CH_2), 1.11–0.98 (m, 4 H, CH_2), 0.95–0.81 (d, ^1J = 10 Hz, 2 H, CH_2), 0.72–0.56 (m, 2 H, CH_2), 0.16 (s, 9 H, CH_3), 0.09 (s, 9 H, CH_3), –0.45 (d, ^1J = 10 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.4 (C), 114.4 (C), 39.3 (C), 37.2 (CH_2), 34.6 (CH_2), 32.6 (CH_2), 31.2 (CH_2), 29.9 (CH_2), 29.6 (CH), 29.5 (CH_2), 29.4 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 23.1 (CH), 1.9 (CH_3), –0.2 (CH_3) ppm. MS: *m*/*z* (%) = 360 (23) $[M]^+$. HRMS: calcd. for $C_{22}H_{40}Si_2$ 360.2669; found 360.2677. $C_{22}H_{40}Si_2$ (360.72): calcd. C 73.25, H 11.18; found C 72.97, H 11.16.

9-(Trimethylsilyl)-1-[9-(trimethylsilyl)bicyclo[6.1.0]nonan-1-yl]bicyclo[6.1.0]non-8-ene (7): Methyllithium (100.0 mL, 1.5 M) in diethyl ether was added to a solution of 1,9,9-tribromobicyclo[6.1.0] nonane (**11**) (18.0 g, 50 mmol) in dry diethyl ether (100.0 mL) at –78 °C over 1 h and trimethylsilyl chloride (9.6 mL, 75 mmol) was then added. The mixture was stirred at –40 °C for 1 h, then warmed to room temperature. Water was added and the solution was extracted with diethyl ether (3 × 25 mL). The ethereal solution was dried, concentrated and purified by chromatography (hexanes) to give 9-(trimethylsilyl)bicyclo[6.1.0]non-1(9)-ene (**5**). Compound **5** was degassed and kept at 50 °C. After 14 d, the mixture was purified by chromatography (hexanes) and recrystallization to give **7** as a white solid (8.74 g, 90%). M.p. 70–71 °C. IR (neat): $\tilde{\nu}$ = 2924, 2851, 1758, 1455, 1245, 874, 836, 753 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.74–2.64 (ddd, ^1J = 4, 5, 10 Hz, 1 H, CH_2), 2.42–2.30 (ddd, ^1J = 5, 11, 14 Hz, 1 H, CH_2), 2.25–2.15 (m, 1 H, CH_2), 2.10–2.00 (dd, ^1J = 8, 14 Hz, 1 H, CH_2), 1.85–1.67 (m, 2 H, CH_2, CH), 1.47–1.31 (m, 9 H, CH_2), 1.29–1.21 (m, 3 H, CH_2), 1.20–1.05 (m, 5 H, CH_2), 0.78–0.63 (m, 1 H, CH_2), 0.50–0.39 (m, 1 H, CH_2), 0.18 (s, 9 H, CH_3), 0.08 (s, 9 H, CH_3), –0.43 (d, ^1J = 10 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 145.9 (C), 118.1 (C), 37.2 (C), 35.0 (C), 34.4 (CH_2), 31.0 (CH_2), 29.5 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 27.7 (CH_2), 27.4 (CH), 26.6 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 25.5 (CH_2), 20.4 (CH_2), 18.0 (CH), 1.9 (CH_3), 0.3 (CH_3) ppm. MS: *m*/*z* (%) = 388

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(8) $[M]^+$, 73 (100). HRMS: calcd. for $C_{24}H_{44}Si_2$ 388.2982; found 388.2978. $C_{24}H_{44}Si_2$ (388.78): calcd. C 74.14, H 11.41; found C 74.11, H 11.30.

[1-(Bicyclo[5.1.0]oct-7-en-1-yl)bicyclo[5.1.0]octan-8-yl]trimethylsilane (8): *n*Bu_4NF (8.3 mL, 1.0 M) in tetrahydrofuran was added to solution of 8-(trimethylsilyl)-1-[8-(trimethylsilyl)bicyclo[5.1.0]-octan-1-yl]bicyclo[5.1.0]oct-7-ene (**6**) (1.0 g, 2.77 mmol) in tetrahydrofuran (5 mL). The mixture was stirred for 4 d at room temperature. Water was added and the solution was extracted with diethyl ether (3×25 mL). The ether phase was dried, concentrated and purified by chromatography (hexanes) to give compound **8** as a yellow liquid (0.73 g, 91%). IR (neat): $\tilde{\nu}$ = 2958, 2916, 2848, 1772, 1461, 1444, 1414, 1245, 1049, 989, 757, 627 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.41 (s, 1 H, CH), 2.75–2.65 (m, 1 H, CH_2), 2.36–2.15 (m, 2 H, CH_2), 2.02–1.89 (m, 2 H, CH_2), 1.87–1.73 (m, 3 H, CH_2), 1.71–1.52 (m, 5 H, CH_2, CH), 1.29–1.03 (m, 5 H, CH_2), 1.00–0.87 (m, 1 H, CH_2), 0.86–0.65 (m, 2 H, CH_2), 0.12 (s, 9 H, CH_3), –0.40 (d, ^1J = 10 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.1 (C), 104.7 (CH), 39.3 (CH), 37.1 (C), 32.7 (C), 31.8 (CH_2), 31.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_3), 27.1 (CH_2), 25.3 (CH_2), 23.0 (CH_3), 1.9 (CH) ppm. MS: *m*/*z* (%) = 288 (9) $[M]^+$. HRMS: calcd. for $C_{19}H_{32}Si$ 288.2273; found 288.2279. $C_{19}H_{32}Si$ (288.54): calcd. C 79.09, H 11.18; found C 78.87, H 11.05.

(1-(Bicyclo[6.1.0]non-8-en-1-yl)bicyclo[6.1.0]nonan-9-yl)trimethylsilane (9): *n*Bu_4NF (4.6 mL, 1.0 M) in tetrahydrofuran was added to a solution of 9-(trimethylsilyl)-1-[9-(trimethylsilyl)bicyclo[6.1.0]-nonan-1-yl]bicyclo[6.1.0]non-8-ene (**7**) (0.6 g, 1.54 mmol) in tetrahydrofuran (5 mL). The mixture was stirred for 2 d at room temperature. Water was added and the solution was extracted with diethyl ether (3×25 mL). The solution was dried, concentrated and purified by chromatography (hexanes) to give **9** as a white powder (0.41 g, 84%). M.p. 47.2–48.3 °C. IR (neat): $\tilde{\nu}$ = 2919, 2847, 2689, 1926, 1760, 1468, 1453, 1245, 1033, 965, 885, 833, 754, 723, 686 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.55 (s, 1 H, CH), 2.67–2.58 (m, ^1J = 5, 14 Hz, 1 H, CH_2), 2.31–2.21 (m, 1 H, CH_2), 2.19–2.11 (dt, ^1J = 4, 14 Hz,1 H, CH_2), 2.03–1.95 (dd, ^1J = 9, 14 Hz, 1 H, CH_2), 1.85–1.80 (m, 1 H, CH_2), 1.74–1.60 (m, 3 H, CH_2, CH), 1.55–1.51 (d, ^1J = 11 Hz,1 H, CH_2), 1.50–1.38 (m, 5 H, CH_2), 1.36–1.24 (m, 3 H, CH_2), 1.24–1.16 (m, 1 H, CH_2), 1.15–1.07 (m, 2 H, CH_2), 1.04–0.97 (m, 2 H, CH_2), 0.96–0.81 (m, 2 H, CH_2), 0.53–0.42 (dd, ^1J = 4, 10 Hz, 1 H, CH_2), 0.10 (s, 9 H, CH_3), –0.4 (d, ^1J = 10 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 125.9 (C), 107.8 (CH), 36.8 (C), 33.6 (CH_2), 31.1 (CH_2), 30.9 (C), 30.0 (C), 28.2 (CH_2), 27.4 (CH_2), 27.3 (CH_2), 27.2 (CH), 26.8 (CH_2), 26.5 (CH_2), 26.5 (CH_2), 25.2 (CH_2), 20.1 (CH_2), 17.5 (CH), 1.9 (CH_3) ppm. MS: *m*/*z* (%) = 316.6 (4) $[M]^+$. HRMS: calcd. for $C_{21}H_{36}Si$ 316.2586; found 316.2581. $C_{21}H_{36}Si$ (316.6): calcd. C 79.67, H 11.46; found C 79.65, H 11.40.

Supporting Information (see also the footnote on the first page of this article): X-ray crystallographic data for compounds **6** and **7** and NMR spectra of compounds **5**–**9**, **11** and **15**.

CCDC-249717 (for **6**) and -249716 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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