Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4371-4382, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01126-5

Synthesis of Camphor-Derived Chiral Cyclopentadienes via the Nazarov Cyclization: Preparation of Chiral Bis(cyclopentadienyl)zirconium and -titanium Dichlorides

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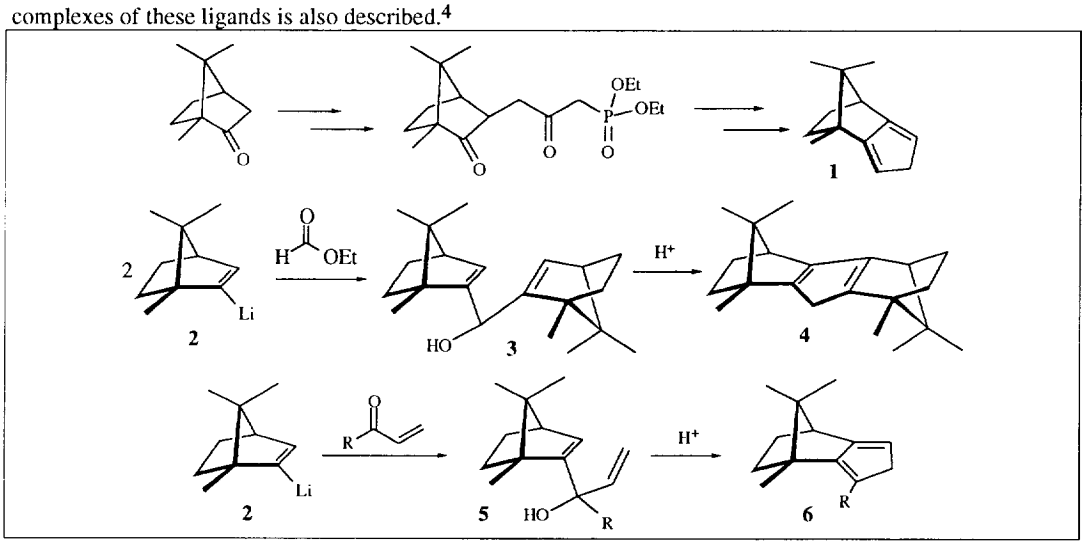
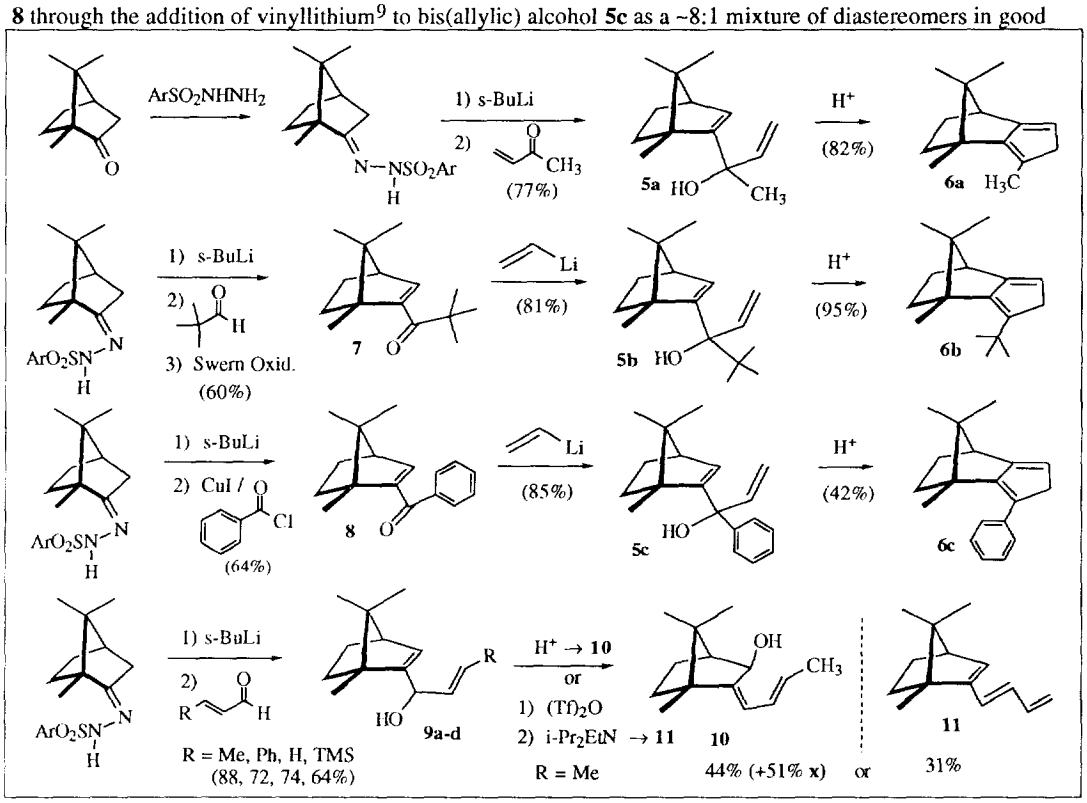
Abstract. Nazarov cationic π-cyclizations were employed in the synthesis of three substituted camphor-derived cyclopentadienyl ligands bearing a 3-methyl, 3-t-butyl or 3-phenyl substituent on the (1R,7S)-1,10,10-trimethyltricyclo[5,2,1,$0^{2,6}$]deca-2,5-diene framework. These ligands were converted to diastereomeric mixtures of bis(cyclopentadienyl)zirconium and -titanium dichlorides. In each case, a C_2-symmetrical isomer was the major isomer in the crude reaction product mixture and in all but one case a pure C_2-symmetrical diastereomer could be obtained by recrstallization.

Of the several possible methods to synthesize chiral, enantiomerically enriched metallocenes,[1] the conversion of a naturally occuring, enantiomerically enriched compound into a chiral cyclopentadienyl ligand is probably the most straightforward concept. To date, the most common method for forming chiral, annulated cyclopentadienes as **1** has been a several step cyclopentannulation sequence (Scheme 1).[2] An interesting alternate cyclopentadiene synthesis was reported in 1990, when Erker described the addition of two equivalents of a camphor-derived vinyl lithium **2** to ethyl formate to form the bis(allylic) alcohol **3** which underwent a Nazarov cationic π-cyclization to form the bis(annulated) C_2-symmetric cyclopentadiene **4** in good yield.[3] By adapting this sequence to add one equivalent of a chiral vinyl lithium reagent **2** to enone derivatives we envisioned a fairly general three-step procedure for the synthesis of substituted camphor-derived mono(annulated) cyclopentadienes **6** through the intermediate bis(allylic) alcohols **5**. By tethering two enones together with an ethano-bridge, we envisioned a bis(Nazarov) cyclization producing bis(cyclopentadienes). We report herein a facile, high-yield route to a series of camphor-derived cyclopentadienes **6a**, **6b** and **6c** (R = Me, Ph, t-Bu). The synthesis of the zirconium and titanium dichloride complexes of these ligands is also described.[4]



Scheme 1

Three routes for the formation of the bis(allylic) alcohols **5** were developed: direct addition of the vinyllithium reagent **2** to an enone or enal, addition of **2** to an aldehyde followed by oxidation and addition of vinyl lithium, and addition of **2** to an acid chloride followed by addition of vinyllithium. In practice each of these methods proved to be optimal for different targets and these three methods are shown in Scheme 2. The methyl-substituted ligand **6a** was prepared in just three steps from camphor. Addition of vinyllithium **2**[3,5] to methyl vinyl ketone yielded the bis(allylic) alcohol **5a** in good yield as a 1:1 mixture of isomers. This mixture cleanly underwent the Nazarov cationic π-cyclization[6] in the presence of acid[7] (p-TsOH in benzene) to give ligand **6a** in good yield. An initially-formed mixture of double bond isomers was converted into isomerically pure **6a** through deprotonation, protonation sequence (n-BuLi; water). In the case of the t-butyl-substituted ligand **6b**, a stepwise formation of the bis(allylic) alcohol **5b** was employed. In this sequence vinyllithium **2** added to pivaloyl aldehyde to give a mixture of allylic alcohols which was oxidized under Swern conditions[8] (oxalyl chloride, DMSO, Et_3N) to enone **7** in 60% overall yield. Vinyllithium[9] added to **7** to give bis(allylic) alcohol **5b** in good yield as a ~10:1 mixture of isomers[10] which cyclized in the presence of acid to form **6b** in high yield. In the case of the phenyl-substituted ligand **6c**, the best route was found to consist of the addition of vinyllithium **2** to a copper iodide/benzoyl chloride mixture[11] to give enone **8** followed by the conversion of **8** through the addition of vinyllithium[9] to bis(allylic) alcohol **5c** as a ~8:1 mixture of diastereomers in good

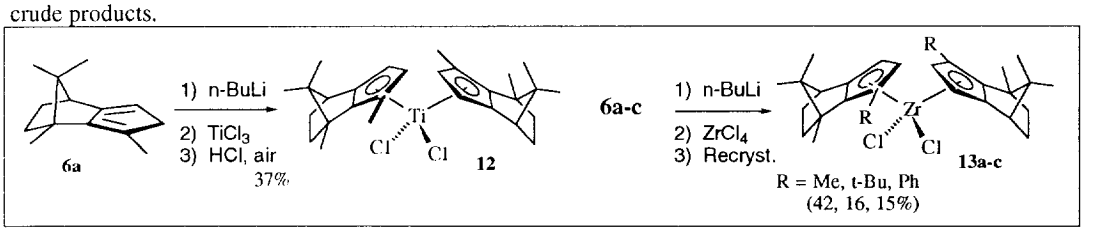


Scheme 2

overall yield. This mixture cyclized in the presence of acid to form the desired phenyl-substituted ligand **6c** in moderate yield. When vinyllithium **2** was added directly to phenyl vinyl ketone, the ensuing 1:1 mixture of diastereomeric alcohols **5c** cyclized to the desired **6c** in only poor yield. Apparently, the minor isomer of bis(allylic) alcohol **5c** formed in the addition of vinyllithium to **7** does not undergo efficient π-cationic cyclization and when it is present in greater amounts, the cyclization yield suffers greatly.

Although vinyllithium **2** adds efficiently to β-substituted acrolein derivatives to give bis(allylic) alcohols **9a-d** (with methyl, phenyl, hydrogen and trimethylsilyl substitution, respectively) in each case as an approximately 1:1 mixture of diastereomers, these intermediate compounds did not undergo clean π-cationic cyclization under the wide variety of conditions studied (varying acid source, Lewis acid, solvent, temperature and time)[12] (Scheme 2). In the case of the methyl-substituted bis(allylic) alcohol **9a**, acid treatment induced the formation of what turned out to be rearranged alcohol **10** in addition to a wide variety of side products. By simply exposing alcohol **9a** to silica gel in methylene chloride, rearranged alcohol **10** was cleanly formed under these mild conditions in addition to recovered starting material. When the acid conditions were made more forcing, no identifiable products were obtained from **9a** and we speculate that norbornyl cation rearrangements are involved. We also feared that exposure of any desired cyclopentadiene product to the sometimes prolonged acidic conditions would lead to decomposition of the product. Thus, we investigated the used of less acidic conditions. When the hydroxyl group in **9a** was converted to a triflate leaving group in the presence of diisopropylethylamine as a proton acceptor,[13] the major product was characterized as the triene elimination product **11**. Exposure of triene **11** to a variey of acid sources did not result in the formation of any desired cyclopentadiene.

With the new chiral, camphor-derived ligands **6a-c** in hand, we investigated the formation of bis(cyclopentadienyl)titanium- and zirconium dichloride complexes. In the case of metalating with titanium trichloride followed by oxidation,[14] only the least hindered methyl-substituted cyclopentadiene **6a** was successfully converted to a titanocene dichloride, complex **12** in Scheme 3. The ratio of the intially formed products indicated a 9:1 mixture of a C_2- and C_1-symmetrical titanocene dichlorides from which pure C_2-symmetrical diastereomer could be isolated by trituration with hexanes. Comparison of the ^{1}H NMR chemical shifts of the cyclopentadienyl hydrogens with known C_2-symmetrical titanocene dichloride complexes derived from ligand **1**[2,15] led to the assignment of the structure of **12**. The t-butyl-substituted ligand **6b** failed to give isolable titanocene complexes in several attempts including simple air oxidationof the initially formed Ti(III) complex. Although the crude metalation product of phenyl-substituted ligand **6c** which was obtained in low yield did show a multitude of signals in the expected cyclopentadienyl hydrogen region of the ^{1}H NMR spectrum, no characterizable titananocene dichloride complex could be isolated from this apparent mixture of crude products.



Scheme 3

In the case of metalating with zirconium, all three cyclopentadienes **6a-c** were successfully converted to their corresponding bis(cyclopentadienyl)zirconium dichloride complexes **13a-c** by reacting the n-butyllithium-generated anion in ether with zirconium tetrachloride. The methyl-substituted complex **13a** was formed in an initial purity of 80% and **13a** was isolable as the pure diastereomer following trituration with hexane in good yield. The t-butyl-substituted complex **13b** was formed as one of several apparent complexes of which **13b** comprised about 30% in the crude mixture, but could be obtained pure by trituration with hexane in low yield. The phenyl-substituted complex **13c** was formed in an initial purity of 40% and **13c** was isolable as the major diastereomer (6:1 ratio with apparently a C_1-symmetrical metallocene) following trituration with hexane in low yield. In each case the isolated or major isomer of **13a-c** was C_2-symmetrical and was assigned the structure shown in Scheme 3 based on comparison to known zirconocene dichloride complexes of camphor-derived ligand **1**.[2,15]

Conclusions. The Nazarov cationic π-cyclization of bis(allylic) alcohols containing a substituent on the central carbon of the pentadienyl moiety underwent clean formation of substituted chiral cyclopentadienes. When the substituent was on the terminal position of the pentadienyl moiety, no cyclization was observed. Camphenyllithium **2** added to enones and enals to give an approximately 1:1 ratio of diastereomeric bis(allylic) alcohols while vinyllithium additions to camphor-derived enones **7** and **8** gave 8:1 to 10:1 selectivity. Metalation of chiral ligand **6a-b** gave varying mixtures of metallocene dichlorides from which a pure C_2-symmetric metallocene was isolable in all cases except the phenyl-substituted ligand **6c**. The ability of the more hindered t-butyl- and phenyl-substituted cyclopentadienes **6b,c** to form complexes with zirconium but not with titanium may be due to the longer carbon-metal bond lengths in zirconocene versus titanocene dichlorides enabling the large ligands to interact less unfavorably with each other.

Experimental

General: Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. Ether, THF, DME, hexanes, toluene, and benzene were distilled under N_2 from sodium and benzophenone. C_6D_6 was distilled from calcium hydride. All reactions involving air or moisture sensitive compounds were performed under argon or nitrogen atmospheres utilizing standard Schlenk line techniques and/or in a Vacuum Atmospheres Dri-Box (under nitrogen). All glassware was oven dried prior to use. Routine solvent removal was performed on a Buchi RE-111 rotary evaporator using water aspiration. Solvent removal in vacuo was accomplished on a vacuum line at < 0.01 mm Hg or on a Schlenk line at <0.001 mm Hg (oil diffusion). All ^1H NMR and ^{13}C NMR spectra were obtained using a Varian XL-300 instrument. Data are reported as follows: chemical shifts (X scale) in parts per million (ppm) relative to residual solvent peaks (multiplicity, coupling constants in hertz (rounded to 0.5 Hz), number of hydrogens). For ^1H NMR spectra, the peaks due to residual $CDCl_3$, C_6D_6, or DMSO-d_6 are listed at 7.24 ppm, 7.15 ppm or 2.49 ppm, respectively, and for ^{13}C spectra, the central peak of the $CDCl_3$, C_6D_6, and DMSO-d_6 multiplets are assigned chemical shifts of 77.0 ppm, 128.0 ppm, or 39.5 ppm, respectively. Unless otherwise noted, multiplicities and compound ratios are deduced from electronic integration. Infrared spectra were recorded on a Bio-Rad FTS-7 FT-IR with a Bio-Rad 3240-SPC computer. Only characteristic and/or strong signals are reported. Low-resolution mass spectra (reported as m/z (relative intensity at 70 eV) were recorded on a Hewlett Packard 5985 instrument. Preparative column chromatography was performed on flash silica gel (E. Merck Reagents

silica gel 60 Å, 230-400 mesh ASTM). Melting Points were determined in Pyrex capillary tubes on a Mel-Temp apparatus and are uncorrected. Analytical thin layer chromatography was performed on 0.2 mm Kieselgel silica gel 60F-254.

(1R)-1,7,7-Trimethyl-2-lithio-bicyclo[2.2.1]hept-2-ene (2). *d*-Camphor 2,4,6-triisopropylbenzene-sulfonylhydrazone was prepared according to a published procedure.[5] A 0.5-L flask equipped with a magnetic stirring bar, and a rubber septum was flushed with nitrogen introduced through the septum of the flask. The flask was charged with *d*-Camphor 2,4,6-triisopropylbenzenesulfonylhydrazone (10.0 g (0.023 mol), resealed, and again flushed with nitrogen. Tetrahydrofuran (200 mL) was added, and the stirred solution was cooled to -78 °C. *sec*-Butyllithium (1.3 *M* in hexane, 41 mL, 53 mmol) was added dropwise. The resulting dark-red solution was stirred for 1 h, and the cold bath was replaced with an ice bath until nitrogen evolution ceased (approximately 25 min). This stirred solution of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) was recooled to -78 °C and ready for the addition of the appropriate electrophile.

(1R)-1,7,7-Trimethyl-2-(3-hydroxy-1-buten-3-yl)bicyclo [2.2.1]hept-2-ene (5a). To a -78 °C THF solution (200 mL) of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) (23 mmol, prepared as described above) was added, via syringe, a THF solution (10 mL) of methylvinyl ketone (2.9 mL, 35 mmol) over a 1-min period under nitrogen atmosphere. The reaction mixture was kept at this temperature for an additional 0.5 h then allowed to warm to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (70 mL) and the mixture extracted with CH_2Cl_2 (3 x 60 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 10% ethyl acetate / petroleum ether) to yield **5a** as a clear colorless oil (3.67 g, 77%) as an approximately equal mixture of two diastereomers. ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (dd, J = 18.0, 11.0 Hz, 0.5 H), 5.91 (dd, J = 18.0, 11.0 Hz, 0.5 H), 5.80 (d, J = 4.0 Hz, 0.5 H), 5.79 (d, J = 4.0 Hz, 0.5 H), 5.27 (dd, J = 18.0, 1.0 Hz, 0.5 H), 5.24 (dd. J = 18.0, 1.0 Hz, 0.5 H), 5.05 (dd, J = 11.0, 1.0 Hz, 1 H), 2.24 (dd, J = 4.0, 4.0 Hz, 0.5 H), 2.22 (dd, J = 4.0, 4.0 Hz, 0.5 H), 1.80 (m, 1 H), 1.48 (m, 1 H), 1.41 (s, 1.5 H), 1.40 (s, 1,5 H), 1.15 (m, 1 H), 1,13 (s, 1.5 H), 1.12 (s, 1.5 H), 0.94 (m, 1 H), 0.78 (s, 1.5 H), 0.77 (s, 1.5 H), 0.71 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.1, 143.8, 128.6, 111.6, 110.1, 77.2, 57.2, 57.1, 55.0, 54.9, 50.9, 29.7, 27.4, 27.3, 25.4, 25.3, 23.6, 19.7, 19.6, 13.3; IR (neat) 3500, 2952, 2923, 2859, 11785, 1753, 1460, 1382, 1100, 1009 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 206 (30 %), 173 (21), 145 (37), 133 (27), 91 (100), 77 (63), 67 (61), 43 (86).

(1R)-1,7,7-Trimethyl-2-(3-hydroxy-4,4-dimethyl-1-buten-3-yl)bicyclo [2.2.1]hept-2-ene (5b). A 100 mL flask was charged with vinyl-tributyltin (4.97 g, 15.7 mmol) and flushed with nitrogen. THF (50 mL) was added and this solution was cooled to -78 °C under an atmosphere of nitrogen. *n*-Butyllithium (2.48 *M* in hexane, 5.5 mL, 13.6 mmol) was added dropwise. The resulting slightly yellow reaction mixture was stirred for 15 min and the THF (8 mL) solution of **8** (2.3 g, 10.45 mmol) was introduced via syringe. The cold bath was removed and the reaction mixture warmed to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (15 mL) and the mixture extracted with CH_2Cl_2 (3 x 15 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 3% ethyl acetate / petroleum ether) to yield **5b** as a clear slightly yellow oil (2.1 g, 81%) as essentially one diastereomer. ^1H NMR (300 MHz, $CDCl_3$) δ 6.25 (dd, J = 17.0, 11.0 Hz, 1 H), 5.75 (d, J = 3.5 Hz, 1 H), 5.13 (dd, J = 17.0, 1.5 Hz, 1 H), 4.98 (dd, J = 11.0, 1.5 Hz, 1 H), 2.25 (dd, J = 3.5, 3.5 Hz, 1 H), 1.75 (m, 1 H), 1.45 (ddd, J = 9.0, 9.0, 3.5 Hz, 1 H), 1.20 (s, 3 H), 1.19 (m, 1 H), 0.95 (s, 9 H), 0.87 (m, 1 H), 0.80 (s, 3 H), 0.69 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 143.3,

132.1, 110.4, 81.8, 56.8, 56.4, 51.4, 38.5, 32.5, 26.0, 25.9, 20.0, 19.7, 14.6; IR (neat) 3613, 2954, 2875, 1473, 1388, 1364, 1290, 1140, 1100, 914 cm^{-1}; (EI 70 eV, *m/z*, rel intensity) 248 (1%), 191 (27), 135 (18), 121 (12), 109 (18), 86 (65), 84 (100), 57 (24), 49 (40).

(1R)-1,7,7-Trimethyl-2-(3-hydroxy-3-phenyl-1-propen-3-yl)bicyclo [2.2.1]hept-2-ene (5c). A 25 mL flask was charged with vinyl-tributyltin (2.57 g, 8.1 mmol) and flushed with nitrogen. THF (10 mL) was added and this solution was cooled to -78 °C under an atmosphere of nitrogen. *n*-Butyllithium (2.48 *M* in hexane, 2.85 mL, 7 mmol) was added dropwise. The resulting slightly yellow reaction mixture was stirred for 15 min and the THF (3 mL) solution of (1R)-1,7,7-trimethyl-2-benzoyl-bicyclo [2.2.1]hept-2-ene **7** (1.3 g, 5.4 mmol) was introduced via syringe. The cold bath was removed and the reaction mixture warmed to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (5 mL) and the mixture extracted with CH_2Cl_2 (3 x 5 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 10% ethyl acetate / petroleum ether) to yield **5c** as a clear colorless oil (1.23 g, 85%) as essentially one diastereomer. ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5 H), 6.39 (dd, J = 17.0, 10.5, Hz, 1 H), 5.87 (d, J = 3.5 Hz, 1 H), 5.25 (dd, J = 17.0, 1.0 Hz, 1 H), 5.14 (dd, J = 10.5, 1.0 Hz, 1 H), 2.26 (dd, J = 3.5, 3.5 Hz, 1 H), 1.80 (m, 1 H), 1.31 (m, 1 H), 0.99 (m, 2 H), 0.87 (s, 3 H), 0.81 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 143.3, 131.6, 127.7, 126.7, 126.3, 126.1, 112.4, 78.0, 58.0, 55.2, 51.1, 32.5, 25.3, 19.7, 19.4, 13.0; IR (neat) 3600, 3478, 3057, 2951, 2874, 1470, 1445, 1290, 998 cm^{-1}; (EI 70 eV, *m/z*, rel intensity) 268 (18%), 235 (22), 207 (24), 148 (19), 133 (35), 115 (38), 105 (100), 91 (80), 77 (89), 55 (55), 43 (24).

(1R,7S)-1,3,10,10-Tetramethyltricyclo[5,2,1,$0^{2,6}$]deca-2,5-diene (6a). To a benzene solution (40 mL) of **5a** (0.64 g, 3.1 mmol) was added the catalytic amount of p-TsOH x H_2O (30 mg, 0.16 mmol). After 16 h the reaction was complete by TLC analysis (SiO_2, 10% ethyl acetate / petroleum ether). Sodium carbonate (1 g, 9.4 mmol) was added to quench the reaction. Filtration and evaporation of the solvent afforded the crude mixture which was purified (SiO_2, petroleum ether) furnishing **6a** as a clear oil (0.48 g, 82%). ^1H NMR (300 MHz, $CDCl_3$) δ 5.41 (bs, 1 H), 3.01 (d, J = 21.5 Hz, 1 H), 2.94 (d, J = 21.5 Hz, 1 H), 2.35 (d, J = 4.5 Hz, 1 H), 1.95 (m, 1 H), 1.93 (m, 3 H), 1.71 (ddd, J = 11.5, 11.5, 4 Hz, 1 H), 1.39 (ddd, J = 13.0, 9.0, 4 Hz, 1 H), 1.23 (ddd, J = 13.0, 9.0, 4 Hz, 1 H), 1.17 (s, 3 H), 0.89 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 150.3, 126.3, 111.3, 54.3, 49.8, 49.3, 48.55, 34.9, 27.2, 20.8, 18.2, 12.9, 12.4; IR (neat) 2955, 2922, 2869, 1466, 1448, 1382, 1153, 739 cm^{-1}; (EI 70 eV, *m/z*, rel intensity) 188 (9%), 173 (22), 145 (100), 131 (26), 129 (23), 115 (23), 91 (21), 77 (16), 43 (15); $[\alpha]^{20}_{589}$ -0.24° (c 1.85, CH_2Cl_2).

(1R,7S)-1,10,10-Trimethyl-3-(1,1-dimethylethyl)-tricyclo [5,2,1,$0^{2,6}$]deca-2,5-diene (6b). To a benzene (10 mL) and dichloromethane (5 mL) solution of **5b** (0.215 g, 0.87 mmol) was added the catalytic amount of p-TsOH x H_2O (9 mg, 0.047 mmol). After 20 h the reaction was complete by TLC analysis (SiO_2, 10% ethyl acetate / petroleum ether). Sodium carbonate (0.5 g, 4.7 mmol) was used to quench the reaction. Filtration and evaporation of a solvent afforded the crude mixture which was purified (SiO_2, petroleum ether) furnishing **6b** as a clear colorless oil (0.19 g, 95%). ^1H NMR (300 MHz, $CDCl_3$) δ 5.42 (bs, 1 H), 3.16 (dd, J = 22.5, 1.5 Hz, 1 H), 3.06 (d, J = 22.5 Hz, 1 H), 2.33 (d, J = 4.0 Hz), 1.93 (m, 1 H), 1.68 (ddd, J = 12.0, 12.0, 4.0 Hz, 1 H), 1.43 (ddd, J = 12.0, 12.0, 4.0 Hz, 1 H), 1.27 (s, 3 H), 1.24 (m, 1 H), 1.17 (s, 9 H), 0.88 (s,3 H), 0.68 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 148.1, 142.5, 110.4, 54.6, 50.8, 48.0, 46.2, 35.5, 32.1, 29.7, 27.4, 20.8, 18.8, 16.0; IR (neat) 2955, 2925, 2861, 1465, 1385, 1362, 1227, 1156, 940 cm^{-1}; (EI 70 eV,

m/z , rel intensity) 230 (16%), 187 (22), 173 (62), 145 (29), 131 (48), 86 (43), 84 (56), 49 (100); $[\alpha]^{20}_{589}$ -7.73 ° (c 0.44, benzene).

(1R,7S)-1,10,10-Trimethyl-3-phenyltricyclo[5,2,1,$0^{2,6}$]deca-2,5-diene (6c). To a benzene solution (50 mL) of **5c** (1 g, 3.7 mmol) was added the catalytic amount of p-TsOH x H_2O (36 mg, 0.19 mmol). After 16 h the reaction was complete by TLC analysis (SiO_2, 10% ethyl acetate / petroleum ether). Sodium carbonate (1g, 9.4 mmol) was used for quenching of the reaction. Filtration and evaporation of a benzene afforded the crude mixture which was purified (SiO_2, petroleum ether) furnishing **6c** as a murky colorless oil (0.39 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.10 (m, 5 H), 5.64 (bs, 1 H), 3.64 (dd, J = 22.5, 1.5 Hz, 1 H), 3.18 (d, J = 22.5 Hz, 1 H), 2.41 (d, J = 4.5 Hz, 1 H), 1.99 (dddd, J = 12.0, 12.0, 9.0, 4.5 Hz, 1 H), 1.79 (ddd, J = 12.0, 12.0, 4.0 Hz, 1 H), 1.59 (ddd, J = 12.0, 9.0, 4.0 Hz, 1 H), 1.31 (ddd, J = 12.0, 9.0, 4.0 Hz, 1 H), 1.06 (s, 3 H), 0.89 (s, 3 H), 0.66 (s,3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 152.8, 137.5, 131.5, 128.3, 127.8, 125.7, 113.9, 55.2, 50.6, 48.0, 47.7, 34.6, 27.1, 20.8, 18.5, 12.9; IR (neat) 3063, 2960, 28744, 2753, 1602, 1494, 1446, 13387, 1233, 1157, 1117 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 250 (61%), 235 (14), 207 (40), 86 (69), 84 (100), 49 (11); $[\alpha]^{20}_{589}$ -1.04° (c 0.55, CH_2Cl_2).

(1R)-1,7,7-Trimethyl-2-(2,2-dimethylpropanoyl)-bicyclo [2.2.1]hept-2-ene (7). A solution of oxalyl chloride (2.14 g, 17 mmol) in anhydrous methylene chloride (60 mL) was cooled to -78 °C under nitrogen. Dimethyl sulfoxide (2.75 g, 2.5 mL, 35 mmol) was added dropwise at a rapid rate, with stirring. After 15 min, the CH_2Cl_2 solution (15 mL) of (1R)-1,7,7-Trimethyl-2-(1-hydroxy-2,2-dimethylpropane-1-yl)bicyclo [2.2.1]hept-2-ene (**14**) (3.0 g, 13.5 mmol) was added dropwise over 10 min. After 15 min stirring, triethylamine (9.5 mL) was added dropwise, keeping the temperature below -50 °C. Stirring was then continued for 15 min. The mixture was allowed to warm to room temperature , and water (60 mL) was added. The aqueous layer was separated and extracted with CH_2Cl_2 (2 x 50 mL). The organic phases were washed with saturated NaCl solution (25 mL) and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue purified (SiO_2, 2% ethyl acetate / petroleum ether) to yield **7** as a clear colorless oil (2.3 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (d, J = 3.5 Hz, 1 H), 2.43 (dd, J = 3.5, 3.5 Hz, 1 H), 1.86 (ddd, J = 12.0, 8.0, 4.0 Hz, 1 H), 1.53 (m, 1 H), 1.27 (m, 1 H), 1.19 (s, 9 H), 1.06 (s, 3 H), 0.96 (ddd, J = 12.0, 8.0, 4.0 Hz, 1 H), 0.83 (s, 3 H), 0.76 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 148.0, 139.8, 55.9, 53.6, 52.5, 44.6, 31.3, 27.4, 25.2, 19.3, 19.0, 11.3; IR (neat) 2363, 2333, 1736, 1657, 1580, 1476, 1460, 1389, 1365, 1310, 1272, 1198, 1133 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 220 (3%), 206 (17), 163 (29), 145 (22), 135 (18), 121 (16), 109 (28), 91 (30), 84 (100), 77 (22), 69 (33), 57 (32), 49 (33), 43 (22); $[\alpha]^{20}_{589}$ -0.84 ° (c 2.0, CH_2Cl_2).

(1R)-1,7,7-Trimethyl-2-benzoyl-bicyclo [2.2.1]hept-2-ene (8). Copper (I) iodide (3.53 g, 19 mmol) was placed in a 250 mL round bottom flask under a nitrogen atmosphere in the glove-box. A THF solution (50 mL) of benzoyl chloride (2.28 g, 16 mmol) was added, via syringe, and this mixture was stirred at room temperature for 3 h under nitrogen. Another 250 mL flask was charged with *d*-camphor 2,4,6-triisopropylbenzenesulfonylhydrazone (5.0 g ,12 mmol) and flushed with nitrogen. Tetrahydrofuran (80 mL) was added, and the stirred solution was cooled to -78 °C with acetone/dry ice bath. *sec*-Butyllithium (1.3 *M*, 20.5 mL, 27 mmol) was added dropwise. The resulting dark-red solution is stirred for 1 h, and the cold bath was replaced with an ice bath until nitrogen evolution ceased (approximately 25 min). This stirred solution of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) was intoduced dropwise, via cannula, into the chilled to -78 °C flask with the benzoyl chloride, copper iodide and THF. The resulting dark-green reaction

mixture was kept at this temperature for an additional 0.5 h then allowed to warm to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (80 mL) and the mixture extracted with CH_2Cl_2 (3 x 50 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 5% ethyl acetate / petroleum ether) to yield **8** as a clear slightly yellow oil (1.84 g, 64%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 7.0 Hz, 2 H), 7.50 (dd, J = 7.0, 7.0 Hz, 1 H), 7.40 (dd, J = 7.0, 7.0 Hz, 2 H), 6.51 (d, J = 3.0 Hz, 1 H), 2.54 (dd, J = 3.5, 3.5 Hz, 1 H), 1.94 (m, 1 H), 1.64 (m, 1 H), 1.31 (m, 1 H), 1.29 (s, 3 H), 0.97 (m, 1 H), 0.95 (s, 3 H), 0.84 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 148.8, 138.7, 131.9, 129.1, 128.1, 55.8, 55.0, 52.9, 31.1, 25.3, 19.7, 18.9, 11.3; IR (neat) 3054, 2955, 2874, 1719, 1641, 1573, 1446, 1383, 1335, 1273, 1241, 1111 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 240 (28%), 225 (35), 197 (31), 135 (12), 105 (100), 91 (21), 77 (71), 51(14); $[\alpha]^{20}_{589}$ -0.87 ° (c 2.2, CH_2Cl_2).

(1R)-1,7,7-Trimethyl-2-(1-hydroxy-2-propen-1-yl)bicyclo [2.2.1]hept-2-ene (9c). To a -78 °C THF solution (10 mL) of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) (0.23 mmol) (prepared as described above) was added, via syringe, a THF solution (2 mL) of acrolein (0.04 mL, 0.6 mmol) over a 1 min period under nitrogen atmosphere. The reaction mixture was kept at this temperature for an additional 0.5 h then allowed to warm to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (5 mL) and the mixture extracted with CH_2Cl_2 (3 x 5 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 5% ethyl acetate / petroleum ether) to yield **9c** as a clear colorless oil (0.033 g, 74%) as an approximately equal mixture of two diastereomers. ^1H NMR (300 MHz, $CDCl_3$) δ 5.99-5.76 (m, 2 H), 5.31-5.07 (m, 2 H), 4.65 (bs, 1 H), 2.27 (dd, J = 3.5, 3.5 Hz, 1 H), 1.82 (m, 1 H), 1.49 (m, 1 H), 1.08 (m, 1 H), 1.04 (s, 3 H), 0.96 (m, 1 H), 0.78 (s, 1.5 H), 0.76 (s, 1.5 H), 0.74 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 139.1, 129.8, 129.1, 114.9, 71.1, 71.0, 57.1, 54.1, 51.4, 34.6, 34.4, 32.3, 31.9, 29.7, 25.2, 19.5, 19.4, 11.7, 11.6; IR (neat) 3360, 2870, 1468, 1261, 1102, 1022, 990 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 192 (100%), 174 (26), 164 (28), 159 (62), 149 (34), 135 (22), 131 (90), 109 (31), 57 (19).

(1R)-1,7,7-Trimethyl-2-(3-hydroxy-1-buten-3-yl)bicyclo [2.2.1]hept-2-ene (9a). To a -78 °C THF solution (50 mL) of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) (5.78 mmol) (prepared as described above) was added via syringe a THF solution (5 mL) of 2-butenal (0.67 mL, 8.1 mmol) over a 1 min period under nitrogen atmosphere. The reaction mixture was kept at this temperature for an additional 0.5 h then allowed to warm to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (15 mL) and the mixture extracted with CH_2Cl_2 (3 x 15 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 10% ethyl acetate / petroleum ether) to yield **9a** as a clear colorless oil (1.05 g, 88%) as an approximately equal mixture of two diastereomers. ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (d, J = 2.5 Hz, 1 H), 5.74-5.36 (m, 2 H), 4.56 (m , 1 H), 2.25 (bs, 1 H), 1.79 (m, 1 H), 1.68 (m, 3 H), 1.49 (m, 1 H), 1.12-0.77 (m, 2 H), 1.00 (s, 3 H), 0.77 (s, 1.5 H), 0.74 (s, 1.5 H), 0.72 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3, 132.5, 128.7, 128.0, 127.1, 70.8, 57.0, 56.8, 53.9, 51.3, 51.2, 32.3, 31.8, 25.4, 25.2, 19.6, 19.5, 19.4, 17.7, 17.6, 11.7, 11.6; IR (neat) 3395, 2952, 2874, 1672, 1447, 1381, 1071, 1014, 966, 878 cm^{-1}; (EI 12 eV, *m/z* , rel intensity) 206 (36%), 188 (21), 178 (14), 173 (44), 163 (47), 145 (60), 135 (32), 119 (26), 109 (55), 91 (64), 84 (83), 77 (43), 71 (71), 49 (100), 43 (44).

(1R)-1,7,7-Trimethyl-2-(1-hydroxy-3-phenyl-2-propen-1-yl)bicyclo [2.2.1]hept-2-ene (9b). This compound was synthesized following the procedure for the synthesis of (1R)-1,7,7-trimethyl-2-(1-hydroxy-2-propen-1-yl)bicyclo [2.2.1]hept-2-ene (**9c**) but using (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene

(**2**) (5.78 mmol), 3-phenyl-propenal (1.07 g, 8.1 mmol) and THF (50 mL). The crude product was purified (SiO_2, 5% ethyl acetate / petroleum ether) to yield **9b** as a clear colorless oil (1.12 g, 72%) as an approximately equal mixture of two diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.18 (m, 5 H), 6.66-6.46 (m, 1 H), 6.32-6.03 (m, 1 H), 5.90 (bs, 1 H), 4.84 (d, J = 4.5 Hz, 1 H), 2.29 (bs, 1 H), 1.85 (m, 1 H), 1.57 (m, 1 H), 1.24 (s, 1,5 H), 1.22-0.80 (m, 2 H), 1.08 (s, 1.5 H), 1.00 (s, 1.5 H), 0.82 (1.5 H), 0.79 (s, 1.5 H), 0.75 (s, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 149.8, 142.4, 136.8, 131.6, 130.8, 130.5, 129.8, 129.1, 128.9, 128.5, 127.6, 127.5, 126.5, 126.3, 126.2, 70.8, 70.7, 34.1, 32.3, 32.0, 29.7, 25.3, 25.2, 24.6, 21.6, 19.9, 19.6, 19.5, 19.4, 12.3, 11.8; IR (neat) 3400, 2950, 2871, 1673, 1616, 1447, 1383, 1016, 965 cm^{-1}; (EI 12 eV, *m/z*, rel intensity) 268 (26%), 253 (9), 225 (9), 158 (100), 129 (64), 115 (19), 84 (17).

(1R)-1,7,7-Trimethyl-2-(1-hydroxy-3-trimethylsilyl-2-propen-1-yl)bicyclo [2.2.1]hept-2-ene (9d). This compound was synthesized following the procedure for the synthesis of (1R)-1,7,7-trimethyl-2-(1-hydroxy-2-propen-1-yl)bicyclo [2.2.1]hept-2-ene above but using (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) (0.39 mmol), 3-trimethylsilyl-propenal (0.06 g, 0.47 mmol) and THF (10 mL). The crude product was purified (SiO_2, 2% ethyl acetate / petroleum ether) to yield **9d** as a clear colorless oil (0.067 g, 64%) as an approximately equal mixture of two diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10-5.84 (m, 2 H), 5.78 (bs, 1 H), 4.63 (bs, 1 H), 2.26 (dd, J = 3.5, 3.5 Hz, 1 H), 1.81 (m, 1 H), 1.51 (m, 1 H), 1.24 (m, 1 H), 1.02 (s, 1.5 H), 1.01 (s, 1.5 H), 0.95 (m, 1 H), 0.77 (s, 1.5 H), 0.75 (s, 1.5 H), 0.73 (s, 3 H), 0.05 (s, 4.5 H), 0.04 (s, 4.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 146.4, 129.6, 129.5, 128.9, 72.8, 72.6, 57.0, 54.1, 51.4, 36.7, 32.3, 31.9, 29.7, 25.3, 19.6, 19.5, 11.8, -1.3; IR (neat) 3357, 2954, 2875, 1616, 1463, 1249, 990, 864, 838 cm^{-1}; (EI 12 eV, *m/z*, rel intensity) 264 (100%), 249 (20), 221 (27), 205 (31), 191 (22), 172 (77), 159 (43), 131 (68), 129 (48), 109 (20), 92 (16), 73 (77).

(1R)-1,7,7-Trimethyl-2-(2-butenyleden-1-yl)-bicyclo [2.2.1]heptan-3-ol (10). A 25 mL flask was charged with SiO_2 (2 g), dichloromethane (4 mL) and water (6 drops). A dichloromethane solution (3 mL) of (1R)-1,7,7-Trimethyl-2-(3-hydroxy-1-buten-3-yl)bicyclo [2.2.1]hept-2-ene (**9a**) (0.5 g, 2.4 mmol) was added and the resulting suspension was vigorously stirred for 12 h. Filtration and evaporation gave a clear oil, which was purified (SiO_2, 10% ethyl acetate / petroleum ether) to yield **10** as a clear colorless oil (0.26 g, 51%, two isomers) along with the recovered starting material **9a** (0.22 g, 44%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50-6.39 (m, 1 H), 5.82 (d, J = 11.0 Hz, 1 H), 5.73-5.28 (m, 1 H), 4.29 (d, J = 5.5 Hz, 1 H), 1.81-1.68 (m, 1 H), 1.76 (dd, J = 7.0, 1.5 Hz, 3 H), 1.52 (m, 1 H), 1.23 (m, 1 H), 1.06 (m, 1 H), 0.97 (s, 3 H), 0.94 (s, 3 H), 0.86 (s, 3 H), 0.76 (m, 1 H);^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 128.6, 123.8, 121.1, 76.4, 52.3, 51.7, 47.2, 34.3, 29.7, 24.5, 19.9, 18,3, 12.3; IR (neat) 3420, 2956, 2924, 2876, 1454, 1375, 1260, 1091, 1023, 800 cm^{-1}; (EI 12 eV, *m/z*, rel intensity) 206 (7), 189 (100), 161 (11), 147 (26), 131 (17), 119 (36), 109 (31), 105 (44), 91 (55), 69 (52), 55 (36), 43 (32).

(1R)-1,7,7-Trimethyl-2-(1,3-butadien-1-yl)bicyclo [2.2.1]hept-2-ene (11). A 25 mL flask was charged with **9a** (36.5 mg, 0.18 mmol) and flushed with nitrogen. Dichloromethane (10 mL) was added and the flask was cooled to -78 °C under nitrogen atmosphere. Diisopropylethylamine (0.063 mL) was added and then Tf_2O (0.05 g, 0.18 mmol) was introduced dropwise. The reaction mixture was allowed to warm to room temperature and quenched with saturated NH_4Cl (2 mL) and then extracted with CH_2Cl_2 (2 x 5 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, petroleum ether) to yield **11** as a clear colorless oil (10 mg, 31%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48-6.24 (m, 2 H), 6.11-6.03

(m, 2 H), 5.16 (dd, J = 15.0, 2.0 Hz, 1 H), 5.01 (dd, J = 10.0, 2.0 Hz, 1 H), 2.28 (dd, 3.5, 3.5 Hz, 1 H), 1.86 (m, 1 H), 1.53 (m, 1 H), 1.10 (s, 3 H), 1.05-0.73 (m, 2 H), 0.76 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8, 146.9, 138.0, 132.4, 128.4, 115.7, 56.7, 54.0, 51.6, 31.5, 29.7, 25.4, 19.6, 12.6; IR (neat) 2953, 2924, 2860, 1660, 1680, 1461, 1382, 1022, 970 cm^{-1}; (EI 12 eV, *m/z* , rel intensity) 188 (17%), 173 (26), 145 (100), 131 (28), 117 (41), 105 (23), 91 (43), 84 (25), 77 (28), 65 (17), 55 (17), 43 (12), $[\alpha]^{20}_{589}$ -0.26° (c 0.9, CH_2Cl_2).

Bis(η^5-(1R,7S)-1,3,10,10-Tetramethyltricyclo[5,2,1,0^{2,6}]dec-3,5-dien-2-yl)dichlorotitanium (12). Into **6a** (0.1 g, 0.53 mmol) in THF (5 mL) at 0 °C, was injected *n*-butyllithium (0.21 mL, 2.68 M in hexane, 0.55 mmol) via syringe under nitrogen. After stirring for 30 min at 0 °C, the solution was transferred to a previously cooled (-78 °C) solution of $TiCl_3$ (0.045 g, 0.29 mmol) in THF (4 mL), to achieve a dark purple color. The solution was gradually warmed to room temperature and then heated under reflux for 8 h. The solvent was removed *in vacuo*, the residue taken in $CHCl_3$ (4 mL) and 6 M HCl (1 mL) added and the solution allowed to stir for 2 h. The organic layer was separated and the water layer extracted with CH_2Cl_2 (2 x 5 mL), dried over $MgSO_4$ and concentrated to provide a dark purple solid. The solid was rinsed with hexanes, filtered and dried *in vacuo* to give a single diastereomer of **12** (0.048 g, 37%) as a dark purple powder: mp 208-211°C. ^1H NMR (300 MHz, $CDCl_3$) δ 6.33 (d, J = 2.5 Hz, 1 H), 5.53 (d, J = 2.5 Hz, 1 H), 2.70 (d, J = 4.0 Hz, 1 H), 2.48 (s, 3 H), 2.33 (ddd, J = 12.5, 9.0, 4.0 Hz, 1 H), 1.96 (s, 3 H), 1.51 (ddd, J = 12.5, 11.0, 4.5 Hz, 1 H), 1.16 (s, 3 H), 1.01 (ddd, J = 12.5, 9.0, 4.0 Hz, 1 H), 0.87 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 143.1, 128.1, 122.9, 108.5, 69.6, 55.7, 50.8, 31.9, 25.9, 21.0, 20.1, 14.5, 12.6; IR (neat) 2952, 2917, 2869, 1469, 1440, 1380, 1370, 1161, 1020, 826 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 493 (2%), 457 (5), 417 (4), 305 (19), 277 (23), 241 (43), 227 (42), 188 (47), 157 (45), 145 (100), 129 (78), 105 (29), 91 (25).

Bis(η^5-(1R,7S)-1,3,10,10-Tetramethyltricyclo[5,2,1,0^{2,6}]dec-3,5-dien-2-yl)dichlorozirconuim (13a). To an Et_2O solution (15 mL) of (1R,7S)-1,3,10,10-Tetramethyltricyclo[5,2,1,0^{2,6}]deca-2,5-diene (**6a**) (0.1 g, 0.53 mmol) at 0 °C under argon in a Schlenk apparatus equipped with a side arm was slowly added *n*-butyllithium (0.21 mL, 2.68 M in hexane, 0.55 mmol) to obtain a slightly yellow solution which was allowed to warm to room temperature for 4 hr. Solid $ZrCl_4$ (0.07 g, 0.29 mmol) was added via side arm and the reaction mixture allowed to stir at room temperature for 24 h. The green suspension was pumped to dryness, triturated with benzene (10 mL) and filtered. The mother liquor was evaporated and the residue was rinsed with hexane (4 mL) and filtered again, providing a single diastereomer of **13a** as a slightly greenish solid (0.061 g, 42%): mp 229-232°C. ^1H NMR (300 MHz, $CDCl_3$) δ 6.15 (d, J = 2.5 Hz, 1 H), 5.55 (d, J = 2.5 Hz, 1 H), 2.61 (d, J = 4.5 Hz, 1 H), 2.51 (ddd, J = 13.0, 9.0, 4.0 Hz, 1 H), 2.34 (s, 3 H), 2.02 (m, 1 H), 1.60 (ddd, J = 13.0, 11.0, 4.5 Hz, 1 H), 1.19 (m, 1 H), 1.17 (s, 3 H), 0.85 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 140.7, 124.2, 115.8, 106.7, 69.7, 54.9, 50.2, 31.5, 26.3, 20.9, 20.1, 13.8, 12.8; IR (neat) 2954, 2877, 1695, 1475, 1451, 1380, 907, 808, 731 cm^{-1}; (FAB, *m/z* , rel intensity) 536 (5%), 499 (68), 464 (24), 351 (5), 321 (5), 283 (40), 269 (23), 187 (100), 171 (21), 159 (26), 145 (30), 129 (28).

Bis(η^5-(1R,7S)-1,10,10-Trimethyl-3-(1,1-dimethylethyl)tricyclo [5,2,1,0^{2,6}]dec-3,5-dien-2-yl)dichlorozirconium (13b). To an Et_2O solution (15 mL) (1R,7S)-1,10,10-trimethyl-3-(1,1-dimethylethyl)-tricyclo[5,2,1,0^{2,6}]deca-2,5-diene (**6b**) (0.314 g, 1.36 mmol) at 0 °C under argon in a Schlenk apparatus equipped with a side arm was slowly added *n*-butyllithium (0.61 mL, 2.45 M in hexane, 1.5 mmol) to obtain a white suspension which was allowed to warm to room temperature for 4 h. Solid $ZrCl_4$ (0.175 g, 0.75 mmol) was added via side arm and the reaction mixture allowed to stir at room temperature for 24 h. The yellow

suspension was pumped to dryness, triturated with benzene (10 mL) and filtered. The mother liquor was evaporated. The ^{1}H NMR spectrum of this residue showed the presence of a complex mixture of isomers (approximately 30% of **13b**). The residue was rinsed with hexane (4 mL) and filtered again, providing a single diastereomer of **13b** (the major isomer) as a yellow solid (0.042 g, 16%): mp 249-252°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08 (d, J = 3.0 Hz, 1 H), 5.73 (d, J = 3.0 Hz, 1 H), 1.99 (m, 1 H), 1.58 (ddd, J = 11.0, 11.0, 4.0 Hz, 1 H), 1.43 (s, 9 H), 1.35 (s, 3 H), 1.19 (m, 1 H), 0.87 (s, 3 H), 0.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 141.4, 140.6, 110.5, 106.4, 68.9, 63.9, 56.0, 50.2, 33.9, 32.4, 25.7, 21.3, 20.4, 17.1; IR (neat) 2656, 1476, 1460, 1390, 1366, 1224, 908, 805 cm^{-1}; (FAB, *m/z* , rel intensity) 585 (28%), 583 (44), 395 (23), 393 (61), 389 (100), 229 (43), 160 (40), 154 (51), 136 (66), 109 (18).

Bis(η^5-(1R,7S)-1,10,10-Trimethyl-3-phenyl-tricyclo [5,2,1,0^{2,6}]dec-3,5-dien-2-yl)dichlorozirconium (13c). To an Et_2O solution (15 mL) of (1R,7S)-1,10,10-trimethyl-3-phenyl-tricyclo[5,2,1,0^{2,6}]deca-2,5-diene (**6c**) (0.112 g, 0.447 mmol) at 0 °C under argon in a Schlenk apparatus equipped with a side arm was slowly added *n*-butyllithium (0.2 mL, 2.45 M in hexane, 0.49 mmol) to obtain a slightly yellow solution which was allowed to warm to room temperature for 4 h. Solid $ZrCl_4$ (0.057 g, 0.25 mmol) was added via side arm and the reaction mixture allowed to stir at room temperature for 24 h. The yellow suspension was pumped to dryness, triturated with benzene (10 mL) and filtered. The mother liquor was evaporated and the residue was rinsed with hexane (3 mL) and filtered again and evaporated providing a yellow solid with **13c** as a major component (6:1) of the mixture (0.022 g, 15%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.21 (m, 5 H), 6.17 (d, J = 2.5 Hz, 1 H), 6.06 (d, J = 2.5 Hz, 1 H), 2.80 (ddd, J = 12.0, 9.0, 4.0 Hz, 1 H), 2.69 (d, J = 4.0 Hz, 1 H), 2.11 (ddd, J = 12.0, 12.0, 4.0 Hz, 1 H), 1.68 (ddd, J = 12.0, 12.0, 5.0 Hz, 1 H), 1.08 (m, 1 H), 0.90 (s, 3 H), 0.86 (s, 3 H), 0.22 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 141.9, 134.2, 129.4, 127.8, 127.2, 127.1, 112.7, 109, 2, 70.3, 55.7, 49.9, 31.1, 26.5, 20.1, 14.1, 13.6; IR (neat) 2958, 2925, 2876, 1700, 1471, 1448, 1386, 1261, 1094, 1024, 805, 763, 732, 697 cm^{-1}; (FAB, *m/z* , rel intensity) 625 (23%), 526 (31), 345 (15), 281 (16), 267 (49), 251 (100), 239 (17), 221 (40), 215 (25), 205 (26), 191 (26), 179 (28), 157 (62), 143 (39), 130 (20), 117 (20), 109 (61), 105 (77).

(1R)-1,7,7-Trimethyl-2-(1-hydroxy-2,2-dimethylpropane-1-yl)bicyclo [2.2.1]hept-2-ene (14). To a -78 °C THF solution (50 mL) of (1R)-1,7,7-trimethyl-2-lithio-bicyclo [2.2.1]hept-2-ene (**2**) (7 mmol) (prepared as described above) was added, via syringe, a THF solution (6 mL) of 2,2-dimethylpropanal (1.8 mL, 20 mmol) over a 1 min period under nitrogen atmosphere. The reaction mixture was kept at this temperature for an additional 0.5 h then allowed to warm to 0 °C. The reaction was quenched at 0 °C with saturated NH_4Cl (20 mL) and the mixture extracted with CH_2Cl_2 (3 x 20 mL). The extracts were dried over $MgSO_4$ and evaporated. The crude product was purified (SiO_2, 4% ethyl acetate / petroleum ether) to yield **14** as a clear colorless oil (1.18 g, 76%) as an approximately equal mixture of two diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (d, J = 3.5 Hz, 0.5 H), 5.87 (d, J = 3.5 Hz, 0.5 H), 3.80 (d, J = 5.0 Hz, 0.5 H), 3.75 (d, J = 5.0 Hz, 0.5 H), 2.34 (dd, J = 3.5, 3.5 Hz, 0.5 H), 2.25 (dd, J = 3.5, 3.5 Hz, 0.5 H), 1.79 (m, 1 H), 1.52 (m, 1 H), 1.17 (m, 1 H), 1. 02 (s, 1.5 H), 1. 02 (m, 1 H), 1.01 (s, 1.5 H), 0.95 (s, 4.5 H), 0.92 (s, 4.5 H), 0.79 (s, 3 H), 0.75 (s, 1.5 H), 0.73 (s, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 150.4, 130.7, 130.6, 75.9, 75.7, 57.7, 55.3, 55.0, 51.8, 51.1, 36.1, 35.3, 32.7, 30.9, 26.5, 26.2, 24.9, 24.8, 19.9, 19.8, 19.6, 12.5, 12.1; IR (neat) 3618, 3490, 2952, 2873, 1601, 1475, 1388, 1363, 1294, 1104, 1035, 987 cm^{-1}; (EI 70 eV, *m/z* , rel intensity) 222 (6%), 205 (2), 137 (93), 109 (67), 93 (57), 91 (39), 81 (42), 57 (99), 43 (100).

Acknowledgements. We thank the Exxon Educational Research Foundation, the Petroleum Research Fund administered by the American Chemical Society (25999-AC1) and the National Institutes of Health (GM 42735) for financial support.

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(*Received* 6 *September* 1994)