Samarium Diiodide-Promoted Intramolecular Radical Cyclization of \( \eta^5 \)-DieneFe(CO)\(_3\) Complexes Bearing Keto Side Chains

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Reaction of samarium diiodide with \( \eta^5 \)-ethylenedieneFe(CO)\(_3\) complexes bearing keto side chains in THF/HMPA/t-BuOH gives fused bicyclo[4.3.0]nonenol derivatives, whereas \( \eta^5 \)-cyclpentadieneFe(CO)\(_3\) analogues produce a bicyclo[5.3.0]decenol ring skeleton. The iron-mediated intramolecular radical addition allows for the direct stereocontrol of three contiguous stereogenic centers of these fused bicyclic skeletons. Under the same reaction conditions, intramolecular ketyl radical cyclization of acyclic \( \eta^5 \)-1,3-butadieneFe(CO)\(_3\) complexes with keto side chains at the terminal position of the diene ligands furnishes disubstituted cyclopentanol and cyclohexanol derivatives with excellent diastereoselectivity.

The chemistry of diene–iron complexes is a subject of continuing interest. The general applications of the complexes are (i) electrophilic reactions with reactive carbon nucleophiles;\(^1\) (ii) nucleophilic reactions with electrophiles;\(^2\) and (iii) additions of nucleophiles to \( \eta^5 \)-pentadienyl(tricarbonyliron(0) and \( \eta^5 \)-cyclopentadienyl-tricarbonyliron(0) cations.\(^3,4\) Surprisingly, reports on the addition of free radical species to the diene ligand of \( \eta^5 \)-1,3-diene(tricarbonyliron(0) complexes are not found. Recently, our attention turned to the intramolecular radical cyclization of diene–iron complexes containing a primary iodide, for example 1, using 1.1 equiv of tributyltin hydride and AIBN (cat.). However, only the reduced product 2 was isolated. Moreover, treatment of complex 1 with 1.2 molar equiv of SmI\(_2\) and a catalytic amount of FeCl\(_3\) using Molander’s protocols also produced 2 in quantitative yield.\(^5\) The primary radical might be formed under these two reaction conditions, however, the low nucleophilicity of the radical prevented its addition to the diene ligand. Inspired by recent successful examples of intramolecular addition of the relative nucleophilic ketyl radical\(^6,7\) to the dihydroanaphthalenicarboxylicinemium(0) and tetralinlicarboxylicinemium(0) complexes developed by Schmalz,\(^6,7\) we turned our efforts on radical cyclizations of this type to \( \eta^5 \)-1,3-diene(tricarbonyliron(0) complexes bearing keto groups. We here report on the first example of intramolecular cyclization of the ketyl radical to \( \eta^5 \)-1,3-diene(tricarbonyliron(0) complexes mediated by samarium(II) iodide.

Results and Discussion

The racemic starting complexes 3–9 required to test the intramolecular radical cyclization were prepared by addition of 2.5 molar equiv of methylithium to the corresponding acid complexes following the literature procedure.\(^2c,8\) Our first experiment began with 3. Treatment of the keto complex 3 with 4.5 molar equiv of samarium(II) diiodide in THF with hexamethylphosphoric acid triamide (HMPA) as a cosolvent and tert-butyl alcohol as a proton source at \( -78 \) °C under nitrogen for 2 h provided a major product in 54% yield, identified as bicyclo[4.3.0]nonenol derivative 11 (entry 1, Table 1). It is important to note that three contiguous stereogenic centers of the racemic bicyclic compound 11 are created with high diastereoselectivity. The product of the relative stereochemistry as shown was isolated

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(7) In our preliminary examples, a simple \( \eta^5 \)-arene(tricarbonylchromium(0) complex, such as \( \eta^5 \)-4-phenyl-2-butane(tricarbonylchromium(0) failed to undergo intramolecular radical cyclization using Schmalz’s conditions. The reduced alcohol was isolated as the major product in 45% yield.

as a single diastereomer. Under the same reaction conditions, intramolecular radical cyclization of complex 4 afforded bicyclo[4.3.0]nonenol derivative 12 (39%) as the sole cyclized product (entry 2, Table 1). The relative stereochemistry of 11 and 12 was assigned on the basis of their close chemical shift values (81.6 and 79.5 ppm, respectively) of the tertiary alcohol carbon in their $^{13}$C NMR spectra. The chemical shift values are consistent with the data of 1,2-cis-dialkyl-substituted cyclopentanol found in the literature.5c,9 Interestingly, the complex with an electron-donating methoxy group, 5 (entry 3, Table 1), also underwent intramolecular radical cyclization to produce the bicyclo[4.3.0]nonanone derivative 13 in 89% yield as the only diastereomer isolated. Since a simple arene–chromium complex such as ($\eta^4$-phenylbutan-2-one)tricarbonylchromium does not undergo intramolecular radical cyclization,7 the result may indicate that iron–diene complexes undergo intramolecular ketyl radical addition easier than do arene–chromium complexes. However, the stereochemistry of the hydroxy group of 13 was assigned at the endo face on the basis of its $^{13}$C NMR spectrum. The chemical shift of 69.6 ppm in 13 was assigned to the tertiary alcohol carbon. The observed upfield chemical shift of 69.6 ppm demands the cis relationship of the hydroxyl group and the adjacent alkyl substituents in the five-membered ring, and the assignment is consistent with the report found in the literature.10 The origin of different stereochemical preferences observed for the formation of bicyclic compounds 11 and 12 and the bicyclo[4.3.0]nonanone derivative 13 was suggested as follows. Reaction of complex 3 with samarium(II) iodide in THF/HMPA/t-BuOH generated ketyl radical anion 14. Due to the steric bulk of the ketyl radical bearing a samarium atom, the ketyl radical points away from the diene moiety in the transition state. Moreover, the anti relationship of the diene ligand and the ketyl oxygen is likely to be favorable in the transition state as noted previously (Scheme 1).5b,11 Thus anti, si-face

### Table 1. Racemic Cyclic Tertiary Alcohols Obtained by Intramolecular Addition of Ketyl Radicals to ($\eta^4$-diene)Fe(CO)$_3$ Complexes in THF/HMPA/t-BuOH

<table>
<thead>
<tr>
<th>No.</th>
<th>keto complex</th>
<th>product</th>
<th>yield [%]</th>
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<tbody>
<tr>
<td>1</td>
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<td><img src="image1" alt="Image" /></td>
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<tr>
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<tr>
<td>4</td>
<td>6a</td>
<td><img src="image4" alt="Image" /></td>
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<tr>
<td>5</td>
<td>6b</td>
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<tr>
<td>6</td>
<td>7a</td>
<td><img src="image6" alt="Image" /></td>
<td>36</td>
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<tr>
<td>7</td>
<td>7b</td>
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<td>8</td>
<td>8a</td>
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<td>8b</td>
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<td>53</td>
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<tr>
<td>10</td>
<td>9</td>
<td><img src="image10" alt="Image" /></td>
<td>63</td>
</tr>
</tbody>
</table>

the allyl anionic complex 16. Protonation of 16 with t-BuOH produced iron–hydride species 17. Addition of the hydride at the less hindered site of the allyl ligand furnished 2-methylbicyclo[4.3.0]non-8-en-2-ol (11). The above reaction pathway involving single electron transfer of Sm(II) species and intramolecular ketyl radical cyclization was first proposed by Schmalz in the case of (η⁶-arene)Cr(CO)₃ derivatives. However, chelation control can be employed to alter the diastereoselectivity for complex 5. As shown in Scheme 2, the methoxy group may provide a chelating center for the samarium species in 18. Anti addition of the ketyl radical at the terminal C-4 position of the diene ligand gave allyl radical intermediate 19, which led to the formation of 13 as the major product in 89% yield.

Under the same reaction conditions, intramolecular radical cyclizations of seven-membered ring substrates 6a afforded bicyclo[5.3.0]decenol 20 (49%) as the only diastereomeric product (entry 4, Table 1). The observed chemical shift of 82.7 ppm for the tertiary alcohol carbon in 20 demands the cis-dialkyl relationship in a five-membered ring as stated previously. Increasing the tether length by 1 with complex 6b (entry 5, Table 1) led to the bicyclo[5.4.0]decenol derivative 21 as the only diastereomer in 21% yield. The relative stereochemistry of 21 was determined by ¹³C NMR spectroscopy. The chemical shift of 72.7 ppm assigned to the carbinol carbon is consistent with those of cis-1,2-disubstituted cyclohexanol found in the literature.

Using the same approach, we are able to obtain 1,2-disubstituted cyclopentanol and cyclohexanol derivatives via intramolecular radical cyclization of acyclic (η⁴-diene)Fe(CO)₃ complexes bearing a methyl ketone side chain at the terminal position of the diene ligand. Intramolecular cyclization of the ketyl radical anion generated by treating complex 7a with 4.5 molar equiv of samarium(II) diiodide in THF/HMPA/t-BuOH afforded cyclopentanol derivative 22 as the only diastereomeric product in 36% yield after purification via flash column chromatography and short-path distillation of the residue. Several examples of radical cyclization of acyclic diene–iron complexes are summarized in Table 1 (entries 6–10). The stereochemical assignments of 22–26 were provided by comparison of their ¹³C NMR chemical shifts of the tertiary alcohol carbon with the data of cis-1,2-dialkycyclopentanol and -cyclohexanol derivatives formed in the literature. The assignment of the stereochemistry of 22–26 is consistent with the reaction pathway proposed for the cyclic precursors (entries 1 and 2, Table 1). It is important to mention that the isolation of cyclohexanol derivative 26 (73.3 ppm for the tertiary carbinol center) with the cis-1,2-dialkyl substituent is consistent with the proposed reaction pathway stated in Scheme 1. Therefore, a methyl group presented at the C-2 position of the diene ligand, for example 9, does not affect the relative stereochemistry of the cyclized product (entry 9, Table 1). The result may further explain the chelation effect (Scheme 2) caused by the methoxy group at the C-2 position of the diene ligand, which leads to the generation of 13 with an endo hydroxy group (entry 3, Table 1). Moreover, the stereochemistry of the double bonds in 22–25 (entries 6–9, Table 1) was assigned as trans on the basis of their ¹H NMR decoupling experiments. For example, the coupling constant of 15.2 Hz for the two vicinal vinyl protons of 22 suggested a trans orientation of the double bond. The allyl anion species 7a followed by samarium diiodide reduction may undergo allyl syn–anti isomerization to give 28. Protonation of 28 with t-BuOH afforded 22. Attempted intramolecular radical cyclization of complexes 29 and 30, however, failed to produce cyclobutanol and cycloheptanol derivatives. The reduced secondary alcohols were isolated after allowing the reaction mixture to proceed for a longer period of time (14 h) at −78 °C. The difficulty in forming cyclobutanol and cycloheptanol
Radical Cyclization of \((\eta^4\text{-Diene})\text{Fe}(\text{CO})_3\) Complexes

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The reactions described herein demonstrate for the first time that intramolecular iron-mediated radical cyclization promoted by SmI\(_2\) can be a convenient method for the formation of fused bicyclic alcohols with excellent regio- and stereochemical control. The ability to achieve stereocontrol of three stereogenic centers in fused bicyclic compounds in a simple reaction may have further applications. This convenient synthetic strategy can also be applied for the diastereoselective synthesis of cis-1,2-diakylcyclopentanol and -cyclohexanol derivatives under very mild reaction conditions.

Experimental Section

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via oven-dried syringe or cannula. Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from a deep blue sodium benzenophenone ketyl solution. Hexamethyl phosphoric acid triamide was distilled from calcium chloride. Flash column chromatography, following the method of Still,\(^{13}\) employed E. Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with silica gel 60 F\(_{254}\) plastic plates of 0.2 mm thickness from E. Merck. The term “concentration” refers to the removal of solvent with an aspirator pump (Yamato Instrument Company model WP-15) with a Buchi Rotovapor-R. The term “under nitrogen” implies that the apparatus was slowly heated in an air bath from 25 to 150 °C under vacuum; vents or reaction mixtures were transferred via oven-dried glassware unless otherwise indicated. Anhydrous solvents under very mild reaction conditions.

The distillate was collected at \(-78^\circ\text{C}\); and boiling points for fractions refers to the bath temperature range. Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. \(^1\text{H}\) nuclear magnetic resonance (NMR) spectra were obtained with J EOL-EX 400 (400 MHz) and Bruker AC-200 (200 MHz) spectrometers. The chemical shifts are reported in ppm with either tetramethylsilane (0.00 ppm) or CHCl\(_3\) (7.26 ppm) as internal standards. \(^{13}\text{C}\) NMR spectra were recorded with J EOL-EX 400 (100.4 MHz) and Bruker AC 200 (50.2 MHz) spectrometers with CDCl\(_3\) (7.70 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a J EOL J MS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (m/z) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a J EOL J MS-HX 110 spectrometer in the Department of Chemistry, Central Instrument Center, Taichung.

General Procedure for Addition of Methylithium to Acid Complexes. Synthesis of Iron Complexes Bearing a Methyl Ketone Side Chain.\(^{12}\) Methylithium (2.5 mol equiv) in hexane was added to a stirred solution of an acid complex in 10 mL of THF at 0 °C under nitrogen. The reaction was stirred at 0 °C for 30 min and then quenched with saturated aqueous ammonium chloride solution. The reaction mixture was diluted with 100 mL of 50% ethyl acetate/hexane. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

General Procedure for Intramolecular Radical Cyclization of \((\eta^4\text{-Diene})\text{Fe}(\text{CO})_3\) Complexes Bearing Keto Side Chains. In a typical procedure, to a solution of freshly prepared SmI\(_2\) (4.5 mmol) and HMPA (20.0 mmol) in 20 mL of THF was added slowly a solution of a diene–iron complex (1.0 mmol) in 4.0 mL of THF followed by addition of 0.22 mL of t-BuOH under nitrogen at \(-78^\circ\text{C}\). The reaction mixture was allowed to stir at \(-78^\circ\text{C}\) for 2 h. The reaction mixture was quenched with saturated aqueous ammonium chloride. The reaction mixture was diluted with ether (100 mL). The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

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(14) Samarium(II) diiodide was prepared from samarium powder and 1,2-dibromoethane following the literature procedure. Kagan, H. B.; Girard, P.; Namy, J. L. J. Am. Chem. Soc. 1980, 102, 2693.

(16) [6–9]-cis-6,8-Nonadien-2-one/tricarbonyliron Complex (7b). The crude mixture obtained from the addition of methylithium (1.55 mmol) to the corresponding acid complex(6.3 g, 0.51 mmol) was purified via flash column chromatography (silica gel, 1.5 ethyl acetate/hexanes) to give 7b (0.5 g, 0.41 mmol, 35%) as a yellow oil: IR (CH2Cl2) 3028, 2955, 2927, 2863, 1507, 1413, 1367, 1300 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.25 (d, J = 7.3 Hz, 1 H), 2.11 (d, J = 7.6 Hz, 1 H), 2.06 (s, 3 H), 1.58 (m, 5 H), 1.49 (m, 2 H), 1.47 (m, 1 H), 1.41 (m, 3 H), 1.12 (m, 1 H), 1.03 (m, 1 H); 13C NMR (100 MHz, CDCl3) δ 151.32, 140.36, 131.80, 121.70, 121.44, 116.19, 21.95, 21.75, 20.43, 20.21, 15.99, 14.82, 14.41, 10.96, 10.83, 10.72; MS (70 eV) m/e (rel intensity) 292 (M+), 264 (M+ − CO), 236 (M+ − 2 CO), 208 (M+ − 3 CO), 180 (M+ − 4 CO), 152 (M+ − 5 CO), 124 (M+ − 6 CO), 96 (M+ − 7 CO), 78 (M+ − 8 CO), 50 (M+ − 9 CO), 22 (M+ − 10 CO), 21 (M+ − 11 CO), 19 (M+ − 12 CO), 18 (M+ − 13 CO).

(17) [7–10]-cis-7,9-Decadien-2-one/tricarbonyliron Complex (8a). The crude mixture obtained from the addition of methylithium (13.3 mmol) to the corresponding acid complex(1.55 g, 5.31 mmol) was purified via flash column chromatography (silica gel, 1.5 ethyl acetate/hexanes) to give 8a (0.54 g, 1.86 mmol, 35%) as a yellow oil: IR (CH2Cl2) 3085, 3069, 3039, 2984, 2982, 2920, 2971, 2191, 1607, 1467, 1279, 1262, cm−1; 1H NMR (400 MHz, CDCl3) δ 8.03 (d, J = 9.0 Hz, 1 H), 5.11 (dd, J = 7.6 Hz, 1 H), 2.12 (m, 1 H), 1.99 (m, 1 H), 1.68 (m, 1 H), 1.51 (m, 2 H), 1.47 (m, 1 H), 1.45 (m, 4 H), 1.08 (m, 1 H); 13C NMR (100 MHz, CDCl3) δ 150.68, 140.44, 131.36, 121.97, 121.84, 116.40, 21.95, 21.74, 20.41, 20.21, 15.97, 14.80, 14.40, 10.96, 10.83, 10.72; MS (70 eV) m/e (rel intensity) 292 (M+), 264 (M+ − CO), 236 (M+ − 2 CO), 208 (M+ − 3 CO), 180 (M+ − 4 CO), 152 (M+ − 5 CO), 124 (M+ − 6 CO), 96 (M+ − 7 CO), 78 (M+ − 8 CO), 50 (M+ − 9 CO), 22 (M+ − 10 CO), 21 (M+ − 11 CO), 19 (M+ − 12 CO), 18 (M+ − 13 CO).

(18) [7–10]-cyl-7,9-Decadien-2-one/tricarbonyliron Complex (8b). The crude mixture obtained from the addition of methylithium (6.53 mmol) to the corresponding acid complex(2.0 g, 0.06 mmol) was purified via flash column chromatography (silica gel, 1.5 ethyl acetate/hexanes) to give 8b (0.76 g, 2.48 mmol, 35%) as a yellow oil: IR (CH2Cl2) 3069, 3039, 2984, 2982, 2920, 2191, 1607, 1467, 1408, 1279, 1262, cm−1; 1H NMR (400 MHz, CDCl3) δ 8.03 (d, J = 9.0 Hz, 1 H), 5.11 (dd, J = 7.6 Hz, 1 H), 2.12 (m, 1 H), 1.99 (m, 1 H), 1.68 (m, 1 H), 1.51 (m, 2 H), 1.47 (m, 1 H), 1.45 (m, 4 H), 1.08 (m, 1 H); 13C NMR (100 MHz, CDCl3) δ 150.68, 140.44, 131.36, 121.97, 121.84, 116.40, 21.95, 21.74, 20.41, 20.21, 15.97, 14.80, 14.40, 10.96, 10.83, 10.72; MS (70 eV) m/e (rel intensity) 292 (M+), 264 (M+ − CO), 236 (M+ − 2 CO), 208 (M+ − 3 CO), 180 (M+ − 4 CO), 152 (M+ − 5 CO), 124 (M+ − 6 CO), 96 (M+ − 7 CO), 78 (M+ − 8 CO), 50 (M+ − 9 CO), 22 (M+ − 10 CO), 21 (M+ − 11 CO), 19 (M+ − 12 CO), 18 (M+ − 13 CO).
Radical Cyclization of (η⁴-Diene)Fe(CO)₃ Complexes

IR (CHCl₃) 3668, 3597, 3385, 3057, 3045, 2989, 2932, 2858, 2062, 1988, 1666, 1608, 1448, 1423, 1377, 1313, 1269, 1248, 1217, 1107, 933, 914, 879, 858, 842, 817, 810, 700, 788 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (m, 1 H), 5.23 (dd, J = 11.2 Hz, 1 H), 2.54 (m, 1 H), 2.13 (m, 3 H), 1.63 (m, 1 H), 1.59 (m, 3 H), 1.44 (m, 2 H), 1.30 (m, 2 H), 1.25 (m, 2 H), 1.21 (s, 3 H); ¹C NMR (100.4 MHz, CDCl₃) δ 130.7, 130.5, 72.7, 49.1, 35.4, 34.2, 34.0, 29.6, 29.4, 27.3, 21.9, 21.2; MS (30 eV) m/e (rel intensity) 180 (M⁺ - 19), 179 (1), 163 (10), 162 (74), 147 (52), 133 (57), 122 (69), 120 (63), 107 (41), 105 (56), 93 (56), 91 (80), 79 (100), 77 (51), 67 (46), 55 (52), 53 (32), 51 (11); HRMS (EI) m/e calcd for C₂₉H₂₇FeO₂ (M⁺) 518.1547, found 518.1545.

(1R*,2S*,5R*)-2-(trans-1-Propenyl)-1-methylcycloptenanol (22). The crude mixture obtained from the intramolecular radical addition of complex 7a (0.15 g, 0.54 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 22 (32 mg, 0.19 mmol, 36%): IR (CHCl₃) 3668, 3597, 3458, 3076, 3057, 2997, 2962, 2876, 2048, 1975, 1834, 1639, 1448, 1379, 1302, 1194, 1122, 1001, 974, 937 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.50 (dt, J = 15.2, 6.4 Hz, 1 H), 5.33 (dd, J = 15.2, 8.3 Hz, 1 H), 1.93 (m, 1 H), 1.80–1.60 (m, 5 H), 1.50–1.25 (m, 4 H), 1.13 (s, 3 H); ¹C NMR (100 MHz, CDCl₃) δ 131.3, 126.4, 80.9, 54.4, 40.1, 29.8, 23.7, 20.6, 18.1.

(1R*,2S*,5R*)-2-(trans-1-Propenyl)-1-methylcyclohexanol (23). The crude mixture obtained from the intramolecular radical addition of complex 7b (0.15 g, 0.51 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 23 (50 mg, 0.34 mmol, 67%) as a colorless oil: IR (CHCl₃) 3680, 3054, 3049, 2991, 2984, 2935, 2910, 2854, 2843, 2829, 2815, 2800, 2790, 2775, 2760, 2740, 2725, 2710, 2695, 2680, 2665, 2650, 2635, 2620, 2605, 2580, 2560, 2540, 2520, 1730, 1715, 1700, 1685, 1675, 1660, 1645, 1518, 1408, 1393, 1373, 1353, 1333, 1313, 1292, 1272, 1252, 1232, 1212, 1192, 1172, 1152, 1132, 1112, 1092, 1072, 1052, 1032, 1012, 992, 972, 952, 932, 912, 892, 872, 852 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.54 (dt, J = 15.0, 6.3 Hz, 1 H), 5.37 (dd, J = 15.0, 8.8 Hz, 1 H), 2.04 (m, 1 H), 1.78–1.65 (m, 3 H), 1.71 (d, J = 6.2 Hz, 3 H), 1.40–1.20 (m, 6 H), 1.13 (s, 3 H); ¹C NMR (100 MHz, CDCl₃) δ 125.7, 121.8, 66.2, 64.1, 38.7, 38.6, 38.5, 38.4, 38.3, 29.8, 28.7, 28.0, 25.7; MS (70 eV) m/e (rel intensity) 154 (M⁺ - 1), 139 (43), 136 (54), 125 (55), 111 (93), 96 (100), 71 (50); HRMS (EI) m/e calcd for C₂₃H₂₉O (M⁺) 325.1538, found 325.1535.

(1R*,2S*,5R*)-2-(trans-1-Butenyl)-1-methylcycloptenanol (24). The crude mixture obtained from the intramolecular radical addition of complex 8a (0.65 g, 2.23 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 24 (0.15 g, 0.78 mmol, 35%): IR (CHCl₃) 3380, 3073, 3039, 2997, 2974, 1988, 1608, 1437 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.44 (m, 2 H), 2.16 (m, 1 H), 1.90 (m, 2 H), 1.77–1.67 (m, 4 H), 1.64–1.58 (m, 2 H), 1.16 (s, 3 H), 0.79 (m, 3 H); ¹C NMR (100 MHz, CDCl₃) δ 130.5, 125.8, 80.7, 50.2, 41.0, 33.6, 29.3, 22.9, 20.13, 17.9; MS (30 eV) m/e (rel intensity) 154 (M⁺ - 3), 153 (10), 136 (17), 123 (10), 107 (53), 89 (35), 77 (100), 57 (67); HRMS (EI) m/e calcd for C₂₃H₂₉O (M⁺ - H₂O) 136.1252, found 136.1246.

(1R*,2S*,5R*)-2-(trans-1-Butenyl)-1-methylcyclohexanol (25). The crude mixture obtained from the intramolecular radical addition of complex 8b (0.24 g, 0.78 mmol) was purified via flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give 25 (72 mg, 0.41 mmol, 53%) as a colorless oil: IR (CHCl₃) 3391, 3063, 3050, 2986, 2936, 1620, 1460, 1258, 857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.43 (m, 2 H), 2.37 (m, 1 H), 1.69–1.54 (m, 2 H), 1.39–1.33 (m, 5 H), 1.09 (s, 3 H), 0.94 (t, J = 11.2 Hz, 3 H); ¹C NMR (100 MHz, CDCl₃) δ 130.9, 126.2, 73.3, 48.0, 42.0, 33.4, 29.1, 25.6, 24.0, 21.0, 17.9; MS (30 eV) m/e (rel intensity) 168 (M⁺ - 15), 153 (17), 151 (100), 135 (5), 125 (16), 110 (17), 95 (22), 79 (25); HRMS (EI) m/e calcd for C₂₃H₂₉O (M⁺) 325.1541, found 325.1530.
colorless oil: IR (CHCl₃) 3596, 3401, 3067, 3050, 2990, 2975, 2935, 2859, 1645, 1445, 1424, 1379, 1157, 1128 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.77 (s, 1 H), 4.71 (s, 1 H), 2.39 (m, 1 H), 1.74 (s, 3 H), 1.76-1.19 (m, 9 H), 0.94 (m, 1 H); ¹³C NMR (100.4 MHz, CDCl₃) δ 145.4, 111.7, 73.3, 45.3, 42.0, 38.8, 29.1, 25.6, 24.0, 22.2, 21.0; MS (70 eV) m/e (rel intensity) 168 (M⁺, 10), 153 (11), 151 (95), 150 (100), 153 (63), 125 (37), 108 (46), 97 (30), 95 (90), 81 (37), 69 (48); HRMS (EI) m/e calcd for C₁₁H₂₀O (M⁺) 168.1514, found 168.1521.

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