Ring-Opening Reactions of Cyclic Allylic Ethers by Zirconocene Complexes of Cyclic Alkynes†

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Summary: Zirconocene complexes of cyclic alkynes can effect ring-opening reactions of cyclic allylic ethers to produce homoallylic alcohols and substituted 2,3-dihydrofurans.

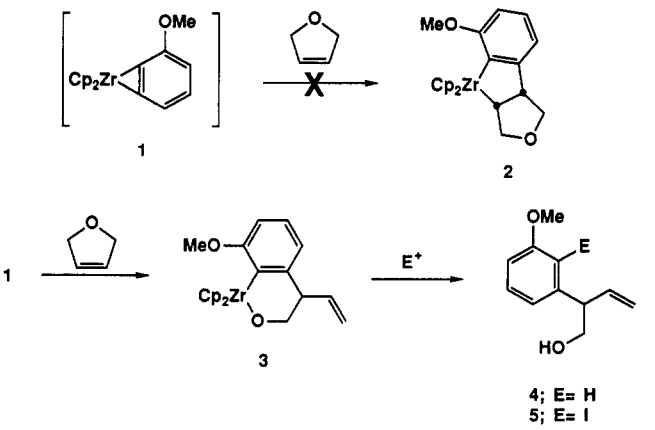
Recently, the utilization of organotransition metal complexes in ring-opening reactions has drawn considerable interest. Transition-metal complexes have been shown to facilitate the ring-opening olefin metathesis polymerization (ROMP) of cyclic olefins,[2] while other complexes participate in ring-opening reactions of epoxides[3] and other cyclic systems.[4] We now report our results in which we have used zirconocene complexes of cyclic alkynes to effect the ring-opening reactions of cyclic allylic ethers.

The zirconocene–3-methoxybenzene complex **1** can be generated by the addition of 2-lithioanisole to methylzirconocene chloride at −78 °C, followed by the thermolysis of the resulting intermediate to effect the loss of methane (70 °C, benzene, 16 h).[5] Since the insertion of olefins into the Zr–C bond of **1** is well documented,[6] we anticipated that generation of **1** in the presence of 2,5-dihydrofuran (1.0 equiv) would produce metallacycle **2** (Scheme I). However, the only observable product was metallacycle **3**, which was transformed by methanolysis (excess MeOH, 30 min) to the homoallylic alcohol **4** (54% overall yield) and by iodinolysis to **5** (51% yield).

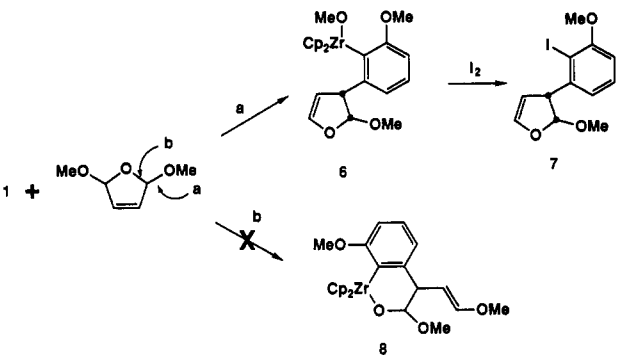
In order to more fully probe this reaction, complex **1** was generated in the presence of 2,5-dimethoxy-2,5-dihydrofuran (1.0 equiv).[7] In this case two reaction pathways are possible; however, the reaction gave **6** (by pathway a) as a single diastereomer (Scheme II). Iodinolysis of **6** yielded **7** (52% yield), which was assigned as the cis diastereomer on the basis of NOE experiments.[8] Here, cleavage of the exocyclic C–O bond is seen exclusively.

The 3,4-relationship of the double bond to the oxygen atom appears necessary for the ring-opening reaction to proceed. When complex **1** was generated in the presence of 2,3-dihydrofuran, no reaction was observed, even at elevated temperatures. However, the oxygen atom and the

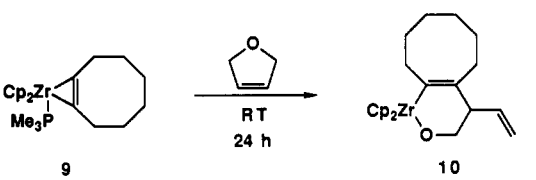
Scheme I



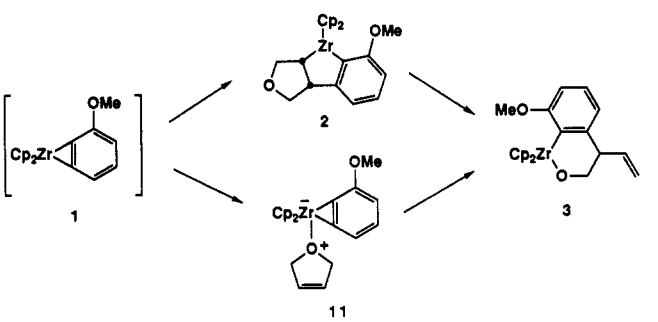
Scheme II



Scheme III



Scheme IV



† Dedicated to the memory of John K. Stille: scholar, friend, and pioneer in the area of organometallic chemistry.

(1) National Science Foundation Predoctoral Fellow 1989–1992.

(2) (a) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 54, p 502. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclic Olefins*; Wiley: New York, 1986.

(3) (a) Kocienski, P.; Yeates, C. *J. Chem. Soc., Chem. Commun.* **1984**, 151. (b) Mori, K.; Tamada, S.; Matsui, M. *Tetrahedron Lett.* **1978**, 901. (c) Annis, G. D.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1977**, 581. (d) Annis, G. D.; Hebblethwaithe, E. M.; Hodgson, S. T.; Holinshead, D. M.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2851.

(4) (a) Lautens, M.; DiFelice, C.; Huboux, A. *Tetrahedron Lett.* **1989**, *30*(49), 6817. (b) Takaya, H.; Suzuki, T.; Kumagai, Y.; Yamakawa, M.; Noyori, R. *J. Org. Chem.* **1981**, *46*, 2846. (c) Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* **1983**, *116*, 2920. (d) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334.

(5) (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *7*, 1044. (b) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (c) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987**, *28*, 3245. (d) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

(6) (a) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (b) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246. (c) Cuny, G. D.; Gutierrez, A.; Buchwald, S. L. Submitted for publication. (d) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324. In the present case, this reaction would necessarily be bimolecular.

(7) Purchased from Aldrich Chemical Co. as a mixture of cis and trans isomers.

(8) A difference NOE experiment was performed on **7** in which the proton in the 3-position of the 2,4-dihydrofuran ring was irradiated and the proton in the 2-position of the 2,3-dihydrofuran showed a 4.0% NOE signal. This relationship defines the 2,3-dihydrofuran ring to have the protons in the 2- and 3-positions in a cis arrangement as shown.

(9) All yields are based on cyclic olefins as limiting reagents.

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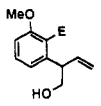
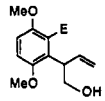
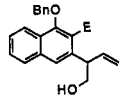
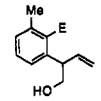
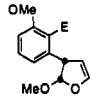
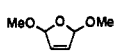
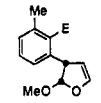
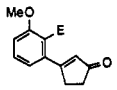
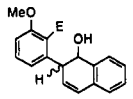
Table I

Olefin	Aromatic	Product	Yield[9]
			4; E= H; 54%[10] 5; E= I; 51%
			12; E= I; 30%
			13; E= I; 50%
			14; E= I; 51%
			15; E= H; 48% 7; E= I; 52%
			16; E= I; 55%
			17; E= H; 49%[11,12]
			18; E= H; 86% trans : cis 2 : 1

double bond need not be in the same ring, as demonstrated by the ring opening of cyclopent-2-en-1-one ethylene ketal (Table I, product **17**). Analogous reactivity was not observed for noncyclic substrates (allyl phenyl ether) or cyclic allylic amines (1-benzyl-3-pyrroline).

Other zirconocene complexes of cyclic alkynes also induce the ring-opening reaction of cyclic allylic ethers. When complex **9** was allowed to react with 2,5-dihydrofuran (benzene, room temperature, 24 h), **10** was the exclusive product (Scheme III).

Several mechanistic possibilities exist that explain the reactions described above. One sequence involves the initial insertion of 2,5-dihydrofuran into the Zr–C bond, in a fashion analogous to that for cyclopentene,[6c] producing the intermediate metallacycle **2**, which subsequently rearranges to product **3** via a β-alkoxide elimination[6d] (Scheme IV). Another possibility involves the complexation of the oxygen atom of the cyclic allylic ether to zirconium, producing the zwitterionic intermediate **11** followed by C–O bond cleavage to give the observed product.

In summary, we have shown that zirconocene complexes of cyclic alkynes can effect the ring opening of cyclic allylic ethers to produce, after workup, homoallylic alcohols and substituted 2,3-dihydrofurans. We are currently probing the generality and mechanistic aspects of this reaction in order to extend this methodology to the synthesis of other cyclic and acylclic systems.

Experimental Section

General Experimental Considerations. All reactions were conducted under an atmosphere of argon with use of standard Schlenk techniques or under nitrogen in a Vacuum Atmospheres Co. drybox. The sealable tubes used in the procedures were single-neck flasks equipped with Kontes Teflon O-ring valves. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-300, Varian Gemini 300, Varian XL-400, or a Varian VXR-500 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Mattson Cygnus Starlab 100 Fourier transform spectrometer. Gas chromatography analyses were performed on a Hewlett-Packard Model 5890 GC instrument with a 3392A integrator and FID detector using a 25-m capillary column with cross-linked SE-30 as a stationary phase. Electron impact mass spectra and high-resolution mass determinations (HRMS) were recorded on a Finnegan MAT System 8200 instrument. Melting points were measured on a Haake Buchler melting point apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Tetrahydrofuran, benzene, and diethyl ether were dried and deoxygenated by refluxing over sodium/benzophenone ketyl followed by distillation. Hexane was deolefinated by stirring over H_2SO_4, from which it was decanted and then stored over CaH_2. The deolefinated hexane thus obtained was dried and deoxygenated by refluxing over sodium/benzophenone ketyl followed by distillation. Cp_2ZrCl_2 was purchased from Boulder Scientific Inc., Mead, CO. All other reagents were either prepared according to published procedures or were available from commercial sources and used without further purification. Unless otherwise stated, preparative flash chromatography was performed on EM Science Kieselgel 60 (230–400 mesh) and spinning-plate chromatography was performed on a Chromatotron Model 7924T instrument from Harrison Research, Palo Alto, CA. The chromatography plates were prepared with EM Science silica gel/$CaSO_4$, #60PF_{254}. Yields, unless otherwise stated, refer to isolated yields of compounds of greater than 95% purity as determined by capillary GC and/or ^1H NMR methods.

Typical Procedure for the Sequential Ring-Opening/Hydrolysis Reaction of Cyclic Allylic Ethers by Organozirconium Intermediates: Preparation of 2-(3-Methoxyphenyl)-3-buten-1-ol (4).[10] To a solution of 2-bromoanisole (262 μL, 0.393 g, 2.10 mmol) in 10 mL of THF at −78 °C was added *n*-butyllithium (1.43 mL of a 1.64 M solution in hexane, 2.20 mmol). After 30 min, this solution was added to a solution of $Cp_2Zr(Me)Cl$ (0.653 g, 2.40 mmol) in 20 mL of THF at −78 °C, and the resulting solution was maintained at −78 °C for 15 min before it was warmed to room temperature. THF was removed in vacuo, and the residue was redissolved in 10 mL of benzene. This mixture was cannula-filtered into a sealable tube, and then 2,5-dihydrofuran (152 μL, 0.140 g, 2.00 mmol) was added. The reaction mixture was maintained at 70 °C for 18 h. The solution was cooled to room temperature, and then methanol (1 mL) was added and the resulting mixture was stirred for 30 min. The reaction mixture was concentrated, and the residue was extracted several times with ether. The extracts were combined and washed sequentially with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, hexane–ether eluent) to give a pale yellow oil (201 mg, 57% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 1.49–1.53 (t, 1 H, J = 6.3 Hz); 3.53 (q, 1 H, J = 7.2 Hz); 3.81 (s, 3 H); 3.82–3.84 (m, 2 H); 5.19 (d, 1 H, J = 8.4 Hz); 5.23 (s, 1 H); 5.94–6.06 (m, 1 H); 6.79–6.85 (m, 3 H); 7.26 (t, 1 H, 9.0 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 52.45, 55.11, 65.97, 112.19, 114.06, 117.30, 120.37, 129.97, 138.28, 142.49, 160.20. IR (neat): 3396 (broad), 1601, 1263, 1050, 1045 cm^{-1}. Molecular formula: $C_{11}H_{14}O_2$. HRMS: calcd, 178.0994 amu; found, 178.0994 ± 0.001 amu.

2,3-Dihydro-2-methoxy-3-(3-methoxyphenyl)furan (15): 48% yield; yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 3.47 (s, 3 H); 3.79 (s, 3 H); 3.82–3.85 (m, 1 H); 5.15–5.18 (m, 2 H); 6.53–6.54 (m, 1 H); 6.74–6.80 (m, 3 H); 7.24 (t, 1 H, J = 8.0 Hz). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 54.69, 55.09, 55.66, 104.25, 112.44, 112.52, 112.98, 119.71, 129.63, 142.42, 144.64, 159.87. IR (neat): 2936, 1601, 1270, 1266, 1038 cm^{-1}. Molecular formula: $C_{12}H_{14}O_3$. HRMS: calcd, 206.0943 amu; found, 206.0943 ± 0.001 amu.

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3-(3-Methoxyphenyl)cyclopent-2-en-1-one (17):[11] 49% yield; white solid; mp 81–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.56–2.60 (m, 2 H); 3.01–3.04 (m, 2 H); 3.86 (s, 3 H); 6.56 (s, 1 H); 7.00–7.40 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.46 (t), 35.03 (t), 55.21 (q), 112.50 (d), 116.52 (d), 119.36 (d), 127.94 (d), 130.04 (d), 135.61 (s), 160.11 (s), 174.14 (s), 209.69 (s).

***cis*-/*trans*-1,2-Dihydro-1-hydroxy-2-(3-methoxyphenyl)-naphthalene (18)**: 86% yield; yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (d, 1 H, J = 7.2 Hz); 2.00 (d, 1 H, J = 4.8 Hz); 3.73 (s, 3 H); 3.87 (s, 3 H); 4.39–4.40 (m, 1 H); 4.84–4.89 (m, 1 H); 6.05–6.10 (m, 2 H); 6.60–7.41 (m, 16 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 40.14, 47.17, 54.93, 55.31, 69.75, 71.06, 110.30, 112.64, 114.69, 120.67, 121.39, 126.18, 126.23, 126.54, 127.42, 127.63, 127.85, 127.91, 128.05, 128.10, 128.13, 128.15, 129.42, 129.50, 129.72, 130.01, 132.25, 132.48, 135.57, 136.00, 139.26, 142.84, 157.07, 159.57. IR (neat): 3430 (broad), 1600, 1489, 1244, 1051, 756 cm^{-1}. Molecular formula: $C_{17}H_{16}O_2$. HRMS: calcd, 252.1150 amu; found, 252.1149 ± 0.001 amu.

Typical Procedure for the Sequential Ring-Opening/Iodinolysis Reaction of Cyclic Allylic Ethers by Organozirconium Intermediates: Preparation of 2-(2-Iodo-3-methoxyphenyl)-3-buten-1-ol (5). To a solution of 2-bromoanisole (262 μL, 0.393 g, 2.10 mmol) in 10 mL of THF at −78 °C was added *n*-butyllithium (1.43 mL of a 1.64 M solution in hexane, 2.20 mmol). After 30 min, this solution was added to a solution of $Cp_2Zr(Me)Cl$ (0.653 g, 2.40 mmol) in 20 mL of THF at −78 °C, and the resulting solution was maintained at −78 °C for 15 min before it was warmed to room temperature. The THF was removed in vacuo, and the residue was redissolved in 10 mL of benzene. The mixture was cannula-filtered into a sealable tube, and then 2,5-dihydrofuran (152 μL, 0.140 g, 2.00 mmol) was added. The reaction mixture was maintained at 70 °C for 18 h. The solution was cooled to room temperature, and then a solution of iodine (0.558 g, 2.20 mmol in 20 mL of benzene) was added, and the resulting mixture was stirred for 3 h. The reaction mixture was washed with saturated Na_2SO_3 and then concentrated. The residue was extracted several times with ether. The extracts were combined and washed sequentially with brine and water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated. The residue was purified by radial plate chromatography (Chromatotron, 4-mm silica plate, hexane–ether eluent) to give a pale yellow oil (329 mg, 54% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66 (s, 1 H); 3.81–3.87 (m, 2 H); 3.90 (s, 3 H); 4.17 (q, 1 H, J = 6.3 Hz); 5.24 (d, 1 H, J = 7.8 Hz); 5.28 (s, 1 H); 5.93–6.05 (m, 1 H); 6.74 (d, 1 H, J = 7.8 Hz); 6.86 (d, 1 H, J = 7.8 Hz); 7.29 (t, 1 H, J = 7.8 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 55.29, 56.23, 64.88, 94.56, 109.32, 117.52, 120.37, 129.18, 137.23, 144.82, 158.44. IR (neat): 3405 (broad), 2938, 1565, 1466, 1463, 1426, 1265, 1057, 1028, 1012, 780 cm^{-1}. Molecular formula: $C_{11}H_{13}IO_2$. HRMS: calcd, 303.9962 amu; found, 303.9960 ± 0.001 amu.

2-(2-Iodo-3,6-dimethoxyphenyl)-3-buten-1-ol (12): 30% yield; white solid; mp 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60–1.64 (t, 1 H); 3.75 (s, 3 H); 3.80 (s, 3 H); 3.87–4.04 (m, 2 H); 4.35–4.40 (m, 1 H); 5.09–5.23 (m, 2 H); 6.18–6.30 (m, 1 H); 6.68 (d, 1 H, J = 9.0 Hz); 6.82 (d, 1 H, J = 9.0 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 56.08, 57.02, 57.63, 64.00, 109.57 (2 carbons), 111.99, 116.89, 133.38, 136.70, 151.82, 152.82. IR (KBr): 3272 (broad), 2939, 1569, 1464, 1432, 1258, 1241, 1064, 1059, 1029, 1013, 992, 795 cm^{-1}. Molecular formula: $C_{12}H_{15}IO_3$. Anal. Calcd: C, 43.13; H, 4.49. Found: C, 43.17; H, 4.47.

2-[2-Iodo-1-(benzyloxy)-3-naphthyl]-3-buten-1-ol (13): 50% yield; yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60–1.62 (bs, 1 H); 3.88–4.03 (m, 2 H); 4.22–4.28 (m, 1 H); 5.10 (s, 2 H); 5.28–5.37 (m, 2 H); 6.06–6.17 (m, 1 H); 7.39–7.54 (m, 6 H); 7.70 (d, 2 H, J = 6.6 Hz); 7.84 (d, 1 H, J = 7.8 Hz); 8.11 (d, 1 H, J = 7.8 Hz). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 55.20, 65.15, 75.39, 94.80, 97.45, 117.86, 122.31, 123.41, 126.57, 127.06, 127.13, 127.82, 128.08, 128.26, 128.57, 134.31, 136.78, 137.46, 140.00. IR (neat): 3375 (broad), 1350, 1075, 1073, 1030, 749,736, 696 cm^{-1}. Molecular formula: $C_{21}H_{19}IO_2$. HRMS: calcd 430.0431 amu; found, 430.0422 ± 0.001 amu.

2-(2-Iodo-3-methylphenyl)-3-buten-1-ol (14): 51% yield; pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67–1.71 (bs, 1 H); 2.48 (s, 3 H); 3.76–3.88 (m, 2 H); 4.11–4.18 (m, 1 H); 5.20–5.26 (m, 2 H); 5.90–6.01 (m, 1 H); 6.99 (d, 1 H, J = 7.5 Hz); 7.13 (d, 1 H, J = 7.5 Hz); 7.19 (d, 1 H, J = 7.5 Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 30.39, 56.09, 65.14, 109.75, 117.62, 125.27, 128.10, 128.60, 137.69, 143.11, 143.65. IR (neat): 3353 (broad), 1461, 1033, 1006, 919, 780 cm^{-1}. Molecular formula: $C_{11}H_{13}IO$. HRMS: calcd, 288.0013 amu; found, 288.0011 ± 0.001 amu.

2,3-Dihydro-2-methoxy-3-(2-iodo-3-methoxyphenyl)furan (7): 52% yield; yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 3 H); 3.90 (s, 3 H); 4.41 (d, 1 H, J = 1.8 Hz); 5.14 (s, 1 H); 5.18 (t, 1 H, J = 3.0 Hz); 6.61 (s, 1 H); 6.74 (d, 1 H, J = 8.7 Hz); 6.76 (d, 1 H, J = 7.4 Hz); 7.25 (dd, 1 H, J = 8.3, 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.74 (q), 56.50 (q), 58.33 (d), 93.01 (s), 104.37 (d), 109.77 (d), 111.93 (d), 120.71 (d), 129.50 (d), 145.03 (d), 158.51 (s). IR (neat): 2935, 2958, 1615, 1566, 1466, 1463, 1266, 1039, 1034 cm^{-1}. Molecular formula: $C_{12}H_{13}IO_3$. HRMS: calcd, 331.9911 amu; found, 331.9907 ± 0.001 amu.

2,3-Dihydro-2-methoxy-3-(2-iodo-3-methylphenyl)furan (16): 55% yield; yellow solid; mp 52–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3 H); 3.51 (s, 3 H); 4.42 (s, 1 H); 5.13 (s, 1 H); 5.16–5.19 (m, 1 H); 6.61 (d, 1 H, J = 2.6 Hz); 6.91–6.96 (m, 1 H); 7.13–7.21 (m, 2 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 30.09, 55.73, 58.96, 104.58, 108.09, 112.01, 125.51, 128.25, 128.87, 142.89, 143.71, 145.41. IR (KBr): 3854, 3040, 2937, 1616, 1462, 1396, 1101, 967 cm^{-1}. Molecular formula: $C_{12}H_{13}IO_2$. Anal. Calcd: C, 45.58; H, 4.12. Found: C, 45.60; H, 4.08.

Additional Spectral Data. Complex 3. ^{1}H NMR (300 MHz, C_6D_6): δ 3.23 (s, 3 H); 3.52–3.60 (m, 1 H); 4.29–4.31 (m, 2 H); 5.01–5.14 (m, 2 H); 5.92 (s, 5 H); 6.05 (s, 5 H); 6.12–6.21 (m, 1 H); 6.41 (d, 1 H, J = 7.9 Hz); 7.07 (d, 1 H, J = 7.4 Hz); 7.20 (dd, 1 H, J = 7.4, 7.9 Hz). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 53.33, 58.59, 75.73, 105.56, 111.40, 111.75, 114.51, 123.38, 127.70, 143.68, 149.29, 163.32, 164.55.

Complex 10. ^{1}H NMR (300 MHz, C_6D_6): δ 1.52–1.82 (m, 9 H); 2.29–2.60 (m, 3 H); 2.88–2.91 (m, 1 H); 4.00–4.12 (m, 2 H); 5.12–5.15 (m, 1 H); 5.18 (s, 1 H); 5.93 (s, 5 H); 5.95 (s, 5 H); 6.12–6.24 (m, 1 H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 26.69, 27.36, 28.38, 29.12, 30.91, 33.19, 58.92, 75.13, 110.75, 111.80, 114.20, 142.00, 143.53, 180.86.

Compound 19. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.68–1.80 (d, 1 H); 2.32–2.52 (m, 4 H); 3.78 (s, 3 H); 3.81–3.95 (m, 5 H); 4.58 (d, J = 1.6 Hz); 6.71–6.84 (m, 3 H); 7.20 (dd, 1 H, J = 7.8, 7.9 Hz). ^{13}C NMR (75 MHz, C_6D_6): δ 31.78, 31.92, 48.13, 54.44, 60.94, 70.90, 98.70, 111.47, 113.40, 119.70, 129.66, 149.79, 160.63, 161.32. IR (neat): 3385 (broad), 1644, 1250, 1048 cm^{-1}.

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Registry No. **1**, 130641-66-6; **3**, 130641-67-7; **4**, 101145-08-8; **5**, 130614-48-1; **6**, 130641-64-4; **7**, 130614-49-2; **9**, 130641-63-3; **10**, 130641-65-5; **12**, 130614-51-6; **13**, 130614-52-7; **14**, 130614-53-8; **15**, 130614-54-9; **16**, 130614-55-0; **17**, 51061-89-3; *cis*-**18**, 130614-56-1; *trans*-**18**, 130614-50-5; **19**, 130614-57-2; $Cp_2Zr(Me)Cl$, 1291-45-8; 2-BrC_6H_4OMe, 578-57-4; 2,5-dihydrofuran, 1708-29-8; 2,5-dihydro-2,5-dimethoxyfuran, 332-77-4; 2-bromo-1,4-dimethoxybenzene, 25245-34-5; 2-bromo-1-(benzyloxy)naphthalene, 76939-81-6; 2-bromo-1-methylbenzene, 95-46-5; 1,4-dioxaspiro-[4.4]non-8-ene, 695-56-7; 1,4-dihydro-1,4-epoxynaphthalene, 573-57-9.

(11) Shirai, H.; Yashiro, T.; Kuwayama, T. *Yakugaku Zasshi* **1973**, *93*(10), 1371.

(12) The initial ring-opening/methanolysis product is **19**, which is unstable and undergoes hydrolysis followed by air oxidation to give **17**: