Additions to $Fe(CO)_3$−Dienal Complexes: Dependence of Diastereoselectivity on Lewis Acid

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Lewis acid mediated additions to $Fe(CO)_3$−2,4-dienal complexes are explored. Silyl enol ether and allylstannane nucleophiles both undergo aldehyde addition with good diastereoselectivity. However, with $TiCl_4$ as the catalyst, the Ψ-exo diastereomer is the major product while with $BF_3{\cdot}Et_2O$ the Ψ-endo diastereomer is favored. Lewis acid/substrate interactions are studied by VT-NMR, and a hypothesis that accounts for the observed diastereoselectivity is presented.

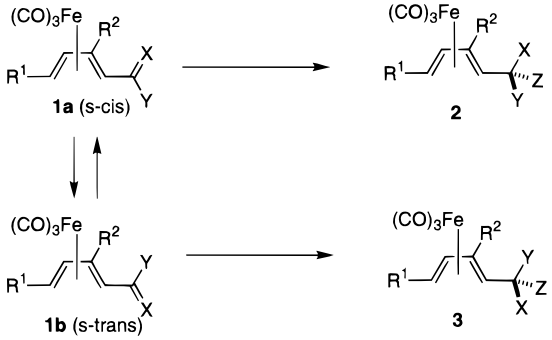
Introduction

Irontricarbonyl-1,3-diene complexes have attracted considerable attention as vehicles for the control of both relative and absolute stereochemistry.[1,2] Particular attention has been focused on the ability of the $Fe(CO)_3$−diene unit to influence the relative stereochemistry created upon functionalization of adjacent prochiral functionality (see Scheme 1). Reactions at the C═X bond of **1** are generally thought to occur anti to the $Fe(CO)_3$ unit for both steric and stereoelectronic reasons. Sterically, one of the carbon monoxide ligands of the $Fe(CO)_3$ unit is located in the vicinity above the C═X substituent, blocking the approach of nucleophiles from the syn face. Stereoelectronically, the electron-rich metal center stabilizes an adjacent cation via coordination to dienyl systems in an η^5-fashion[3−6] and is expected to strongly interact with the π*-orbital of the C═X bond, especially when the C═X bond is electron deficient.

The principal stereocontrol element in such reactions is generally envisioned to be the conformation of the σ bond between the diene complex and the adjacent functionality.[7] Both s-cis (**1a**) and s-trans (**1b**) conformations are possible, with the preferred conformation being highly dependent upon the nature of the substituents X, Y, and R^2. Addition to the face of the C═X bond anti to the $Fe(CO)_3$ moiety via the s-cis conformation (**1a**) leads to **2**, while anti-addition to the s-trans conformation (**1b**) leads to **3**.

Reactions upon an alkene appendage (**1**, X = CR_2, Y = H) are strongly biased toward anti-addition to the s-trans conformation (**1b**). Nitrile oxide cycloaddition (85:15 to 91:9 selectivity),[8] Diels−Alder cycloadditions (100:0 selectivity),[9] OsO_4 addition (100:0 selectivity),[10] cyclopropanations,[11−13] and 1,4-addition of organometallic reagents (generally 100:0 selectivity)[5,14,15] all appear to react via anti-addition to the s-trans conformation of **1**. Similarly, enolate alkylation (X = C(O^-)OR, Y = H) also appears to occur via anti-addition to the s-trans conformation.[16] Preference for the s-trans conformation (**1b**) is attributed to the presence of severe steric interactions in the s-cis conformation (**1a**) between the alkene substituents (X) and the substituent at the C^2 position of the diene complex (R^2).

Scheme 1



Conversely, hydride reduction of ketone-substituted complexes (X = O, Y = alkyl) appears to occur via anti-addition to the s-cis conformation (**1a**), leading to **2** (X = O, Y = alkyl, Z = H), with excellent (>95:5) selectivity.[3,4,17,18] Preference for the s-cis conformation in this case has been attributed to the presence of significant steric interactions in the s-trans conformation between the alkyl substituent (Y) and the substituent at the C^2 position of the diene complex (R^2).

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In contrast, the diastereoselectivity when nucleophiles are added to aldehyde-substituted $Fe(CO)_3$−diene complexes (X = O, Y = H) is generally modest. The addition of Grignard reagents and alkyllithiums to such aldehydes generally occurs preferentially to the s-cis conformation, leading to **2** (X = OH, Y = H, Z = Nuc) rather than **3** with, at best, 80:20 selectivity.[2,19−21] Alkynyllithium reagents add in a similar fashion with a slightly higher level of diastereoselectivity.[22] In contrast, Ti(IV)- and Al(III)-based reagents have been reported to modestly favor the production of **3** over **2** (X = OH, Y = H, Z = Nuc; 75:25 selectivity).[2] This reversal of stereoselectivity has been suggested to be due to initial addition of the nucleophile to one of the carbon monoxide ligands with subsequent transfer to the syn face of the aldehyde in the s-cis conformation.[23] Lewis acid-catalyzed diene−aldehyde cyclocondensation reactions have been reported to behave similarly. With $BF_3{\cdot}Et_2O$ as the catalyst, the s-trans-derived addition product (75:25) is favored while with $TiCl_4$ the s-cis-derived product (79:21 selectivity) is favored, though in considerably reduced yield.[24,25] Indium-mediated aldehyde allylation proceeds with a slight preference (55:45) for the s-cis conformation.[26] Nucleophilic addition to the corresponding imine (X = NCH_2-Ph, Y = H) proceeds via the s-trans conformation with a high level of diastereoselectivity (100:0).[27]

In connection with the development of general approaches to the control of acyclic stereochemistry, we sought to broaden the scope of the nucleophilic addition to $Fe(CO)_3$−2,4-dienal complexes by studying whether higher levels of diastereoselectivity could be obtained via employment of Lewis acid mediated pathways. Signficant improvements in diastereoselectivity have been noted previously in connection with studies of Lewis acid catalyzed additions to aldehydes containing neighboring stereogenic centers.[28,29]

Results

Dienal complex **4**, which is readily available via thermolysis of 2,4-nonadienal in the presence of an $Fe(CO)_3$ source, was used throughout these studies.[30,31] Treatment of **4** in methylene chloride at −78 °C with $BF_3{\cdot}Et_2O$ (1.5 equiv) followed by addition of silyl enol ether **5**[32,33] produced an 84:16 mixture of β-hydroxy ketones **6** and **7**

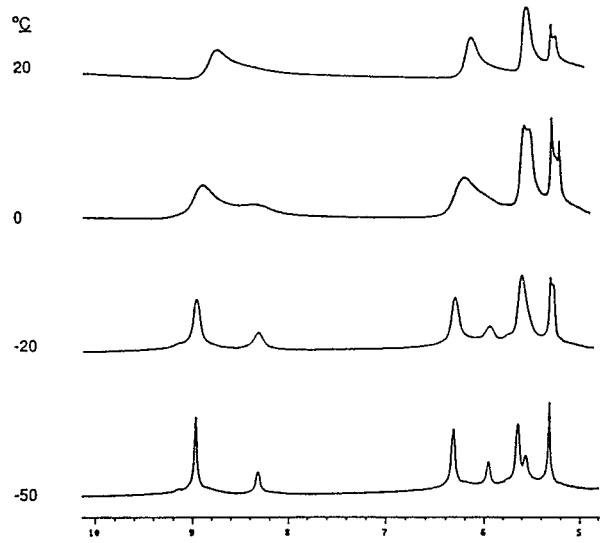
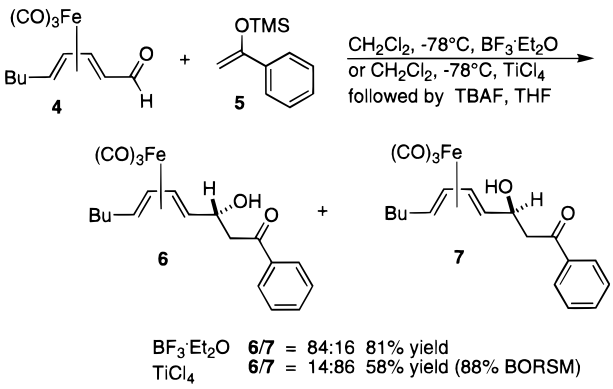


Figure 1. Variable-temperature NMR study of **4** with $BF_3{\cdot}Et_2O$.

Scheme 2



in 81% yield. Careful workup was required in order to avoid dehydrative elimination of **6** and **7** to the corresponding complexed trienone. The major isomer, **6**, is envisioned to arise via anti-addition of the silyl enol ether to the s-cis conformation of **4**.

In contrast, employment of $TiCl_4$ (0.86 equiv) as the catalyst, again in CH_2Cl_2 at −78 °C, led initially to a mixture of **6** and **7** and the corresponding silyl ethers. Treatment with TBAF in THF provided a 14:86 ratio of **6**/**7** in 58% yield (88% yield based on recovered starting material). The major product with this catalyst can be viewed as being derived from anti-addition of the silyl enol ether to the s-trans conformation of **4** (Scheme 2).

The stereochemistry of **6** and **7** was assigned on the basis of consideration of the chemical shifts of the protons on the diene as well as the relative polarity of the compounds on silica. It has been empirically observed that the signal for the α-H of the Ψ-exo isomer, in general, appears upfield relative to that of the Ψ-endo

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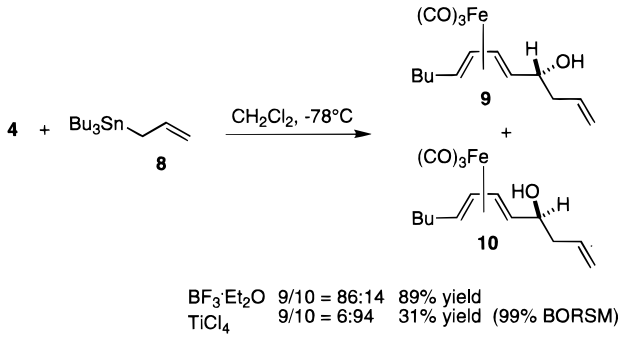
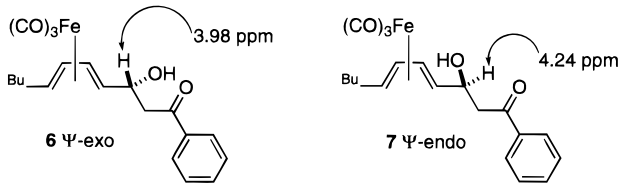
Scheme 3



isomer (Figure 1).[34−36] The significant polarity difference between such compounds was first observed by Gresham, Lillya, Uden, and Walter[37] and has routinely been used to assign relative stereochemistry to such systems.[24]



To determine whether the diastereoselectivity was nucleophile dependent, the Lewis acid catalyzed addition of allyltributylstannane to dienal complex **4** was investigated. With BF_3·Et_2O (1.2 equiv) as the catalyst, a 86:14 mixture of **9** and **10** was produced in 89% yield. As with silyl enol ether **5**, alcohol **9** is considered to be derived from anti-addition to the s-cis conformation of **4**. Conversely, $TiCl_4$ (0.50 equiv) catalyzed addition of **8** to **4** produced a 6:94 mixture of **9** and **10** in 37% yield (99% yield based on recovered starting material) (Scheme 3). As before, the major product produced with $TiCl_4$ catalysis can be viewed as being derived from anti addition of the allyl group to the s-trans conformation of **4**. These results follow the same trend previously seen in the Lewis acid-catalyzed addition of a siloxydiene to an $Fe(CO)_3$−dienal complex.[15]

Variable-Temperature NMR Studies. In an attempt to develop a better understanding of the nature of the interaction between complex **4** and these two Lewis acids, variable-temperature NMR studies of **4** in the presence of BF_3·Et_2O and $TiCl_4$ were conducted. An initial VT-NMR study of the aldehyde complex in the absence of any Lewis acid demonstrated that its spectrum did not change when the temperature was lowered from rt to −60 °C. With $TiCl_4$, at least 1.0 equiv. of the Lewis acid was employed with no significant change observed upon addition of additional equivalents. With BF_3·Et_2O 1.5 equiv. were necessary to eliminate signals corresponding to free aldehyde. The free aldehyde was thought to be due to competitive coordination of BF_3 to Et_2O and the aldehyde. No significant change was observed upon addition of additional equivalents of BF_3.

With BF_3·Et_2O (Figure 1), at 20 °C broadening of all of the signals was observed. As the temperature was incrementally lowered to −50 °C, many of the signals resolved into two distinct signals of unequal intensity. In particular, the aldehyde C−H absorption resolved into two distinct peaks, at 8.3 and 9.0 ppm in approximately a 1:4 ratio. With $TiCl_4$ (Figure 2), similar behavior was seen. At 40 °C broadening was seen with resolution of

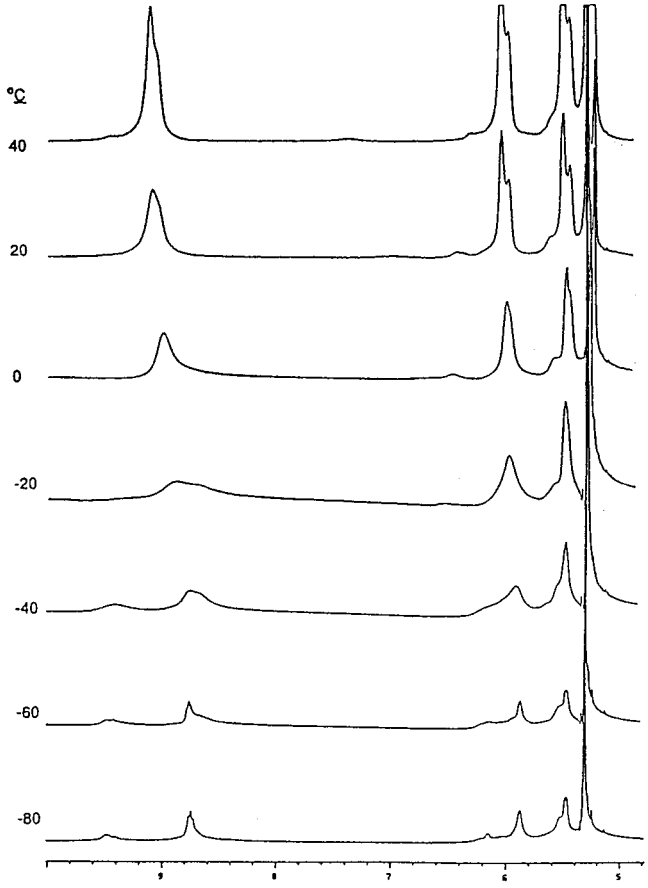


Figure 2. Variable-temperature NMR study of **4** with $TiCl_4$.

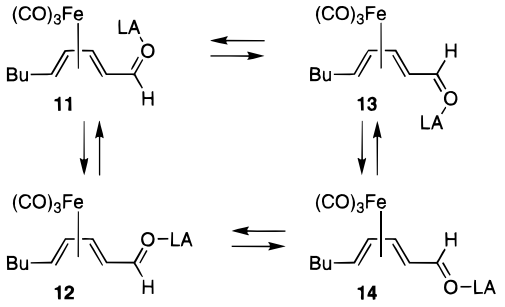
the aldehyde absorption at less than −40 °C into two signals at approximately 8.7 and 9.4 ppm in approximately a 10:1 ratio.

Discussion

It is feasible for these Lewis acids to coordinate to either the aldehyde oxygen or to an oxygen of one of the carbon monoxide ligands. If coordination to an oxygen of one of the carbon monoxide ligands were to occur, reduced fluxionality about the diene−Fe bond would be expected at lower temperature and, minimally, three conformational isomers would be expected.[38] Since only two conformational isomers were detected at low temperature, the mode of interaction of these Lewis acids with **4** appears to be exclusively via coordination to the aldehyde oxygen. This suggests that initial addition of the nucleophile to one of the carbon monoxide ligands, followed by intramolecular transfer of the nucleophile to the syn face of the aldehyde in the s-cis conformation, as suggested previously by Franck-Neumann et al.,[23] is highly unlikely.

Assuming that BF_3 and $TiCl_4$ both have a similar effect on the chemical shift of the aldehyde proton, it appears that each Lewis acid causes a different conformation to be favored. With BF_3, the aldehyde proton of the major isomer is downfield of the minor isomer while with $TiCl_4$ the major isomer is significantly upfield of the minor isomer. The outcome of the addition reactions suggests that with BF_3 conformation **12** is preferred. Donaldson et al. also proposed that the major isomer in their BF_3 catalyzed reaction arose from addition to the carbonyl

Scheme 4



group in the s-cis conformation.[24] In the case of $TiCl_4$, addition via the s-trans conformation **14** dominates.

Though coordination to the aldehyde oxygen in a wide array of orientations is possible,[39] it is illustrative to first consider in plane coordination to the s-cis and s-trans conformations of **4** in both *E* and *Z* orientations. These four possibilities are shown in Scheme 4. Coordination in the *Z*-orientation to the s-cis isomer (**11**) is unlikely because of steric interactions between the Lewis acid and the C-2 hydrogen of the diene complex. Complexation in the *Z*-orientation to the s-trans isomer (**13**) is also expected to be unlikely because of steric interactions between the Lewis acid and the endo hydrogen at the C-1 position of the diene complex. Coordination in the *E*-orientation to the s-cis (**12**) and s-trans (**14**) conformations is expected to be preferred.[39]

The degree of out-of-plane bending of the Lewis acid and the C−O−LA bond angle are also important variables. Crystal structures of systems containing carbonyl−boronic Lewis acid complexes generally have the Lewis acid within 11° of the plane of the carbonyl. Such complexes also generally have a C−O−B bond angle between 112 and 119°. In contrast, there is considerably greater variability seen with titanium complexes. Extreme out-of-plane bending is seen in some cases and Ti−O−C bond angles greater than 150° have been noted.[39]

These two Lewis acids also have considerably different coordination geometries. If all three fluorine ligands remain bound, the boron based Lewis acid has only a single coordination site available and is expected to react with a Lewis base to form tetrahedral complex **15**. In contrast, the titanium based system has two available coordination sites and can form either a trigonal bipyramid complex (**16**) or, if both additional sites are occupied, octahedral complexes (**17** or **18**). Oligomeric complexes of titanium have also been characterized.

A final noteworthy feature is the impact of the electron rich $Fe(CO)_3$-diene moiety. Electron donation by this group is anticipated to allow the aldehyde oxygen to function as a four-electron donor to titanium (**19**). When bound to complex **4**, such an intermediate might best be viewed as a titanoxy-substituted dienyl cation system with the $Fe(CO)_3$ moiety involved in coordination to the "cationic" aldehyde carbon (see **20** and **21**). The carbon−oxygen−titanium bond angle in such a system would likely approach 180°, which would increase significantly the steric interaction between the chloride ligands on titanium and the C^2-hydrogen of the diene complex in the s-cis conformation (**15**), causing the s-trans conformation (**16**) to be preferred. Overall, this analysis suggests

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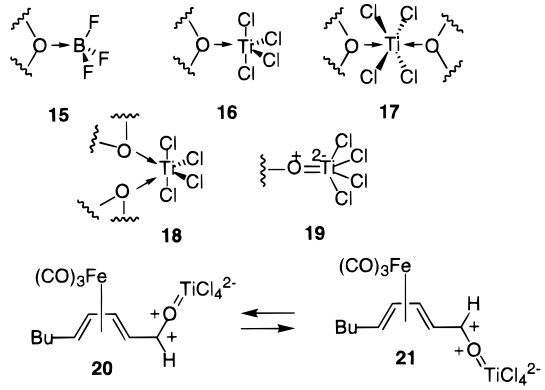
Scheme 5



that with BF_3 reaction via **12** is favored while with $TiCl_4$ reaction via conformation **21** is expected (Scheme 5).

Conclusions

In this study, we found that the stereoselectivity of the Lewis acid mediated addition to complex **4** was strongly Lewis acid dependent. Based on VT-NMR studies of Lewis acid/aldehyde complexes, we speculate that the major diastereomer obtained in each case corresponds to attack of the nucleophile anti to the $Fe(CO)_3$ moiety but that the face of the aldehyde that is positioned anti to the $Fe(CO)_3$ with each Lewis acid is different. With BF_3 catalysis the reaction appears to occur via addition to the s-cis conformation **12** to generate the Ψ-endo alcohol, while $TiCl_4$ appears to react via s-trans conformation **21** to preferentially generate the Ψ-exo alcohol.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR spectra were recorded on either 500 or 300 MHz spectrometers in the solvents indicated. IR spectra were recorded on a FT-IR spectrophotometer. Column chromatography was performed with Florisil (100−200 mesh) or silica gel (200−425 mesh) with a gradient elution ethyl acetate/hexane solvent system unless otherwise indicated. All reagents were obtained from commercial suppliers and used as received unless otherwise indicated. Tetrahydrofuran was distilled from potassium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane was distilled from calcium hydride under a nitrogen atmosphere. All reactions were carried out under a nitrogen atmosphere.

Variable-Temperature NMR. To an NMR tube containing CD_2Cl_2 (approximately 0.5 mL) was added aldehyde tricarbonyl[(2,3,4,5-η)-2,4-nonadienal]iron (**4**) (5.0 mg, 0.018 mmol). This solution was degassed via three cycles of freeze/pump/thaw and flushed with nitrogen. The Lewis acid was added, and the sample was introduced into the spectrometer. Each sample was incrementally cooled and allowed to equilibrate at the given temperature for a period of 15 min. To ensure that the composition of the sample had not changed upon prolonged exposure to the Lewis acid, each sample was then incrementally warmed to room temperature. Spectra obtained as the sample was warmed were found to be essentially identical to those previously obtained as the sample was cooled.

BF_3·Et_2O-Mediated Addition of Trimethyl[(1-phenylethenyl)oxy]silane (5) to Tricarbonyl[(2,3,4,5-η)-2,4-nonadienal]iron (4). Tricarbonyl[(2,3,4,5-η)-2,4-nonadienal]-iron (**4**) (117.4 mg, 0.422 mmol) in CH_2Cl_2 (8.0 mL) under nitrogen at −78 °C was treated with BF_3·Et_2O (78.0 μL, 0.634 mmol) followed after 10 min by trimethyl[(1-phenylethenyl)-oxy]silane (**5**) (155 mg, 0.806 mmol). After 15 min, saturated $NaHCO_3$ solution was added and the reaction mixture was warmed to room temperature. After extraction with CH_2Cl_2,

the combined organics were dried over sodium sulfate, concentrated in vacuo, and purified by silica gel chromatography to give keto alcohols **6** and **7** (135 mg, 81% yield) in an 84:16 ratio.

$TiCl_4$-Mediated Addition of Trimethyl[(1-phenylethenyl)oxy]silane (5) to Tricarbonyl[(2,3,4,5-η)-2,4-nonadienal]iron (4). To a solution of complex **4** (58.0 mg, 0.209 mmol), in CH_2Cl_2 (5.0 mL) at −78 °C, was added $TiCl_4$ (11.0 μL, 0.104 mmol) turning the yellowish solution dark orange-brown. After 5 min, trimethyl[(1-phenylethenyl)oxy]silane (**5**) (86.0 mg, 0.447 mmol) was added. After 5.5 h, additional trimethyl[(1-phenylethenyl)oxy]silane (**5**) (65.0 mg, 0.338 mmol) was added. After an additional 6.5 h, additional $TiCl_4$ (8.0 μL, 0.076 mmol) was added. After a further 8 h, the reaction was quenched with saturated $NaHCO_3$ solution, allowed to warm to room temperature, and extracted with CH_2Cl_2. The combined organics were dried over sodium sulfate and concentrated in vacuo.

To a solution of this crude material in THF (10 mL) at 0 °C was added tetrabutylammonium fluoride (1.0 mL, 1.0 mmol). The reaction was allowed to warm to room temperature, and after 30 min saturated $NaHCO_3$ solution was added. The reaction mixture was then extracted with CH_2Cl_2, and the combined organics were dried over sodium sulfate, concentrated in vacuo, and purified by silica gel chromatography to give keto alcohols **6** and **7** (48 mg, 58%) in a 14:86 ratio, as well as **4** (20.0 mg; yield of **6**/**7** based on recovered starting material = 88%). Ψ-*endo*-tricarbonyl[(3,4,5,6-η)-3-hydroxy-1-phenyl-4,6-undecadien-1-one]iron **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3H), 1.03−1.09 (m, 2H), 1.25−1.44 (m, 4H), 1.53−1.72 (m, 2H), 3.11 (d, J = 2.9 Hz, 1H), 3.14 (dd, J = 17.6, 8.8 Hz, 1H), 3.30 (dd, J = 17.6, 2.9 Hz, 1H), 4.27−4.31 (m, 1H), 5.07 (dd, J = 8.3, 4.9 Hz, 1H), 5.32 (dd, J = 8.8, 4.9 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.96 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.3, 33.8, 34.3, 47.9, 64.6, 66.1, 68.8, 80.3, 84.1, 128.1, 128.7, 133.7, 136.5, 199.7; IR (CH_2Cl_2) 3575, 2931, 2042, 1970, 1678, cm^{-1}. Ψ-*exo*-Tricarbonyl[(3,4,5,6-η)-3-hydroxy-1-phenyl-4,6-undecadien-1-one]iron **7**: ^{1}H NMR (500 MHz,$CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 8.5 Hz, 1H), 1.20−1.43 (m, 4H), 1.54−1.74 (m, 3H), 3.22 (dd, J = 18.1, 8.8 Hz, 1H), 3.33 (dd, J = 18.1, 1.7 Hz, 1H), 3.60 (d, J = 3.6 Hz, 1H), 3.92−4.10 (m, 1H), 5.14 (dd, J = 8.8, 4.9 Hz, 1H), 5.38 (dd, J = 8.2, 4.9 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.2, 33.8, 34.2, 45.8, 62.3, 65.8, 70.4, 82,8, 85,7, 128.1, 133.8, 136,4, 200,5; IR (CH_2Cl_2) 3549,3056, 2985, 2931,2874, 2042, 1973, 1677, 1598, cm^{-1}.

BF_3·Et_2O-Mediated Addition of Allyltributyltin (8) to 4. To a solution of **4** (57 mg, 0.21 mmol), in CH_2Cl_2 (5.0 mL), under a nitrogen atmosphere at −78 °C, was added BF_3·Et_2O (30.0 μL, 0.245 mmol), turning the yellow solution orange-brown. After 20 min, allyltributyltin (**8**) (190 μL, 0.613 mmol) was added. After 30 min the reaction was quenched with saturated $NaHCO_3$ solution and allowed to warm to room temperature. This mixture was extracted with CH_2Cl_2, and the combined organics were dried over $MgSO_4$ and concentrated in vacuo. The crude product was immediately chromatographed, giving a mixture of alcohols **9** and **10** (55.4 mg, 89%) in a 86:14 ratio.

$TiCl_4$-Mediated Addition of Allyltributyltin (8) to 4. To a solution of **4** (92.8 mg, 0.334 mmol) in CH_2Cl_2 (7.0 mL) at −78 °C was added $TiCl_4$ (18.0 μL, 0.164 mmol), turning the yellow solution a dark orange-brown. After 20 min, tributylallyltin (205 μL, 0.661 mmol) was added. After 2 h, the reaction was quenched with saturated $NaHCO_3$ solution and allowed to warm to room temperature. This mixture was extracted with CH_2Cl_2, and the combined organics were dried over sodium sulfate, concentrated in vacuo, and immediately chromatographed to give a mixture of alcohols **9** and **10** (33.4 mg, 31%) in a 5:95 ratio as well as 63.7 mg of aldehyde **4** (yield of **9**/**10** = 99% yield based on recovered starting material). Ψ-*endo*-Tricarbonyl[(5,6,7,8-η)-1,5,7-dodecatrien-4-ol]iron **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 6.6 Hz, 3H) 1.00 (t, J = 8.3 Hz, 1H), 1.08 (q, J = 7.6 Hz, 1H), 1.26−1.43 (m, 4H), 1.52−1.62 (m, 2H), 1.66−1.73 (m, 1H), 2.21−2.31 (m, 1H), 2.34−2.39 (m, 1H), 3.51−3.57 (m, 1H), 5.06 (dd, J = 8.5, 5.1 Hz, 1H), 5.15−5.18 (m, 3H), 5.77−5.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 22.3, 33.8, 34.2, 44.8, 64.9, 67.2, 72.8, 80.8, 84.3, 118.6, 134.1; IR (CH_2Cl_2) 3597, 3060, 2930, 2041, 1965 cm^{-1}.

Ψ-*exo*-Tricarbonyl[(5,6,7,8-η)-1,5,7-dodecatrien-4-ol]iron **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 8.3 Hz, 1H), 1.18 (q, J = 7.6 Hz, 1H), 1.26−1.43 (m, 3H), 1.53−1.60 (m, 2H), 1.68 (p, J = 7.3 Hz, 1H), 1.79 (d, J = 3.9 Hz, 1H), 2.25 (dt, J = 14.6, 7.6 Hz, 1H), 2.45−2.52 (m, 1H), 3.47 (tt, J = 7.9, 3.9 Hz, 1H), 5.08 (dd, J = 8.8, 4.9 Hz, 1H), 5.19 (apparent d, J = 12.7 Hz, 2H), 5.26 (dd, J = 8.3, 4.9 Hz, 1H), 5.81−5.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 22.3, 33.8, 34.2, 43.0, 63.4, 65.4, 72.9, 82.4, 85.5, 119.0, 134.0; IR (CH_2Cl_2) 3597, 3055, 2986, 2961, 2931, 2859, 2042, 1964 cm^{-1}.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra of **6**, **7**, **9**, and **10** and VT NMR studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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