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Iron Tricarbonyl Stabilized Pentadienyl Cation as Initiator for Cascade Polycyclizations: A Diastereoselective Entry into Octahydrophenanthrenes

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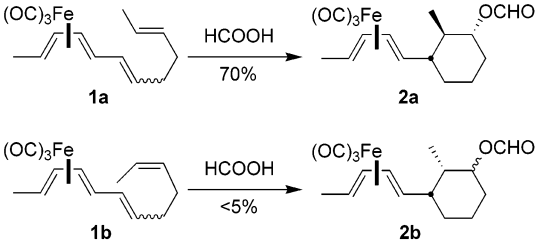
Abstract: A new example is provided of completely diastereoselective polycyclization, affording the octahydrophenanthrene framework. Generation of an iron tricarbonyl stabilized pentadienyl carbocation is the triggering event of the cascade reaction. The carbocation is generated by anchimerically assisted regiospecific protonation of a double bond adjacent to the iron tricarbonyl diene moiety. Tetrafluoroboric acid ether complex appears to be the optimum reagent, affording good yields, even under catalytic conditions.

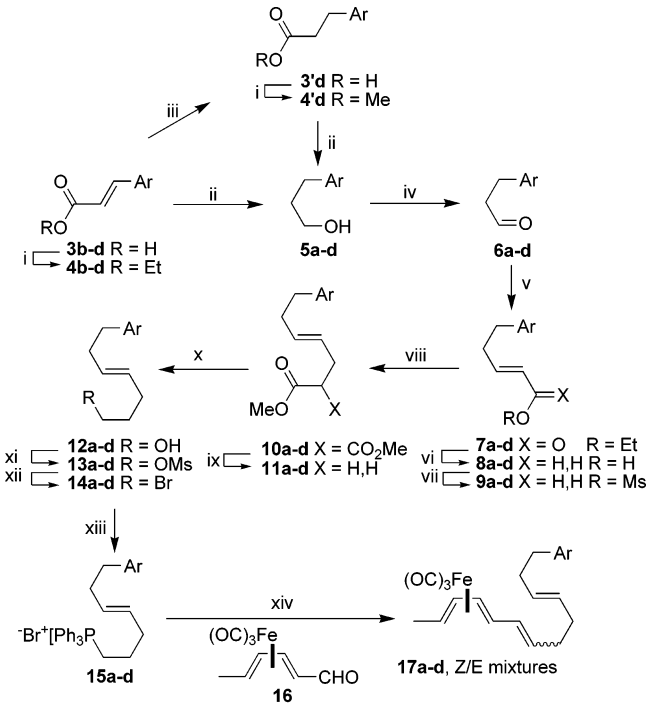
Iron tricarbonyl diene complexes continue to evolve as useful auxiliaries in synthetic organic chemistry.[1] A recent example of biomimetic double cyclization of polyolefinic substrates, using the iron tricarbonyl pentadienyl cation as initiator, illustrates its versatility in generating diastereoselectivity.[2] This work has its roots in Johnson's seminal work on "Nonenzymic Biogenetic-like Olefinic Cyclizations" and related works,[3] the first to prove correct the Stork−Eschenmoser postulate,[4] which inspired numerous research groups in developing new methods for this type of tandem reaction, seeking to improve and introduce new ways to achieve diastereoselectivity and enantioselectivity. The high appeal of this reaction lies in its ability to create a number of new C−C bonds and introduce several stereocenters in one step.

Herein we present another protocol for this transformation, derived from our new method to generate carbocations that are stabilized by a neighboring diene-$Fe(CO)_3$ group.[5] Several substrates were prepared, which cyclized in very good yields, even under catalytic conditions, and complete diastereoselectivity was observed. Our focus was on pendant *E*-substituted olefins, since a simple cyclization employing a pendant *Z*-substituted olefin afforded only traces of the desired cyclization product (Scheme 1). We believe that the *Z*-substituted double bond in **1b** places a high steric demand on the cyclization reaction.

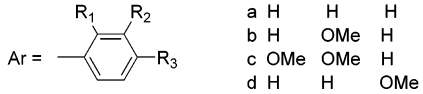
SCHEME 1. *E* vs *Z* Pendant Olefin Behavior



SCHEME 2. Synthesis of Polyene Substrates



i: EtOH, H_2SO_4; ii: $LiAlH_4$; iii: H_2, Pd/C; iv: PCC;
v: $(C_2H_5O)_2P(O)CH_2CO_2C_2H_5$, LiCl, DBU; vi: DIBAL-H;
vii: $MeSO_2Cl$, Et_3N; viii: $CH_2(CO_2Me)_2$, NaH; ix: NaCl, H_2O, DMF, 150°C;
x: $LiAlH_4$; xi: $MeSO_2Cl$, Et_3N; xii: LiBr; xiii: PPh_3; xiv: nBuLi, **16.**



	R^1	R^2	R^3
a	H	H	H
b	H	OMe	H
c	OMe	OMe	H
d	H	H	OMe

The substrates were prepared as described in Scheme 2, starting with commercially available cinnamyl and hydrocinnamyl derivatives, following literature procedures.[6] Whereas 3-methoxy- (**4b**) or 2,3-dimethoxy-

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(2) Franck-Neumann, M.; Geoffroy, P.; Hanss, D. *Tetrahedron Lett.* **2002**, *43*, 2277−2280.

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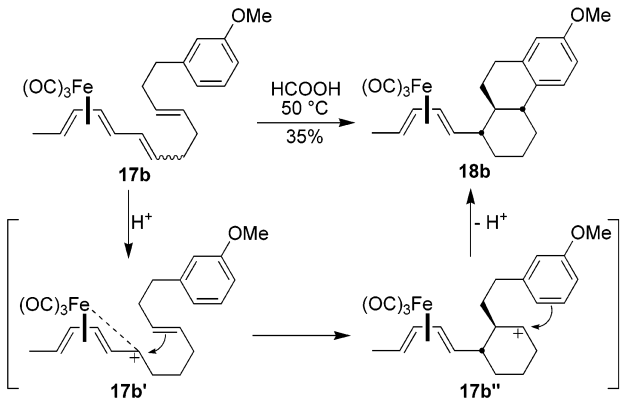
SCHEME 3. Double Cyclization Mechanism



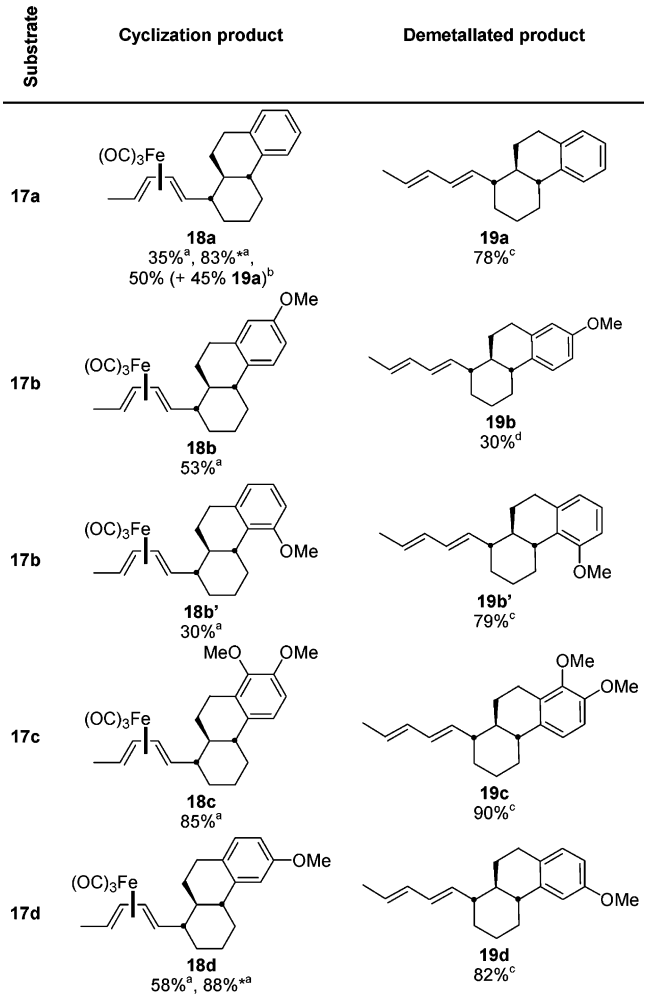
substituted (**4c**) esters were readily reduced by $LiAlH_4$ to afford the corresponding saturated alcohols (**5b**,**c**) in high yields, the 4-methoxy-substituted cinnamic ester (**4d**) yielded only 20% of the corresponding alcohol (**5d**) along with a complex mixture of inseparable compounds, presumably due to the electron rich nature of the substrate. An alternate hydrogenation/esterification/reduction route had to be employed in this case. Horner–Emmons olefination of aldehydes **6a**–**d** provided the disubstituted olefins **7a**–**d** in very good yields and with complete *E* selectivity.

We began our exploration of cationic polycyclization with substrate **17b**, which was considered to bear the most reactive terminator (*p*-OMe-substituted phenyl ring with respect to the cyclization position). We initially used our previously reported cyclization method, HCOOH neat, 50 °C.[5] Disappointingly, only 35% yield of cyclization product **18b** could be isolated from a very complex product mixture (Scheme 3). This is not surprising because formic acid will not only protonate the double bond adjacent to the iron tricarbonyl diene moiety, an event that triggers the cyclization reaction, but is sufficiently nucleophilic to compete with the pendant olefin for the same cation. In the case of the polycyclization reaction, an extra cationic intermediate **17b″** appears on the reaction pathway, increasing the possibility of side reactions (Scheme 3).

Simple pendant olefin substrates follow a "cyclization–nucleophile insertion" pathway, affording formyloxy derivatives,[5] thus benefitting from the double role of the formic acid. At the same time, simple pendant aromatic substrates, or combined olefin/aromatic terminators, only require the acid to perform the protonation step. Since the proton is being regenerated in the termination step, a catalytic amount of acid should be sufficient to promote the reaction. Therefore we decided to replace formic acid with an acid that has a less nucleophilic conjugate base. Tetrafluoroboric acid ether complex proved to be the best reagent, affording very clean cyclizations in dry dichloromethane at 0 °C. Both stoichiometric and catalytic amounts (ca. 25% molar) of acid were employed. Along with the expected cyclization product **18b**, obtained in 53% yield, its regioisomer **18b′** was also isolated in 30% yield (Chart 1). The remaining substrates followed a similar path. Substrate **17a** afforded the expected cyclization product **18a**, albeit in low yield under catalytic conditions, due to the reduced nucleophilicity of the unactivated phenyl ring. However, most of the unreacted starting material was recovered. While extending the reaction time was considered a logical way to improve the yield, demetalation of the starting material over longer reaction time was somewhat of a drawback and prevented the overall increase of the yield. Under stoichiometric conditions complex **18a** was obtained in 50% yield, along with ca. 45% demetalated product **19a**, which suggests a near quantitative cyclization reaction. Substrates **17c** and **17d**, designed to cyclize unambiguously to a single product, also performed very well, with **17c** affording a superior yield, while **17d** was somewhat lower, due to the less favorable position of the methoxy activating substituent (Chart 1).

To establish stereochemistry we relied on NMR analysis. This proved to be a difficult endeavor for the cyclization products **18a**–**d**, due to extensive overlapping of diagnostic resonances. Two mild methods of demeta-

CHART 1. Cyclization Products and Their Demetalated Counterparts[a]



[a] Reagents and conditions: (a) 25% molar $HBF_4{\cdot}OEt_2$, 0 °C, CH_2Cl_2, 4 h. (b) Stoichiometric $HBF_4{\cdot}OEt_2$, 0 °C, CH_2Cl_2, 4 h. (c) 10–30 equiv of Me_3NO, acetone, room temperature, overnight. (d) Saturated $CuCl_2$ in ethanol. An asterisk indicates numbers based on reacted starting material.

lation[7] were employed to afford the tricyclic demetalated products **19a**−**d**, for which extensive 1D and 2D (COSY) analysis revealed the expected all-trans cyclization products, consistent with the Stork−Eschenmoser hypothesis.[4]

By employing correlation spectroscopy (COSY) the angular hydrogen resonances were easily assigned. Analysis of coupling constants reveals that hydrogen atoms H_1, H_{4a}, and H_{10a} are all axial, consistent with a trans ring junction and equatorial position for the demetalated diene moiety (1D and 2D spectra included in Supporting Information).

In conclusion, we have described new examples of a catalytic, completely diastereoselective double cyclization reaction of polyolefinic substrates, using an iron tricarbonyl-stabilized pentadienyl cation as the initiator. With the advent of new methods for the preparation of enantiopure iron tricarbonyl diene complexes[8] such as **16**, enantiospecific cyclizations should be easily available.

Experimental Section

Complexes **1a** and **2a** are already reported.[5] Complex **2b** was not fully characterized due to extremely low yields that could not be improved.

Representative Experimental Procedure for the Preparation of Polyene Substrates 1b, 17a−d. Phosphonium salt **15c** (0.49 g, 0.85 mmol, 1 equiv) was concentrated from dichloromethane and dried overnight in vacuo. Under Ar atmosphere, 10 mL of dry THF was added via syringe. *n*-BuLi (2.5 M in hexanes, 0.68 mL, 2 equiv[9]) was added dropwise at −78 °C. The mixture was stirred for 30 min at −78 °C. A solution of 0.36 g (1.8 equiv) of iron tricarbonyl sorbaldehyde complex **16** in 5 mL of dry THF was transferred by cannula into the reaction flask. Stirring was continued for 30 min at −78 °C, the cold bath was removed, and the reaction flask was allowed to warm to room temperature. Reaction progress was monitored by TLC. The reaction was quenched by addition of saturated NH_4Cl solution (5 mL). The organic phase was diluted with diethyl ether, washed with saturated $NaHCO_3$ solution, water, and brine, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and flash chromatography separation afforded 319.5 mg (83%) of complex **17c** as a yellow oil.

^{1}H NMR spectra are reported for the *Z*/*E* mixtures; as the *Z* isomer is the major one, it is assumed that the resolved signals belong to it. Whenever possible, two sets of ^{13}C NMR are reported; major signals are again assumed to belong to the major *Z* isomer.

(±)-Tricarbonyl[(2*S*)-2-5-η-(2*E*,4*E*,10*Z*)-2,4,6,10-dodecatetraene]iron, inseparable mixture of 6*Z* and 6*E* isomers (1b): yellow oil, 51% yield (82% borsm). TLC R_f 0.6 (hexanes). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 5.53−5.32 (4H), 5.14 (dd, *J* = 9.0, 4.8 Hz, 1H), 5.03 (dd, *J* = 8.2, 5.1 Hz, 1H), 2.23−2.03 (4H), 1.94 (t, *J* = 9.1 Hz, 1H), 1.61 (d, *J* = 5.2 Hz, 3H), 1.45−1.32 (4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) *Z* isomer (major) 212.4, 130.9, 130.7, 129.6, 124.5, 85.3, 82.2, 56.9, 56.7, 27.8, 26.5, 19.2, 12.8, and *E* isomer (minor) 131.8, 131.7, 130.8, 129.5, 124.3, 84.7, 81.0, 62.2, 56.7. IR (film, cm^{-1}) 2045, 1966. HRMS (FAB) M^+ calcd for $C_{15}H_{18}O_3Fe$ 302.0605, found 302.0612.

(±)-Tricarbonyl[(2*S*)-2-5-η-(2*E*,4*E*,10*E*)-13-phenyltrideca-2,4,6,10-tetraene]iron, inseparable mixture of 6*Z* and 6*E* isomers (17a): yellow oil, 80% yield. TLC R_f 0.4 (hexanes). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.35−7.15 (5H), 5.51−5.29 (4H), 5.15 (dd, *J* = 8.6, 5.1 Hz, 1H), 5.04 (dd, *J* = 7.7, 5.0 Hz, 1H), 2.68 (dd, *J* = 9.4, 7.1 Hz, 2H), 2.37−2.27 (2H), 2.17−2.03 (4H), 1.94 (t, *J* = 9.1 Hz, 1H), 1.50−1.30 (4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) *Z* isomer (major) 212.5, 142.2, 130.9, 130.7, 130.2, 130.1, 128.5, 128.3, 125.8, 85.4, 82.3, 57.0, 56.9, 36.1, 34.5, 32.2, 28.0, 19.3, and *E* isomer (minor) 131.8, 131.7, 130.1, 128.4, 125.8, 84.8, 81.1, 62.3, 56.8, 32.8. IR (film, cm^{-1}) 3027, 2923, 2855, 2037, 1966. HRMS (EI) $M^+ - 2CO$ calcd for $C_{20}H_{24}OFe$ 336.1177, found 336.1172.

(±)-Tricarbonyl[(2*S*)-2-5-η-(2*E*,4*E*,10*E*)-13-(3-methoxyphenyl)trideca-2,4,6,10-tetraene]iron, inseparable mixture of 6*Z* and 6*E* isomers (17b): yellow oil, 69% yield. TLC R_f 0.4 (EtOAc:hexanes = 1:24). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.20 (dd, *J* = 8.8, 7.5 Hz, 1H), 6.81−6.70 (3H), 5.50−5.25 (4H), 5.14 (ddd, *J* = 8.8, 5.1, 0.6 Hz, 1H), 5.03 (ddd, *J* = 8.2, 5.4, 0.7 Hz, 1H), 3.80 (s, 3H), 2.65 (dd, *J* = 10.0, 7.2 Hz, 2H), 2.38−2.23 (2H), 2.22−2.00 (4H), 1.93 (t, *J* = 8.72 Hz, 1H), 1.45−1.35 (4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) *Z* isomer (major) 212.4, 159.5, 143.8, 130.8, 130.6, 130.1, 130.0, 129.1, 120.9, 114.2, 111.0, 85.3, 82.2, 56.8, 56.7, 55.1, 36.1, 34.3, 32.1, 27.9, 19.2, and *E* isomer (minor) 131.7, 84.7, 81.0, 62.2, 56.7, 36.0, 34.2, 29.5. IR (film, cm^{-1}) 2039, 1967. HRMS (FAB) M^+ calcd for $C_{23}H_{26}O_4Fe$ 422.1180, found 422.1166.

(±)-Tricarbonyl[(2*S*)-2-5-η-(2*E*,4*E*,10*E*)-13-(2,3-dimethoxyphenyl)trideca-2,4,6,10-tetraene]iron, inseparable mixture of 6*Z* and 6*E* isomers (17c): yellow oil, 83% yield. TLC R_f 0.35 (EtOAc:hexanes = 1:10). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.98 (dd, *J* = 8.5, 7.3 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 5.60−5.25 (4H), 5.13 (dd, *J* = 8.6, 4.9 Hz, 1H), 5.02 (ddd, *J* = 8.1, 4.7, 0.8 Hz, 1H), 3.86 (s, 1H), 3.82 (s,1H), 2.68 (dd, *J* = 10.0, 5.7 Hz, 2H), 2.34−2.22 (2H), 2.17−2.00 (4H), 1.94 (t, *J* = 8.9 Hz, 1H), 1.50−1.30 (4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) Z isomer (major) 212.4, 152.7, 147.1, 136.0, 130.8, 130.7, 130.5, 129.7, 123.6, 121.9, 110.0, 85.3, 82.1, 60.6, 56.9, 56.8, 55.6, 33.7, 32.1, 30.0, 27.9, 19.2. HRMS (FAB) $M^+ - 3CO$ calcd for $C_{20}H_{28}O_2Fe$ 368.1439, found 368.1399.

(±)-Tricarbonyl[(2*S*)-2-5-η-(2*E*,4*E*,10*E*)-13-(4-methoxyphenyl)trideca-2,4,6,10-tetraene]iron, inseparable mixture of 6*Z* and 6*E* isomers (17d): yellow oil, 51% yield. TLC R_f 0.36 (EtOAc:hexanes = 1:25). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.10 (unresolved AA′ quartet, 2H), 6.82 (unresolved AA′ quartet, 2H), 5.50−5.25 (4H), 5.14 (dd, *J* = 8.8, 4.8 Hz, 1H), 5.03 (ddd, *J* = 7.8, 5.3, 0.5 Hz, 1H), 3.79 (s, 3H), 2.61 (dd, *J* = 9.8, 7.3 Hz, 2H), 2.35−2.00 (6H), 1.93 (t, *J* = 9.3 Hz, 1H), 1.45−1.30 (4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) Z isomer (major) 212.5, 157.7, 134.3, 130.9, 130.8, 130.3, 130.0, 129.4, 113.7, 85.4, 82.3, 57.0, 56.9, 55.3, 35.2, 34.8, 32.2, 28.0, 19.3. HRMS (FAB) M^+ calcd for $C_{23}H_{26}O_4Fe$ 422.1180, found 422.1095.

Representative Experimental Procedure for the Cyclization Reactions. To 45.5 mg (0.1 mmol) of complex **17c** in 1 mL of CH_2Cl_2, under Ar at 0 °C, was added 1 drop of $HBF_4 \cdot OEt_2$ (85% in diethyl ether, ca. 0.25 equiv). After 4 h at 0 °C, no further conversion by TLC could be observed. The reaction was quenched by addition of water (2 mL). The organic phase was diluted with diethyl ether, then washed with satd aq $NaHCO_3$ solution, water, and brine. Evaporation of solvents under reduced pressure and recrystallization with dichloromethane/pentane afforded 39 mg (85% yield) of complex **18c**.

(±)-Tricarbonyl((2*S*)-2-5-η-5-((1*R*,4a*R*,10a*R*)-1,2,3,4,4a,9,-10,10a-octahydrophenanthren-1-yl)-(2*E*,4*E*)-pentadiene)-iron (18a): yellow solid, mp 173 °C, 35% yield (83% yield borsm). TLC R_f 0.38 (hexanes). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.35−7.30 (1H), 7.20−7.06 (3H), 5.03 (unresolved AB quartet, 2H), 1.43 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 140.1, 136.7, 128.9, 126.1, 125.8, 125.6, 84.3, 83.9, 70.3, 57.6, 48.3, 46.8, 43.2, 37.0, 31.4, 30.1, 26.9, 26.7, 19.2. IR (KBr pellet, cm^{-1}) 2946, 2925, 2911, 2865, 2853, 2837, 2035, 1968. HRMS (EI) M^+ calcd for $C_{22}H_{24}O_3Fe$ 392.1075, found 392.1115.

(±)-Tricarbonyl((2*S*)-2-5-η-5-((1*R*,4a*R*,10a*R*)-7-methoxy-1,2,3,4,4a,9,10,10a-octahydro-phenanthren-1-yl)-(2*E*,4*E*)-pentadiene)iron (18b): yellow solid, mp 170 °C, 53% yield. TLC R_f 0.28 (EtOAc:hexanes = 1:25). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.21 (d, *J* = 8.5 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 5.02 (unresolved AB quartet, 2H), 3.77 (s, 3H), 2.85−2.73 (2H), 2.48−2.20 (3H), 1.99−1.85 (2H), 1.62−

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(9) Careful NMR analysis of the phosphonium salts revealed 0.5 to 1.0 equiv of water present, thus requiring excess of base.

1.49 (3H), 1.41 (d, J = 6.2 Hz, 3H), 1.36−1.27 (2H), 1.19−0.93 (3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 157.4, 137.9, 132.4, 127.0, 113.4, 111.8, 84.2, 83.8, 70.3, 57.5, 55.2, 48.1, 46.9, 42.6, 37.0, 31.5, 30.3, 26.9, 26.5, 19.1. IR (KBr pellet, cm^{-1}) 2039, 1967, 1953. HRMS (FAB) M$^+$ calcd for $C_{23}H_{26}O_4Fe$ 422.1180, found 422.1168.

(±)-Tricarbonyl((2*S*)-2-5-η-5-((1*R*,4a*R*,10a*R*)-5-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-(2*E*,4*E*)-pentadiene)iron (18b′): yellow oil, 30% yield. TLC R_f 0.50 (EtOAc:hexanes = 1:25). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.07 (t, J = 8.0 Hz, 1H), 6.74−6.64 (2H), 5.08−4.94 (2H), 3.78 (s, 3H), 1.42 (d, J = 6.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 158.8, 139.8, 128.9, 126.1, 121.5, 108.1, 84.2, 84.1, 70.3, 57.4, 55.0, 49.8, 48.7, 42.7, 37.8, 31.8, 31.7, 27.3, 25.9, 19.2.

(±)-Tricarbonyl((2*S*)-2-5-η-5-((1*R*,4a*R*,10a*R*)-7,8-dimethoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-(2*E*,4*E*)-pentadiene)iron (18c): yellow solid, 85% yield. TLC R_f 0.26 (EtOAc:hexanes = 1:10). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.02 (d, J = 9.0 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 5.03 (unresolved AB quartet, 2H), 3.84 (s, 3H), 3.79 (s, 3H), 3.03 (dd, J = 17.4, 4.2 Hz, 1H), 2.55 (ddd, J = 18.0, 12.6, 6.0 Hz, 1H), 2.41−2.38 (2H), 2.28 (t, J = 9.0 Hz, 1H), 1.96−1.89 (2H), 1.48 (qt, J = 13.2, 3.6 Hz, 1H), 1.42 (d, J = 6.0 Hz, 3H), 1.33−1.23 (2H), 1.19−1.11 (2H), 1.01−0.95 (2H), 0.81 (t, J = 9.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 150.2, 146.1, 133.6, 131.2, 121.2, 109.8, 84.2, 83.8, 70.3, 59.8, 57.5, 55.7, 48.1, 46.3, 42.6, 36.9, 31.5, 26.5, 26.4, 24.0, 19.2. HRMS (EI) M$^+$ − CO calcd for $C_{23}H_{28}O_4Fe$ 424.1337, found 424.1323.

(±)-Tricarbonyl((2*S*)-2-5-η-5-((1*R*,4a*R*,10a*R*)-6-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)-(2*E*,4*E*)-pentadiene)iron (18d): yellow solid, mp 169 °C, 58% yield (88% yield based on reacted starting material). TLC R_f 0.24 (EtOAc:hexanes = 1:25). ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.00 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.3, 2.6 Hz, 1H), 5.03 (unresolved AB quartet, 2H), 3.79 (s, 3H), 1.42 (d, J = 6.2 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 157.8, 141.4, 129.7, 128.9, 111.6, 111.3, 84.3, 83.9, 70.3, 57.6, 55.3, 48.3, 46.8, 43.4, 37.0, 31.4, 29.3, 27.1, 26.7, 19.2. IR (KBr pellet, cm^{-1}) 2944, 2915, 2851, 2835, 2035, 1956. HRMS (FAB) M$^+$ calcd for $C_{23}H_{26}O_4Fe$ 422.1180, found 422.1128.

Representative Experimental Procedure for the Demetalation Reactions. Trimethylamine *N*-oxide (50 mg, 10 equiv) was added to 30 mg (1 equiv) of complex **18c** in 2 mL of 1:1 acetone and ethanol. While the reaction was stirred at room temperature for 24 h, ca. 15 equiv of Me_3NO was added after checking the reaction progress by TLC. The reaction mixture was filtered through a Celite plug and evaporated. Recrystallization from dichloromethane/pentane afforded 18.7 mg (90%) of compound **19c**. Preparative TLC was also used for purification of the demetalated products, both liquids and solids.

(±)-(1*R*,4a*R*,10a*R*)-1-((1*E*,3*E*)-Penta-1,3-dienyl)-1,2,3,4,-4a,9,10,10a-octahydrophenanthrene (19a): pale yellow oil, 78% yield. TLC R_f 0.50 (hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31 (d, J = 7.8 Hz, 1H), 7.14 (tm, J = 7.2 Hz, 1H), 7.11 (tm, J = 7.5 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.09−6.01 (2H), 5.65−5.59 (1H), 5.43−5.39 (1H), 2.80 (dd, J = 8.4, 3.6 Hz, 2H), 2.48−2.46 (1H), 2.38 (td, J = 12.0, 3.0 Hz, 1H), 2.05−2.01 (1H), 1.93 (dquint, J = 13.8, 3.0 Hz, 1H), 1.90−1.84 (1H), 1.77−1.74 (1H), 1.53 (qt, J = 13.2, 4.2 Hz, 1H), 1.34−1.19 (3H), 1.14 (qd, J = 10.8, 2.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 140.5, 137.2, 136.3, 131.8, 130.3, 129.0, 127.2, 125.6, 125.5, 47.6, 44.7, 43.2, 33.7, 30.9, 30.0, 27.7, 26.1, 18.1. IR (film, cm^{-1}) 3014, 2919, 2854. HRMS (EI) M$^+$ calcd for $C_{19}H_{24}$ 252.1878, found 252.1875.

(±)-(1*R*,4a*R*,10a*R*)-7-Methoxy-1-((1*E*,3*E*)-penta-1,3-dienyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (19b): off-white solid, mp 64 °C, 30% yield. TLC R_f 0.34 (EtOAc:hexanes = 1:25). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.14 (d, J = 8.4 Hz, 1H), 6.64 (dd, J = 9.0, 3.0 Hz, 1H), 6.53 (d, J = 3.0 Hz, 1H), 6.01−5.93 (2H), 5.57−5.51 (1H), 5.33 (dd, J = 13.8, 9.0 Hz, 1H), 3.70 (s, 3H), 2.72−2.68 (2H), 2.35 (dd, J = 12.6, 3.0 Hz, 1H), 2.24 (t, J = 11.4 Hz, 1H), 1.94 (dm, J = 12.6 Hz, 1H), 1.84 (dquint, J = 13.2, 3.0 Hz, 1H), 1.78 (qd, J = 10.4, 3.6 Hz, 1H), 1.68 (d, J = 7.8 Hz, 3H), 1.44 (qt, J = 13.2, 3.6 Hz, 1H), 1.03 (qd, J = 10.8, 3.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 157.4, 138.5, 136.4, 132.8, 131.8, 130.3, 127.1, 126.6, 113.6, 111.7, 55.2, 47.5, 44.9, 42.7, 33.7, 31.1, 30.3, 27.8, 26.0, 18.1. IR (KBr pellet, cm^{-1}) 2926, 2855. HRMS (FAB) M$^+$ calcd for $C_{20}H_{26}O$ 282.1984, found 282.1975.

(±)-(1*R*,4a*R*,10a*R*)-5-Methoxy-1-((1*E*,3*E*)-penta-1,3-dienyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (19b′): pale yellow oil, 79% yield. TLC R_f 0.42 (pentane). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.06 (t, J = 7.8 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.08−5.98 (2H), 5.64−5.56 (1H), 5.43 (dd, J = 15.0, 9.6 Hz, 1H), 3.79 (s, 3H), 2.92 (d, J = 12.6 Hz, 1H), 2.77 (td, J = 14.7, 4.8 Hz, 1H), 2.66 (dq, J = 16.2, 2.2 Hz, 1H), 2.49 (t, J = 10.5 Hz, 1H), 1.98 (qd, J = 10.4, 4.2 Hz, 1H), 1.89 (dquint, J = 12.6, 2.4 Hz, 1H), 1.86−1.77 (2H), 1.75 (d, J = 6.6 Hz, 3H), 1.60 (qt, J = 13.2, 4.2 Hz, 1H), 1.09 (qd, J = 12.6, 4.2 Hz, 1H), 0.97 (qd, J = 12.0, 3.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 158.9, 140.2, 136.7, 131.8, 130.0, 129.1, 127.0, 126.1, 121.7, 108.1, 55.0, 48.0, 47.8, 43.0, 34.6, 31.9, 31.5, 26.9, 26.5, 18.1. IR (film, cm^{-1}) 2923, 2855. HRMS (FAB) M$^+$ calcd for $C_{20}H_{26}O$ 282.1984, found 282.1984.

(±)-(1*R*,4a*R*,10a*R*)-7,8-Dimethoxy-1-((1*E*,3*E*)-penta-1,3-dienyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (19c): off-white solid, mp 124 °C, 90% yield. TLC R_f 0.36 (EtOAc:hexanes = 1:10). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.01 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.08−5.99 (2H), 5.64−5.57 (1H), 5.40 (dd, J = 13.2, 9.0 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.93 (ddd, J = 17.4, 5.4, 1.8 Hz, 1H), 2.58 (ddd, J = 18.0, 12.0, 6.0 Hz, 1H), 2.41 (m, 1H), 2.29 (td, J = 11.4, 3.0 Hz, 1H), 2.05 (ddt, J = 12.6, 6.0, 2.4 Hz, 1H), 1.90 (dquint, J = 13.2, 3.0 Hz, 1H), 1.83 (qd, J = 10.4, 3.6 Hz, 1H), 1.75−1.71 (4H), 1.50 (qt, J = 13.2, 4.2 Hz, 1H), 1.26−1.14 (3H), 1.05 (qd, J = 10.8, 2.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 150.2, 146.2, 136.3, 134.0, 131.7, 131.6, 130.2, 127.1, 120.9, 109.7, 59.8, 55.7, 47.4, 44.3, 42.7, 33.6, 31.1, 27.2, 25.9, 23.9, 18.0. IR (KBr pellet, cm^{-1}) 3013, 3002, 2924, 2855, 2833. HRMS (FAB) M$^+$ calcd for $C_{21}H_{28}O_2$ 312.2089, found 312.2093.

(±)-(1*R*,4a*R*,10a*R*)-6-Methoxy-1-((1*E*,3*E*)-penta-1,3-dienyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (19d): off-white solid, mp 93 °C, 82% yield. TLC R_f 0.36 (EtOAc:hexanes = 1:25). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.98 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 1.8 Hz, 1H), 6.68 (dd, J = 7.8, 1.8 Hz, 1H), 6.07−5.99 (2H), 5.64−5.58 (m, 1H), 5.40 (dd, J = 13.8, 9.0 Hz, 1H), 3.78 (s, 3H), 2.74−2.71 (2H), 2.43−2.40 (m, 1H), 2.34 (t, J = 12.0 Hz, 1H), 2.01 (dm, J = 12.6 Hz, 1H), 1.92 (dquint, J = 13.2, 3.6 Hz, 1H), 1.85 (qd, J = 10.2, 3.0 Hz, 1H), 1.74 (d, J = 6.6 Hz, 3H), 1.52 (qt, J = 13.2, 3.6 Hz, 1H), 1.30−1.19 (3H), 1.11 (qd, J = 11.0, 2.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 157.7, 141.8, 136.3, 131.8, 130.3, 129.7, 129.4, 127.1, 111.4, 111.1, 55.3, 46.6, 44.7, 43.4, 33.7, 31.0, 29.2, 27.9, 26.1, 18.1. IR (KBr pellet, cm^{-1}) 3015, 2917, 2853. HRMS (FAB) M$^+$ calcd for $C_{20}H_{26}O$ 282.1984, found 282.1979.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **1b, 17a**−**d**, **18a**−**d**, and **19a**−**d**, as well as COSY spectra for compound **19c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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