Synthesis of 1,2- and 1,4-Disubstituted Tricarbonyl(pentadienyl)iron(+1) Cations and Reactions with Heteroatom Nucleophiles

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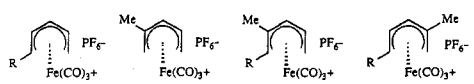
Tricarbonyl(1,2-dimethylpentadienyl)iron(+1) (**3a**), tricarbonyl(2-methyl-1-phenylpentadienyl)iron(+1) (**3b**), tricarbonyl(1,4-dimethylpentadienyl)iron(+1) (**4a**), and tricarbonyl(4-methyl-1-phenylpentadienyl)iron(+1) (**4b**) were prepared as their hexafluorophosphate salts by the dehydration of the appropriately substituted dienol complexes. The reaction of each cation with methanol and with triphenylphosphine proceeds with excellent regioselectivity to afford the corresponding methyl ethers and phosphonium salts, respectively. The reduction of each cation with sodium cyanoborohydride was also examined. Only for cation **3b** was good regioselectivity observed; the other cations gave mixtures of diene complexes.

Introduction

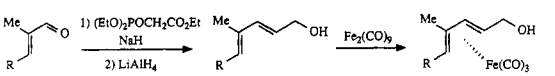
Nucleophilic attack on coordinated polyenes is one of the paradigms of π-organometallic chemistry.[1] Where these types of reactions occur with predictable regioselectivity they can be of synthetic utility. For example, the tricarbonyl((1–5-η)-4-methoxy-1-methylcyclohexadienyl)iron(+1) cation is known to undergo nucleophilic attack at Cl with a wide range of nucleophiles,[2] and for this reason it has been useful for the synthesis of trichothecenes, Aspidosperma alkaloids, and steroids.[3] There is great potential for the application of the corresponding *acyclic* (pentadienyl) cation systems to the synthesis of linear polyenes (e.g., 5-HETE methyl ester).[4] We and others have reported on attack at 1-substituted (pentadienyl)-$Fe(CO)_3$(+1) cations (1) by carbon[5] and heteroatom



nucleophiles.[6] Recently, the reactivity of tricarbonyl(2-methylpentadienyl)iron(+1) cation (**2**) with nucleophiles has been described.[7] These studies have indicated the regiochemical directing effects which can be expected for a single substituent; however, the relative strength of these directing effects is unknown. In this paper we describe the synthesis of a series of 1,2-disubstituted (**3a** and **3b**) and 1,4-disubstituted (pentadienyl)$Fe(CO)_3$ cations (**4a** and **4b**) and their reactivity with heteroatom nucleophiles.

Results and Discussion[8]

Synthesis and Characterization of Pentadienyl Cations. The most common method for the preparation of tricarbonyl(pentadienyl)iron(+1) cations involves the dehydration of coordinated pentadienols with strong acid.[6a,b,f,7,9] The requisite tricarbonyl(dienol)iron complexes can be prepared by reduction of the corresponding complexed dienals, dienones, or dienoates or by direct complexation of the dienol ligand. The electrophilic acylation of tricarbonyl(diene)iron complexes is known to produce complexed dienones.[10] However, in general, this reaction proceeds at the unsubstituted terminus of 1-substituted diene complexes,[10a] and for 2-substituted complexes it occurs with low regioselectivity.[10b] Thus, in order to obtain regiospecifically substituted pentadienyl cations, it was deemed prudent to first prepare the dienol ligands. 4-Methyl-2,4-hexadien-1-ol (**5a**) was prepared from the



condensation of tiglic aldehyde with ethyl diethylphosphonacetate (NaH/C_6H_6) followed by reduction with

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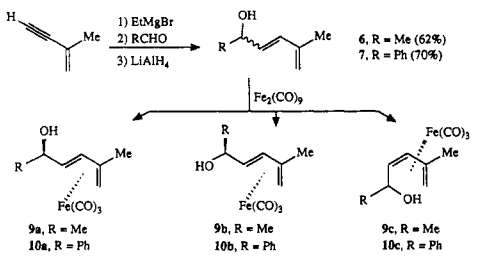
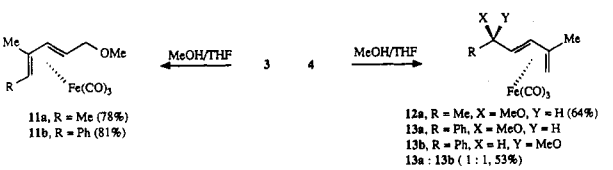
$LiAlH_4$ (Et_2O) according to the literature procedure.[11] 4-Methyl-5-phenyl-2,4-pentadien-1-ol (**5b**) was prepared in a similar fashion starting from α-methyl-*trans*-cinnamaldehyde. 5-Methyl-3,5-hexadien-2-ol (**6**) and 4-methyl-1-phenyl-2,4-pentadien-1-ol (**7**) were each prepared from 3-methyl-3-buten-1-yne by deprotonation ($EtMgBr/Et_2O$) and condensation with acetaldehyde or benzaldehyde, followed by reduction ($LiAlH_4/Et_2O$) in a fashion similar to the preparation of 4-methyl-2,4-pentadien-1-ol.[12] Reduction by $LiAlH_4$ afforded mixtures of (*E*)-**6**:(*Z*)-**6**[13a] (ca. 5.5:1) and (*E*)-**7**:(*Z*)-**7** (ca. 8:1).[13b]

Complexation of the dienols was accomplished by treating the dienol with $Fe_2(CO)_9$ in benzene at 50 °C. For dienols **5a** and **5b** a single product was obtained (**8a** and **8b**, respectively). Reaction of dienol **6** with $Fe_2(CO)_9$ gave a mixture of Ψ-exo- and Ψ-endo-3*E*-dienol complexes (**9a** and **9b**)[14] and a single 3*Z*-dienol complex (**9c**) in a 4:3:1 ratio. In a similar fashion, dienol **7** gave Ψ-exo- and Ψ-endo-complexes **10a** and **10b** and a 3*Z*-dienol complex **10c** (3.3:3.3:1 ratio). In both cases, the Ψ-exo diastereomer could be separated from the mixture of Ψ-endo and 3*Z*-dienol diastereomers. The relative stereochemistry of the Ψ-exo and Ψ-endo diastereomers in each set is based on a combination of ^1H NMR spectral data and chromatographic mobility. It has been empirically found that the signal for the alcohol methine proton of a Ψ-exo isomer appears upfield of that for the corresponding Ψ-endo isomer.[15] In addition, the Ψ-exo isomer was found to be more polar than the Ψ-endo isomer.[16]

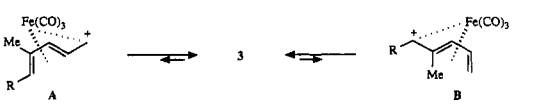


Reaction of the complexed dienols **8a**, **8b**, **9**, and **10** with hexafluorophosphoric acid in acetic anhydride/ether, followed by reprecipitation from CH_3NO_3/ether, gave the corresponding tricarbonyl(pentadienyl)iron(+1) cations (**3a**, **3b**, **4a**, **4b**) as their PF_6^- salts. In CD_3NO_2 solution, only the "U" or cisoid conformation[17] was observed for these cations, as determined by ^1H NMR chemical shifts and coupling constants.[7,9]

Reaction of Pentadienyl Cations with Heteroatom Nucleophiles. The reactions of cations **3a**, **3b**, **4a**, and **4b** with three *heteroatom* nucleophiles were studied. The reaction of monosubstituted pentadienyl cations with water has been previously examined.[6a,b,e,7] In general, this reaction has been found to produce 2(*E*),4-pentadien-1-ol complexes via attack by water on the "S" or transoid form of the pentadienyl ligand. The reaction of cations **3a**, **3b**, **4a**, and **4b** each with water gave a complex mixture of the corresponding dienols and two diastereomeric dimeric dienyl ethers. Since it had been previously observed that dimeric ethers were formed from the reaction of other dienyl cations with water,[18] methanol was chosen as the oxygen nucleophile. The reaction of **3a**, **3b**, and **4a** with methanol each gave a single 1-methoxy-2(*E*),4-diene complex in good yield (**11a**, **11b**, and **12a**, respectively). The chemical shift and coupling constant for H2 of each ($\delta \sim 1, J_{2,3} \approx 8$ Hz) are characteristic of a proton in an endo position. The relative stereochemistry of the newly developed sp^3 center (Ψ-exo) is assigned by analogy to the stereochemistry for nucleophilic attack of water on the (1-methylpentadienyl)$Fe(CO)_3$ cation.[19] The reaction of **4b** with methanol gave a mixture of Ψ-exo and Ψ-endo methyl ethers **13a** and **13b**. The structures of **13a** and **13b** were assigned by comparison of their ^1H NMR spectral data to that of the corresponding Ψ-exo and Ψ-endo alcohols **10a** and **10b**.



For cations **4a** and **4b** the regiochemical directing effects of the two substituents are "matched" for attack by an alcohol nucleophile (i.e., they both direct attack at the same dienyl terminus); however, for cations **3a** and **3b** the regiochemical directing effects of the substituents are "mismatched". Thus, while excellent regioselectivity was expected for reaction of cations **4a** and **4b** with methanol, it was not simple a priori to predict the regiospecificity which was eventually observed for the reaction of **3a** and **3b** with methanol. For these two "mismatched" cases, the directing effect of the 2-methyl substituent is dominant over the 1-substituent. This may be rationalized on the basis of the relative energy of the two possible "S" or transoid cations (**A** and **B**). The transoid cation **B** involves



steric hindrance between the endo methyl substituent and the C5 terminus which is not present in **A**. This type of rationale has previously been presented for the regiodirecting effect of the 2-methyl substituent.[7]

The reactions of the 1- and 2-methylpentadienyl cations with triphenylphosphine have been previously reported.[6d,e,7] The reaction of (1-phenylpentadienyl)iron cation **1b**[6b] with PPh_3 gave a single product, ((5-phenyl-2(*Z*),4(*E*)-pentadienyl)triphenylphosphonium)$Fe(CO)_3^+$ (**14**). From these results it appears that attack by Ph_3P occurs on the cisoid form of the pentadienyl cation at the sterically less hindered terminus.

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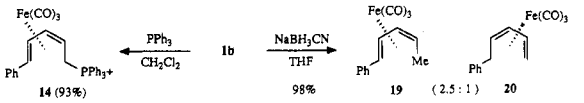
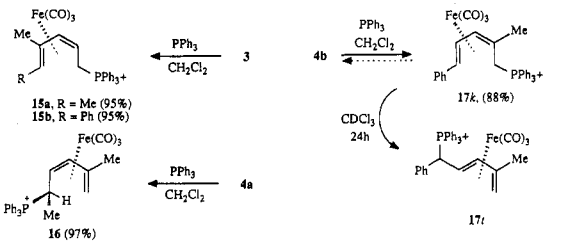


For PPh_3 as nucleophile, the substituents present on cations **3a** and **3b** have "matched" regiochemical directing effects. Thus, as expected, the reaction of cations **3a** and **3b** with Ph_3P each gave a single (2(*Z*),4(*E*)-pentadienyl)-triphenylphosphonium salt, **15a** and **15b**, in excellent yield



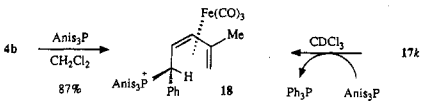
arising from attack at the unsubstituted terminus of the cisoid cation. The chemical shift for H2 ($\delta \sim 2$) and $J_{2,3}$ coupling constant (7.3 Hz) are characteristic of a cis-C2–C3 orientation.

Although the substituent patterns present on cations **4a** and **4b** constitute "mismatched" regiochemical directing effects, the reaction of each with Ph_3P gave a single product (**16** and **17***k*, respectively). While both arise via attack on the cisoid form of the cation, **16** represents attack at the substituted terminus while **17***k* represents attack at the unsubstituted terminus. The structural assignments are based on ^1H NMR spectroscopy. For **16**, the presence of a single downfield nonaryl signal (δ 4.80, d, J = 7.0, H3) and the chemical shift for H2 (δ 1.80) and $J_{2,3}$ coupling (7.0 Hz) are characteristic of a cis-1,3-disubstituted (butadiene)$Fe(CO)_3$ functionality. In comparison, for **17***k*, the presence of two downfield nonaryl signals (δ 5.53, dd, J = 5.1, 9.8 Hz, and δ 5.03, d, J = 5.1 Hz) are characteristic of a 1,1,4-trisubstituted (butadiene)$Fe(CO)_3$ functionality. The chemical shift for Me-2 (δ 1.42) is characteristic of a methyl group in an exo orientation.

While kinetic nucleophilic attack occurs at the unsubstituted terminus of **4b**, the phosphonium salt **17***k* rearranges in $CDCl_3$ solution, over the period of a few hours, to give the phosphonium salt **17***t*. The structure of **17***t* was assigned on the basis of its ^1H NMR spectral data. In particular, the presence of a single downfield nonaryl signal (δ 5.02, H3) and two upfield signals (δ 0.90, H2endo, and δ 0.46, H5endo) are characteristic of a trans-1,3-disubstituted (butadiene)$Fe(CO)_3$. This novel, unprecedented rearrangement[20] might occur by cleavage of the carbon–PPh_3 bond to give the cation **4b** and Ph_3P. The thermodynamically favored product **17***t* is formed by isomerization of the cation **4b** from the cisoid form to the transoid form, followed by nucleophilic attack by Ph_3P. Alternatively, an intramolecular mechanism for the rearrangement of **17***k* to **17***t* might be imagined.

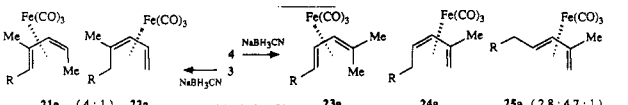
The reaction of **4b** with tris(*p*-methoxyphenyl)phosphine [$Anis_3P$] gave the phosphonium salt **18**. In comparison to **17***k*, **18** is stable in both CH_2Cl_2 and $CDCl_3$ solutions.[21] The structure of **18** was assigned on the basis of its ^1H NMR spectral data. In particular, the signals at δ 4.96 (H3), 2.04 (H5exo), and 1.65 (H5endo) are characteristic of a cis-1,3-disubstituted (butadiene)$Fe(CO)_3$ complex. The product **18** results from attack of $Anis_3P$ on the cisoid cation at Cl. In comparison, attack by Ph_3P at this site occurs on the transoid cation. Since $Anis_3P$ is more nucleophilic than Ph_3P, it might be rationalized that $Anis_3P$ will attack the more stable (and therefore less reactive) cisoid cation, while Ph_3P will only attack Cl of the less stable (and more reactive) transoid form of the cation.

The phosphonium resonance signals of **17***k*, **17***t*, and **18** appear at δ 20.1, 18.3, and 23.7 ppm, respectively. A $CDCl_3$ solution of **17***k* and $Anis_3P$ was monitored by ^{31}P NMR spectroscopy. As the reaction proceeded, the signals at δ 20.1 (**17***k*) and −9.0 ($Anis_3P$) disappear and are replaced by signals at δ 23.7 (**18**) and −4.2 (Ph_3P). Thus, in the presence of $Anis_3P$ **17***k* is transformed into **18**. This reaction must be *inter*molecular, and it seems likely that the transformation of **17***k* to **17***t* is also intermolecular. For the reaction of cation **4a** with Ph_3P and the reaction of **4b** with $Anis_3P$, the regiospecificity observed may be attributed to dominance of the 4-methyl substituent over the 1-substituent.



The reduction of pentadienyl iron cations with a variety of anionic hydride donors has been reported. Reduction by $NaBH_4$ or $LiEt_3BH$ is known to give mixtures consisting of *Z*- and *E*-diene complexes,[6a,c] while the mild reducing agent $NaBH_3CN$ is reported to react with 1-alkyl- or 2-methyl-substituted pentadienyl cations to give primarily *Z*-diene complexes.[6c,7] Since it was desired to maximize the amount of *Z*-diene products $NaBH_3CN$ was chosen for examination. The reaction of **1b** with $NaBH_3CN$ gave a mixture of (1-phenyl-1(*E*),3(*Z*)-pentadiene)$Fe(CO)_3$ (**19**) and the known[22] (5-phenyl-1,3(*Z*)-pentadiene)$Fe(CO)_3$ (**20**) in a 2.5:1 ratio.

The reaction of cations **3a**, **3b**, **4a**, and **4b** with $NaBH_3CN$ each gave a mixture of diene complexes. The diene complexes **23a** and **25a** were identified by comparison to literature spectral data.[23,24] The structural assignments



for the other diene products are based upon their characteristic ^1H NMR spectral data. Separation of the product mixtures was not attempted. Only in the case of cation **3b** was the reduction highly regioselective (>90%). A prediction of the product composition can be made in each case on the basis of a combination of the directing effects for the individual substituents.[25] Notably for cations **3a**, **3b**, and **4b** the predicted product ratios closely

(20) Previously, only $Z \rightarrow E$ isomerization of the dienyl phosphonium salts, in $CDCl_3$ or acetone-d_6, has been observed.[6d,e]

(21) Dienylphosphonium salt **18** undergoes $Z \rightarrow E$ isomerization in acetone-d_6.

(22) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954–7.

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(25) The predicted ratios are as follows: **3a** → **21a**:**22a** (3.3:1); **3b** → **21b**:**22b** (13:1); **4a** → **23a**:**24a** (1:8); **4b** → **23b**:**24b** (1:2.1).

approximate the observed ratios. Thus, while the selectivity for nucleophilic attack by $NaBH_3CN$ on disubstituted pentadienyl cations appears to be due to an indeterminate combination of steric and electronic factors, the outcome is predictable to a certain extent.

Summary

The 1,2- and 1,4-disubstituted (pentadienyl)iron(+1) cations can be prepared by dehydration of the appropriately substituted dienol complexes in good yield. Reaction of these cations with methanol or triphenylphosphine proceeds with excellent regioselectivity to afford dienol products. Reduction of the cations with $NaBH_3CN$ affords mixtures of diene complexes. For substituent combinations which have "matched" directing effects, the observed regiochemical outcome is predictable. In general, for substituent combinations which have "mismatched" directing effects, the regioselectivity of nucleophilic attack is controlled by the 2- or 4-methyl substituent. The reactivity of cations **3a**, **3b**, **4a**, and **4b** with carbon nucleophiles will be reported in due course.

Experimental Section

General Data. All reactions were carried out in flame-dried glassware under an atmosphere of nitrogen. Spectrograde solvents were used without further purification with the exception of diethyl ether (Et_2O) and tetrahydrofuran (THF), which were distilled from the sodium and potassium benzophenone ketyls, respectively, methylene chloride (CH_2Cl_2), which was distilled from phosphorus pentoxide, and hexanes, which was fractionally distilled before use. Column chromatography was performed using silica gel 62 (60–200 mesh, Aldrich). Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. Carbon and proton NMR spectra were recorded on either a GE Omega GN-300 or a Varian EM360L spectrometer. Microanalyses were sent to Midwest Microlab, Ltd., Indianapolis, IN. High-resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry. 4-Methyl-2,4-hexadien-1-ol (**5a**) was prepared from the condensation of tiglic aldehyde with ethyl diethylphosphonacetate (NaH/C_6H_6) followed by reduction with $LiAlH_4$ (Et_2O) according to the literature procedure (73%).[11] 4-Methyl-5-phenyl-2,4-pentadien-1-ol (**5b**) was prepared in a similar fashion starting from α-methyl-*trans*-cinnamaldehyde (44%): mp 41–43 °C; 60-MHz ^1H NMR ($CDCl_3$) δ 7.5–7.2 (br s, 5 H), 6.54 (s, H5), 6.46 (d, J = 15.6 Hz, H3), 5.94 (dt, J = 15.6, 6 Hz, H2), 4.29 (br d, J = 6 Hz, H1), 2.03 (s, Me), 1.67 (br s, OH). 5-Methyl-3,5-hexadien-2-ol (**6**) and 4-methyl-1-phenyl-2,4-pentadien-1-ol (**7**) were each prepared from 3-methyl-3-buten-1-yne by deprotonation ($EtMgBr/Et_2O$) and condensation with acetaldehyde or benzaldehyde, followed by reduction ($LiAlH_4/Et_2O$) in a fashion similar to the preparation of 4-methyl-2,4-pentadien-1-ol.[12] The $LiAlH_4$ reduction afforded mixtures of (*E*)-**6**:(*Z*)-**6** (ca. 5.5:1, 62%) and (*E*)-**7**:(*Z*)-**7** (ca. 8:1, 70%). **6**: Kugelrohr distilled at 37–40 °C/0.6 mmHg; 300-MHz ^1H NMR ($CDCl_3$) δ 6.30 (d, J = 15.7 Hz, *E*-H4), 5.88 (d, J = 11.9 Hz, *Z*-H4), 5.71 (dd, J = 15.7, 6.4 Hz, *E*-H3), 5.45 (dd, J = 11.9, 9.1 Hz, *Z*-H3), 4.98 (br s, *E*-C=CH_2), 4.85 (br s, *Z*-C=CH_2), 4.38 (dq, J = 6.4, 6.4 Hz, *E*-H2), 3.64 (dq, J = 9.1, 6.4 Hz, *Z*-H2), 1.84 (s, Me-5), 1.70 (br s, OH), 1.31 (d, J = 6.4 Hz, *Z*-Me-1), 1.30 (d, J = 6.4 Hz, *E*-Me-1). **7**: Kugelrohr distilled at 45–50 °C/0.7 mmHg; 300-MHz ^1H NMR ($CDCl_3$) δ 7.45–7.25 (m, 5 H), 6.43 (d, J = 15.5 Hz, *E*-H3), 6.06 (d, J = 10.6 Hz, *Z*-H3), 5.85 (dd, J = 15.5, 6.6 Hz, *E*-H2), 5.67 (m, *Z*-H2), 5.30 (dd, J = 6.6, 2.6 Hz, *E*-H1), 5.02 (br s, *E*-C=CH_2), 4.94 (br s, *Z*-H1), 4.71 (br s, *Z*-C=CH_2), 1.99 (d, J = 2.6 Hz, *Z*-OH), 1.93 (s, *Z*-Me-4), 1.84 (s, *E*-Me-4), 1.73 (br s, OH). Anal. Calcd for $C_{12}H_{14}O \cdot {}^1/_{20}H_2O$: C, 82.29; H, 8.11. Found: C, 82.16; H, 8.04.

General Procedure for Complexation of Dienols. To a solution of dienol (7–26 mmol) in C_6H_6 (ca. 50 mL) was added solid $Fe_2(CO)_9$ (1.5 molar equiv). The solution was heated to 50 °C for 5 h until all of the solid $Fe_2(CO)_9$ had disappeared. The solvent was removed under reduced pressure and the product purified by chromatography. The following dienols were treated by this method:

Complexation of 4-Methyl-2,4-hexadien-1-ol. The product was purified by chromatography (C_6H_6) to afford **8a** as a pale yellow solid (66%): mp 44–45 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 5.11 (d, J = 8.0 Hz, H3), 3.73 (m, H1), 3.60 (m, H1′), 2.14 (s, Me-4), 2.10 (br s, OH), 1.45 (d, J = 6.4 Hz, Me-6), 1.14 (q, J = 6.4 Hz, H5endo), 0.98 (m, H2endo); HRMS m/z 252.0088 [calcd for $C_{10}H_{12}O_4Fe$, 252.0084].

Complexation of 4-Methyl-5-phenyl-2,4-pentadien-1-ol. The product was purified by chromatography (Et_2O–hexanes (1:1)) to afford **8b** as a golden yellow oil (90%): ^1H NMR ($CDCl_3$) 300 MHz δ 7.4–7.2 (m, 5 H), 5.23 (d, J = 8.1 Hz, H3), 3.85 (m, H1), 3.70 (m, H1′), 2.38 (s, Me-4), 2.00 (s, H5endo), 1.60 (br s, OH), 1.27 (dt, J = 5.4, 7.8 Hz, H2endo). This compound was used without further characterization.

Complexation of 5-Methyl-3,5-hexadien-2-ol. The product was separated by chromatography (hexanes–ethyl acetate (32:1)) into two fractions. The less polar fraction consisted of a mixture of **9b** and **9c** (3:1, 20%). **9b**: 300-MHz ^1H NMR ($CDCl_3$) δ 5.24 (d, J = 8.2 Hz, H4), 3.75 (ddq, J = 3.6, 7.7, 6.3 Hz, H2), 2.18 (s, Me-5), 1.82 (d, J = 2.2 Hz, H6exo), 1.36 (d, J = 3.6 Hz, OH), 1.33 (d, J = 6.3 Hz, Me-1), 0.86 (br t, J = 7.9 Hz, H3endo), 0.36 (d, J = 2.2 Hz, H6endo). **9c**: 300-MHz ^1H NMR ($CDCl_3$) δ 5.12 (d, J = 7.8 Hz, H4), 3.22 (m, H2), 2.51 (dd, J = 7.8, 9.5 Hz, H3), 2.18 (s, Me-5), 1.95 (d, J = 3.2 Hz, H6exo), 1.45 (d, J = 4.0 Hz, OH), 1.43 (d, J = 3.2 Hz, H6endo), 1.17 (d, J = 6.1 Hz, Me-1). The more polar fraction consisted of **9a** (20%): mp 37–38 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 5.31 (d, J = 8.0 Hz, H4), 3.61 (m, H2), 2.17 (s, Me-5), 1.83 (d, J = 2.4 Hz, H6exo), 1.66 (br s, OH), 1.35 (d, J = 6.2 Hz, Me-1), 0.75 (t, J = 8.1 Hz, H3endo), 0.46 (d, J = 2.4 Hz, H6endo); 75-MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.4, 100.7, 86.3, 71.1, 64.3, 43.7, 25.0, 22.6. Anal. Calcd for $C_{10}H_{12}O_4Fe$: C, 47.65; H, 4.80. Found: C, 48.15; H, 4.97.

Complexation of 4-Methyl-1-phenyl-2,4-pentadienol. The product was separated by chromatography (hexanes–ethyl acetate (32:1)) into two fractions. The less polar fraction consisted of a mixture of **10b** and **10c** (3.5:1, 26%). **10b**: 300-MHz ^1H NMR ($CDCl_3$) δ 7.4–7.3 (m, 5 H), 5.29 (d, J = 8.1 Hz, H3), 4.49 (dd, J = 2.5, 8.2 Hz, H1), 2.14 (s, Me-4), 1.88 (d, J = 2.5 Hz, OH), 1.83 (br d, J = 1.9 Hz, H5exo), 1.03 (t, J = 8.1 Hz, H2endo), 0.39 (d, J = 1.9 Hz, H5endo). **10c**: 300-MHz ^1H NMR ($CDCl_3$) δ 7.4–7.3 (m, 5 H), 5.04 (d, J = 7.6 Hz, H3), 4.02 (dd, J = 3.4, 10.2 Hz, H1), 2.69 (dd, J = 7.6, 10.2 Hz, H2exo), 2.10 (br d, J = 2.0 Hz, H5exo), 2.05 (s, Me-4), 1.86 (d, J = 3.4 Hz, OH), 1.74 (d, J = 2.0 Hz, H5endo). The more polar fraction consisted of **10a** (20%): mp 85–86 °C; 300-MHz ^1H NMR ($CDCl_3$) δ 7.4–7.2 (m, 5 H), 5.53 (d, J = 7.8 Hz, H3), 4.51 (d, J = 7.8 Hz, H1), 2.14 (s, Me-4), 2.09 (br s, OH), 1.81 (br s, H5exo), 1.00 (br t, J = 7.8 Hz, H2endo), 0.46 (br s, H5endo); 75 MHz $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.0, 144.0, 128.6, 128.0, 125.8, 100.4, 86.0, 76.8, 63.7, 43.6, 22.6. Anal. Calcd for $C_{15}H_{14}O_4Fe$: C, 57.35; H, 4.49. Found: C, 57.35; H, 4.39.

General Procedure for the Preparation of Pentadienyl Cations. To a cold solution of HPF_6 (3.5 mL, 60% in H_2O) in acetic anhydride (3.5 mL) was added dropwise a solution of tricarbonyl(dienol)iron (ca. 7 mmol) in acetic anhydride (3 mL) and Et_2O (8 mL). The mixture was added dropwise to a large excess of Et_2O (ca. 400 mL). The precipitate was collected by vacuum filtration, dissolved in CH_3NO_2, and reprecipitated by dropwise addition of excess Et_2O (ca. 400 mL). The precipitate was collected by vacuum filtration and dried in vacuo. The following cations were prepared by this method:

Tricarbonyl(1,2-dimethylpentadienyl)iron(+1) Hexafluorophosphate (3a). The product was isolated as a pale yellow solid (68%): mp 148–153 °C dec; 300-MHz ^1H NMR (CD_3NO_2) δ 6.90 (d, J = 7.2 Hz, H3), 6.06 (ddd, J = 7.2, 10.1, 12.8 Hz, H4), 3.63 (dd, J = 3.8, 10.1 Hz, H5exo), 2.68 (q, J = 6.3 Hz, H1endo), 2.56 (dd, J = 3.8, 12.8 Hz, H5endo), 2.44 (s, Me-2), 1.80 (d, J =

6.3 Hz, Me-1). Anal. Calcd for $C_{10}H_{11}O_3FePF_6$: C, 31.61; H, 2.92. Found: C, 31.66; H, 2.89.

Tricarbonyl(2-methyl-1-phenylpentadienyl)iron(+1) Hexafluorophosphate (3b). The product was isolated as a golden yellow solid (72%): mp 152–158 °C dec; 60-MHz ^{1}H NMR (CD_3NO_2) δ 7.4–7.3 (m, 5 H), 7.00 (d, J = 8 Hz, H3), 6.20 (ddd, J = 8, 10, 13 Hz, H4), 3.80 (dd, J = 3.5, 10 Hz, H5exo), 3.33 (s, H1endo), 3.00 (dd, J = 3.5, 13 Hz, H5endo), 2.67 (s, Me-2); 15-MHz ^{13}C{^{1}H} NMR (CD_3NO_2) δ 129.5, 126.0, 125.3, 125.1, 117.2, 98.0, 91.9, 88.4, 60.3, 16.3. Anal. Calcd for $C_{15}H_{13}O_3FePF_6$: C, 40.75; H, 2.96. Found: C, 40.71; H, 2.89.

Tricarbonyl(1,4-dimethylpentadienyl)iron(+1) Hexafluorophosphate (4a). The product was isolated as a pale yellow solid (70%): mp 153–159 °C dec; 300-MHz ^{1}H NMR (CD_3NO_2) δ 6.83 (d, J = 6.6 Hz, H3), 5.90 (dd, J = 7.1, 12.4 Hz, H2), 3.49 (m, H5exo and H1endo), 2.44 (s, Me-4), 1.94 (d, J = 4.1 Hz, H5endo), 1.85 (d, J = 6.0 Hz, Me-1); 75-MHz ^{13}C{^{1}H} NMR (CD_3NO_2) δ 126.3, 104.1, 96.1, 93.6, 26.3, 21.6, signal for C5 obscured by CD_3NO_2. Anal. Calcd for $C_{10}H_{11}O_3FePF_6$: C, 31.61; H, 2.92. Found: C, 31.58; H, 2.82.

Tricarbonyl(4-methyl-1-phenylpentadienyl)iron(+1) Hexafluorophosphate (4b). The product was isolated as a golden yellow solid (38%): mp 178–180 °C dec; 300-MHz ^{1}H NMR (CD_3NO_2) δ 7.6 (m, 2 H), 7.5 (m, 3 H), 7.03 (d, J = 7.1 Hz, H3), 6.65 (dd, J = 7.1, 12.9 Hz, H2), 4.49 (d, J = 12.9 Hz, H1endo), 3.69 (d, J = 4.0, H5exo), 2.44 (d, J = 4.0 Hz, H5endo), 2.52 (s, Me-4); 75-MHz ^{13}C{^{1}H} NMR (CD_3NO_2) δ 129.7, 127.4, 125.8, 123.7, 120.5, 91.1, 89.9, 89.2, 58.0, 20.9. Anal. Calcd for $C_{15}H_{13}O_3FePF_6$: C, 40.75; H, 2.96. Found: C, 40.72; H, 2.95.

General Procedure for Reaction of Pentadienyl Cations with MeOH. To a suspension of tricarbonyl(pentadienyl)iron(+1) cation (ca. 0.25 mmol) in THF (2 mL) was added methanol (2 mL). The suspension immediately went into solution, and the mixture was stirred for 1 h at rt. The solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was dried and the solvent evaporated. The residue was purified by chromatography (hexanes–ethyl acetate (2:1)). The following methyl ethers were prepared in this fashion:

Tricarbonyl(1-methoxy-4-methyl-2(*E*),4(*E*)-hexadiene)iron (11a). The product was isolated as a yellow oil (78%): 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.10 (d, J = 8.3 Hz, H3), 3.60 (dd, J = 4.5, 10.3 Hz, H1), 3.34 (s, OMe), 3.22 (dd, J = 8.9, 10.3 Hz, H1′), 2.12 (s, Me-4), 1.44 (d, J = 6.4 Hz, Me-6), 1.13 (q, J = 6.4 Hz, H5endo), 0.91 (br dt, J = 8.6, 4.6 Hz, H2endo); HRMS m/z 266.0247 (calcd for $C_{11}H_{14}O_4Fe$, 266.0244).

Tricarbonyl(1-methoxy-4-methyl-5-phenyl-2(*E*),4(*E*)-pentadiene)iron (11b). The product was isolated as a yellow oil (81%): 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 5 H), 5.19 (d, J = 8.3 Hz, H3), 3.66 (dd, J = 4.6, 10.7 Hz, H1), 3.34 (dd, J = 8.1, 10.7 Hz, H1′), 3.39 (s, OMe), 2.37 (s, Me-4), 1.97 (s, H5endo), 1.22 (dt, J = 8.1, 4.6 Hz, H2endo); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 211.4, 139.3, 129.4, 128.2, 126.4, 99.0, 84.8, 74.3, 65.6, 58.3, 54.2, 19.7; HRMS m/z 328.0413 (calcd for $C_{16}H_{16}O_4Fe$, 328.0401).

Tricarbonyl(2-methoxy-5-methyl-3(*E*),5-hexadiene)iron (12a). The product was isolated as a yellow oil (64%): 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.28 (d, J = 8.1 Hz, H4), 3.34 (s, OMe), 3.08 (br dq, J = 8.0, 6.2 Hz, H2), 2.17 (s, Me-5), 1.84 (br s, H6exo), 1.32 (d, J = 6.2 Hz, Me-1), 0.64 (br t, J = 8.0 Hz, H3endo), 0.44 (br s, H6endo); HRMS m/z 266.0246 (calcd for $C_{11}H_{14}O_4Fe$, 266.0244).

Tricarbonyl(1-methoxy-4-methyl-1-phenyl-3(*E*),5-pentadiene)iron (13). The product was isolated as a 1:1 mixture of two diastereomers as a yellow oil (53%): 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.45–7.20 (m, 5 H), 5.52 (d, J = 8.1 Hz, Ψ-exo H3) and 5.21 (d, J = 8.5 Hz, Ψ-endo H3), 3.96 (d, J = 7.3 Hz) and 3.91 (d, J = 7.5 Hz, both H1), 3.20 and 3.19 (2 × s, OMe), 2.16 and 2.11 (2 × s, Me-4), 1.75 (m, HW = 9.7 Hz, H5exo), 0.94 (t, J = 7.9 Hz) and 0.90 (d, J = 7.7 Hz, both H2), 0.39 and 0.30 (br s, both H5endo); HRMS m/z 328.0397 (calcd for $C_{16}H_{16}O_4Fe$, 328.0401).

General Procedure for Reaction of Pentadienyl Cations with PPh_3. To a solution/suspension of tricarbonyl(pentadienyl)iron(+1) hexafluorophosphate (0.25–0.50 mmol) in CH_2Cl_2 (15 mL) was added to one portion solid triphenylphosphine (1 molar equiv). The reaction mixture rapidly became clear and was stirred for 30–60 min. The solvent was evaporated under reduced pressure, and the resultant solid was washed with ether (3 × 25 mL) and dried in vacuo. The following compounds were prepared by this method:

Tricarbonyl((5-phenyl-2(*Z*),4(*E*)-pentadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (14). The product was isolated as bright yellow crystals (93%): mp 180–185 °C (foams); 60-MHz ^{1}H NMR ($CDCl_3/CH_3CN$) δ 7.9–7.6 (m, 20 H), 6.00 (dd, J = 9.1, 5.0 Hz, H4), 5.21 (br t, J = 5.7 Hz, H3), 3.60 (m, H1 and H2), 3.51 (d, J = 9.2 Hz, H5endo), 3.06 (br d, J_{PH} = 13.2 Hz, H1′); 15-MHz ^{13}C{^{1}H} NMR ($CDCl_3/CH_3CN$) δ 136.0, 134.6 (J_{PC} = 10.5 Hz), 131.2 (J_{PC} = 13.5 Hz), 129.5, 127.9, 127.1, 91.4, 825, 67.3, 63.0, 42.6, peaks for PPh_3 ipso and C5 obscured by peaks for CD_3CN); ^{31}P{^{1}H} NMR ($CDCl_3/CH_3CN$) δ 24.2 wrt H_3PO_4. Anal. Calcd for $C_{32}H_{26}O_3FeP_2F_6$: C, 55.67; H, 3.80. Found: C, 56.17; H, 3.83.

Tricarbonyl((4-methyl-2(*Z*),4(*E*)-hexadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (15a). The product was isolated as a pale yellow solid (95%): mp 69–70 °C; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.9–7.6 (m, 15 H), 4.91 (d, J = 7.3 Hz, H3), 3.13 (dd, J_{HH} = 1.6 Hz, J_{PH} = 13.5 Hz, H1), 3.10 (dd, J_{HH} = 5.6 Hz, J_{PH} = 13.5 Hz, H1′), 2.45 (q, J = 6.3 Hz, H5endo), 2.20 (s, Me-4), 1.91 (m, H2exo), 1.53 (d, J = 6.3 Hz, Me-6); 75-MHz ^{13}C{^{1}H} NMR ($CDCl_3$) δ 136.0 (J_{PC} = 3.1 Hz), 134.3 (J_{PC} = 9.1 Hz), 131.3 (J_{PC} = 12.1 Hz), 118.2 (J_{PC} = 84.2 Hz), 112.2, 82.1, 61.1, 38.0 (J_{PC} = 8.5 Hz), 19.0, 17.3. Anal. Calcd for $C_{28}H_{26}O_3FeP_2F_6 \cdot {}^1/_2Et_2O$: C, 53.04; H, 4.60. Found: C, 53.41; H, 4.20.

Tricarbonyl((4-methyl-5-phenyl-2(*Z*),4(*E*)-pentadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (15b). The product was isolated as a bright yellow solid (95%): mp 183–185 °C (foams); 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.9–7.6 (m, 15 H), 7.4–7.2 (m, 5 H), 5.09 (d, J = 7.3 Hz, H3), 3.38 (ddd, J_{HH} = 4.4, 15.9 Hz, J_{PH} = 13.8 Hz, H1), 3.15 (ddd, J_{HH} = 9.5, 15.9 Hz, J_{PH} = 13.8 Hz, H1′), 3.12 (s, H5endo), 2.20 (m, H2exo), 2.13 (s, Me-4); 75-MHz ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.7 (J_{PC} = 12.0 Hz), 130.2, 128.3, 127.0, 117.3 (J_{PC} = 84.1 Hz), 110.6, 81.7 (J_{PC} = 4.9 Hz), 66.6, 38.6, 25.1 (J_{PC} = 43.6 Hz), 20.2. Anal. Calcd for $C_{33}H_{28}O_3FeP_2F_6 \cdot {}^1/_2H_2O$: C, 55.56; H, 4.10. Found: C, 55.46; H, 3.93.

Tricarbonyl((5-methyl-3(*Z*),5-hexadien-2-yl)triphenylphosphonium)iron Hexafluorophosphate (16). The product was isolated as a pale yellow solid (97%): mp 145–148 °C; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.9–7.6 (m, 15 H), 4.80 (d, J = 7.0 Hz, H3), 3.15 (m, H1), 2.20 (d, J = 3.6 Hz, H5exo), 1.87 (s, Me-4), 1.80 (dd, J = 7.0, 14.0 Hz, H2exo), 1.80 (m, H5endo), 1.40 (dd, J_{HH} = 6.5 Hz, J_{PH} = 18.6 Hz, Me-1); 75-MHz ^{13}C{^{1}H} NMR ($CDCl_3$) δ 135.0 (J_{PC} = 3 Hz), 133.9 (J_{PC} = 9.1 Hz), 130.5 (J_{PC} = 12.1 Hz), 117.3 (J_{PC} = 79.9 Hz), 110.8, 83.6 (J_{PC} = 2.5 Hz), 48.5 (J_{PC} = 10.3 Hz), 45.3, 28.2 (J_{PC} = 35.8 Hz), 23.6, 17.4. Anal. Calcd for $C_{28}H_{26}O_3FeP_2F_6$: C, 52.36; H, 4.08. Found: C, 52.37; H, 3.99.

Tricarbonyl((2-methyl-5-phenyl-2(*Z*),4-pentadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (17*k*). The product was isolated by recrystallization from CH_2Cl_2/Et_2O as a golden yellow solid (88%): mp 145–150 °C dec; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.9–7.6 (m, 15 H), 7.3–7.1 (m, 5 H), 5.53 (dd, J = 5.1, 9.8 Hz, H4), 5.03 (d, J = 5.1 Hz, H3), 4.25 (br t, J = 13.3 Hz, H1), 3.05 (br t, J = 14.1, H1′), 2.77 (d, J = 10.1 Hz, H5), 1.42 (d, J = 1.8, Me-2); ^{31}P NMR ($CDCl_3$) δ 20.1 (PR_4^+), −143.2 (pent, J_{PF} = 780 Hz, PF_6^-) with respect to H_3PO_4. Anal. Calcd for $C_{33}H_{28}O_3FeP_2F_6$: C, 56.27; H, 4.01. Found: C, 56.22; H, 4.10. If the product is allowed to stand in $CDCl_3$ solution overnight it is transformed into tricarbonyl(4-methyl-1-phenyl-2(*E*),4-pentadien-1-yl)triphenylphosphonium)iron hexafluorophosphate (17*t*): ^{1}H NMR ($CDCl_3$) δ 8.0–6.8 (m, 20 H), 5.02 (d, J = 8.3, H3), 4.28 (t, J = 11.8 Hz, H1), 2.02 (s, Me-4), 1.86 (br s, H5exo), 0.90 (m, H2endo), 0.46 (br s, H5endo); ^{31}P NMR ($CDCl_3$) δ 18.3 (PR_4^+), −143.2 (pent, J_{PF} = 780 Hz, PF_6^-) with respect to H_3PO_4.

Tricarbonyl((4-methyl-1-phenyl-2(*Z*),4-pentadien-1-yl)-tris(*p*-methoxyphenyl)phosphonium)iron Hexafluorophosphate (18). The reaction of **4b** with tris(*p*-methoxyphenyl)-phosphine was carried out in the same fashion as the preparation of **17*k*** in 87% yield. **18**: mp 113–114 °C dec; 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.5–6.9 (m, 17 H), 4.96 (m, H3), 3.80 (s, 3 × OMe), 3.48 (br t, J = 11 Hz, H1), 2.44 (br m, H2exo), 2.04 (br s, H5exo), 1.90 (s, Me-4), 1.65 (br s, H5endo); 300-MHz ^{1}H NMR (acetone-d_6) δ 7.9–6.9 (m, 17 H), 5.44 (br d, J = 6.8 Hz, H3), 4.31 (br t, J = 13.9 Hz, H1), 3.96 (s, 3 × OMe), 2.93 (br m, H2exo), 2.24 (br d, J = 2.7 Hz, H5exo), 2.14 (br d, J = 2.7 Hz, H5endo), 2.07 (s, Me-4); ^{31}P NMR ($CDCl_3$) δ 23.7 (PR_4^+), −143.2 (pent, J_{PF} = 780 Hz, PF_6^-) with respect to H_3PO_4. Anal. Calcd for $C_{36}H_{34}O_6FeP_2F_6 \cdot 2^1/_4H_2O$: C, 51.78; H, 4.65. Found: C, 51.50; H, 4.24.

General Procedure for Reaction of Pentadienyl Cations with $NaBH_3CN$. To a suspension of the cation (0.3–0.5 mmol) in THF (25 mL) at 0 °C was added solid $NaBH_3CN$ (1 molar equiv). The reaction mixture was stirred for 5 h, during which time the solution was slowly warmed to rt. The solution was diluted with water (50 mL) and extracted with petroleum ether (3 × 30 mL). The combined extracts were dried, the solvent was evaporated, and the residue was purified by chromatography (hexanes). The following cations were reduced by this method:

Reaction of 1b with $NaBH_3CN$. The product was isolated as a yellow oil (98%). This was identified as a mixture of **19** and the known compound **20**[22] (2.5:1) by NMR spectroscopy. **19**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 5 H), 5.98 (ddd, J = 1.2, 5.2, 9.7 Hz, H2), 5.30 (br dd, J = 5.2, 7.4 Hz, H3), 3.33 (d, J = 9.8 Hz, H1endo), 2.77 (m, H4exo), 1.30 (d, J = 7.3 Hz, Me-4endo); ^{13}C{^{1}H} NMR ($CDCl_3$, partial) δ 88.4, 83.8, 60.5, 52.9, 14.5. **20**: ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 5 H), 5.50 (m, H2), 2.28 (dt, J = 3.6, 11.3 Hz, H4exo), 1.97 (dd, J = 3.2, 7.8 Hz, H1exo), 1.66 (dd, J = 3.1, 9.6 Hz, H1endo), the signal for H3 of **20** is obscured by the signal for H3 of **19**, and the signals for H5/5′ of **20** are obscured by the signal for H4exo of **19**; ^{13}C{^{1}H} NMR ($CDCl_3$, partial) δ 91.1, 86.5, 60.1, 41.2, 34.8.

Reaction of 3a with $NaBH_3CN$. The product was isolated as a yellow oil (80%). This was identified as a mixture of **21a** and **22a** (4:1) by NMR spectroscopy. **21a**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.09 (d, J = 7.8 Hz, H3), 2.45 (pent, J = 7.5 Hz, H4exo), 2.19 (q, J = 6.5 Hz, H1endo), 2.15 (s, Me-2), 1.47 (d, J = 6.5 Hz, Me-1exo), 1.11 (d, J = 7.3 Hz, Me-4endo). **22a**: ^{1}H NMR ($CDCl_3$) δ 5.27 (ddd, J = 5.2, 8.0, 9.8 Hz, H2), 1.78 (br d, J = 8.0 Hz, H1exo), 1.58 (br d, J = 9.8 Hz, H1endo), 1.57 (s, Me-4exo), 1.4 (m, 2 H), 0.88 (t, J = 7.5 Hz, Me-6), the signal for H3 of **22a** is obscured by the signal for H3 of **21a**.

Reaction of 3b with $NaBH_3CN$. The product was isolated as a yellow oil (55%). This was identified as a mixture of **21b** and **22b** (>10:1) by NMR spectroscopy. **21b**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.5–7.3 (m, 5 H), 5.19 (d, J = 8.0 Hz, H3), 3.27 (s, H1endo), 2.63 (pent, J = 7.3 Hz, H4exo), 2.37 (s, Me-2), 1.30 (d, J = 7.2 Hz, Me-4endo). **22b**: δ 7.5–7.3 (m, 5 H), 5.40 (ddd, J = 5.3, 7.5, 9.6 Hz, H2), 5.14 (d, J = 5.3 Hz, H3), 2.90 (d, J = 12.7, H5), 1.97 (dd, J = 3.0, 7.5 Hz, H1exo), 1.60 (dd, J = 3.0, 9.6 Hz, H1endo), 1.48 (s, Me-4exo); the signal for H5′ of **22b** is obscured by the signal for H4exo of **21b** (δ 2.6).

Reaction of 4a with $NaBH_3CN$. The product was isolated as a yellow oil (81%). This was identified as a mixture of **23a**, **24a**, and **25a** (2.8:4.7:1) by comparison to literature NMR spectral data.[23,24] **23a**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.07 (dd, J = 5.3, 9.1 Hz, H2), 4.98 (d, J = 5.3 Hz, H3), 1.51 (s, Me-4exo), 1.42 (d, J = 6.0 Hz, Me-1exo), 1.17 (s, Me-4endo). **24a**: δ 5.19 (d, J = 7.9 Hz, H3), 2.17 (s, Me-2), 1.87 (d, J = 2.4, H1exo), 1.49 (d, J = 2.4, H1endo), 0.92 (t, J = 7.2, Me-5). **25a**: δ 5.12 (d, J = 8.4 Hz, H3), 2.15 (s, Me-2), 1.72 (d, J = 2.0, H1exo), 1.03 (t, J = 7.3, Me-6), 0.30 (d, J = 2.0, H1endo), the signals for H-4exo of **24a** (ddd) and for H1endo of **23a** (q) overlap at ca. δ 2.4; the complex multiplets corresponding to the methylene CH_2's of **24a** and **25a** are obscured by signals at ca. δ 1.4 and 1.2; HRMS m/z 236.0144 (calcd for $C_{10}H_{12}O_3Fe$, 236.0135).

Reaction of 4b with $NaBH_3CN$. The product was isolated as a yellow oil (81%). This was identified as a mixture of **23b** and **24b** (1:3.5) by NMR spectroscopy. **23b**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 5.81 (dd, J = 5.5, 10.0 Hz, H2), 5.19 (d, J = 5.5 Hz, H3), 3.40 (d, J = 10.0 Hz, H1endo), 1.61 (s, Me-4exo), 1.41 (s, Me-4endo). **24b**: δ 7.5–7.1 (m, 5 H), 5.25 (d, J = 7.5 Hz, H3), 2.77 (dd, J = 4.3, 14.1 Hz, H5), 2.64 (ddd, J = 4.3, 7.5, 10.3 Hz, H4exo), 2.33 (dd, J = 10.3, 14.1 Hz, H5′), 2.23 (s, Me-2), 2.00 (d, J = 3.0 Hz, H1exo), 1.70 (d, J = 3.0, H1endo); HRMS m/z 298.0295 (calcd for $C_{15}H_{14}O_3Fe$, 298.0291).

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Supplementary Material Available: ^{1}H NMR spectra for compounds **8a**, **8b**, **11a**, **11b**, **12a** and the mixtures **13a/b**, **19/20**, **21a/22a**, **21b/22b**, and **23b/24b** (10 pages). Ordering information is given on any current masthead page.

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