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Iron Carbonyl Promoted Cyclocarbonylation of 3-Hydroxy α,ω-Diynes To Give (Cyclopentadienone)iron Tricarbonyl Complexes

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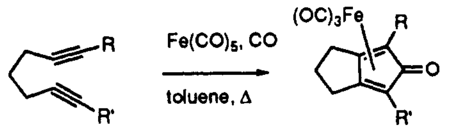
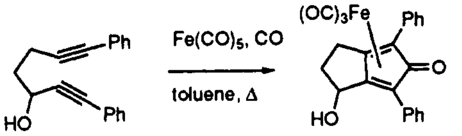
Reactions of a number of hydroxy-substituted diynes with pentacarbonyliron in toluene at 125–130 °C, under moderate pressures of carbon monoxide, afforded bicyclic cyclopentadienone–$Fe(CO)_3$ complexes. No significant diastereoselectivity was observed during the cyclocarbonylation reactions. The secondary alcohols could be converted to ketones by oxidation with pyridinium chlorochromate without detriment to the diene–$Fe(CO)_3$ group. Reaction of nucleophiles ($NaBH_4$ and vinylmagnesium bromide) with the ketones thus formed is completely stereoselective, attack occurring *anti* to the metal. During the demetalation of complex **19**, using trimethylamine *N*-oxide, an intermediate was isolated and characterized as a diene–$Fe(CO)_2(Me_2NH)$ complex, suggesting the possible generality of an unexpected mechanism that has previously been proposed for this reaction.

Introduction

An earlier paper[1] from this laboratory described reaction conditions for effecting high-yield conversion of α,ω-diynes to cyclopentadienone–$Fe(CO)_3$ complexes, exemplified by eq 1. In that study we also noted that hydroxyl substitution can be tolerated (eq 2), but the diynes that we studied do not lead to compounds that may be of interest as intermediates for the synthesis, e.g., of polyquinane natural products, such as coriolin.[2] Additionally, in order to be synthetically useful, decomplexation of the product cyclopentadienone–$Fe(CO)_3$ must be effected in good yield. The problem here lies within the inherent instability of the free cyclopentadienone and its tendency to undergo dimerization, although Vollhardt and co-workers have reported the decomplexation of related cobalt complexes of cyclopentadienones that are (kinetically) stabilized by the presence of bulky trimethylsilyl substituents.[3] More recently, Knölker and co-workers have described iron carbonyl mediated cyclocarbonylations that are almost identical with our reactions, as well as the demetalation of the product complexes, but yields and spectral data for the products were not recorded.[4]



(1)



(2)

The intramolecular Pauson–Khand reaction[5] has been extensively investigated as a method for delivering highly functionalized diquinanes, leading to the synthesis of a number of sesquiterpenoid natural products. This reaction usually does not proceed well in the presence of unprotected hydroxyl functionality or when electron-deficient alkynes are used, but such problems are now being overcome.[6] This paper describes the cyclocarbonylation of hydroxy-substituted α,ω-diynes, as well as an electron-deficient diyne. In addition, we show that a sterically crowded diyne also undergoes high-yielding cyclocarbonylation, to give molecules of potential value in natural products synthesis. Finally, demetalation of the cyclopentadienone complexes can be accomplished in a number of cases using trimethylamine *N*-oxide,[7] and evidence of a possibly general and unusual mechanism for this reaction is uncovered.

Results and Discussion

Reaction of the known[8] aldehydes **1** and **2** with lithium (trimethylsilyl)acetylide furnished the diynols **3** and **4**, respectively (eq 3). The diynol **7** was prepared by reaction of the Grignard reagent from **5** with (trimethylsilyl)propynal (**6**; eq 4). Oxidation of **3** with pyridinium chlorochromate (PCC) afforded the electron-deficient diyne **8** (eq 5).

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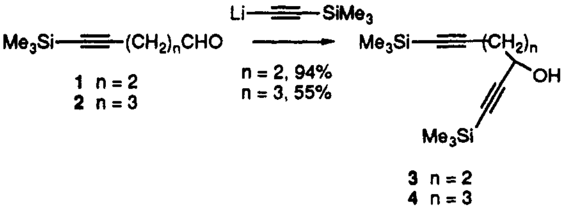
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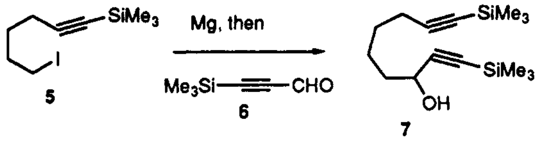
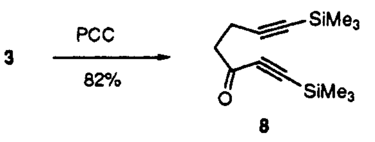

(4)

The *gem*-dimethyl-substituted hydroxy diynes **10**–**12** were prepared by a modification of the route described by Magnus and co-workers for the synthesis of the related enyne (Scheme 1).[9] Treatment of the aldehyde **9** with lithium (trimethylsilyl)acetylide gave **9**, as expected, and this was converted to a mixture of **11** (50%) and **12** (14%) using standard methodology. The silyl ether **11** could be isolated by chromatography and was used in the cyclocarbonylation reaction for comparison with the free alcohol **12**, which can be obtained by treatment of the mixture with ion exchange resin. No attempt was made to optimize the preparation of **11**, since our interest was focused on the free alcohol **12**.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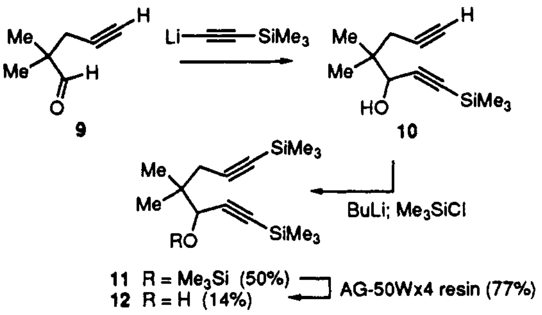
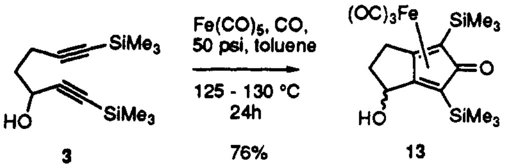
Scheme 1

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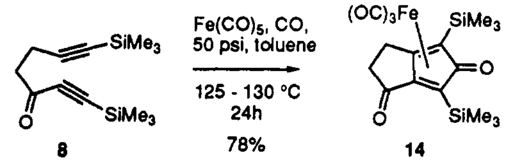
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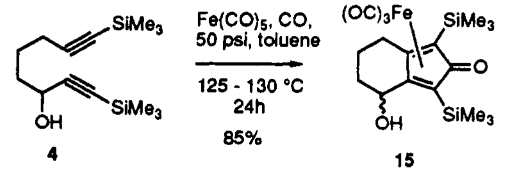
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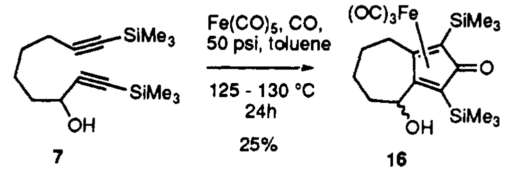
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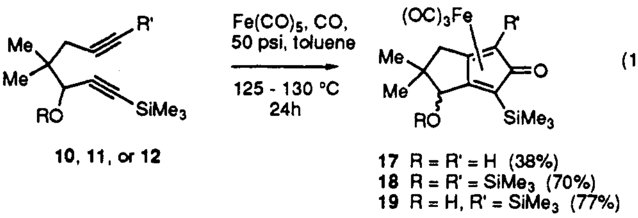
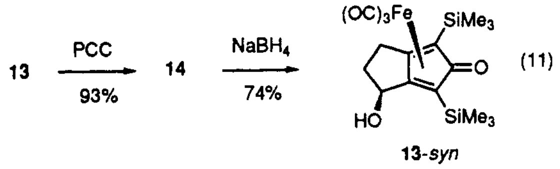

(10)

Cyclocarbonylation of the above diynes was effected by using the reaction conditions that we have previously described,[1] as summarized in eqs 6–10. The lower yield of **16** is a reflection of the greater difficulty of forming seven-membered rings; no other products were observed, and the yield quoted is based on diyne consumed. Little or no diastereoselectivity was obtained during these reactions, approximately equimolar amounts of *syn* and *anti* alcohols (with respect to iron) being formed in each case. In most cases the diastereomers could be separated chromatographically. The structures were assigned on the basis of the following experiments. Oxidation of the mixture of alcohols **13**, **15**, and **19** (PCC, CH_2Cl_2) afforded the ketones **14**, **20**, and **21**, respectively, in high yield without detriment to the $Fe(CO)_3$ moiety (eqs 11–13). Reduction of each ketone with sodium borohydride gave a single alcohol, assigned *syn* stereochemistry on the basis of the known stereochemical directing power of the $Fe(CO)_3$ group.[10] It may be noted that on TLC the *syn* isomer is usually more polar and the C*H*OH proton is found at lower field in the ^{1}H NMR spectrum than that for the *anti* compound. In the ^{13}C NMR spectra, the ring junction carbons (C.1 and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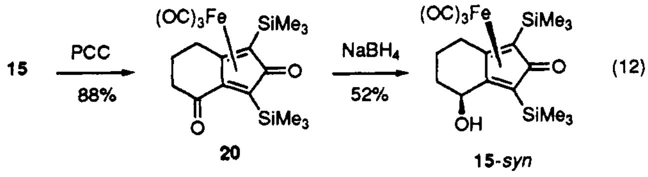
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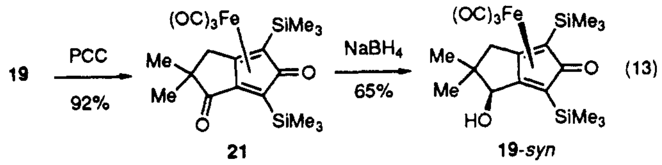
(13)

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[9] Magnus, P.; Slater, M. J.; Principe, L. M. *J. Org. Chem.* **1989**, *54*, 5148.

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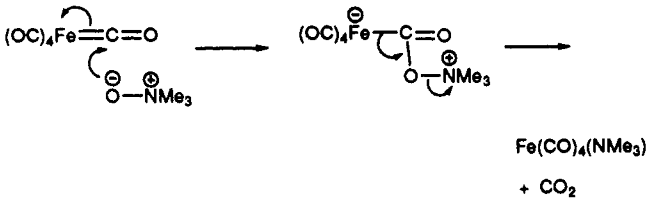
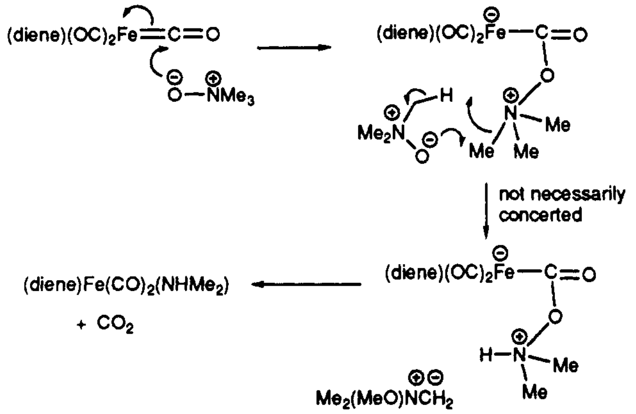
Scheme 2

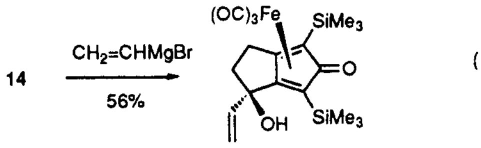


Scheme 3



C.5) show consistent trends for *syn* vs *anti* diastereomers, two close peaks being observed for the former (δ 117.5 and 116.8 for **19**), whereas the *anti* isomers have these peaks further apart (δ 118.8 and 113.8).

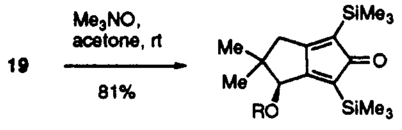
Nucleophiles other than hydride also add to the ketone in a completely stereoselective manner;[1] for example, vinylmagnesium bromide reacts with **14** to give **22** (eq 14).



(14)

22

The carbonyl group therefore provides a valuable center with which to introduce functionality into the uncomplexed ring, which we intend to pursue further in the future. For the present study we have focused our attention on the demetalation of the (cyclopentadienone)iron derivatives. Complexes **19** and **22** provide excellent candidates for the demetalation reaction, since the steric crowding of the product cyclopentadienones is expected to prevent dimerization. Since the trimethylsilyl groups are removable after subsequent manipulations of this type of system, access to more interesting, less highly substituted molecules is possible. In any event, treatment of each of these complexes with excess trimethylamine *N*-oxide in acetone at room temperature afforded the cyclopentadienones **23** and **24** in 81% and 43% yield, respectively. We expect that the double Michael acceptor potential of these dienones will allow the construction of densely functionalized di- and triquinane derivatives, and future efforts will be directed toward the cyclocarbonylation of unsymmetrical diynes, so that the reactivity of each enone moiety can be differentiated.



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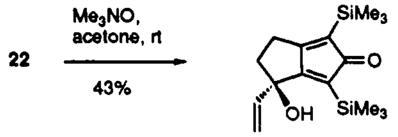
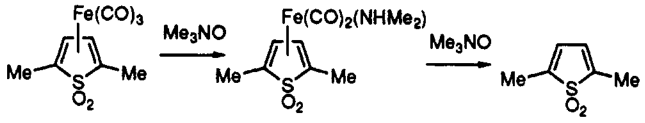
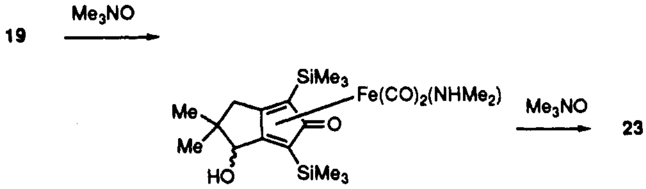


24

Observations on the Mechanism of Decarbonylation using Trimethylamine *N*-Oxide. It is commonly assumed that the amine oxide promoted removal of a carbonyl ligand from all transition-metal carbonyls proceeds according to the mechanism shown in Scheme 2, for the reaction of $Fe(CO)_5$ with Me_3NO. Evidence for this mechanism lies in the isolation and characterization of $Fe(CO)_4(NMe_3)$.[11] A few years ago Eekhof *et al.*[12] reported the characterization of the unusual *di*methylamine complex intermediate **26**, isolated from the reaction of complex **25** with Me_3NO. A mechanism, reproduced in Scheme 3, was proposed to account for this rather unexpected demethylation reaction. An alternative mechanism (Scheme 4) is also plausible, analogous to the Polonovski reaction,[13] in which the dimethylamine ligand results from hydrolysis of the iminium species that results from the Polonovski sequence. During our studies on the decomplexation of **19**, we observed a putative intermediate on TLC. Treatment of *anti*-**19** with Me_3NO at room temperature gave an isolable compound, the NMR spectrum of which was consistent with the dimethylamine complex structure **27** (see Experimental Section for details). While the *syn* alcohol also gave a similar intermediate (TLC) its instability precluded its isolation and characterization. Further treatment of **27** with Me_3NO effected its conversion to the cyclopentadienone **23**. Thus, it appears that the mechanism proposed by Eekhof *et al.* may have some generality. While our result represents only the second observation of a dimethylamine complex intermediate, it may be noted that ligand *exchanges* promoted



25 **26**



27
anti stable
syn unstable

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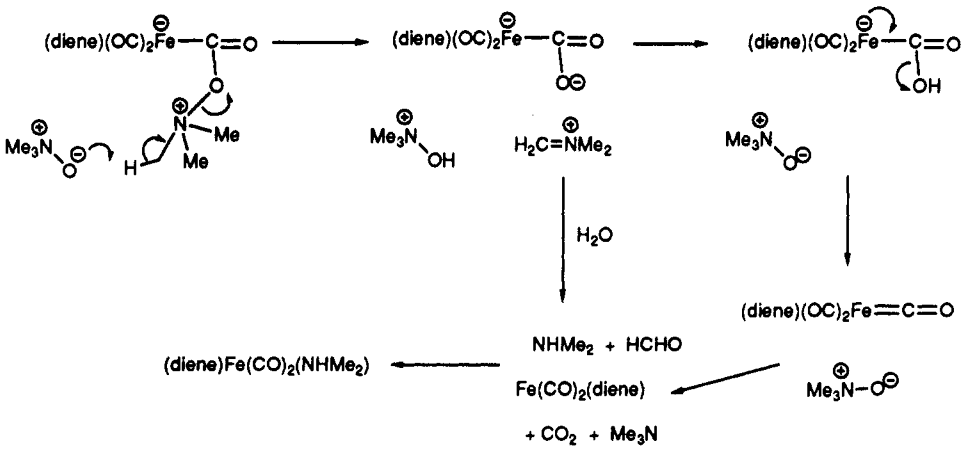
Scheme 4



by Me_3NO commonly require at least 2 equiv of the amine oxide.[14] Such observations are also consistent with the mechanisms of Schemes 3 and 4. We suggest that efforts should be directed at examining the details of amine oxide promoted demetalations of diene–$Fe(CO)_3$ complexes in order to establish the details of this reaction more rigorously.

Conclusions

Bicyclo[3.3.0]octadienone–$Fe(CO)_3$ complexes were prepared with a hydroxyl group in the uncomplexed ring. Although the diastereoselectivity was negligible, the complexes were prepared in higher yield for five-, six-, and seven-membered fused rings than the complexes without hydroxyl substitution that were described in our earlier work.[1] The hydroxyl substitution gives a synthetic handle for the further functionalization of these complexes, and nucleophiles add exclusively to the *anti* face of the ketone derived from the alcohol. Future work will focus on exploitation of the steric influences of the metal in the *multiple* functionalization of these complexes, in particular, those with a six-membered ring. The inclusion of *gem*-dimethyl substitution gave ring systems similar to those found in some triquinane natural products (e.g., coriolin). Decomplexation may be effected by treatment of the complexes with Me_3NO. The mechanism of the amine oxide promoted decomplexation of diene–$Fe(CO)_3$ complexes requires additional study to determine the generality of the formation of diene–$Fe(CO)_2(NHMe_2)$ intermediates.

Experimental Section

For general methods of characterization and analysis and of purification of solvents and reagents, see ref 1.

1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-ol (3). Butyllithium (9.75 mL, 24.4 mmol) was added to a solution of (trimethylsilyl)acetylene in 20 mL of THF at −78 °C. The solution was warmed to room temperature to ensure complete deprotonation. The solution was cooled back to −78 °C, and a solution of 1 in 10 mL of THF was added via cannula. The solution was slowly warmed to room temperature and stirred for 3 h, until TLC indicated consumption of the starting material. The reaction mixture was quenched with water and worked up as usual. The diyne was used without further purification (4.786 g, 94%), although a sample was purified by flash chromatography for analysis: R_f 0.43 (20% EtOAc/hexanes). IR (neat): 3370 (–OH), 2183 (C≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.43 (q, J = 6.6 Hz, 1H, H-3), 2.48 (d, J = 6.6 Hz, 1H, –OH), 2.34 (AB quartet of triplets, J = 15.1, 6.6, 2H, H-5, diastereotopic), 1.84 (q, J = 6.6 Hz, 2H, H-4), 0.11 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 106.1, 105.9, 89.8, 85.3, 61.6, 36.2, 15.8, 0.0, −0.2.

1,7-Bis(trimethylsilyl)hepta-1,6-diyn-3-one (8). Pyridinium chlorochromate (PCC; 362.1 mg, 1.68 mmol) was added to a solution of 3 in CH_2Cl_2. After the mixture was stirred at room temperature for 18 h, TLC indicated complete loss of starting material. The reaction mixture was filtered through silica gel using 25% EtOAc/hexanes as the solvent. Removal of the solvent gave the product (286.3 mg, 82%) as a pale oil: R_f 0.60 (25% EtOAc/hexanes). IR (neat): 2179 (C≡C), 1682 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.82 (dd, J = 8.6, 6.4 Hz, 2H), 2.55 (dd, J = 8.6, 6.4 Hz, 2H), 0.24 (s, 9H), 0.13 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 185.2, 104.6, 101.3, 98.8, 85.5, 44.0, 14.5, 0.0, −0.8. HRMS: calcd for $C_{13}H_{22}OSi_2$ (M) 250.1209, found 250.1209. MS: *m/e* (%) 250 (1), 235 (2), 178 (9).

1,8-Bis(trimethylsilyl)octa-1,7-diyn-3-ol (4). A solution of (trimethylsilyl)acetylene (0.50 mL, 3.5 mmol) in 30 mL of THF was cooled to −78 °C. A hexane solution of butyllithium (1.45 mL, 3.52 mmol) was added, followed by 1 h of stirring at −78 °C. A solution of the aldehyde 2 (488.6 mg, 2.90 mmol) in 10 mL of THF was added. After the mixture was stirred for 20 min at room temperature, TLC indicated complete loss of starting material. The reaction was quenched with water and extracted with ether. The pure product (425.3 mg, 55%) was obtained by flash chromatography using 20% EtOAc/hexanes as the solvent system: R_f 0.38 (20% EtOAc/hexanes). IR (neat): 3348 (br, –OH), 2175 (C≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.36 (q, J = 7 Hz, 1H, H-3), 2.28 (t, J = 7 Hz, 2H, H-6), 2.07 (d, J = 7 Hz, 1H, –OH), 1.84–1.65 (m, 4H, H-4, H-5), 0.17 (s, 9H, $SiMe_3$), 0.14 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 106.8, 106.6, 89.3, 84.8, 62.1, 36.5, 24.2, 19.4, 0.1, −0.2. HRMS: calcd for $C_{14}H_{26}OSi_2$ (M) 266.1522, found 266.1565 MS: *m/e* (%) 266 (1), 251 (6), 193 (35), 178 (43), 161 (100).

1,9-Bis(trimethylsilyl)nona-1,8-diyn-3-ol (7). A solution of the iodide 5 in 5 mL of ether was added to magnesium. The Grignard reagent formed after the addition of an I_2 crystal. The ether solution was transferred by cannula to a solution of the aldehyde 6 that was cooled to −78 °C. After the mixture was stirred for 30 min, 6 was consumed. Following aqueous workup, TLC indicated two products which were isolated by flash chromatography using 10% EtOAc/hexanes as the solvent. The major product was 1,10-bis(trimethylsilyl)-1,9-decadiyne (R_f 0.79). 7 was also formed (237.0 mg, 9%): R_f 0.39, 10% EtOAc/hexane. IR (neat): 3388 (–OH), 2174 (C≡C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.28 (q, J = 5.9 Hz, 1H, H-3), 2.18 (t, J = 6.8 Hz, 2H, H-7), 1.90 (d, J = 5.9 Hz, 1H, –OH), 1.65–1.44 (m, 6H), 0.10 (s, 9H, $SiMe_3$), 0.08 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 107.2, 106.7, 89.5, 84.5, 62.7, 37.18, 28.2, 24.4, 19.8, 0.1, −0.2. HRMS: calcd for $C_{15}H_{28}OSi_2$ 280.1679, found 280.1679. MS: *m/e* (%) 280 (1), 265 (3), 207 (21), 175 (54).

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1-(Trimethylsilyl)-4,4-dimethylhepta-1,6-diyn-3-ol (10). Butyllithium (25 mL, 2.5 M) was added to a solution of (trimethylsilyl)acetylene (7.9 mL, 55.9 mmol) in 125 mL of THF cooled to −78 °C. After the mixture was stirred for 1.5 h, the solution was warmed to room temperature and then cooled again to −78 °C. A solution of **9** (5.464 g, 50.5 mmol) in 20 mL of THF was added via cannula. After the mixture was stirred for 1 h, the solution was warmed to room temperature and quenched with saturated NH_4Cl solution. The product was extracted into 100 mL of ether and washed with 50 mL of saturated NaCl solution. The organic layer was dried with $MgSO_4$. Following solvent removal and vacuum distillation the pure diyne (8.087 g, 39.2 mmol, 78%) was obtained. IR (neat): 3431 (–OH), 3312 (C≡CH), 2172 (C≡CSi), 2118 (C≡CH) cm^{-1}. ^1H NMR: δ 4.16 (d, *J* = 1H, H-3), 2.30 (dd, *J* = 16.6, 2.7 Hz, 1H, H-5), 2.16 (dd, *J* = 16.6, 2.7 Hz, 1H, H-5), 2.1 (br s, 1H, –OH), 1.97 (t, *J* = 2.7 Hz, 1H, H-7), 1.03 (s, 3H, Me), 1.01 (s, 3H, Me), 0.13 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 104.7, 90.9, 81.8, 70.5, 69.5, 38.4, 27.8, 22.7, 22.1, 0.2.

1,7-Bis(trimethylsilyl)-4,4-dimethyl-3-(trimethylsiloxy)-1,6-heptadiyne (11). For the procedure, see that for **12**: R_f 0.79 (10% EtOAc/hexanes). IR (neat): 2174 (C≡C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.16 (s, 1H, H-3), 2.30 (d, *J* = 16.7 Hz, 1H, H-5), 2.14 (d, *J* = 16.7 Hz, 1H, H-5), 1.00 (s, 3H, Me), 0.98 (s, 3H, Me), 0.14 (s), 0.13 (s, 27H, 3 × $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 105.7, 105.3, 90.0, 86.3, 69.4, 38.9, 29.1, 22.8, 21.9, 0.1, −0.2.

1,7-Bis(trimethylsilyl)-4,4-dimethylhepta-1,6-diyn-3-ol (12). The diyne **10** (3.496 g, 16.9 mmol) was treated with butyllithium (15.0 mL, 37.5 mmol) at −78 °C. The solution was stirred for 4 h, during which time it was warmed to room temperature. The solution was cooled to −78 °C, and chlorotrimethylsilane (4.3 mL, 33.9 mmol) was added. The solution was stirred at room temperature overnight, quenched with ammonium chloride solution, and worked up as usual. TLC indicated two products which were separated by flash chromatography, **11** (2.940 g, 50%) and **12** (0.651 g, 14%). The ion exchange resin AG 50W-X4 (2.50 mL) was added to a solution of the silyl ether **11** (1.579 g, 4.50 mmol) in 40 mL of Et_2O. The mixture was stirred for 2 days until TLC indicated consumption of the silyl ether. The solution was filtered, dried with $MgSO_4$, and filtered again. The product was obtained essentially pure by evaporation of solvent (0.9673 g, 77%): R_f 0.29 (10% EtOAc/hexanes). IR (neat): 3420, 2172 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.22 (d, *J* = 6.2, 1H, H-3), 2.39 (d, *J* = 16.8, 1H), 2.22 (d, *J* = 16.8, 1H), 2.06 (d, *J* = 6.2, 1H, –OH), 1.08 (s, 3H, –Me), 1.05 (s, 3H, –Me), 0.18 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 104.8, 104.7, 90.8, 87.0, 69.9, 38.6, 29.3, 22.9, 22.3, 0.1, −0.2.

General Procedure for the Preparation of Tricarbonyl(cyclopentadienone)iron Complexes. A solution of the appropriate dyne in 8–10 mL of toluene was injected into a 60-mL quartz Griffen–Worden pressure vessel (Kontes Glassware). To this solution was added a 5-fold excess of freshly filtered $Fe(CO)_5$. The solution was degassed by the freeze–pump–thaw method. After it was warmed to room temperature, the vessel was charged with CO (50 psi). The vessel was held in an oil bath at 125–135 °C for 24 h. After the mixture was cooled and the pressure was released, the reaction mixture was diluted in CH_2Cl_2 or EtOAc and then filtered through Celite. The solvent was removed by rotary evaporation. The solid was dried further on a vacuum line to ensure complete removal of any residual $Fe(CO)_5$, and the complexes were purified by flash chromatography.

Tricarbonyl(2,4-bis(trimethylsilyl)-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one)iron (13). 1,7-Bis(trimethylsilyl)-3-hydroxy-1,6-heptadiyne (0.427 g, 1.69 mmol) and $Fe(CO)_5$ (2.5 mL, 8.8 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC (30% EtOAc/hexanes) indicated the presence of two diastereomers: R_f(*syn*) 0.36, R_f(*anti*) 0.34. Flash chromatography afforded the product as an inseparable mixture of the diastereomers (711 mg, 76%). Data for *syn* isomer (obtained via borohydride reduction, see below): IR (CCl_4) 3398 (br, –OH), 2067, 2013, 1991, 1628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (dt, *J* = 8.2, 4.8 Hz, 1H, H-6), 2.66–2.49 (m, 2H), 2.41 (d, *J* = 4.8 Hz, 1H, –OH), 1.78–1.70 (m, 1H), 0.28 (s, 9H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 208.4, 183.1, 118.9, 118.0, 71.1, 70.4, 68.3, 35.5, 24.9, −0.1, −0.7; HRMS calcd for $C_{16}H_{24}FeO_4Si_2$ (M − CO) 392.0562, found 392.0566; MS *m/e* (%) 392 (1), 364 (7), 336 (43). Data for *anti* isomer: ^1H NMR ($CDCl_3$) δ 4.99 (t, *J* = 4.7 Hz, 1H, H-6), 3.01–2.90 (m, 1H), 2.53 (dd, *J* = 16.3, 17.4 Hz, 1H), 2.43 (d, *J* = 4.7 Hz, 1H, –OH), 2.35–2.14 (m, 2H), 0.28 (s, 9H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 208.4, 183.7, 119.7, 114.0, 72.8, 70.8, 70.0, 36.4, 25.4, −0.1, −0.7.

Tricarbonyl(2,4-bis(trimethylsilyl)-6-hydroxybicyclo[3.4.0]nona-1,4-dien-3-one)iron (15). 1,8-Bis(trimethylsilyl)-3-hydroxy-1,7-heptadiyne (0.182 g, 0.68 mmol) and $Fe(CO)_5$ (1.0 mL, 3.5 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC indicated the presence of two diastereomers. The pure complexes (295 mg, 85%) were obtained by flash chromatography. Data for *syn* isomer: R_f 0.31 (25% EtOAc/hexanes); mp 192–193 °C dec; IR (CCl_4) 3385, 2066, 2012, 1990, 1629 cm^{-1}; ^{H} NMR ($CDCl_3$) δ 4.62 (q, *J* = 4.2 Hz, 1H, H-6), 2.61 (dt, *J* = 17.1, 4.2 Hz, 1H), 2.46 (dt, *J* = 17.1, 4.2 Hz, 1H), 2.42 (d, *J* = 4.2 Hz, 1H, –OH), 1.96–1.77 (m, 4H, H-8, H-9), 0.32 (s, 9H, $SiMe_3$), 0.27 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 208.6, 181.0, 114.6, 113.1, 70.3, 70.1, 62.5, 33.4, 25.7, 17.7, 0.0 −0.3; HRMS calcd for $C_{18}H_{26}FeO_5Si_2$ (M) 434.0668, found 434.0685; MS *m/e* (%) 434 (1), 406 (9), 378 (11), 350 (100). Data for *anti* isomer: R_f 0.24 (25% EtOAc/hexanes); mp 147 °C dec; IR (CCl_4) 3398, 2063, 2005, 1983, 1629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (q, *J* = 5.3 Hz, 1H, H-6), 2.60 (t, *J* = 6.2 Hz, 2H), 2.12–1.66 (m, 4H), 1.96 (d, *J* = 5.3 Hz, 1H, –OH), 0.32 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 208.6, 181.5, 112.4, 109.6, 73.6, 71.7, 63.7, 31.6, 24.3, 17.7, −0.4; HRMS calcd for $C_{18}H_{26}FeO_5Si_2$ (M) 434.0668, found 434.0664; MS *m/e* (%) 434 (2), 406 (5), 378 (24), 350 (100).

Tricarbonyl(2,4-bis(trimethylsilyl)-6-hydroxybicyclo[3.5.0]deca-1,4-dien-3-one)iron (16). 1,8-Bis(trimethylsilyl)-3-hydroxy-1,7-heptadiyne (0.333 g, 1.19 mmol) and $Fe(CO)_5$ (1.7 mL, 6.0 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC (20% EtOAc/hexanes) indicated the presence of two diastereomers, which were purified by flash chromatography (77 mg, 14%). The unreacted diyne (142 mg) was recovered; therefore, the recovered yield was 25%. Data for *syn* isomer: R_f 0.32 (20% EtOAc/hexanes); IR (CCl_4) 3299, 2071, 2015, 1998, 1637 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.74 (dd, *J* = 6.0, 3.2 Hz, 1H, H-6), 2.91 (t, *J* = 13.6 Hz, 1H), 2.56 (dd, *J* = 13.6, 6.2 Hz, 1H), 2.41–1.43 (m, 7H), 0.30 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$); HRMS calcd for $C_{19}H_{28}FeO_5Si_2$ (M) 448.0824, found 448.0822; MS *m/e* (%) 448 (1), 420 (8), 342 (11), 364 (100). Data for *anti* isomer: R_f 0.14 (20% EtOAc/hexanes); ^1H NMR ($CDCl_3$) δ 4.77 (d, *J* = 6.0 Hz, 1H), 2.67 (dd, *J* = 7.7, 4.3 Hz, 2.29–2.19 (m, 1H), 2.08–1.69 (m, 4H), 1.58–1.44 (m, 1H), 0.32 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 208.8, 182.6, 116.1, 111.8, 75.8, 73.0, 68.7, 36.3, 29.5, 29.0, 23.4, 0.5, 0.2; HRMS calcd for $C_{19}H_{28}FeO_5Si_2$ (M) 448.0824, found 448.0829; MS *m/e* (%) 448 (1), 420 (9), 342 (9), 364 (100).

Tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[3.3.0]octa-1,4-diene-3,6-dione)iron (14). 1,7-Bis(trimethylsilyl)-1,7-heptadiyn-3-one (0.197 g, 0.79 mmol) and $Fe(CO)_5$ (1.2 mL, 4.2 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. The pure complex (236 mg, 77%) was obtained by flash chromatography: R_f 0.48 (30% EtOAc/hexanes); mp 107 °C. IR (cm^{-1}): 2074, 2023, 2001, 1727, 1641. ^1H NMR: δ 3.13 (dt, *J* = 17.3, 6.9 Hz, 1H, H-7), 2.99 (dt, *J* = 17.3, 5.0 Hz, 1H, H-7), 2.76 (dd, *J* = 6.9, 5.0 Hz, 2H, H-6), 0.31 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 204.5, 183.4, 129.8, 97.9, 78.9, 67.4, 36.8, 23.5, −0.5, −0.9. HRMS: calcd for $C_{17}H_{22}FeO_5Si_2$ 418.0355, found 418.0333. MS: *m/e* (%) 418 (5), 390 (23), 362 (47), 334 (100).

Tricarbonyl(2,4-bis(trimethylsilyl)-7,7-dimethyl-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one)iron (19). 1,7-Bis(trimethylsilyl)-4,4-dimethylhepta-1,6-diyn-3-ol (0.483 g, 1.73 mmol) and $Fe(CO)_5$ (2.5 mL, 8.8 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC (30% EtOAc/hexanes) indicated the presence of two diastereomers, which were purified by flash chromatography (772 mg, 77%). Data for the *syn* isomer: R_f 0.52 (30% EtOAc/hexanes); mp 182–183 °C; IR (CCl_4) 3379, 2069, 2013, 1992, 1625 cm^{-1}; ^{H} NMR 4.79 (d, J = 5.9 Hz, 1H, H-6), 2.63 and 2.54 (AB q, J_{Ab} = 16.8 Hz, 2H, H-8), 2.16 (d, J = 5.9 Hz, 1H, –OH), 1.31 (s, 3H, Me), 1.22 (s, 3H, Me), 0.32 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$); ^{13}C NMR δ 208.3, 182.5, 117.5, 116.8, 78.3, 69.3, 67.3, 44.3, 40.6, 30.2, 24.7, –0.1, –0.7; HRMS calcd for $C_{19}H_{28}FeO_5Si_2$ (M) 448.0825, found 448.0939; MS *m/e* (%) 448 (1), 420 (4), 364 (100), 308 (8), 318 (28). Data for the *anti* isomer: R_f 0.44 (30% EtOAc/hexanes); mp 190–193 °C dec; IR (CCl_4) 3353, 2067, 2011, 1988, 1629 cm^{-1}; ^1H NMR 4.52 (d, J = 6.2 Hz, 1H, H-6), 2.76 (d, J = 17.0 Hz, 1H, H-8), 2.50 (d, J = 17.0 Hz, 1H, H-8), 1.97 (d, J = 6.2 Hz, 1H, –OH), 1.36 (s, 3H, Me), 1.29 (s, 3H, Me), 0.32 (s, 9H, $SiMe_3$), 0.27 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 208.3, 183.0, 118.8, 113.8, 79.7, 71.2, 68.8, 45.4, 41.3, 31.4, 24.6, –0.8, –0.9; HRMS calcd for $C_{19}H_{28}FeO_5Si_2$ (M) 448.0825, found 448.0851 MS *m/e* (%) 448 (1), 420 (5), 392 (22), 364 (100), 318 (11), 308 (5).

Tricarbonyl(2,4-bis(trimethylsilyl)-7,7-dimethyl-6-(trimethylsilyloxy)bicyclo[3.3.0]octa-1,4-dien-3-one)iron (18). 1,7-Bis(trimethylsilyl-4,4-dimethyl-3-(trimethylsiloxy)-1,6-heptadiyne (0.205 g, 0.58 mmol) and $Fe(CO)_5$ (0.82 mL, 2.9 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC (20% EtOAc/hexanes) indicated the presence of one complex, which was purified by flash chromatography (209 mg, 70%), but by NMR was shown to be a mixture of diastereomers that were not separated. IR (CCl_4): 2062, 2005, 1991, 1629 cm^{-1}. ^1H NMR: δ 4.94 (s, 1H), 4.63 (s, 1H), 2.73 (d, J = 16.9 Hz, 1H), 2.56 (d, J = 12.3 Hz, 1H), 2.50 (d, J = 12.3 Hz, 1H), 2.40 (d, J = 16.9 Hz, 1H), 1.34 (s, 3H, Me), 1.32 (s, 3H, Me), 1.22 (s, 3H, Me), 1.19 (s, 3H, Me), 0.30, 0.26, 0.25, 0.24, 0.23. ^{13}C NMR: δ 208.5, 208.4, 183.3, 183.2, 118.3, 117.8, 115.4, 115.3, 82.0, 80.5, 70.6, 68.5, 68.1, 66.7, 46.0, 44.0, 41.3, 40.9, 31.1, 30.2, 27.1, 25.0, 1.5, 1.4, 0.6, –0.4, –0.7. HRMS: calcd for $C_{22}H_{36}FeO_5Si_3$ (M) 520.1220, found 520.1232. MS *m/e* (%) 520 (1), 492 (3), 464 (24), 436 (100).

Tricarbonyl(4-(trimethylsilyl)-7,7-dimethyl-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one)iron (17). 1-(Trimethylsilyl)-4,4′-dimethyl-1,6-heptadiyn-3-ol (0.677 g, 3.28 mmol) and $Fe(CO)_5$ (4.9 mL, 17 mmol) were heated for 1 day, under 50 psi of CO, and the reaction mixture was worked up as described previously. TLC (80% EtOAc/hexanes) indicated the presence of two diastereomers, which were purified by flash chromatography (460 mg, 38%). Data for the *syn* isomer: R_f 0.51 (80% EtOAc/hexanes); IR (CCl_4) 3199, 2071, 2016, 1996, 1636 cm^{-1}; ^{H} NMR 4.74 (d, J = 5.7 Hz, 1H, H-6), 3.95 (s, 1H), 2.56 (s, 2H), 2.54 (s, 2H), 1.28 (s, 3H), 1.20 (s, 3H), 0.32 (s, 9H, $SiMe_3$); ^{13}C NMR δ 207.8, 178.2, 116.6, 110.6, 78.2, 67.2, 61.2, 48.9, 39.2, 30.0, 24.5, –0.2; HRMS calcd for $C_{16}H_{20}FeO_5Si$ (M) 376.0429, found 376.0428, m/e (5) 376 (1), 348 (12), 320 (23), 292 (100). Data for the *anti* isomer: R_f 0.39 (80% EtOAc/hexanes); mp 182–183 °C dec; IR (CCl_4) 3300, 2073, 2018, 1999, 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (d, J = 5.5 Hz, 1H), 4.01 (s, 1H), 3.71 (s, broad, 1H), 2.86 (d, J = 17.0 Hz, 1H), 2.35 (d, J = 17.0 Hz, 1H), 1.32 (s, 3H), 1.27 (s, 3H), 0.31 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 207.7, 178.9, 113.4, 112.3, 79.7, 68.1, 62.2, 45.6, 39.8, 31.2, 24.4, –0.2; HRMS calcd for $C_{16}H_{20}FeO_5Si$ (M) 376.0429, found 376.0437; MS *m/e* (%) 376 (6), 320 (9), 292 (100).

Procedure for the Oxidation of 13. To a suspension of PCC (231 mg, 1.07 mmol) in 3 mL of CH_2Cl_2 was added solution of **13** (287 mg, 0.68 mmol) in 2 mL of CH_2Cl_2. The mixture was stirred for 11 h, until TLC indicated complete loss of **12**. The solution was decanted from the reduced chromium polymer, which was washed three times with 2 mL of CH_2Cl_2. The solution was filtered through silica gel. Removal of solvent gave the pure product **14** (263 mg, 93%; see above for complete spectral data).

Tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[3.4.0]nona-1,4-diene-3,6-dione)iron (20). To a suspension of PCC (80 mg, 0.37 mmol) in 2 mL of CH_2Cl_2 was added a solution of **15** (106 mg, 0.24 mmol) in 2 mL of CH_2Cl_2. The mixture was stirred for 18 h, until TLC indicated complete loss of **15**. The solution was decanted from the reduced chromium residue, which was washed three times with 2 mL of CH_2Cl_2. The combined solution was filtered through silica gel. Removal of solvent gave the pure product (89 mg, 88%). R_f 0.43 (25% EtOAc/hexanes). IR (CCl_4): 2069, 2020, 1999, 1701, 1645 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.75 (t, J = 3.9 Hz, 1H), 2.68 (dd, J = 8.6, 3.9 Hz, 2H), 2.45 (ddd, J = 18.1, 13.2, 5.2 Hz, 1H), 2.27–2.18 (m, 1H), 1.98–1.86 (m, 1H), 0.24 (s, 9H, $SiMe_3$), 0.23 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 199.4, 182.1, 119.5, 96.3, 79.2, 66.9, 39.2, 24.0, 22.6, 0.0, –0.5. HRMS: calcd for $C_{17}H_{24}FeO_4Si_2$ (M – CO) 404.0562, found 404.0566. MS: *m/e* (%) 404 (1), 376 (31), 348 (100).

Tricarbonyl(2,4-bis(trimethylsilyl)-7,7-dimethylbicyclo[3.3.0]octa-1,4-diene-3,6-dione)iron (21). PCC (49.9 mg, 0.37 mmol) was added to a CH_2Cl_2 solution of **19** (53.9 mg, 0.12 mmol). The mixture was stirred for 20 h, when TLC indicated consumption of **19**. The solution was decanted from the reduced chromium polymer, which was washed three times with 2 mL of CH_2Cl_2. The solution was filtered through alumina. Removal of solvent gave the pure product (49.1 mg, 92%): R_f 0.55 (30% EtOAc/hexanes). IR (CCl_4): 2078, 2015, 1996, 1725, 1644 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.98 and 2.89 (AB q, J_{AB} = 17.4 Hz, 2H, H-8), 1.39 (s, 3H, Me), 1.33 (s, 3H, Me), 0.35 (s, 9H, $SiMe_3$), 0.31 (s, 9H, $SiMe_3$). ^{13}C NMR: δ 210.9, 206.8, 183.3, 126.7, 97.2, 77.8, 66.5, 47.4, 39.4, 29.9, 26.3, –0.5, –0.9. HRMS: calcd for $C_{19}H_{26}FeO_5Si_2$ (M) 446.0668, found 446.0671. MS: *m/e* (%) 446 (4), 418 (14), 390 (40), 362 (100).

Procedure for the Borohydride Reduction of 13, 20, and 21. To a stirred suspension of the ketone (0.22 mmol) in EtOH (2 mL) was added $NaBH_4$ (12.4 mg, 0.328 mmol). After it was stirred for 2–5 min, the reaction mixture became clear and TLC indicated complete reaction. Aqueous workup, followed by flash chromatography, gave the pure alcohol complex.

Tricarbonyl(2,4-bis(trimethylsilyl)-6-*syn*-hydroxy-6-*anti*-vinylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (22). A stirred solution of **14** in 4 mL of THF was cooled to –78 °C. Vinylmagnesium bromide was added, and after the mixture was stirred for 7 min, TLC indicated complete conversion of starting material to product. The reaction mixture was quenched with saturated NH_4Cl solution. The aqueous layer was extracted three times with 6 mL of Et_2O. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The pure product (122 mg, 56%) precipitated from the cold Et_2O solution: R_f 0.46 (30% EtOAc/hexanes); mp 188–189 °C dec. IR (CCl_4): 2068, 2014, 1992, 1628 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.17 (dd, J = 17.3, 10.6 Hz, 1H, H-9), 5.26 (d, J = 10.6 Hz, 1H, H-10_{cis}), 5.20 (d, J = 17.3 Hz, 1H, H-10_{trans}), 2.67–2.48 (m, 2H), 2.39 (dd, J = 12.5, 6.0 Hz, 1H), 2.25 (s, 1H, –OH), 2.17–2.07 (m, 1H), 0.28 (s, 9H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 208.3, 183.0, 140.1, 119.2, 118.7, 114.6, 80.3, 70.6, 68.0, 41.1, 24.7, 0.0, –0.6. HRMS: calcd for $C_{19}H_{26}FeO_5Si_2$ (M) 446.0668, found 446.0682. MS: *m/e* (%) 446 (1), 362 (100).

2,4-Bis(trimethylsilyl)-7,7-dimethyl-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one (23). Trimethylamine *N*-oxide (137.8 mg, 1.83 mmol) was added to a solution of **19** (101 mg, 0.23 mmol) in 10 mL of acetone. The solution was stirred for 1 h at room temperature. The acetone was removed on the rotary evaporator, and the red solid was dissolved in 10 mL of Et_2O. The Et_2O solution was washed five times with NaCl solution, dried with $MgSO_4$, and filtered. The Et_2O solution was then filtered through a short column of alumina to remove any residual iron impurities. The pure product (57 mg, 81%) was obtained by flash chromatography: R_f 0.52 (30% EtOAc/hexanes). IR (CCl_4): 3398, 1691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.29 (d, J = 5.2 Hz, 1H, H-6), 2.54 (d, J = 18.2 Hz, 1H, H-8), 2.33 (d, J = 18.2 Hz, 1H, H-8), 1.62 (d, J = 5.2 Hz, 1H, –OH), 1.12 (s, 3H, Me), 0.99 (s, 3H, Me), 0.22 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 212.0, 176.0, 175.8, 128.3, 124.7, 76.8, 44.4, 39.9, 26.6, 21.4, –0.5, –0.8. HRMS: calcd for $C_{16}H_{28}O_2Si_2$ (M) 308.1628, found 308.1629. MS: *m/e* (%) 308 (64), 293 (54), 278 (22).

2,4-Bis(trimethylsilyl)-6-hydroxy-6-vinylbicyclo[3.3.0]octa-1,4-dien-3-one (24). Using the procedure as for **23**, the complex **22** (66.6 mg, 0.15 mmol) was treated with Me_3NO (90.3 mg, 1.20 mmol) in acetone (10 mL) at room temperature for 30 min. The usual workup and flash chromatography afforded **24** (19.1 mg, 43%). IR (CCl_4): 3390, 1690, 1646 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.1 (dd, J = 17.5, 10.5 Hz, 1H, vinyl), 5.98 (s, 1H, OH), 5.18 (d, J = 17.5 Hz, vinyl), 5.18 (d, J = 17.5 Hz, vinyl), 3.0 (s, 2H), 2.92 (s, 2H), 0.25 (s, 18H, 2 × $SiMe_3$). HRMS: calcd for $C_{16}H_{26}O_2Si_2$ 306.1471, found 306.1473.

Dicarbonyl(dimethylamine)(2,4-bis(trimethylsilyl)-7,7-dimethyl-6-*anti*-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one)iron (27). Trimethylamine *N*-oxide (90 mg, 1.2 mmol) was added to a solution of **19**-*anti* (67 mg, 0.15 mmol) in 10 mL of acetone. The solution was stirred for 20 min at room temperature. The acetone was removed on the rotary evaporator, and the red solid was dissolved in 10 mL of Et_2O. The Et_2O solution was washed five times with NaCl solution, dried with $MgSO_4$, and filtered. The Et_2O solution was then filtered through a short column of alumina to remove any residual iron impurities. The pure product (26 mg, 37%) was obtained by flash chromatography: R_f 0.27 (30% EtOAc/hexanes). IR (CCl_4): 1992, 1938 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.21 (d, J = 6.7 Hz, 1H, H-6), 2.88 (d, J = 6.0 Hz, 3H, NMe_2), 2.80 (d, J = 6.0 Hz, 3H, NMe_2), 2.47 (d, J = 16.5 Hz, 1H), 2.19 (d, J = 16.5 Hz, 1H), 1.71 (d, J = 6.7 Hz, 1H, –OH), 1.26 (s, 3H), 1.23 (s, 3H), 0.40 (s, 9H), 0.36 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 213.4, 213.0, 175.6, 114.3, 108.3, 79.6, 72.2, 68.9, 50.9, 50.8, 45.2, 40.3, 31.0, 24.9, 0.13.

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