

Selectivity in the Pentacarbonyliron-Promoted Cyclocarbonylation of Eneidyne

Anthony J. Pearson* and Alvis Perosa

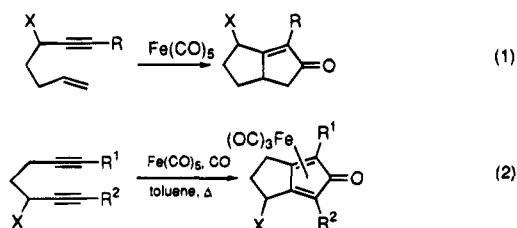
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received June 19, 1995[⊗]

Cyclocarbonylation reactions of a series of eneidyne, promoted by pentacarbonyliron, proceed selectively on the diyne, resulting in the formation of cyclopentadienone–iron tricarbonyl complexes, without competing enyne cyclocarbonylation.

Introduction

Previous papers from our laboratory have described the preparation and intramolecular cyclocarbonylation reactions of a number of different enynes and α,ω -diynes to give the corresponding cyclopentenones (Pauson–Khand type reaction) or the corresponding cyclopentadienone–Fe(CO)₃ complexes, exemplified by eqs 1 and 2.^{1–4}



It was found that these reactions tolerate the presence of different functionalities. Hydroxy-substituted, electron-deficient acetylenes, as well as sterically crowded ones, undergo high-yielding intramolecular cyclocarbonylations. It was also shown that the hydroxy-substituted cyclopentadienone complexes can be oxidized to the corresponding ketones and that the products can be subjected to stereoselective nucleophilic addition. Demetalation was accomplished in some cases using trimethylamine *N*-oxide, and evidence of an unexpected mechanism for this reaction mechanism was obtained.¹

Further studies of this cyclocarbonylation reaction were needed if it is to be employed in organic synthesis. The construction of the bicyclo[3.3.0]octadienone skeleton is of interest for the synthesis of a number of natural polyquinanes, some of which have already been approached by similar and by more traditional chemistry, such as coriolin,^{5,6} pentalenene,^{7–9} pentalenic acid,^{7,10} crinipellin,¹¹ silphinene,^{7,12} hirsutene,¹³ and hirsutic acid.⁶

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

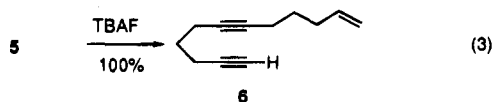
- (1) Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578.
 (2) Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096.
 (3) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, *91*, 202.
 (4) Pearson, A. J.; Dubbert, R. A. *Organometallics* **1994**, *13*, 1656.
 (5) Magnus, P.; Exon, C. *J. Am. Chem. Soc.* **1983**, *105*, 2477.
 (6) Magnus, P.; Exon, C.; Albaugh-Robertson, G. J. *Tetrahedron* **1985**, *41*, 5861.
 (7) Schore, N. E.; Rowley, E. G. *J. Org. Chem.* **1992**, *57*, 6853.
 (8) Yamamura, S.; Shizuri, Y.; Maki, S.; Ohkubo, M. *Tetrahedron Lett.* **1990**, *31*, 7167.
 (9) Burnell, D. J.; Zhu, Y.-Y.; Wu, Y.-J. *J. Org. Chem.* **1994**, *59*, 104.
 (10) Schore, N. E.; Rowley, E. G. *J. Organomet. Chem.* **1991**, *413*, C5.
 (11) Curran, D. P.; Schwartz, C. E. *J. Am. Chem. Soc.* **1990**, *112*, 9272.

In the present work our first objective was to study the selectivity of these cyclocarbonylation reactions for substrates containing both acetylenic and olefinic functionalities. We will show how, under our conditions, the iron-promoted cyclocarbonylation reaction of eneidyne occurs specifically on the diyne moiety.

Next, demetalation of the cyclopentadienone–Fe(CO)₃ complexes had to be accomplished efficiently in order for the global scheme to be synthetically useful. Recently similar demetalation reactions have been reported from our laboratory¹ and from Knölker and co-workers,^{14,15} by the use of Me₃NO. We will describe the problems encountered and the applicability of such demetalation procedures to our cases.

Results and Discussion

A series of eneidyne was prepared starting from 4-pentyn-1-ol (Scheme 1). In the presence of 2 equiv of lithium amide in liquid ammonia at –40 °C, 4-pentyn-1-ol reacted regioselectively with 5-bromo-1-pentene to give the kinetically preferred substitution product **1**.¹⁶ The resulting alcohol **1** was converted, via the methanesulfonate **2**, to the corresponding iodide **3**, which acts as a better leaving group in the subsequent acetylide addition.¹⁷ It was then added to the appropriate acetylide to afford the desired eneidyne **4** and **5**. Desilylation of **5** with TBAF gave **6** (eq 3).



Alcohol **1** was oxidized using the Swern¹⁸ procedure to give the aldehyde **7**, which was then treated with the appropriate acetylide to give the desired eneidyne alcohols **8** and **9** in good yields. This sequence can be easily performed on multigram scale, and rigorous purification of the intermediates is unnecessary.

Cyclocarbonylation of the eneidyne was then investigated. An interesting feature of this reaction is its

(12) Franck-Neumann, M.; Miesch, M.; Gross, L. *Tetrahedron Lett.* **1991**, *32*, 2135.

(13) Castro, J.; Sorensen, H.; Riera, A.; Morin, C.; Moyano, A.; Pericas, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388.

(14) Knölker, H.-J.; Heber, J.; Mahler, C. H. *Synlett* **1992**, 1002.

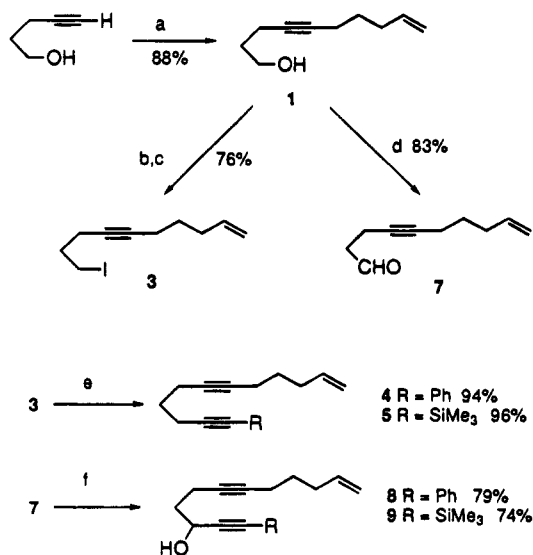
(15) Knölker, H.-J.; Heber, J. *Synlett* **1993**, *12*, 924.

(16) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; Vol. 34.

(17) Ho, T. L. *Chem. Rev.* **1975**, *75*, 1.

(18) Swern, D.; Huang, S.-L.; Mancuso, A. J. *J. Org. Chem.* **1978**, *43*, 2480.

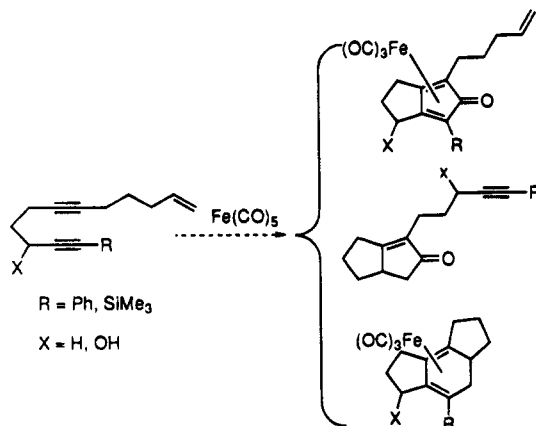
Scheme 1



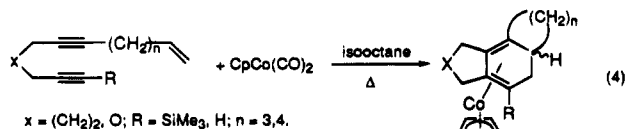
Reagents:

- a: 5-bromo-pent-1-ene, liq. NH_3 , Li, $\text{Fe}(\text{NO})_5$, THF, -40°C to RT, 12 h;
 b: NEt_3 , $\text{CH}_3\text{SO}_3\text{Cl}$, CH_2Cl_2 , RT, 12 h;
 c: NaI , acetone, reflux, 12 h;
 d: $(\text{ClCO})_2$, Me_2SO , NEt_3 , CH_2Cl_2 , -60°C to RT, 30 min;
 e: $\text{R}-\text{C}\equiv\text{C}-\text{H}$, $n\text{-BuLi}$, THF, reflux, 72 h;
 f: $\text{R}-\text{C}\equiv\text{C}-\text{H}$, $n\text{-BuLi}$, THF, -30°C to RT, 30 min.

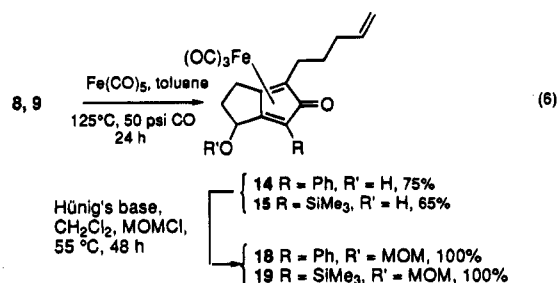
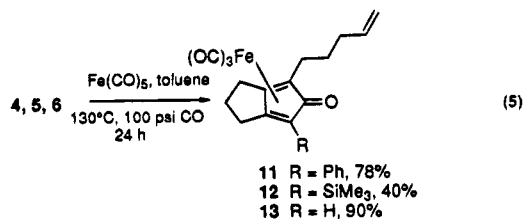
Scheme 2



possible chemoselectivity deriving from the presence of the diyne and enyne moieties. Iron pentacarbonyl has been shown to promote cyclocarbonylation of 1,6-enynes to the corresponding bicyclo[3.3.0]pentenones (eq 1),⁴ and diynes react with iron pentacarbonyl under CO pressure to generate the tricarbonylironbicyclo[3.3.0]dienones;¹⁻³ a competing effect was thus possible, although we have observed that the enyne cyclocarbonylation is generally much slower than the diyne reaction. Vollhardt and co-workers have shown that acetylenic and olefinic functionalities present in the same molecule can participate in a cobalt-mediated annulation reaction to give a tricyclic complex (eq 4).¹⁹ Thus, a mixture of products arising from multiple concurrent reaction pathways might have been expected (Scheme 2).

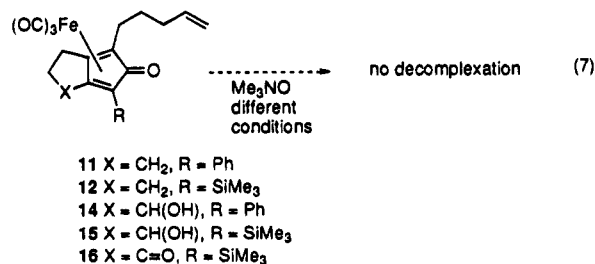


Very rewardingly it was found that the above eneynes, when subjected to the cyclocarbonylation conditions that have been previously described,¹⁻³ react cleanly to give solely the complexes arising from diyne cyclocarbonylation, as summarized in eqs 5 and 6.



Proton NMR spectra of the crude products from all the above reactions showed no evidence of any cyclopentenones arising from participation of the olefin in the reaction. In the cases of eq 6 a roughly equimolar mixture of the *syn* and *anti* diastereomers was obtained, which were usually not separated in view of the subsequent demetalation reaction which destroys the chirality of the organometallic.

At this point it seemed interesting to develop a general and efficient demetalation procedure for our complexes, which would hopefully lead to the corresponding bicyclo[3.3.0]octadienones. In our case an added curiosity derives from the possibility that the free olefin side chain might react in an intramolecular Diels-Alder fashion with the highly reactive cyclopentadienone upon decomplexation. The demetalation reactions of complexes 11, 12, and 14-16 proved quite difficult to accomplish (eq 7). Initial attempts using the



known procedures with Me_3NO ^{4,15,20,21} in acetone or benzene as solvents at various temperatures, and using ceric ammonium nitrate,²² proved unsuccessful. It was thought that decreasing the electron density on the complexed cyclopentadienone ring might help in the demetalation. The hydroxy-substituted complex was

(19) Vollhardt, K. P. C.; Sternberg, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 4839.

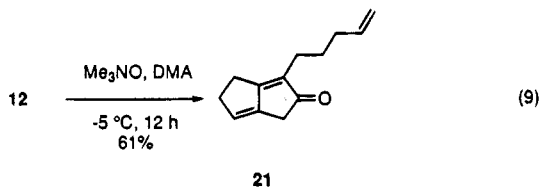
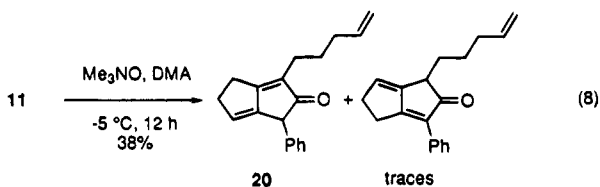
(20) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 74, 336.

(21) Hogeveen, H.; Eekhof, J. H.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1976**, 76, 657.

(22) Vollhardt, K. P. C.; Gesing, E. R. F.; Tane, J. P. *Synlett* **1980**, 1002.

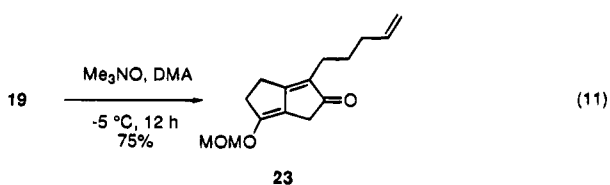
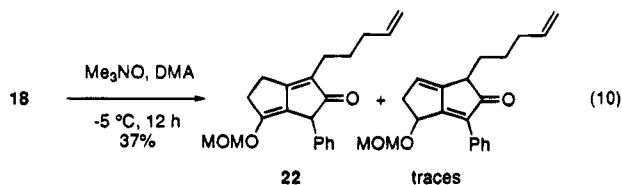
oxidized to the corresponding ketone **16** by standard treatment with PCC, but attempts to decomplex this compound by the usual methods also failed.

The importance of solvent is illustrated by the use of Me_3NO in *N,N*-dimethylacetamide (DMA), which led to successful demetalation at -5°C .²³ The results are shown in eqs 8 and 9. As can be seen in each case, a



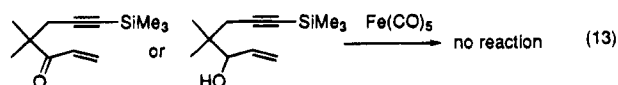
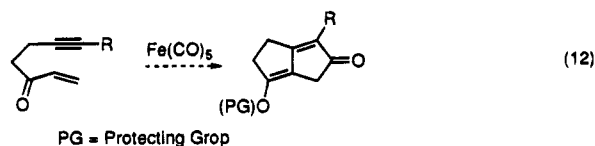
migration of one double bond occurs during this reaction, as has been observed previously by Knölker and co-workers.¹⁵ We believe this is due to the increased basicity of Me_3NO in DMA that allows for an easy deprotonation at the γ -carbon followed by reprotonation at the α -position, followed by desilylation. The trimethylsilyl group plays a very important role in controlling the site of deprotonation and accompanying deconjugation.

Surprisingly, decomplexation of the hydroxy complexes **14** and **15** did not occur under the preceding conditions. There appears to be some oxidation occurring at the hydroxyl oxygen, but the products were extremely unstable and were uncharacterizable. To overcome this, the hydroxy complex **15** was protected as the trimethylsilyl ether **17**. Although some TLC evidence of the demetalated product was obtained, it was not possible to isolate and characterize it. A second attempt was made by protecting **14** and **15** as their MOM ethers: **18** and **19**. Upon subjecting these compounds to our demetalation conditions, we were able to isolate the bicyclic enones **22** and **23** in moderate to good yields (eqs 10 and 11).



As in the preceding cases migration of a double bond and desilylation were observed. It should be noted that compounds **22** and **23** are each the protected and

masked enol form of an enedione, which can be considered as the products of a Pauson–Khand type reaction of an electron-deficient α,β -unsaturated enyne such as that shown in eq 12. This is noteworthy since



electron-deficient alkenes are usually poor substrates for Pauson–Khand reactions,^{24,25} there being only a few examples in the literature.^{26–28} The pentacarbonyliron promoted Pauson–Khand type reaction on such electron-deficient alkenes also does not occur in the presence of pentacarbonyliron; unpublished attempts from our group to achieve the reaction shown in eq 13 proved unsuccessful. The scope of our pentacarbonyliron promoted cyclocarbonylation is thus extended to formally include intramolecular Pauson–Khand type cyclizations of electron deficient α,β -unsaturated enynes.

Experimental Section

General Methods. The syntheses were carried out under a purified nitrogen atmosphere. THF and Et_2O were distilled from Na/benzophenone, CH_2Cl_2 from CaH_2 , and acetone from CaSO_4 . All other solvents were used as purchased. All nonvolatile compounds were dried of residual solvents by exposure to high vacuum prior to analysis.

Infrared spectra were recorded on a Nicolet Impact FT-IR spectrometer in NaCl chambers. ^1H (^{13}C) NMR spectra were recorded at 300 (75) MHz on a Varian Gemini spectrometer, unless otherwise noted, and were referenced to the solvent or to TMS. NMR assignments for some complexes were made on separated pure diastereomers; in several other cases the assignments were made on the mixtures of diastereomers by comparison with the purified materials. Mass spectra were recorded on a Kratos MS25A instrument.

Gas chromatography was performed on an Hewlett Packard 5890 Series II instrument fitted with a HP-5 30 m \times 0.32 mm capillary column coated with a 0.25 mm film of 5% PhMe Silicone, equipped with a flame ionization detector, using He as carrier gas. The temperature gradient program, in each case the same, was the following: start at 120°C , increase to 150°C at $5^\circ\text{C}/\text{min}$, and then to 250°C at $10^\circ\text{C}/\text{min}$, for 2 min.

Deca-9-en-4-yne-1-ol (1). To 300 mL of liquid ammonia at -78°C is added enough lithium metal (~ 30 mg, ~ 4.3 mmol) to turn the solution deep blue. After addition of a catalytic amount of ferric nitrate nonahydrate (5 mg, 0.02 mmol) the solution turns brownish, at which point the remaining lithium is added (200 mg, 28.8 mmol). The solution turns blue again, and as it is warmed to -40°C , it becomes a whitish suspension (LiNH_2). 4-Pentyn-1-ol (840 mg, 10 mmol) is added to the suspension at -40°C over 20 min, followed by 1.49 g (10 mmol) of 5-bromopent-1-ene over 30 min. The solution is stirred at the boiling point of ammonia (-33°C) for 3 h after which 50 mL of THF is added; the ammonia is then left to evaporate overnight. The resulting THF solution is quenched with 100

(24) Pauson, P. L.; Khand, I. U. *J. Chem. Soc. Chem., Commun* **1974**, 379.

(25) Schore, N. E. *Org. React.* **1991**, *40*, 1.

(26) Veretenov, A. L.; Smit, W. A.; Vorontsova, L. G.; Kurella, M. G.; Caple, R.; Gybin, A. S. *Tetrahedron Lett.* **1991**, *32*, 2109.

(27) Costa, M.; Mor, A. *Tetrahedron Lett.* **1995**, *36*, 2867.

(28) Krafft, M. E.; Wright, C. *Tetrahedron Lett.* **1992**, *33*, 151.

(23) Bandara, B. M. R.; Birch, A. J.; Kelly, L. F. *J. Org. Chem.* **1984**, *49*, 2496.

mL of cold water, the aqueous layer is extracted three times with ethyl ether, and the combined organic layers are washed twice with brine. After drying over MgSO_4 and removal of the solvent, the product is purified by flash chromatography ($R_f = 0.40$ in 10% EtOAc/hexanes) and obtained as a yellow oil in 88% yield: GC Rt = 5.3 min; IR (CCl_4) 3641, 3323, 3079, 2937 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.84–5.60 (m, 1H), 5.02–4.92 (m, 2H), 3.73 (t, 2H, $J = 6.1$ Hz), 2.25 (td, 2H, $J = 4.3, 2.4$ Hz), 2.12 (m, 4H), 1.80–1.66 (m, 3H), 1.55 (p, 2H, $J = 7.29$ Hz); ^{13}C NMR (CDCl_3) δ 138, 115, 81, 80, 62, 33, 32, 28, 18, 15. HRMS: calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ (M^+), m/e 152.1201; found, m/e 152.1191.

1-(Methylsulfonyl)oxydeca-9-en-4-yne (2). To **1** (0.507 g, 3.3 mmol) in 25 mL of CH_2Cl_2 are added 1 mL of Et_3N and, at -30°C , 0.25 mL (3.3 mmol) of methanesulfonyl chloride. The solution is stirred at room temperature overnight. The solvent is removed, and the solid mass is diluted with 30 mL of ethyl ether. Workup with 10% NaHCO_3 and brine, followed by drying over magnesium sulfate and removal of the solvent, affords the product as a yellow oil ($R_f = 0.74$ in 10% EtOAc/hexanes), in 86% yield: GC Rt = 12.1 min; IR (CCl_4) 3161, 3085, 2945, 2262, 1807, 1645 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.80–5.72 (m, 1H), 5.03–4.93 (m, 2H), 4.33 (t, 2H, $J = 6.1$ Hz), 3.00 (s, 3H), 2.32–2.27 (m, 2H), 2.13 (m, 4H), 1.93–1.84 (m, 2H), 1.54 (p, 2H); ^{13}C NMR (CDCl_3) δ 138, 115., 81, 77, 69, 37, 33, 28, 28, 18, 15. HRMS: calcd for $\text{C}_{10}\text{H}_{15}\text{O}$ ($\text{M}^+ - \text{SO}_2\text{CH}_3$), m/e 151.1123; found, m/e 151.1123.

1-Iodo-deca-9-en-4-yne (3). A solution of **2** in 25 mL of acetone (0.685 g, 2.85 mmol) was refluxed overnight with 0.500 g (3.2 mmol) of NaI. Removal of the acetone, dilution with ether, and aqueous workup, followed by drying over magnesium sulfate and removal of the solvent, affords the product as a yellow oil, which over time tends to darken (88% yield) ($R_f = 0.61$ in 10% EtOAc/hexanes): GC Rt = 8.1 min; IR (CCl_4) 3315, 3160, 2951, 2260 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.82–5.72 (m, 1H), 5.04–4.94 (m, 2H), 3.28 (t, 2H, $J = 6.7$ Hz), 2.30–2.24 (m, 2H), 2.13 (m, 4H), 1.98–1.89 (m, 2H), 1.55 (p, 2H); ^{13}C NMR δ 138, 115, 81, 78, 33, 32, 28, 20, 18, 6. HRMS: calcd for $\text{C}_{10}\text{H}_{15}\text{I}$ (M^+), m/e 262.0219; found, m/e 262.0203.

12-Phenyldodeca-6,11-diyne-1-ene (4) and 12-(Trimethylsilyl)dodeca-6,11-diyne-1-ene (5). These products were prepared by following an identical procedure. The appropriate acetylene (3 mmol) dissolved in 10 mL of THF is treated at -78°C with 3 mmol of a 1.6 M solution of *n*-BuLi in hexanes. The solution is warmed to 0°C to ensure complete deprotonation, 2 mmol of **3** is added, and the solution is brought to reflux. Small aliquots (1–2 mmol) of preformed acetylide are added via cannula until complete conversion of 10-iododec-6-yne-1-ene is observed by GC (1 to 2 days). The mixture is then worked up as usual and dried over MgSO_4 . Removal of the solvent affords a clear yellow oil which is purified by flash chromatography. **4:** Yield 94%; $R_f = 0.46$ (10% EtOAc in hexanes); IR (CHCl_3) 2940, 2250 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.38–7.35 (m, 2H), 7.27–7.22 (m, 3H), 5.82–5.73 (m, 1H), 2.50 (t, 2H), 2.31 (m, 2H), 2.14 (m, 4H), 1.76 (p, 2H), 1.56 (p, 2H); ^{13}C NMR (CDCl_3) δ 138, 132, 128, 128, 124, 115, 89, 81, 80, 79, 33, 28, 28, 19, 18, 18. HRMS: calcd for $\text{C}_{18}\text{H}_{20}$ (M^+), m/e 236.1565; found, m/e 236.1567. **5:** Yield 96%; $R_f = 0.75$ (10% EtOAc in hexanes); GC Rt = 10.7 min; IR 2945, 1649, 1248 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.82–5.73 (m, 1H), 5.04–4.93 (m, 2H), 2.31 (t, 2H, $J = 7.14$ Hz), 2.23 (m, 2H), 2.14 (m, 4H), 1.67 (p, 2H, $J = 7.07$ Hz), 1.55 (p, 2H, $J = 7.28$ Hz), 0.12 (s, 9H); ^{13}C NMR (CDCl_3) δ 138, 115, 107, 85, 80, 79, 33, 28, 19, 18, 0. HRMS: calcd for $\text{C}_{14}\text{H}_{21}\text{Si}$ ($\text{M}^+ - \text{CH}_3$), m/e 217.1412; found m/e 217.1412.

Dodeca-6,11-diyne-1-ene (6). To **5** dissolved in THF is added 1.5 equiv of tetrabutylammonium fluoride (1.0 M in THF) at RT (room temperature) for 20 min. Usual workup affords a quantitative yield of the product ($R_f = 0.56$ in 10% EtOAc/hexanes): IR (CCl_4) 3308, 2934, 1552 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.73–5.62 (m, 1H), 5.04–4.85 (m, 2H), 2.21 (qd, 2H, $J_1 = 7.8$ Hz, $J_2 = 2.9$ Hz), 2.09 (m, 4H), 1.88 (7, 1H, $J = 2.9$

Hz), 1.64 (p, 2H, $J = 8.0$ Hz), 1.51 (p, 2H, $J = 7.8$ Hz); ^{13}C NMR δ 138.0, 115.0, 83.8, 80.6, 79.1, 68.6, 32.8, 28.2, 28.0, 18.1, 17.8, 17.5. HRMS: calcd for $\text{C}_{12}\text{H}_{16}$ (M^+), m/e 160.1252; found, m/e 160.1251.

Deca-9-en-4-yne-1-ol (7). Via the Swern procedure, to a solution of CH_2Cl_2 (25 mL) and oxalyl chloride (13.7 mL, 15.1 mmol) is added, at -55°C , Me_2SO (23.3 mL, 30.2 mmol) dissolved in 5 mL of CH_2Cl_2 . After the mixture is stirred for 2 min, 2.08 g (13.7 mmol) of **1** is added over 5 min, and the solution is stirred for an additional 15 min, after which triethylamine (9.6 mL, 68.5 mmol) is added. The reaction is then stirred below -50°C for 5 min and then allowed to warm to room temperature. Water (50 mL) is added, and the aqueous layer is reextracted with additional 50 mL of CH_2Cl_2 . The combined organic layers are washed with saturated NaCl solution (100 mL), then with 1% HCl, water, and 5% Na_2CO_3 , and finally with water. After drying over MgSO_4 and removal of the solvent, the product is purified for analytical purposes by flash chromatography: $R_f = 0.31$ in 10% EtOAc in hexanes; yield 1.70 g (11.3 mmol), 83%; GC Rt = 4.5 min; IR (CCl_4) 1729, 1546 cm^{-1} ; ^1H NMR (CDCl_3) δ 9.77 (t, $J = 1.4$ Hz), 5.75 (ddt, 1H, $J_{trans} = 17.0$ Hz, $J_{cis} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.99 (dd, 1H, $J_{trans} = 17.0$ Hz, $J_{gem} = 1.6$ Hz), 4.94 (dd, 1H, $J_{cis} = 10.3$ Hz, $J_{gem} = 1.6$ Hz), 2.60 (dt, 2H, $J_1 = 7.1$ Hz, $J_2 = 1.4$ Hz), 2.46 (m, 2H), 2.11 (m, 4H), 1.53 (p, 2H); ^{13}C NMR (CDCl_3) δ 201.0, 137.9, 115.0, 81.1, 78.1, 43.0, 32.7, 28.0, 18.0, 12.1. HRMS: calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ (M^+), m/e 150.1045; found, m/e 150.1041.

3-Hydroxy-1-phenyldodeca-1,6-diyn-12-ene (8) and 3-Hydroxy-1-(trimethylsilyl)dodeca-1,6-diyn-12-ene (9). These products were prepared following an identical procedure. The appropriate acetylene (3 mmol) dissolved in 10 mL of THF is treated at -78°C with 3 mmol of a 1.6 M solution of *n*-BuLi in hexanes. The solution is warmed to 0°C to ensure complete deprotonation, it is cooled to between -50 and -60°C , and dec-6-yne-10-ene-1-ol (2.5 mmol) is added over 5–10 min. After the reaction mixture is allowed to warm to 0°C , it is poured into a mixture of ice and 10% NH_4Cl , the aqueous layer is reextracted with ethyl ether, and the combined organic layers are dried over anhydrous MgSO_4 ; after removal of the solvent the crude product is purified by flash chromatography. **8:** Yield = 79%; $R_f = 0.19$ (10% EtOAc in hexanes); GC Rt = 16.6 min; IR (CCl_4) 3679, 3605, 3035, 2943, 1224 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32 (m, 2H), 7.21 (m, 3H), 5.70 (ddt, 1H, $J_{trans} = 17.0$ Hz, $J_{cis} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.94 (dd, 1H, $J_{trans} = 17.0$ Hz, $J_{gem} = 1.6$ Hz), 4.89 (dd, 1H, $J_{cis} = 10.3$ Hz, $J_{gem} = 1.6$ Hz), 4.66 (dt, 1H, $J_a = J_b = 6.0$ Hz), 4.71 (s, 1H), 2.31 (m, 2H), 2.06 (m, 4H), 1.89 (td, 4H, $J_a = J_b = 6.9$ Hz), 1.49 (q, 2H, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3) δ 138, 132, 128, 128, 122, 115, 89, 85, 81, 79, 62, 37, 33, 28, 18, 15. HRMS: calcd for $\text{C}_{18}\text{H}_{20}\text{O}$ (M^+), m/e 252.1514; found, m/e 252.1509. **9:** Yield = 74%; $R_f = 0.23$ (10% EtOAc in hexanes). IR (CCl_4) 3600, 2936, 1547, 1245 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.77 (ddt, 1H, $J_{trans} = 17.0$ Hz, $J_{cis} = 10.3$ Hz, $J_1 = 6.6$ Hz), 5.01 (dd, 1H, $J_{trans} = 17.0$ Hz, $J_{gem} = 1.6$ Hz), 4.96 (dd, 1H, $J_{cis} = 10.3$ Hz, $J_{gem} = 1.6$ Hz), 4.49 (dt, 1H, $J_a = J_b = 6.0$ Hz), 2.44–2.20 (m, 2H), 2.18–2.04 (m, 4H), 1.98 (d, $J = 7.3$ Hz, 1H), 1.85 (dt, $J_a = J_b = 6.7$ Hz, 2H), 1.55 (m, 2H); ^{13}C NMR (CDCl_3) δ 138, 115, 106, 90, 81, 79, 62, 37, 33, 28, 18, 15, 0. HRMS: calcd for $\text{C}_{15}\text{H}_{23}\text{OSi}$ ($\text{M}^+ - 1$), m/e 247.1518; found, m/e 247.1516.

3-(Trimethylsilyloxy)-1-(trimethylsilyl)dodec-1,6-diyn-12-ene (10). To **9** (500 mg, 2.02 mmol) dissolved in 10 mL of THF are added 16 mmol of triethylamine and, after cooling to 0°C , 6.1 mmol of trimethylsilyl chloride. The solution is stirred overnight and then worked up as usual to afford, after flash chromatography, the desired product: Yield = 82%; $R_f = 0.73$ (10% EtOAc in hexanes); GC Rt = 11.3 min; IR (CCl_4) 3320, 2965, 2184, 1259 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.78 (ddt, 1H, $J_{trans} = 17.0$ Hz, $J_{cis} = 10.3$ Hz, $J_1 = 6.6$ Hz), 5.01 (dd, 1H, $J_{trans} = 17.0$ Hz, $J_{gem} = 1.6$ Hz), 4.95 (dd, 1H, $J_{cis} = 10.3$ Hz, $J_{gem} = 1.6$ Hz), 2.23–2.20 (m, 2H), 2.18–2.06 (m, 4H), 1.88–1.74 (m, 2H), 1.54 (q, 2H, $J = 7.5$ Hz); ^{13}C NMR (CDCl_3) δ

138, 115, 107, 89, 80, 79, 62, 38, 33, 28, 18, 15, 0.1, -0.2. HRMS: calcd for $C_{18}H_{32}OSi_2$ (M^+), m/e 320.1992; found, m/e 320.1992.

General Procedure for the Cyclocarbonylation Reactions. To 2 mmol of the enediyne in 10 mL of toluene in a Fisher-Porter vessel is added 10 mmol of pentacarbonyliron filtered through a short pad of Celite. The reaction vessel is sealed and degassed by three freeze-pump-thaw cycles. During the last cycle it is charged with 100 psi of CO (50 psi for the hydroxy- and trimethylsilyloxy-substituted enediynes), and then it is heated at 125–130 °C for 22 hours. After cooling and release of the pressure, the reaction mixture is diluted with 10 mL of methylene chloride and filtered through a 30 mm Celite column to remove iron impurities; the solvent is evaporated and the dark residue chromatographed through a short column of silica gel to afford, after removal of the solvent, pure complex.

Tricarbonyl{2-(pent-4-enyl)-4-phenylbicyclo[3.3.0]octa-1,4-dien-3-one}iron (11). This was obtained from **4**: Yield 78%; R_f = 0.35 (EtOAc); IR (CDCl₃) 2063, 2011, 1979 cm^{-1} ; ¹H NMR (CDCl₃) δ 7.94–7.90 (m, 2H), 7.35–7.20 (m, 3H), 5.82 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, J_1 = 6.6 Hz), 5.01 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.95 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 2.99–2.86 (m, 2H), 2.64–2.57 (m, 2H), 2.57–2.37 (m, 2H), 2.18–1.98 (m, 4H), 1.75–1.58 (m, 2H); ¹³C NMR (CDCl₃) δ 208.9, 172.0, 138.0, 132.4, 128.6, 127.9, 127.6, 115.0, 108.5, 103.8, 82.2, 77.9, 33.8, 28.9, 28.4, 26.1, 25.8, 24.4. HRMS: calcd for $C_{19}H_{24}O_4SiFe$ (M^+), 0404.0711. Found: 404.0716.

Tricarbonyl{2-(pent-4-enyl)-4-(trimethylsilyl)bicyclo[3.3.0]octa-1,4-dien-3-one}iron (12). This was obtained from **5**: Yield 58%; R_f = 0.08 (10% EtOAc in hexanes); IR (CDCl₃) 2067, 2006, 2000 cm^{-1} ; ¹H NMR (CDCl₃) δ 5.79 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, J_1 = 6.6 Hz), 5.01 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.95 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 2.57–2.48 (m, 4H), 2.46–2.22 (m, 2H), 2.11 (dt, 2H, $J_1 = J_2 = 7.2$ Hz), 2.03–1.80 (m, 2H), 1.79–1.53 (m, 2H), 0.25 (s, 9H); ¹³C NMR (CDCl₃) δ 209.0, 178.7, 138.1, 115.0, 112.3, 112.2, 85.1, 67.2, 33.9, 28.9, 27.4, 25.9, 25.8, 24.4, -0.7. HRMS: calcd for $C_{19}H_{24}O_4SiFe$ (M^+), m/e 400.0793; found, m/e 400.0832.

Tricarbonyl{2-(pent-4-enyl)bicyclo[3.3.0]octa-1,4-dien-3-one}iron (13). This was obtained from **6**: Yield = 90%; R_f = 0.21 (30% EtOAc in hexanes); IR (CCl₄) 2071, 2014, 1991, 1653 cm^{-1} ; ¹H NMR (CDCl₃) δ 5.77 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, J_1 = 6.6 Hz), 5.00 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.93 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 4.02 (s, 1H), 2.66–2.48 (m, 4H), 2.44–2.29 (m, 2H), 2.22–1.85 (m, 4H), 1.67–1.51 (m, 2H); ¹³C NMR (CDCl₃) δ 208.4, 174.1, 137.8, 115.0, 110.7, 105.7, 82.2, 84.7, 59.8, 33.7, 28.8, 26.7, 26.1, 26.0, 24.3. HRMS: calcd for $C_{16}H_{16}O_4Fe$ (M^+), m/e 328.0398; found, m/e 328.0390.

Tricarbonyl{2-(pent-4-enyl)-4-phenyl-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one}iron (14). This was obtained from **8**: Yield = 75% (mixture of diastereomers); R_f = 0.12–0.25 (30% EtOAc in hexanes); IR (CCl₄) 2071, 2026, 2000 cm^{-1} ; ¹H NMR (CDCl₃) δ 8.14 (dd, 2H, $J_1 = 8.2$ Hz, $J_2 = 1.5$ Hz), 7.36–7.25 (m, 3H), 5.70 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.38 (t, 1H), 5.02 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.96 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 4.06 (d, 1H), 3.04–2.90 (m, 1H), 2.51–2.25 (m, 3H), 2.12–1.93 (m, 3H), 1.91–1.56 (m, 2H), 1.40–1.23 (m, 1H); ¹³C NMR (CDCl₃) δ (1st diastereomer) 208.2, 171.0, 137.9, 131.4, 129.1, 128.3, 127.8, 115.1, 110.1, 104.8, 81.9, 77.7, 71.2, 35.7, 33.7, 28.9, 24.1, 23.0, δ (2nd diastereomer) 208.0, 172.4, 137.9, 131.8, 128.7, 128.2, 127.6, 114.9, 111.3, 98.9, 85.1, 75.2, 72.3, 36.8, 33.8, 29.3, 23.7, 23.6. HRMS: calcd for $C_{22}H_{20}O_5Fe$ (M^+), m/e 420.0660; found, m/e 420.0641.

Tricarbonyl{2-(pent-4-enyl)-4-(trimethylsilyl)-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one}iron (15). This was obtained from **9**: Yield = 65% (mixture of diastereomers); R_f = 0.09 (10% EtOAc in hexanes); IR (CCl₄) 2069, 2016, 1989

cm^{-1} ; ¹H NMR (CDCl₃) δ 5.78 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.13 (t, 1H, $J = 9.7$ Hz), 4.99 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.94 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 3.11 (s, 1H), 3.00–1.51 (m, 10H), 0.23 (s, 9H); ¹³C NMR (CDCl₃) δ 209, (179, 178), 138, 115, (114, 112), (113, 109), (87, 85), (72, 71), (66, 65), (36, 35), 34, 29, (24, 23), 24, (-0.1, -0.8). HRMS: calcd for $C_{19}H_{24}O_5SiFe$ (M^+), m/e 416.0742; found, m/e 416.0590.

Tricarbonyl{2-(pent-4-enyl)-4-(trimethylsilyl)-6-oxobicyclo[3.3.0]octa-1,4-dien-3-one}iron (16). To 132 mg (0.32 mmol) of **15** in 5 mL of CH₂Cl₂ is added 103 mg (0.48 mmol) of PCC, and the reaction is stirred at room temperature overnight. Aqueous workup, drying over MgSO₄ and removal of the solvent afford the desired ketone: Yield = 90%; R_f = 0.40 (20% EtOAc in hexanes); IR (CCl₄) 2081, 2027, 2001, 1723, 1653 cm^{-1} ; ¹H NMR (CDCl₃) δ 5.77 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.01 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.96 (dd, 1H, J_{cis} = 10.3 Hz, $J_{syn} = 1.6$ Hz), 3.14–2.91 (m, 2H), 2.75 (t, 2H, $J = 5.3$ Hz), 2.35–2.01 (m, 4H), 1.76–1.52 (m, 2H); ¹³C NMR (CDCl₃) δ 207, 179, 137, 123, 115, 93, 92, 65, 64, 37, 34, 29, 24, 22, -0.6. HRMS: calcd for $C_{19}H_{22}O_5SiFe$ (M), m/e 414.0586; found, m/e 414.0586.

Tricarbonyl{2-(pent-4-enyl)-4-(trimethylsilyl)-6-((trimethylsilyloxy)bicyclo[3.3.0]octa-1,4-dien-3-one}iron (17). This was obtained from **10**: Yield = 81% (mixture of diastereomers); R_f = 0.46–0.56 (20% EtOAc in hexanes); IR (CCl₄) 2963, 2070, 2014, 1990, 1641, 1257 cm^{-1} ; ¹H NMR (CDCl₃) δ 5.77 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.09 (t, 1H, $J = 7.5$ Hz), 4.98 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.93 (dd, 1H, J_{cis} = 10.3 Hz, $J_{gem} = 1.6$ Hz), 2.92–1.50 (m, 10H), 0.25 (2s, 9H), 0.15 (2s, 9H); ¹³C NMR (CDCl₃) δ 209 (2), (179, 178), 138, 115, (115, 112), (114, 109), (87, 84), (73, 72), (66, 65), 36 (2), 34, 29 (2), (24, 23), 24, (0.7, 0.2), (0.1, -0.9). HRMS: calcd for $C_{22}H_{32}O_5Si_2Fe$ (M^+), m/e 488.1138; found, m/e 488.1151.

Tricarbonyl{2-(pent-4-enyl)-4-phenyl-6-((methoxymethylene)oxy)bicyclo[3.3.0]octa-1,4-dien-3-one}iron (18). The corresponding alcohol **14** (145 mg, 0.35 mmol) is dissolved in CH₂Cl₂ with 2.8 mmol of Hünigs base, 1.7 mmol of methoxymethyl chloride is added at 0 °C, and the reaction is warmed to 55 °C for 48 h. Aqueous workup, followed by drying over MgSO₄ and flash chromatography, affords the desired methoxymethyl ether as a 2:1 mixture of diastereomers: Yield = 100% (mixture of diastereomers); R_f = 0.30–0.40 (30% EtOAc in hexanes); IR (CCl₄) 2945, 2069, 2018, 1990, 1645 cm^{-1} ; ¹H NMR (1st diastereomer, R_f = 0.4) (CDCl₃) δ 8.05 (d, 2H, $J = 7.3$ Hz), 7.32 (m, 3H), 5.82 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.37 (d, 1H, $J = 4.7$ Hz), 5.03 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.98 (dd, 1H, J_{cis} = 10.3 Hz, J_{gem} = 1.6 Hz), 4.74 (d, 1H, $J_{gem} = 7.0$ Hz), 4.64 (d, 1H, $J_{gem} = 7.0$ Hz), 3.31 (s, 3H), 3.00–1.60 (m, 10H), (2nd diastereomer, R_f = 0.3) (CDCl₃) δ 7.90 (d, 2H, $J = 7.3$ Hz), 7.26 (m, 3H), 5.79 (ddt, 1H, J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz, $J_1 = 6.6$ Hz), 5.21 (t, 1H, $J = 7.4$ Hz), 5.03 (dd, 1H, J_{trans} = 17.0 Hz, J_{gem} = 1.6 Hz), 4.96 (dd, 1H, J_{cis} = 10.3 Hz, $J_{gem} = 1.6$ Hz), 4.74 (s, 2H), 3.37 (s, 3H), 2.85–1.55 (m, 10H); ¹³C NMR (1st diastereomer, R_f = 0.4) (CDCl₃) δ 208, 173, 138, 132, 129, 128, 128, 115, 110, 99, 95, 84, 77, 56, 34, 33, 29, 24, 23, (2nd diastereomer, R_f = 0.3) (CDCl₃) δ 208, 171, 138, 131, 129, 128, 127, 115, 109, 101, 96, 82, 78, 76, 56, 34, 33, 29, 24, 23. HRMS: calcd for $C_{21}H_{28}O_6SiFe$ (M^+), m/e 464.0922; found, m/e 464.0922.

Tricarbonyl{2-(pent-4-enyl)-4-(trimethylsilyl)-6-((methoxymethylene)oxy)bicyclo[3.3.0]octa-1,4-dien-3-one}iron (19). The corresponding alcohol **15** (80 mg, 0.19 mmol) is dissolved in CH₂Cl₂ with 1.52 mmol of Hünigs base, 0.80 mmol of methoxymethyl chloride are added at 0 °C, and the reaction is warmed to 55 °C for 48 h. Aqueous workup, followed by drying over MgSO₄ and flash chromatography, affords the desired methoxymethyl ether as a mixture of diastereomers: Yield = 100% (mixture of diastereomers); R_f = 0.68 (20% EtOAc in hexanes); IR (CCl₄) 2956, 2066, 2013,

1990, 1641 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.76 (ddt, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{cis}} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.98 (dd, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.94 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.84 (2t, 1H, $J = 6.7$ Hz), 4.74 (d, 1H, $J_{\text{gem}} = 7.0$ Hz), 4.68 (d, 1H, $J_{\text{gem}} = 7.0$ Hz), 3.38 (s, 3H), 2.92–1.50 (m, 10H), 0.25 (s, 9H); ^{13}C NMR (CDCl_3) δ 208, (179, 178), 138, 127, 125, 120, 115, 114, 113, 107, 98, 95, 87, 78, 77, 76, 57, 56, 33, 28, 24, 24, 23, -0.1, -1. HRMS: calcd for $\text{C}_{21}\text{H}_{28}\text{O}_6\text{SiFe}$ (M^+), m/e 460.1004; found, m/e 460.1003.

Decomplexation Reactions. The general procedure consists in dissolving the desired complex (0.2 mmol) in 5 mL of *N,N*-dimethylacetamide and cooling to -10 °C under air, followed by addition of 0.8 mmol of trimethylamine *N*-oxide. The mixture is then stirred for 1 h after which time the temperature is raised to -5 °C followed by additional 11 h of stirring. With care taken to maintain the product at around 0 °C, 10 mL of ethyl ether is added, and the solution is filtered through a short column of Celite, diluted with additional 10 mL of ether, and washed at least 6 times with 15 mL aliquots of cold half-saturated brine. The organic layer is dried over MgSO_4 in an ice bath and the solvent removed by rotary evaporation without heating. In all cases the crude ^1H NMR spectrum shows very few peaks due to impurities; the GC trace on the other hand shows a purity, relative to the crude mixture, of around 70%. After purification by HPLC the yield is somewhat lower due to losses in the chromatographic process. The three different yields are reported in each case.

2-(Pent-4-enyl)-4-phenylbicyclo[3.3.0]octa-1,5-dien-3-one (20). This was obtained from 11: Yield, crude 65%, GC 38%, HPLC 10%; $R_f = 0.28$ (30% EtOAc in hexanes); GC Rt = 18.6 min; IR (CCl_4) 3558, 2939, 1716, 1634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38–7.24 (m, 5H), 6.16 (t, 1H, $J = 2.6$ Hz), 5.79 (ddt, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{cis}} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.99 (dd, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.94 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J_{\text{gem}} = 1.6$ Hz), 2.93 (s, 2H), 2.90 (m, 2H), 2.84 (m, 2H), 2.33 (m, 2H), 2.06 (m, 2H), 1.62 (m, 2H); ^{13}C NMR (CDCl_3) δ 208, 182, 151, 140, 138, 130, 130, 128, 127, 125, 115, 76, 36, 34, 27, 26, 24. HRMS: calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ (M^+), m/e 264.1514; found, m/e 264.1512.

2-(Pent-4-enyl)bicyclo[3.3.0]octa-1,5-dien-3-one (21). This was obtained from 12: Yield, crude 61%, GC 45%, HPLC 12%; $R_f = 0.32$ (20% EtOAc in hexanes); IR (CCl_4) 2951, 1717, 1634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.96 (t, 1H, $J = 2.5$

Hz), 5.79 (ddt, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{cis}} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.99 (dd, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.93 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J_{\text{gem}} = 1.6$ Hz), 2.85 (s, 2H), 2.83 (m, 2H), 2.72 (m, 2H), 2.25 (t, 2H, $J = 7.7$ Hz), 2.03 (q, 2H, $J = 7.7$ Hz), 1.62 (p, 2H, $J = 7.7$ Hz); ^{13}C NMR (CD_3Cl) δ 208, 182, 144, 138, 134, 129, 115, 36, 36, 34, 27, 25, 23. HRMS: calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (M^+), m/e 188.1201; found, m/e 188.1202.

2-(Pent-4-enyl)-4-phenyl-6-((methoxymethylene)oxy)-bicyclo[3.3.0]octa-1,5-dien-3-one (22). This was obtained from 18: Yield, crude 58%, GC 37%, HPLC 8%; $R_f = 0.40$ (20% EtOAc in hexanes); IR (CCl_4) 2986, 2940, 2866, 1697 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.28–7.05 (m, 5H), 5.73 (ddt, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{cis}} = 10.3$ Hz, $J_1 = 6.6$ Hz), 4.92 (dd, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.86 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.82 (d, 1H, $J = 6.2$ Hz), 4.54 (d, 1H, $J = 6.2$ Hz), 3.96 (s, 1H), 3.24 (s, 3H), 2.98–2.80 (m, 4H), 2.16 (td, 2H, $J_1 = 2.9$ Hz, $J_2 = 7.5$ Hz), 1.96 (dt, 2H, $J_1 = 6.6$ Hz, $J_2 = 7.5$ Hz), 1.50 (p, 2H, $J = 7.5$ Hz); ^{13}C NMR (CDCl_3) δ 206, 183, 157, 139, 129, 128, 127, 127, 120, 115, 95, 57, 53, 34, 34, 27, 23, 23. HRMS: calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$ (M^+), m/e 324.1725; found, m/e 324.1721.

2-(Pent-4-enyl)-6-((methoxymethylene)oxy)bicyclo[3.3.0]octa-1,5-dien-3-one (23). This was obtained from 19: Yield, crude 75%, GC 49%, HPLC 15%; $R_f = 0.30$ (30% EtOAc in hexanes); IR (CCl_4) 2933, 1694, 1669, 1620 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.79 (ddt, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{cis}} = 10.3$ Hz, $J_1 = 6.6$ Hz), 5.05 (s, 2H), 4.98 (dd, 1H, $J_{\text{trans}} = 17.0$ Hz, $J_{\text{gem}} = 1.6$ Hz), 4.92 (dd, 1H, $J_{\text{cis}} = 10.3$ Hz, $J_{\text{gem}} = 1.6$ Hz), 3.43 (s, 3H), 2.98 (s, 2H), 2.84 (m, 2H), 2.75 (m, 2H), 2.19 (t, 2H, $J = 7.6$ Hz), 2.03 (q, 2H, $J = 7.6$ Hz), 1.54 (p, 2H, $J = 7.6$ Hz); ^{13}C NMR (CDCl_3) δ 207, 183, 156, 139, 129, 115, 114, 95, 57, 37, 35, 34, 27, 23, 23. HRMS: calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3$ (M^+), m/e 248.1412 found, m/e 248.1413.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 93-08105 to A.J.P.), the CNR (Italy; to A.P.) and the Fulbright Commission (to A.P.) for financial support of this research.

Supporting Information Available: Figures showing NMR spectra (49 pages). Ordering information is given on any current masthead page.

OM950465B