Studies on Intramolecular Coupling of Tricarbonyl(diene)iron Systems with Pendant Olefinic Groups: Configurational Requirements for Reactions of Acyclic Diene Complexes and Mechanistic Implications

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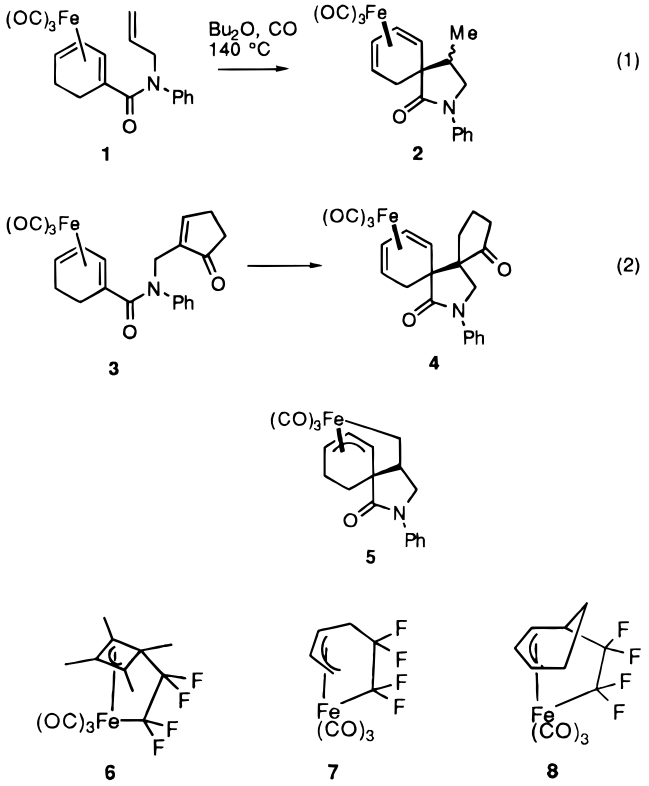
A photothermal cyclization reaction, which involves intramolecular coupling between a diene−$Fe(CO)_3$ complex and a pendant olefinic group, has been studied for a number of acyclic diene complexes in which the olefinic group is attached as an ester, amide, keto, or alcohol derivative. While the cyclization will occur for complexes in which a methyl group is in the *E* stereochemical arrangement about the diene terminus, the transfer of hydrogen from this methyl to the metal, followed by reductive elimination to give a final cyclized material, does not occur. The latter process is shown to require a methyl group at the diene terminus in a *Z* configuration.

Introduction

We have previously described an interesting and potentially useful cyclization reaction that involves thermal coupling between a (cyclohexadiene)iron tricarbonyl complex and an attached alkene, exemplified by the conversions of **1** and **3** to lactams **2** and **4**.[1] These



reactions were proposed to involve the intermediate formation of the σ,η^3-complex **5**, on the basis of a precedent for intermolecular reactions of tricarbonyl(diene)iron complexes with olefins observed by Green, who reported that iron complexes, including (tetramethylcyclobutadiene)-, (butadiene)-, and (cyclohexadiene)iron tricarbonyls, react with perfluoroolefins (such as tetrafluoroethene and hexafluoropropene) when irradiated to form stable 1:1 adducts such as **6**−**8**.[2]

The mechanism of Green's reaction was studied by Kerber using reactions of (diene)iron tricarbonyl complexes with 1,1-dichloro-2,2-difluoroethene.[3] It was found that when a polyhaloethylene was added to a THF solution of **9**, initially irradiated for 15 h, adduct **10** was formed readily at room temperature. Furthermore, when the reaction was run in the presence of ^{13}CO, a significant amount of labeled carbon monoxide was incorporated into the product. On the basis of these observations, the mechanism shown in Scheme 1 was proposed by Kerber. Initial loss of carbon monoxide and complexation with halogenated olefin is followed by carbon−carbon bond formation to give the σ,η^3-complex **10**.

The overall transformations shown in eqs 1 and 2 require hydrogen atom transfer from the diene ligand to the metal, followed by reductive elimination to form the methyl or methylene group in the product lactam. Such a process does not occur with halogenated complex **8**, presumably due to the electron-withdrawing nature of fluoro substituents, which stabilizes the metal−carbon σ-bond. Interestingly, when even one of the fluorine atoms is changed to the less electron-withdraw-

(1) Pearson, A. J.; Zettler, M. W. *J. Am. Chem. Soc.* **1989**, *111*, 3908.

(2) (a) Bond, A.; Green, M. *J. Chem. Soc., Chem. Commun.* **1971**, 12. (b) Bond, A.; Green, M.; Lewis, B.; Lowrie, S. F. W. *J. Chem. Soc., Chem. Commun.* **1971**, 1230. (c) Bond, A.; Green, M.; Taylor, S. H. *J. Chem. Soc., Chem. Commun.* **1973**, 112. (d) Green, M.; Lewis, B. *J. Chem. Soc., Chem. Commun.* **1973**, 114. (e) Green, M.; Heathcock, S.; Wood, D. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1564. (f) Bond, A.; Lewis, B.; Green, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1109. (g) Green, M.; Lewis, B.; Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1975**, 1118.

(3) Kerber, R. C.; Koerner von Gustorff, E. A. *J. Organomet. Chem.* **1976**, *110*, 345−357.

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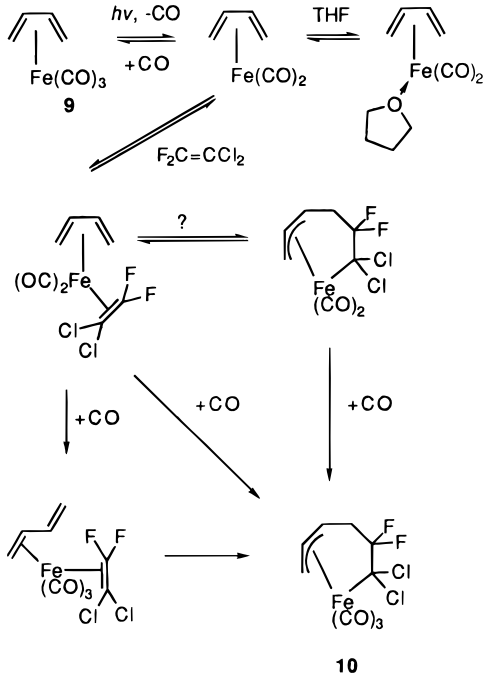
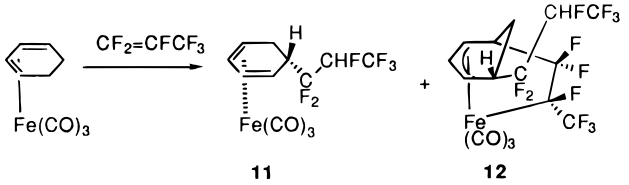
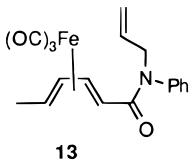
Scheme 1. Kerber's Mechanism of Formation of σ,η^3-Complexes



ing CF_3 group, hydrogen migration does take place and products **11** and **12** result.[2g]



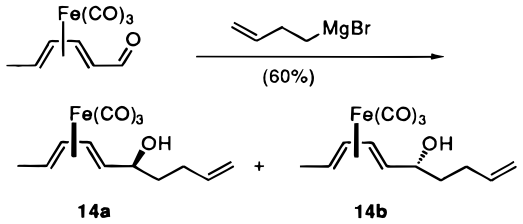
In the case of metal-assisted spirocyclization, it is the migration of a hydrogen atom from C5 of the ring that furnishes the diene. However, it is unclear whether a *cis* configuration of the intermediate is an essential requirement in order for the reaction to take place. That question cannot be answered by studying cyclic substrates, since the resulting intermediate (σ,η^3-organo)iron complex can only exist in the *cis* form. Therefore, one would need to compare the reactivities of acyclic complexes in order to gain a deeper understanding of the mechanism of the cyclization reaction. It has been observed earlier that amide complex **13** with a *trans*-



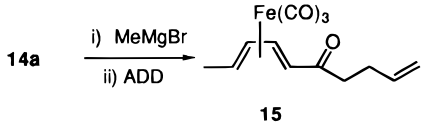
methyl substituent is unreactive under thermal cyclization conditions.[4] It is then necessary to compare the reactivity of this and similar complexes with the corresponding *gem*-dimethyl-substituted complexes having a *cis* substituent. It should be noted that, apart from the aforementioned attempted cyclization of **13**, the reactivity of acyclic (diene)iron tricarbonyl complexes with pendant alkenes under the cyclization conditions has not been studied. Therefore, the goals of the following studies were examination of the cyclization of acyclic complexes with and without an alkyl substituent in a *cis* configuration about the diene and, thus, elucidation of the configurational requirements for successful completion of the reaction.

Results and Discussion

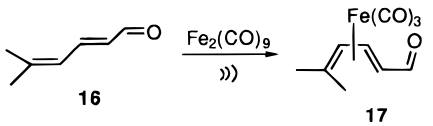
Preparation of Acyclic (Diene)iron Tricarbonyl Complexes Having Pendant Alkenes. Tricarbonyl-(1,6,8-decatrien-5-ol)iron (**14**) was prepared by Grignard addition to the known (2,4-hexadienal)iron tricarbonyl.[5] Alcohol **14** was obtained as a 2:1 mixture of diastereomers (Ψ-endo and Ψ-exo isomers **14a** and **14b**; assignment of stereochemistry of diastereomeric (dienol)iron tricarbonyl complexes is based on literature precedent[6]). The diastereomers were separated by chromatography (60% total yield; unoptimized).



Swern oxidation[7] of **14a** with a hydroxy group α to a (diene)iron tricarbonyl was found to cause extensive decomposition. Therefore, a milder method described by Mukaiyama was used,[8] involving *in situ* transformation of alcohol **14a** to the magnesium alkoxide by treatment with MeMgBr and subsequent oxidation with 1,1′-(azodicarbonyl)dipiperidine (ADD) to give ketone **15**.



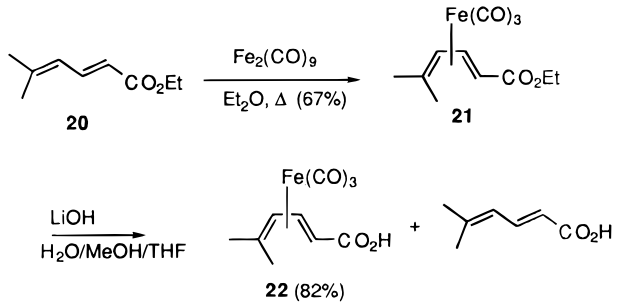
5-Methyl-2,4-hexadienal (**16**) was prepared from 3-methyl-2-butenal.[9] Sonication[10] of **16** with diiron nonacarbonyl in toluene afforded complex **17**, but in only 12% yield. Other complexation methods proved to be less efficient. Aldehyde **17** is unstable and decomposes readily, especially in solution, and should be used shortly after preparation.



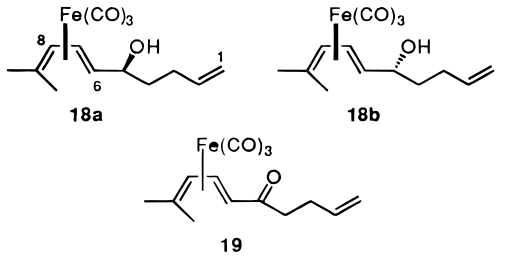
(4) Zettler, M. W. Ph.D. Dissertation, Case Western Reserve University, 1988.

(5) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955.
(6) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058.
(7) Mancuso, A. J.; Huang, S.-H.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(8) (a) Mukaiyama, T.; Takahashi, K.; Kuwajima, I. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1491. (b) Narasaka, K.; Morikawa, A.; Saigo, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2733.
(9) (a) Nazarov, I. N.; Krasnaia, Z. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1958**, *28*, 2477. (b) Nazarov, I. N.; Makin, S. M.; Kruptsov, B. K. *J. Gen. Chem. USSR (Engl. Transl.)* **1959**, 3641.
(10) Ley, S. V.; Low, C. M. R. *Ultrasound in Synthesis*; Springer-Verlag: Berlin, 1989; Vol. 27, p 133.

Scheme 2



Grignard addition to **17** afforded diastereomeric alcohols **18a** and **18b** as a 5:1 mixture of diastereomers, readily separable by chromatography (56% combined yield). As with **14a** and **14b**, the assignment of relative

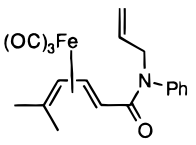
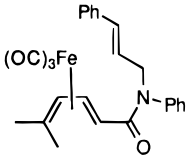
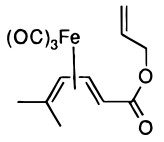


stereochemistry to these alcohols is based on relative polarity. This result illustrates the favorable influence of the *cis*-diene substituent on selectivity of nucleophilic addition to an aldehyde α to the (diene)iron tricarbonyl, which has not been previously reported. The effect is presumably the result of amplification of the known conformational preference for the *s-cis*-aldehyde.[11] Ketone **19** was prepared from alcohol **18** by ADD oxidation.

It is interesting to note the difference in spectral characteristics of alcohols **14** and **18**. Signals of *anti* H6 in the ^{1}H NMR spectra of **14a** and **14b** appear at 1.03 and 0.98 ppm, respectively, while that of **18a** occurs at 2.33 ppm. The corresponding signal of H6 in **18b** is obscured by peaks from allylic protons and appears at ca. 2.3 ppm. The geometry of (diene)iron tricarbonyl complexes is such that the four-carbon diene unit is planar (or nearly planar); *anti* substituents are displaced from the plane of the diene away from iron, while *syn* substituents are slightly bent toward the metal. A large downfield shift of *anti* H6 in the case of trisubstituted complex **18** presumably reflects further distortion of its geometry from the planar structure. That distortion can be held responsible for the observed lower thermal stability of dimethyl-substituted complexes (see later).

Preparation of various allyl amide and ester complexes analogous to **19** was also examined. Complexation of ester **20** with diiron nonacarbonyl (Et_2O, 35 °C, 5 h) yielded complex **21** in 67% yield. Initial attempts to hydrolyze ester **21** (30% KOH/MeOH, 24 h; HCl/H_2O/dioxane; LiOH/H_2O/THF; LiOH/MeOH/H_2O, 0 °C or room temperature) failed dismally, yielding only the free dienoic acid, resulting from complete demetalation (Scheme 2). However, use of dilute base in a mixed

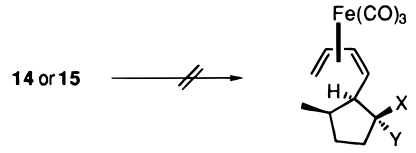
Table 1. Acyclic Complexes Derived from Acid 22

Complex	Yield (%)
 **23**	92
 **24**	94
 **25**	84

solvent system (0.8 N LiOH in H_2O/THF/MeOH) afforded complex **22** and uncomplexed acid in a 4.5:1 ratio (82% yield of complex **22**). The product was used for further derivatization as a mixture, since their coupling products are easier to separate.

Coupling of acid **22**, via its acid chloride, with *N*-phenyl-*N*-allylamine, *N*-phenyl-*N*-cinnamylamine,[12] or allyl alcohol afforded amides **23** and **24** and ester **25** (Table 1; yields are based on the amount of consumed complex **22**). These complexes were readily separated by chromatography from the respective uncomplexed dienes that were present.

Cyclizations of Acyclic (Diene)iron Tricarbonyl Complexes Having Pendant Alkenes. Alcohols **14** and ketone **15** did not yield any desired cyclization products when subjected to thermal or photochemical cyclization conditions:



Reflux of a Bu_2O solution or irradiation in benzene of diastereomer of **14a** (the Ψ-endo isomer) under a CO atmosphere resulted only in partial decomposition of the substrate. The unreacted alcohol was recovered as a 2:1 mixture of diastereomers, indicating that two diastereomers, **14a** and **14b**, exist in equilibrium under the reaction conditions. (Thermal epimerization of acyclic (diene)iron tricarbonyl complexes is a well-precedented phenomenon and proceeds through dechelation followed by bond rotation to the transoid diene, migration of the metal, and further complexation with the double bond.[13])

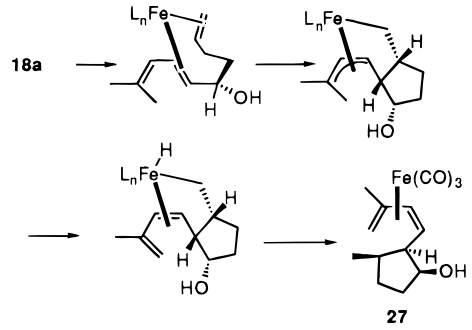
Dimethyl-substituted alcohol **18** and ketone **19** also proved unreactive under thermal cyclization conditions

(11) Howell, J. A. S.; Squibb, A. D.; Bell, A. G.; McAdrie, P.; Cunningham, D.; Goldshmidt, Z.; Gottlieb, H. E.; Hezroni-Langerman, D.; Grée, R. *Organometallics* **1994**, *13*, 4336.

(12) von Braun, J.; Tauber, L. *Ann. Chem.* **1927**, *458*, 102.

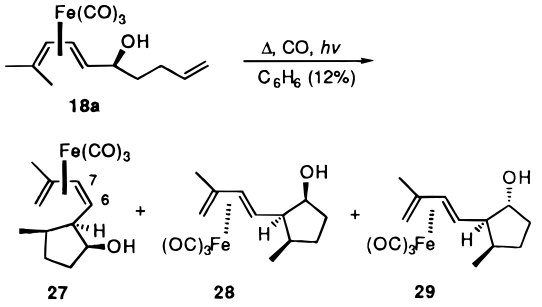
(13) (a) Whitlock, H. W.; Markezich, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5290. (b) Markezich, R. L.; Whitlock, H. W. *J. Am. Chem. Soc.* **1971**, *93*, 5291.

Scheme 3. Mechanism of Formation of Alcohol 27



and ketone **19** also under photochemical conditions (only traces of desired product could be observed in the ^{1}H NMR spectrum). On the other hand, alcohol **18a**, when subjected to photochemical cyclization conditions, afforded an equimolar mixture of three isomeric complexes, readily separable by chromatography, in 12% combined yield. All three products had a characteristic doublet in the olefinic region of their ^{1}H NMR spectra, corresponding to H7 of the complex. Only one product showed a signal corresponding to *syn*-H6 (δ 2.51 ppm, dd, J = 11.3, 8 Hz). Therefore, that product was assigned the structure **27** with *Z* configuration, the expected result of metal-assisted cyclization. The stereochemistry shown is based on the mechanism of formation of **27** (Scheme 3), and the product was obtained as a single epimer, since the epimerization process characteristic of cyclic (diene)iron tricarbonyl complexes is impossible in this case.[1]

The remaining two products were assigned structures **28** and **29**. Complex **28** likely arises from thermally



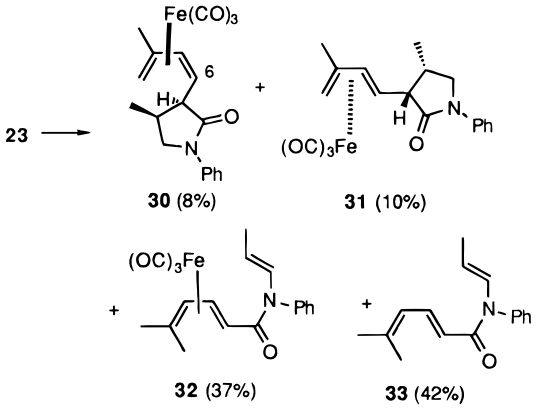
induced *cis*−*trans* isomerization of **27**, a known process for acyclic diene−Fe(CO)$_3$ complexes.[14] Alcohol **29** is formed as a result of epimerization of starting alcohol **18a**, followed by cyclization and *cis*−*trans* isomerization. This assignment is based on the identity of spectral characteristics of this product and that arising from irradiation of the diastereomeric alcohol **18b**. Whitesides' studies of *cis*−*trans* isomerization of deuterium-labeled (diene)iron tricarbonyl complexes[14] lead to the conclusion that metal epimerization must be much faster than hydrogen abstraction to give the (π-allyl)-metal hydride (that is an intermediate in the isomerization). Therefore, products arising from epimerization of *Z* complex **27** and further *cis*−*trans* isomerization can hypothetically also be formed. However, the intermediate π-allyl complex in that case would be sterically more crowded. In agreement with that, only one set of isomers resulting from alcohol **18a** has been isolated.

The minor diastereomer **18b** under the same conditions yielded only *E* complex **29** (6% yield). The fact that the products corresponding to epimerization of **18b** and further cyclization are not produced in this case can be explained by the greater stability of Ψ-exo (dienol)-iron tricarbonyl complexes (**18b** in this case) over Ψ-endo isomers (**18a**).

The low yields of cyclization products can be ascribed to the thermal instability of acyclic alcohol complexes having a terminal *gem*-dimethyl group, as noted earlier, resulting in their demetalation. Nevertheless, the results described show the general possibility of cyclization of acyclic (diene)iron tricarbonyl complexes with pendant alkenes. The fact that the reaction takes place only under the photochemical conditions is also noteworthy. More importantly, complexes lacking an alkyl group in the *cis* orientation were found to be completely unreactive, while disubstituted complexes (having a cis substituent) cyclize under the same reaction conditions. This supports the original assumption that there is a configurational requirement for the cyclization, and a *cis*-alkyl substituent is necessary for completion of the hydrogen transfer process, as indicated in Scheme 3.

Analogous to the alcohol complexes, carboxylic acid derivatives did not yield any cyclization products when refluxed in Bu_2O under CO atmosphere. All complexes proved to be unstable under the reaction conditions, and only demetalated dienes were obtained. For amide **23** and ester **25**, olefin migration in the allyl side chain was found to be a major process. In the case of complex **25**, the resulting vinyl ester was hydrolyzed to acid **22** during separation of the products on silica gel. The isomerization is presumably a metal-assisted process and takes place even in the case of complex **24** with the double bond stabilized by conjugation. Interestingly, a small amount of product of formal hydrogenation of the nonconjugated double bond was formed from amide **23**. The mechanism of that reduction is unclear at this time, although it is possible that a water-gas reaction could occur, with small amounts of water as impurity.

Irradiation of amide **23** under the standard conditions (benzene, 80 °C) afforded *cis*- and *trans*-lactams **30** (8% yield) and **31** (ca. 10% yield). The ^{1}H NMR spectrum

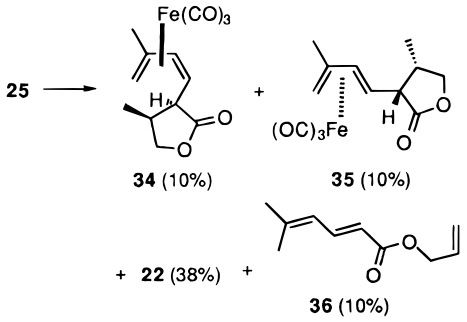


of lactam **30** shows the characteristic doublet for H7 at δ 5.56 ppm (broad), a singlet for the methyl substituent on the diene at 2.22 ppm, and a doublet corresponding to the lactam methyl group at 1.2 ppm. The signal for

(14) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63.

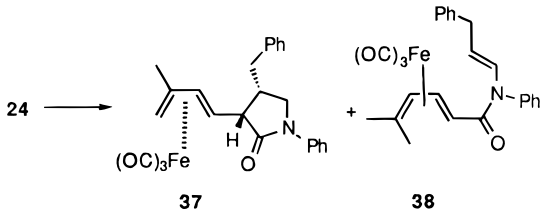
H6 appears as a doublet of doublets at 2.28 ppm, which is characteristic of a *syn* hydrogen atom on the diene, thus indicating the *Z* configuration. Signals of the remaining two diene protons appear at 1.97 (H9 syn) and 1.37 ppm (H9 anti); these assignments are supported by a COSY experiment. Lactam **31**, formed as a result of isomerization of **30** under the reaction conditions, was contaminated with an inseparable impurity; however, analyses of ^{1}H NMR and IR spectra support its formation. The major products of this reaction are amides **32** (37%) and **33** (42%), derived from double-bond migration.

Ester **25** under photochemical cyclization conditions afforded *cis*- and *trans*-lactones **34** (10% yield) and **35** (10% yield) as single diastereomers (along with 38% of acid **22** and 10% of demetalated ester **36**). It should be



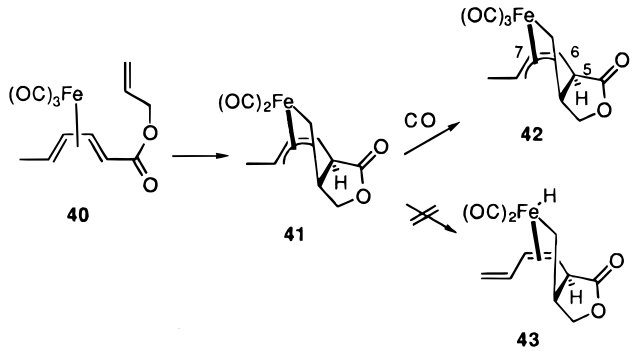
noted that the use of lower temperatures does not favorably affect the outcome of the reaction; irradiation of complex **25** at 30 °C yielded ester **36** and acid **22** as the only products. Therefore, it can be concluded that in this series, similar to the case of cyclic ester complexes, and unlike the reactions with fluoroolefins reported by Green, elevated temperature is necessary in combination with near-UV irradiation for carbon−carbon bond formation to take place leading to cyclization.

Amide **24**, with the olefin stabilized by conjugation with a phenyl group, under the photochemical conditions yielded a 4:3 inseparable mixture of *trans*-lactam **37** (a product of cyclization followed by isomerization) and amide **38** (product of olefin migration; 15% combined yield). Partial demetalation to form **39**, the free diene corresponding to **24**, and decomposition were also observed in this case.



The behavior of the substrates described above indicates that metal-assisted intramolecular coupling of acyclic (diene)iron tricarbonyl complexes with pendant alkenes does take place in the cases of allylic amides and esters. Similar to the case for alcohol complexes, initially formed (*Z*)-dienes rearrange to *E* isomers. Double-bond migration is, however, a competing reaction and, unlike the case of cyclic (diene)iron tricarbonyls, a dominant process.

Scheme 4



Formation of cyclization products (lactones **34** and **35** and lactams **30**, **31**, and **37**) in the series of dimethyl-substituted carboxylic acid derivatives is in agreement with the assumed configurational requirement for hydrogen atom transfer. It should be noted, though, that the behavior of these dimethyl-substituted complexes was compared to an earlier observation that monosubstituted amide **13** is unreactive under the thermal cyclization conditions. However, complexes **23**, **24**, and **25** also failed to cyclize under the thermal conditions. Therefore, it was necessary to examine the behavior of the corresponding monosubstituted derivatives, lacking a *cis*-alkyl substituent, under photochemical conditions.

Accordingly, ester **40** was prepared from the known (2,4-hexadienoic acid)iron tricarbonyl.[15] Complex **40** remained unchanged upon reflux in Bu_2O under a CO atmosphere. This result once again demonstrates the effect of *cis*-alkyl substituents on the thermal stability of acyclic complexes (no demetalation was observed, in contrast to the results with the *gem*-dimethyl systems noted earlier). When it was irradiated in benzene under a CO atmosphere, ester **40** afforded σ,η^3-complex **42**, which is believed to be an intermediate in the cyclization reaction, as a stable product (Scheme 4; 5% yield).

The IR spectrum of the complex **42** shows the characteristic signal of the five-membered lactone (1768 cm^{-1}). The ^{1}H NMR spectrum has signals of π-allyl protons H6 and H7 as a doublet and doublet of doublets at 4.68 and 4.55 ppm, respectively. Splitting of H6 and H5 is not observed, presumably due to a 90° dihedral angle. Signals of the methylene group σ-bonded to metal appear as an AB part of a pseudo-ABX system at 1.43−1.37 ppm (assignments were confirmed by a COSY experiment). It should be noted that **42** is the first example of a σ,η^3-complex isolated as a stable compound formed under the *cyclization* conditions. (The other known examples of these complexes are the ones reported by Green[2f,g] and Whitesides.[14])

Formation of complex **42** under the reaction conditions is further evidence that σ,η^3-complexes are intermediates in the cyclization reaction. Together with the results of the cyclizations of dimethyl-substituted complexes, it indicates that a *Z* configuration about the diene is necessary for successful hydrogen atom transfer from the ligand to the metal and completion of the reaction. Such transfer does not happen in the case of substrates with *E* configuration (transformation of **41** to **43**), since the metal would have to span a transoid

(15) Cais, M.; Maoz, N. *J. Organomet. Chem.* **1966**, *5*, 370.

diene-like system in the transition state, resulting in poor orbital overlap and high energy.

Conclusions

The possibility of application of photochemically induced metal-assisted cyclization of acyclic diene−Fe(CO)$_3$ complexes with pendant olefinic groups has been shown. The products of the reaction are initially formed as single epimers. However, thermally induced *cis*−*trans* isomerization of products takes place. The yields are generally low due to a competing olefin migration, a process that we envisage can be blocked by appropriate substitution in the allylic side chain, leading to a synthetically useful reaction, though such an approach has not yet been investigated. Partial mechanistic evaluation of the cyclization reaction has been performed. Formation of (σ,η^3-organo)iron complexes as reaction intermediates was indicated, and it is strongly indicated that metal-assisted hydrogen atom transfer to complete the reaction can only take place from an alkyl substituent having a *Z* configuration about diene.

Experimental Section

General procedures are as described elsewhere.[16]

Tricarbonyl[(6−9-η)-1,6,8-decatrien-5-ol]iron (14a). A solution of 4-bromo-1-butene (0.243 mL, 1.25 equiv) in anhydrous ether (1 mL) was added to a flask containing Mg (58 mg, 1.25 equiv) and anhydrous ether (1.5 mL) under Ar with stirring, so that the mixture slowly refluxed. The reaction mixture was then refluxed on a warm water bath for 30 min (until Mg dissolved) and then transferred *via* a cannula to a solution of (2,4-hexadienal)iron tricarbonyl (0.361 g, 1 equiv) in anhydrous ether (1.5 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then at room temperature for 3 h and quenched by the addition of saturated NH_4Cl solution. The ether layer was separated, and the aqueous layer was washed twice with ether. The combined organic fraction was washed with $NaHCO_3$ solution and water and dried over $MgSO_4$, and solvent was evaporated under vacuum. Flash chromatography separation (silica gel, EtOAc/hexanes, 1:19−1:9) afforded alcohols **14a** (0.224 g, 40% yield) and **14b** (0.111 g, 20% yield). Alcohol **14a**: R_f 0.58 (EtOAc/hexane, 3:7). IR ($CHCl_3$ solution; cm^{-1}): 3618, 2050, 1983, 1644; ^{1}H NMR (δ, ppm, $CDCl_3$): 5.83 (ddt, 1H, J = 17, 10.3, 6.7 Hz), 5.15 (dd, 1H, J = 8, 5 Hz), 5.1−4.97 (m, 3H), 3.49 (ddt, 1H, J = 8, 5, 3.6 Hz), 2.27−2.15 (m, 2H), 1.75−1.55 (m, 2H), 1.42 (d, 3H, J = 4.7 Hz), 1.39 (d, 1H, J = 3.6 Hz, OH); 1.2−1.1 (m, 1H); 1.03 (dd, 1H, J = 8 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 212, 138.1, 115.16, 85.34, 80.78, 73.40, 68.41, 58.18, 38.87, 30.20, 19.11. HRMS: for M^+ ($C_{13}H_{16}FeO_4$) calculated 292.0398 found 292.0391. Alcohol **14b**: R_f 0.3 (EtOAc/hexane, 3:7). IR ($CHCl_3$ solution, cm^{-1}): 3609, 2922, 2051, 1978, 1643. ^{1}H NMR (δ, ppm, $CDCl_3$): 5.84 (ddt, 1H, J = 17, 10.2, 6.7 Hz), 5.24 (dd, 1H, J = 8, 5 Hz), 5.1−4.98 (m, 3H), 3.47−3.42 (m, 1H), 2.3−2.13 (m, 2H), 1.82−1.5 (m, 2H), 1.42 (d, 3H, J = 6 Hz), 1.24 (ddq, 1H, J = 14.5, 6, 1.2 Hz), 1.14 (d, 1H, J = 5.5 Hz, OH), 0.98 (dddd, 1H, J = 8.2, 8.2, 1.2, 1.2 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 212.06, 138.16, 115.26, 86.43, 82.13, 73.71, 64.55, 58.35, 37.64, 29.91, 19.18. HRMS: for M^+ ($C_{13}H_{16}FeO_4$) calculated 292.0398, found 292.0402; for $M^+ - 2CO$ ($C_{11}H_{16}FeO_2$) calculated 236.0499, found 236.0496.

Tricarbonyl[(6−9-η)-1,6,8-decatrien-5-one]iron (15). Alcohol **14a** (56 mg) was dissolved in 0.5 mL of anhydrous THF at 0 °C under Ar, and MeMgBr (2.8 M solution in Et_2O, 1.25 equiv) was slowly added. The reaction mixture was stirred at 0 °C for 30 min, and then a solution of ADD (58 mg, 1.2 equiv) in 1 mL of dry THF was added. The reaction mixture was stirred at 0 °C for 45 min and at room temperature for 1.5 h and then was quenched by the addition of brine and extracted with ether. The organic fraction was washed with 1 M $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. Flash chromatography separation (EtOAc/hexane, 1:19−1:1) afforded ketone **15** (27 mg, 55% yield at 88% conversion; 7 mg of starting material recovered). IR ($CHCl_3$ solution, cm^{-1}): 2060, 1997, 1672. ^{1}H NMR (δ, ppm, $CDCl_3$): 5.86−5.75 (m, 2H), 5.25 (dd, 1H, J = 8, 5 Hz), 5.07−4.97 (m, 2H), 2.5−2.29 (m, 4H), 1.59−1.5 (m, 1H), 1.48 (d, 3H, J = 6 Hz), 1.22 (d, 1H, J = 8 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 204.68, 191.43, 137.18, 115.29, 88.73, 81.33, 59.23, 53.48, 41.7, 28.46, 19.2.

Tricarbonyl(2−5-η)-5-methyl-2,4-hexadien-1-al]iron (17). A mixture of aldehyde **16** (117 mg) and diiron nonacarbonyl (774 mg, 2 equiv) in toluene (2.5 mL) was sonicated under an Ar atmosphere for 14 h. The reaction mixture was diluted with ether, filtered through Celite, and concentrated. Unreacted starting material was removed under high vacuum. Chromatographic purification (basic alumina, EtOAc/hexane, 1:19) afforded the unstable complex **17** (32 mg, 12% yield). IR (thin film; cm^{-1}): 2056, 1982, 1685. ^{1}H NMR (δ, ppm, $CDCl_3$): 9.29 (d, 1H, J = 4 Hz), 5.86 (dd, 1 H, J = 8.7, 5 Hz), 5.27 (d, 1 H, J = 5 Hz), 2.53 (dd, 1 H, J = 8.7, 4 Hz), 1.65 (s, 3H), 1.34 (s, 3H).

Tricarbonyl[(6−9-η)-9-methyl-1,6,8-decatrien-5-ol]iron (18a). Magnesium (47 mg, 1.25 equiv) and 1 mL of anhydrous ether were placed in a flask equipped with a reflux condenser. A solution of 4-bromo-1-butene (0.2 mL, 1.25 equiv) in 1 mL of anhydrous ether was slowly added under Ar so that the solution gently refluxed. The mixture was refluxed for a further 30 min until all Mg dissolved. The resulting solution of Grignard reagent was slowly added to the solution of aldehyde **17** in 1.5 mL of anhydrous ether at −78 °C under Ar. The reaction mixture was stirred at −78 to −40 °C for 2 h and at 0 °C for 1 h and then was quenched with saturated aqueous NH_4Cl. The ether layer was separated, and the aqueous layer was washed twice with ether. The combined organic fraction was washed with $NaHCO_3$ solution and water and dried over $MgSO_4$, and solvent was evaporated under vacuum. Flash chromatography separation (silica gel, EtOAc/hexane, 1:30−1:4) afforded alcohols **18a** (179 mg, 47%) and **18b** (35 mg, 9% yield). Complex **18a**: R_f 0.57 (EtOAc/hexane, 3:7). IR ($CHCl_3$ solution, cm^{-1}): 2921, 2040, 1971, 910. ^{1}H NMR (δ, ppm, $CDCl_3$): 5.85 (ddt, 1H, J = 17, 10.2, 6.6 Hz), 5.21 (dd, 1H, J = 9, 5.3 Hz), 5.11−4.98 (m, 3H), 3.53−3.3 (m, 1H), 2.33 (dd, 1H, J = 9 Hz), 2.26−2.18 (m, 2H), 1.79−1.6 (m, 2H), 1.57 (s, 3H), 1.44 (d, 1H, J = 3.4 Hz, OH), 1.21 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 212.03, 138.17, 115.15, 87.75, 84.9, 74.36, 71.91, 68.35, 38.9, 33.51, 30.21, 21.25. HRMS: for $M^+ - CO$ ($C_{13}H_{18}FeO_3$) calculated 278.0605, found 278.04999; for $M^+ - 2CO$ ($C_{12}H_{18}FeO_2$) calculated 250.0656, found 250.0643. Complex **18b**: R_f 0.36 (EtOAc/hexane, 3:7). IR ($CHCl_3$ solution, cm^{-1}): 2048, 1979, 914. ^{1}H NMR (δ, ppm, $CDCl_3$): 5.85 (ddt, 1H, J = 17, 10.2, 6.7 Hz), 5.3 (dd, 1H, J = 8.9, 5.3 Hz), 5.12−4.98 (m, 3H), 3.47−3.41 (m, 1H), 2.31−2.13 (m, 2H), 1.87−1.6 (m, 3H), 1.57 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 211.93, 138.21, 115.23, 88.75, 86.48, 75.06, 72.19, 64.66, 37.48, 33.47, 30, 21.41. HRMS for $M^+ - 2CO$ ($C_{12}H_{18}FeO_2$) calculated 250.0656, found 250.0655.

Tricarbonyl[(6−9-η)-9-methyl-1,6,8-decatrien-5-one]iron (19). Alcohol **18a** (47 mg) was dissolved in 0.5 mL of anhydrous THF under an Ar atmosphere, and MeMgBr (64 μL of a 3 M solution in ether, 1.25 equiv) was added at 0 °C. The reaction mixture was stirred for 30 min at the same temperature; then a solution of 48 mg of ADD in 1 mL of anhydrous THF was added. The mixture was stirred at 0 °C for 1 h and then was then quenched with brine and extracted with ether. The organic fraction was washed with 1 M $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated.

(16) Pearson, A. J.; Gontcharov, A. *J. Org. Chem.* **1998**, *63*, 152.

Flash chromatography purification (silica gel, EtOAc/hexane, 1:30−1:5) afforded ketone **19** (31 mg, 67% yield): R_f 0.24 (ether/hexane, 1:7). IR ($CHCl_3$ solution, cm^{-1}): 2054, 1990, 1680. ^1H NMR (δ, ppm, $CDCl_3$): 5.9 (dd, 1H, J = 8.8, 5.4 Hz), 5.83 (ddt, 1H, J = 17, 10.2, 6 Hz), 5.24 (d, 1H, J = 5.4 Hz), 5.11−4.96 (m, 2H), 2.55−2.31 (m, 5H), 1.62 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 205.39, 137.26, 115.28, 90.92, 85.23, 73.35, 53.34, 41.85, 33.26, 28.52, 21.93. HRMS: for $M^+ - CO$ ($C_{13}H_{16}FeO_3$) calculated 276.0449, found 276.0447.

1-Carbethoxy-5-methylhexa-2,4-diene (20). Sodium hydride (1 mmol, 42 mg of 60% suspension in oil) was placed in a round-bottom flask. Anhydrous THF (2 mL) and 15-crown-5 (5.4 μL) were added under Ar. A solution of 3-methyl-2-butenal (0.1 mL, 1 mmol) and triethyl phosphonoacetate (0.2 mL, 1 mmol) in 3 mL of anhydrous THF was added at 0 °C with stirring. The reaction mixture was stirred at room temperature for 2.5 h and then was poured into 20 mL of water and extracted with ether. The organic fraction was dried over $MgSO_4$ and concentrated to afford 151 mg of ester **20** (98% yield). IR (cm^{-1}, thin film): 2986, 2913, 1714, 1645, 1279, 1146. ^1H NMR (δ, ppm, $CDCl_3$): 7.56 (dd, 1H, J = 15, 1.7 Hz), 5.98 (d, 1H, J = 11.7 Hz); 5.76 (d, 1H, J = 15 Hz), 4.2 (q, 2H, J = 7 Hz), 1.9 (s, 3H), 1.88 (s, 3H), 1.3 (t, 3H, J = 7 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 167.67, 146.11, 140.93, 123.75, 118.62, 60.06, 26.5, 18.91, 14.33. HRMS: for M^+ ($C_9H_{14}O_2$) calculated 154.0994, found 154.0952; for $M^+ - CH_3$ ($C_8H_{11}O_2$) calculated 139.0759, found 139.0753.

Tricarbonyl(1-carbethoxy-5-methylhexa-2,4-diene)iron (21). Ester **20** (2.0 g) was dissolved in 80 mL of anhydrous ether. Diiron nonacarbonyl (9.45 g, 2 equiv) was added. The reaction mixture was refluxed under Ar for 3 h and then was cooled to room temperature, and 1 equiv more of diiron nonacarbonyl (4.7 g) was added. The reaction mixture was refluxed for an additional 1 h and then cooled to room temperature and filtered through a column of basic alumina. The column was washed with ether. Unreacted starting diene was removed under high vacuum (0.5 mmHg). Flash chromatography purification (silica gel, CH_2Cl_2/hexane) afforded complex **21** (2.573 g, 67% yield). IR ($CHCl_3$ solution, cm^{-1}): 2059, 1997, 1712, 1328, 1199. ^1H NMR (δ, ppm, $CDCl_3$): 5.87 (dd, 1H, J = 8.7, 5.4 Hz), 5.21 (d, 1H, J = 5.4 Hz), 4.2 (m, 2H), 2.26 (d, 1H, J = 8.7 Hz), 1.6 (s, 3H), 1.27 (s, 3H), 1.26 (t, 3H, J = 7.1 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 209.81, 173.01, 90.56, 86.89, 73.04, 60.48, 46.23, 33.24, 21.63, 14.28. HRMS: for $M^+ - CO$ ($C_{11}H_{14}FeO_4$) calculated 266.0241, found 266.0240.

Tricarbonyl[5-methyl-(2*E*)-2,4-hexadienoic acid]iron (22). Complex **21** (1.052 g) was placed in a round-bottom flask. Methanol (12.7 mL, oxygen free) and THF (12.7 mL, oxygen free) were added, followed by 17.1 mL of a 2 N solution of LiOH (oxygen free), and the mixture was stirred at room temperature under Ar for 18 h. The reaction mixture was acidified with 2 N HCl, extracted with ether, and dried over $MgSO_4$, and the solvent was evaporated under vacuum to afford 881 mg of 4.5:1 mixture of complex **22** and acid **23** (82% yield of **22**). IR (KBr pellet, cm^{-1}): 3200−2800 (br), 2061, 1979, 1677, 1399. ^1H NMR (δ, ppm, $CDCl_3$): 5.88 (dd, 1H, J = 7, 6 Hz), 5.21 (d, 1H, J = 6 Hz), 2.22 (d, 1H, J = 7 Hz), 1.6 (s, 3H), 1.28 (s, 3H). HRMS: for M^+ ($C_{10}H_{10}FeO_5$) calculated 265.9878, found 265.9904; for $M^+ - CO$ ($C_9H_{10}FeO_4$) calculated 237.9928, found 237.9923.

Tricarbonyl[(2−5-η)-*N*-allyl-*N*-phenyl-(2*E*)-5-methyl-2,4-hexadienamide]iron (23). Acid **22** (143 mg; 4.5:1 mixture with uncomplexed acid) was treated with oxalyl chloride (89 mL), pyridine (82 mL), and *N*-allylaniline (68 mg) according to the general procedure. Flash chromatography separation (CH_2Cl_2/hexane, 3:7, then CH_2Cl_2, followed by CH_2Cl_2/EtOAc, 9:1) yielded amide **23** (137 mg, 92% yield based on the amount of consumed complex **22**), uncomplexed amide (40 mg), and a 5:1 mixture of acid **22** and its uncomplexed derivative (26 mg). IR ($CHCl_3$ solution; cm^{-1}): 2053, 1989, 1630, 1600. ^1H NMR (δ, ppm, $CDCl_3$): 7.45−7.23 (m, 5H), 5.97 (dd, 1H, J = 8.6, 5.5 Hz), 5.88 (ddt, 1H, J = 16.6, 10.5, 6.2 Hz), 5.16 (d, 1H, J = 5.5 Hz), 5.13−5.05 (m, 2H), 4.36 (dddd, 1H, J = 14.7, 6.2, 1.2, 1.2 Hz), 4.22 (dddd, 1H, J = 14.7, 6.2, 1.2, 1.2 Hz), 1.94 (d, 1H, J = 8.6 Hz), 1.44 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 211.06, 171.13, 142.31, 133.46, 129.58, 128.78, 127.99, 117.68, 90.09, 87.27, 72.2, 52.31, 48.24, 33, 20.7. HRMS: for $M^+ - 2CO$ ($C_{17}H_{19}FeNO_2$) calculated 325.0765, found 325.0767.

Tricarbonyl{(2−5-η)-*N*-phenyl-*N*-[(*E*)-3-phenyl-2-propenyl]-(2*E*)-5-methyl-2,4-hexadienamide}iron (24). Acid **22** (254 mg; as above) was treated with oxalyl chloride (0.185 mL, 2 equiv), pyridine (0.184 mL, 2 equiv) and *N*-cinnamylaniline (266 mg, 1.2 equiv) according to the general procedure. Flash chromatography separation (EtOAc/hexane, 1:19−1:1) yielded complex **24** (307 mg, 94% yield based on the amount of consumed complex **22**), uncomplexed amide (108 mg) ,and a 5:1 mixture of acid **2.67** and its demetalation product (36 mg). IR ($CHCl_3$ solution; cm^{-1}): 2050, 1980, 1630, 1593. ^1H NMR (δ, ppm, $CDCl_3$): 7.44−7.2 (m, 10H), 6.43−6.26 (m, 2H), 6.0 (dd, 1H, J = 8.7, 5 Hz), 5.17 (d, 1H, J = 5 Hz), 4.53 (dd, 1H, J = 14, 6 Hz), 4.35 (dd, 1H, J = 14, 6 Hz), 1.96 (d, 1H, J = 8.7 Hz), 1.45 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 209.99, 171.26, 142.24, 136.87, 133.08, 129.68, 128.83, 128.55, 128.09, 127.61, 126.47, 124.72, 90.17, 87.2, 72.33, 51.82, 48.26, 33.01, 20.73. HRMS: for $M^+ - 2CO$ ($C_{23}H_{23}FeNO_2$) calculated 401.1078, found 401.1062.

Tricarbonyl[(2−5-η)-allyl-(2*E*)-5-methyl-2,4-hexadienoato]iron (25). Acid **22** (274 mg of mixture as above) was treated with oxalyl chloride (0.2 mL), pyridine (0.184 mL), and allyl alcohol (0.154 mL) according to the general procedure. Flash chromatography separation (EtOAc/hexane, 1:19−1:1) yielded complex **25** (148 mg, 84% yield based on the amount of consumed complex **22**), uncomplexed ester (28 mg), and a 4:1 mixture of acid **22** and its uncomplexed derivative (77 mg). IR ($CHCl_3$ solution; cm^{-1}): 2053, 1989, 1707. ^1H NMR (δ, ppm, $CDCl_3$): 5.92 (ddt, 1H, J = 17, 10, 5.7 Hz), 5.88 (dd, 1H, J = 8.6, 5.4 Hz), 5.36−5.21 (m, 3H), 4.63 (dddd, 1H, J = 13.3, 5.7, 1.4, 1.4 Hz), 4.53 (dddd, 1H, J = 13.3, 5.7, 1.4, 1.4 Hz), 2.82 (dd, 1H, J = 8.6, 1 Hz), 1.6 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (δ, ppm, $CDCl_3$): 209.67, 172.76, 132.41, 118.19, 90.66, 86.87, 73.21, 65.13, 45.71, 33.26, 21.66. HRMS: for $M^+ - 2CO$ ($C_{11}H_{14}FeO_3$) calculated 250.0292, found 250.0297.

General Procedure for the Photothermally Induced Cyclization. The appropriate ester or amide was dissolved in freshly distilled benzene in a quartz tube equipped with a reflux condenser under argon. The solution was purged with CO for 1 min. The reaction mixture was irradiated in a Rayonet reactor with a 350 nm light source at 80 °C with magnetic stirring for 2.5 h (unless otherwise noted). The product mixture was diluted with ether, filtered through Celite, and concentrated. Flash chromatography or preparative TLC separation (CH_2Cl_2/hexane, 1:1, unless otherwise noted) yielded the desired product. Deviations from this procedure are noted in the experimental data for the specific compound.

Tricarbonyl{(6−9-η)-3-methyl-2-[(1*Z*)-3-methyl-1,3-butadienyl]-1-cyclopentanol}iron (27). Complex **18a** (24 mg) was irradiated according to the general procedure for 2.5 h. Preparative TLC separation (CH_2Cl_2/hexane, 1:1) afforded alcohols **27** (1 mg, 4% yield), **28** (1 mg, 4% yield), and **29** (1 mg, 4% yield). Complex **27**: IR ($CHCl_3$ solution, cm^{-1}) 3500 (broad), 2044, 1986, 1596; ^1H NMR (δ, ppm, $CDCl_3$) 5.31 (apparent d, 1H, J = 8 Hz), 3.7−3.6 (m, 1H), 2.51 (dd, J = 11.3, 8 Hz), 2.2 (s, 3H), 1.94 (dd, 1H, J = 2.8, 1.8 Hz), 1.8−1.23 (m, 7H), 1.1 (d, 3H, J = 7.3 Hz); HRMS for M^+ ($C_{14}H_{18}FeO_4$) calculated 306.0554, found 306.0588. Complex **28**: IR ($CHCl_3$ solution, cm^{-1}) 3640 (broad), 2050, 1970, 1609; ^1H NMR (δ, ppm, $CDCl_3$) 5.25 (d, 1H, J = 7.5 Hz), 4.2−4.1 (m, 1H), 2.19 (s, 3H), 2.17−1.23 (m, 8H), 0.87 (d, 3H, J = 6.9 Hz); HRMS for $M^+ - CO$ ($C_{13}H_{18}FeO_3$) calculated 278.0605, found 278.0606. Complex **29**: IR ($CHCl_3$ solution, cm^{-1}) 3637

(broad), 2047, 1971, 1602; ^{1}H NMR (δ, ppm, $CDCl_3$) 5.26 (d, 1H, J = 8.3 Hz), 3.79−3.67 (m, 1H), 2.21 (s, 3H), 2.19−2.0 (m, 1H), 1.93 (dd, 1H, J = 3, 1.7 Hz), 1.85−1.1 (m, 7H), 0.97 (d, 3H, J = 7.1 Hz); HRMS for M^+ ($C_{14}H_{18}FeO_4$) calculated 306.0554, found 306.0554.

Tricarbonyl{(6−9-η)-4-methyl-3[(1*Z*)-3-methyl-1,3-butadienyl]-1-phenyl-2-pyrrolidinone}iron (30). Complex **23** (24 mg) was irradiated according to the general procedure for 2.5 h. Preparative TLC separation afforded lactam **30** (2.5 mg, 10% yield), amide **32** (9 mg, 37% yield), lactam **31** (1.8 mg, 8% yield), and amide **33** (6.5 mg, 42% yield). Complex **30**: IR ($CHCl_3$ solution; cm^{-1}) 2050, 1982, 1695, 1600, 911; ^{1}H NMR (δ, ppm, $CDCl_3$; the assignments are confirmed by a COSY experiment) 7.62−7.09 (m, 5H), 5.56 (d, 1H, J = 7.5 Hz), 3.84 (dd, 1H, J = 9.7, 6 Hz), 3.38 (dd, 1H, J = 9.7, 1.5 Hz), 2.64 (ddq, 1H, J = 7, 7, 6 Hz), 2.28 (dd, 1H, J = 11.5, 7.5 Hz), 2.22 (s, 3H), 2.09 (dd, 1H, J = 11.5, 7 Hz), 1.97 (dd, 1H, J = 3.1, 1.5 Hz), 1.37 (dd, 1H, J = 3.1, 1.1 Hz), 1.2 (d, 3H, J = 7 Hz); ^{13}C NMR (δ, ppm, $CDCl_3$) 139.61, 128.69, 124.22, 119.27, 108.64, 86.88, 53.57, 49.59, 46.48, 43.21, 30.6, 24.33, 14.48 (amide carbonyl and iron carbonyl peaks are not seen in the spectrum); HRMS for $M^+ - 2CO$ ($C_{17}H_{19}FeNO_2$) calculated 325.0765, found 325.0774. Lactam **31** was obtained in impure form. Only the significant signals are reported for the NMR spectrum. IR ($CHCl_3$ solution; cm^{-1}): 2056, 1982, 1708, 1600. ^{1}H NMR (δ, ppm, $CDCl_3$): 7.7−7.1 (m, 5H), 5.34 (d, 1H, J = 7.3 Hz), 4.01−3.9 (m, 1H), 3.8 (dd, 1H, J = 9.6, 6 Hz), 2.57−2.4 (m, 2H), 2.22 (s, 3H), 2.0 (dd, 1H, J = 3, 1.5 Hz), 1.88 (d, 3H, J = 7 Hz), 0.59 (dd, 1H, J = 10.3, 7.3 Hz), 0.49 (d, 1H, J = 3 Hz). HRMS: for $M^+ - CO$ ($C_{17}H_{19}FeNO_2$) calculated 325.0765, found 325.0744; for $M^+ - 3CO$ ($C_{16}H_{19}FeNO$) calculated 297.0816, found 297.0825.

Tricarbonyl{(6−9-η)-4-methyl-3[(1*Z*)-3-methyl-1,3-butadienyl]tetrahydro-2-furanone}iron (34). Complex **25** (29 mg) was irradiated according to the general procedure for 3.5 h. Preparative TLC separation (EtOAc/hexane, 3:7, multiple development) afforded lactone complexes **34** (3 mg, 10% yield, light yellow oil) and **35** (3 mg, 10% yield) and acid **22** (4.5 mg, 38% yield). Complex **34**: IR ($CHCl_3$ solution; cm^{-1}): 2060, 1981, 1773, 915; ^{1}H NMR (δ, ppm, $CDCl_3$) 5.51 (apparent d, 1H, J = 7.5 Hz), 4.16 (dd, 1H, J = 8.9, 5.2 Hz), 3.96 (d, 1H, J = 8.9 Hz), 2.66−2.63 (m, 1H), 2.22 (s, 3H), 2.14 (dd, J = 11, 7.5 Hz), 2.01 (dd, J = 11, 7 Hz), 1.99 (dd, J = 3.5, 1.6 Hz), 1.3 (dd, J = 3.5, 1.1 Hz), 1.17 (d, 3H, J = 7 Hz); HRMS for $M^+ - CO$ ($C_{12}H_{14}FeO_4$) calculated 278.0241, found 278.0227, for $M^+ - 2CO$ ($C_{11}H_{14}FeO_3$) calculated 250.0292, found 250.0299. Complex **35**: IR ($CHCl_3$ solution; cm^{-1}) 2053, 1982, 1766; ^{1}H NMR (δ, ppm, $CDCl_3$) 5.41 (d, J = 7.8 Hz), 4.28 (dd, 1H, J = 8.9, 5.2 Hz), 3.99 (dd, 1H, J = 8.9, 1.2 Hz), 2.61 (ddq, 1H, J = 7, 7, 5.2 Hz), 2.39 (dd, 1H, J = 10.2, 7 Hz), 2.22 (s, 3H), 1.92 (dd, 1H, J = 2.7, 1.5 Hz), 1.18 (d, 3H, J = 7 Hz), 0.49 (d, 1H, J = 2.7 Hz), 0.44 (dd, 1H, J = 10.2, 7.8 Hz); ^{13}C NMR (δ, ppm, $CDCl_3$) 159.65, 102.22, 88.4, 73.05, 50.25, 49.93, 44.07, 35.31, 22.74, 14.23; HRMS for $M^+ - CO$ ($C_{12}H_{14}FeO_4$) calculated 278.0241, found 278.0271, for $M^+ - 2CO$ ($C_{11}H_{14}FeO_3$) calculated 250.0292, found 250.0290.

Tricarbonyl{(6−9-η)-4-methyl-3[(1*Z*)-3-benzyl-1,3-butadienyl]-1-phenyl-2-pyrrolidinone}iron (37). Complex **24** (28 mg) was irradiated according to the general procedure for 3 h 40 min. Preparative TLC separation (EtOAc/hexane, 1:4, multiple development) afforded 4.2 mg of an inseparable mixture of complexes **37** (12% yield at 70% conversion) and **38** (9% yield at 70% conversion), amide **39** (3 mg), and starting complex **24** (8.5 mg). Complex **37**: ^{1}H NMR (δ, ppm, $CDCl_3$) 7.66−7.03 (m, 10H), 5.53 (d, 1H, J = 8 Hz), 3.61 (dd, 1H, J = 10, 5.4 Hz), 3.48 (dd, 1H, J = 10, 1.5 Hz), 3.21 (dd, 1H, J = 13, 3.2 Hz), 2.73−2.66 (m, 1H), 2.6 (dd, 1H, J = 10, 7 Hz), 2.4 (dd, 1H, J = 13 Hz), 2.26 (s, 3H), 1.95−1.94 (s, br, 1H), 0.69 (dd, 1H, J = 10, 8 Hz), 0.58 (d, 1H, J = 2.7 Hz). Complex **38** was isolated as a 3:4 mixture with lactam **37**: ^{1}H NMR (δ, ppm, $CDCl_3$) 7.66−7.07 (m, 11H), 5.98 (dd, 1H, J = 8.6, 5.5 Hz), 5.16 (d, 1H, J = 5.5 Hz), 4.55 (dt, 2H, J = 14.2, 7.2 Hz), 3.33 (d, 2H, J = 7.2 Hz), 1.76 (d, 1H, J = 8.6 Hz), 1.45 (s, 3H), 0.59 (s, 3H).

Tricarbonyl[(2−5-η)-allyl-(2*E*)-2,4-hexadienoato]iron (40). Tricarbonyl(2,4-hexadienoic acid)iron (133 mg) was treated with oxalyl chloride (0.092 mL), pyridine (0.085 mL), and allyl alcohol (0.072 mL) according to the general procedure. Flash chromatography separation (EtOAc/hexane, 1:19−1:1) yielded complex **40** (102 mg, 91% yield based on the amount of consumed starting material; 36 mg of starting acid recovered). IR ($CHCl_3$ solution; cm^{-1}): 2950, 2062, 1999, 1707, 1175, 910. ^{1}H NMR (δ, ppm, $CDCl_3$): 5.91 (ddt, 1H, J = 17.2, 10.3, 5.6 Hz), 5.79 (dd, 1H, J = 8.1, 4.6 Hz), 5.37−5.18 (m, 3H), 4.62 (dddd, 1H, J = 13.4, 5.6, 1.4 Hz), 4.52 (dddd, 1H, J = 13.4, 5.6, 1.4 Hz), 1.48−1.44 (m, 1H), 1.47 (s, br, 3H), 1.01 (dd, 1H, J = 8.1, 1 Hz). ^{13}C NMR (δ, ppm, $CDCl_3$): 209.92, 171.86, 132.26, 117.91, 88.28, 82.77, 64.96, 59.07, 45.57, 19.06. HRMS: for $M^+ - 2CO$ ($C_{10}H_{12}FeO_3$) calculated 236.0135, found 236.0116, for $M^+ - 3CO$ ($C_9H_{12}FeO_2$) calculated 208.0186, found 208.0177.

Tricarbonyl{(1′−3′-η)-(1′′-σ)-3-[3′-(*E*)-methyl-(1′−3′-π)-allyl]-4-methylenyl}iron (42). Ester **40** was irradiated according to the general procedure for 4 h. Preparative TLC separation (EtOAc/hexane, 3:7, multiple development) afforded complex **42** (1.6 mg, 5% yield), starting ester **40** (4 mg), and tricarbonyl(2,4-hexadienoic acid)iron (2 mg, 9% yield). IR ($CHCl_3$ solution, cm^{-1}): 2060, 1999, 1768. ^{1}H NMR (δ, ppm, $CDCl_3$): 4.68 (d, 1H, J = 8.4 Hz), 4.55 (dd, 1H, J = 12, 8.4 Hz), 4.24 (dd, 1H, J = 9, 4.8 Hz), 4.02 (d, 1H, J = 9 Hz), 3.41 (dq, J = 12, 6 Hz), 3.15 (d, 1H, J = 7.8 Hz), 2.34 (m, 1H), 1.84 (d, 3H, J = 6 Hz), 1.43−1.37 (AB part of pseudo-ABX system, 2H, J_{AB} = 9.6 Hz; appear as two dd with centers at 1.41, 1.37 ppm, J = 12, 9.6 Hz). HRMS: for $M^+ - CO$ ($C_{11}H_{12}FeO_4$) calculated 264.0085, found 264.0079.

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Supporting Information Available: Figures giving NMR spectra for new compounds (37 pages). Ordering information is given on any current masthead page.

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