Substitution (as in eq A3) and simplification (as in eq A4) gives

$$H_\infty = \frac{(1 - x)(3 - 3y)}{4 - 3y - z} \qquad \text{(A12)}$$

Use of the value of f (0.50) established at the beginning of the $Cp_2W(H)^{13}CH_3/Cp_2W(H)CD_3$ experiment with K_1 in eq A9 gave the value of y to be expected at the end of that experiment; eq A1 gave the expected value of z, and eq A10 and A12 gave the expected values of C_∞ and H_∞.

Registry No. CD_3MgBr, 77491-27-1; CD_3Br, 1111-88-2; Cp_2WCl_2, 12184-26-8; $Cp_2W(CD_3)_2$, 119908-43-9; $Cp_2W(CD_3)(OC(O)Ph)$, 119908-44-0; $Cp_2W(H)CD_3$, 94370-31-7; $Cp_2W(CH_3)(OC(O)Ph)$, 73210-66-9; $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4D)W(CH_3)H$, 94370-29-3; $Cp_2W(^{13}CH_3)_2$, 119908-45-1; $^{13}CH_3Br$, 51624-21-6; $[Cp_2WHLi]^4$, 53322-18-2; Cp_2WHz, 1271-33-6; $Cp_2WH(Li\cdot PMDT)$, 119908-47-3; $Cp_2W(H)CH_3$, 72415-89-5; $(\eta^5\text{-}C_5H_5)_2WD_2$, 11082-26-1; $Cp_2W(D)CH_3$, 94370-30-6; $Cp_2W(D)CD_3$, 94370-33-9; $Cp_2W(\eta^2\text{-}CH_3CN)$, 119908-48-4; $Cp_2W(H)Ph$, 11077-71-7; $Cp_2W(CO)_3H$, 12128-26-6; $Os(CO)_4H_2$, 22372-70-9; D_2, 7782-39-0; $Cp_2W(H)^{13}CH_3$, 94370-32-8; $Li[AlD_2(OCH_2CH_2OCH_3)_2]$, 119908-49-5.

Intramolecular Coupling between Tricarbonyl(diene)iron Complexes and Pendant Alkenes

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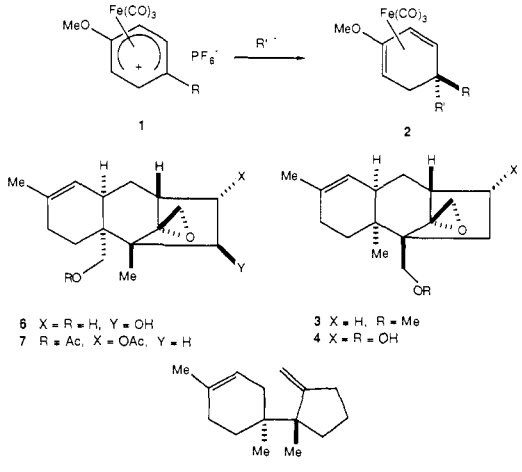
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received September 16, 1988*

Abstract: New methodology for carbon–carbon bond formation, suitable for the construction of quaternary carbon centers, is described. The procedure involves the intramolecular reaction of an alkene with a cyclohexadiene–$Fe(CO)_3$ complex at elevated temperature (140 °C), resulting in the formation of spirolactones and spirolactams. The simple example is conversion of tricarbonyl(allyl 1–4-η-cyclohexa-1,3-dienecarboxylate)iron (**24a**) to tricarbonyl(6–9-η-1-oxo-4-methyl-2-oxaspiro[4.5]-deca-6,8-diene)iron (**25a**). A fairly extensive study of the scope of the reaction is reported, and it is shown that cyclopentenes will couple with the cyclohexadiene–$Fe(CO)_3$, giving tricyclic intermediates of potential value for the synthesis of trichothecene derivatives. Methods for controlling the stereochemical outcome of the reaction, by suppressing pre- and postcyclization rearrangement of the diene–$Fe(CO)_3$ moiety, are described. A discussion of the mechanism of the coupling reaction, which involves prior dissociation of CO ligand from the organometallic group, is presented.

The studies described in this paper were undertaken in an attempt to overcome a number of shortcomings in the use of (cyclohexadienyl)iron complexes for the construction of sterically congested quaternary carbon centers. For several years we have been exploring the reactions of carbon nucleophiles with dienyl complexes of general structure **1**, in which electronic deactivation



of C(5) by the 4-methoxy group directs nucleophile addition to C(1), giving products of structure **2**, even when this position is substituted.[1] This behavior has been exploited in the total synthesis of unnatural trichothecene analogues **3**[2] and **4**[3] and more recently in a short diastereoselective synthesis of trichodiene[4] (**5**), the biogenetic precursor of naturally occurring trichothecenes.[5] Because of the interesting biological activity of many of the trichothecenes (e.g., antibiotic, antitumor, and antifungal), especially those having hydroxyl functionality at C(15), exemplified by verrucarol (**6**) and calonectrin (**7**), we also investigated the generality of using complexes related to **1** as synthetic precursors for this family of natural products.

In order to generate intermediates of potential value for synthesis of **6** and **7**, we initially considered using dienyl–$Fe(CO)_3$ complexes **1** (R = CH_2OP) or **1** (R = CO_2Me). By analogy with the conversion of **1** (R = Me) to complexes **8** (used in the synthesis of **3** and **4**) and **9** (used as a precursor to **5**), we expected that various enolates of cyclopentanone would react with the requisite dienyl precursors to generate intermediates such as **10** or **11**. In view of the well-precedented hydride abstractions[6] from cyclohexadiene complexes **12** and **13**, we fully anticipated that complex **15** would give **1** (R = CO_2Me) upon treatment with triphenylmethyl hexafluorophosphate.

Many attempts in our laboratory to secure the conversion of **15** to **1** (R = CO_2Me) failed dismally, the reaction leading to decomposition of the organometallic system. Similar lack of

(1) Reviews: Pearson, A. J. In *Chemistry of the Carbon–Metal Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1987; Vol. 4, Chapter 10. Pearson, A. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 58.

(2) Pearson, A. J.; Ong, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 6686.

(3) Pearson, A. J.; Chen, Y. S. *J. Org. Chem.* **1986**, *51*, 1939.

(4) Pearson, A. J.; O'Brien, M. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1445.

(5) Selected reviews: McDougal, P. G.; Schmuff, R. N. *Prog. Chem. Org. Nat. Prod.* **1985**, *47*, 153. Miroca, C. J.; Pathre, S. V.; Christenson, C. M. *Mycotoxic Fungi, Mycotoxins, Mycotoxicoses*; Marcell Dekker: New York, 1977; Vol. 1, pp 365–409. Pathre, S. V.; Mirocha, C. J. *J. Am. Oil Chem. Soc.* **1979**, *56*, 820.

(6) (a) Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882. (b) Birch, A. J.; Williamson, D. H. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1982.

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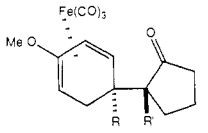
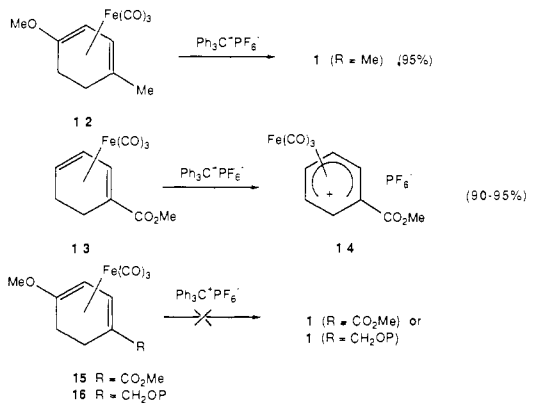


8 R = Me, R' = CO_2Me
9 R = R' = Me
10 R = CH_2OP, R' = Me
11 R = CO_2Me, R' = Me



12

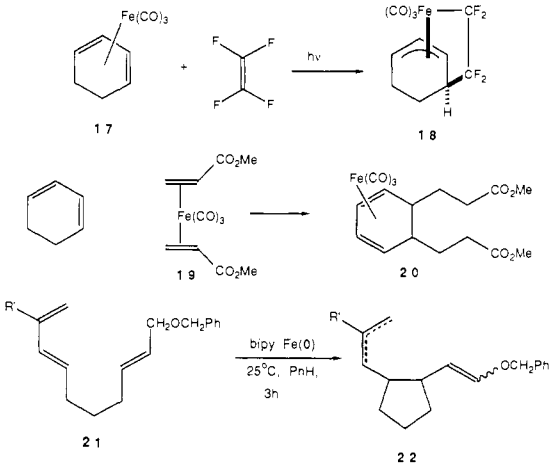
13

14 (90-95%)

15 R = CO_2Me
16 R = CH_2OP

success was encountered during attempts to convert **16** (P = Ac, Me, CH_2Ph) to **1** (R = CH_2OP). Therefore, if we were to use these types of diene complex in the construction of contiguous quaternary carbon centers of the type encountered in verrucarol or calonectrin, new methodology was required that overcomes the difficulties in the hydride abstraction step, as well as potential difficulties in the subsequent nucleophile addition.

Several years ago, Green and co-workers[7] described a novel photochemically induced coupling reaction between diene–Fe(CO)$_3$ complexes and polyhalogenated or polycyano-substituted alkenes, exemplified by the conversion of cyclohexadiene–Fe(CO)$_3$ (**17**) to complex **18**. More recently, Grevels and co-workers[8]



17 **18**

19 **20**

21 **22**

showed that cyclohexa-1,3-diene reacts with the bis(methyl acrylate)Fe(CO)$_3$ complex **19** to give complex **20**, and Takacs and co-workers[9] have described the iron(0)-catalyzed coupling of dienes and olefins exemplified by the conversion of **21** to **22**.

These results, in particular the work of Green, prompted us to examine intramolecular coupling of diene–Fe(CO)$_3$ complexes with alkenes, in anticipation of generating new methodology for

(7) Bond, A.; Green, M. *J. Chem. Soc.* **1971**, 12. Bond, A.; Green, M.; Loweie, S. F. W. *J. Chem. Soc., Chem. Commun.* **1971**, 1230. Bond, A.; Green, M.; Taylor, S. H. *J. Chem. Soc., Chem. Commun.* **1973**, 112. Bond, A.; Green, M. *J. Chem. Soc., Dalton Trans.* **1974**, 763. Bond, A.; Lewis, B.; Green, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1109. Green, M.; Lewis, B.; Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1975**, 1118.
(8) Goddard, R.; Grevels, F. W.; Schrader, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 353.
(9) Takacs, J. M.; Anderson, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 2200.

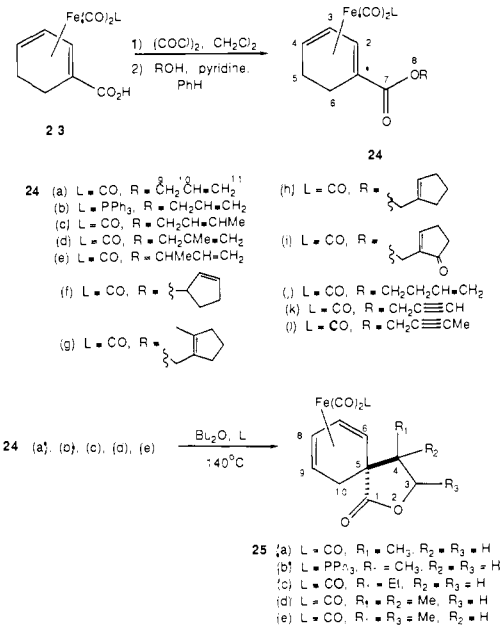
Table I. Cyclization Reactions of Allylic Ester Derivatives **24a–e**

entry	substrate	reaction conditions	product (yield, %)
1	**24a**	Bu_2O, N_2, reflux, 11 h	**25a** (15–20)
2	**24a**	Bu_2O, N_2, PPh_3, reflux, 11 h	**25b** (20) + **24b** (75)
3	**24a**	Bu_2O, CO, reflux, 11 h	**24a** (88)
4	**24c**	Bu_2O, CO, reflux, 12 h	no reaction
5	**24c**	sunlamp, benzene, CO, reflux, 8 h	**25c** (40)
6	**24d**	Bu_2O, CO, reflux, 12 h	**25d** (15)
7	**24d**	sunlamp, benzene, CO, reflux, 12 h	no reaction
8	**24e**	Bu_2O, CO, reflux, 10 h	**25e** (89)

constructing sterically congested quaternary carbon centers. The results of our investigation are described in this paper.[10]

Results and Discussion

(1) The Cyclization Reaction. In order to test the feasibility of diene–Fe(CO)$_3$/alkene intramolecular coupling, a number of unsaturated esters **24** were prepared from tricarbonyl(2,3-di-



23 **24**

24 (a) L = CO, R = $CH_2CH{=}CH_2$
(b) L = PPh_3, R = $CH_2CH{=}CH_2$
(c) L = CO, R = $CH_2CH{=}CHMe$
(d) L = CO, R = $CH_2CMe{=}CH_2$
(e) L = CO, R = $CHMeCH{=}CH_2$
(f) L = CO, R =
(g) L = CO, R =
(h) L = CO, R =
(i) L = CO, R =
(j) L = CO, R = $CH_2CH_2CH{=}CH_2$
(k) L = CO, R = $CH_2C{\equiv}CH$
(l) L = CO, R = $CH_2C{\equiv}CMe$

24 (a), (b), (c), (d), (e) $\xrightarrow[140^\circ C]{Bu_2O,\ L}$

25 (a) L = CO, R_1 = CH_3, R_2 = R_3 = H
(b) L = PPh_3, R_1 = CH_3, R_2 = R_3 = H
(c) L = CO, R_1 = Et, R_2 = R_3 = H
(d) L = CO, R_1 = R_2 = Me, R_3 = H
(e) L = CO, R_1 = R_3 = Me, R_2 = H

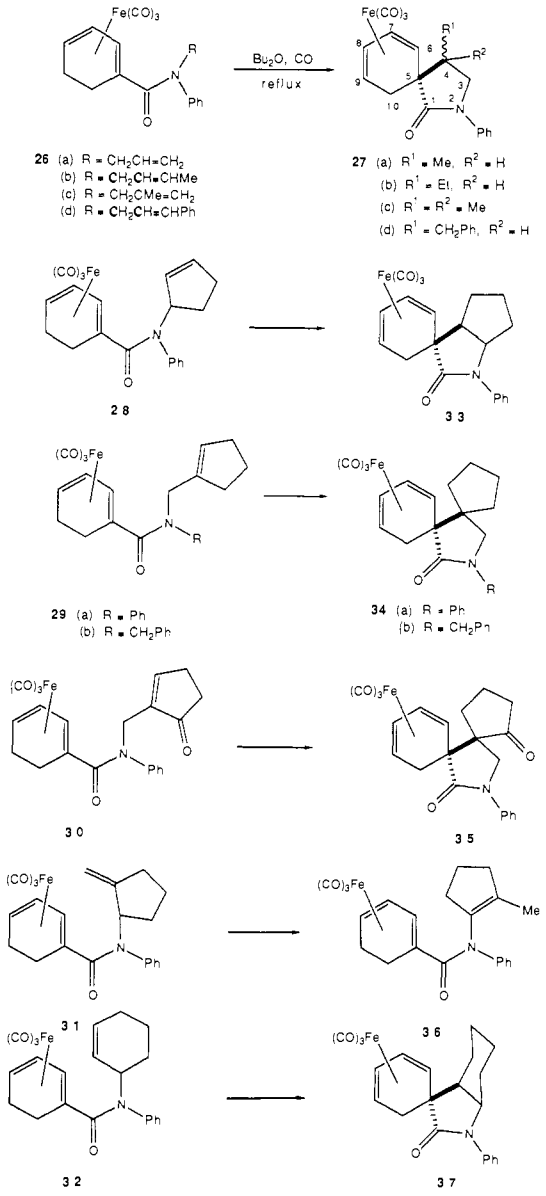
hydrobenzoic acid)iron[6b] (**23**) by conversion to the acid chloride followed by reaction of this material with the appropriate unsaturated alcohol. When the simple allyl ester was heated under reflux in di-*n*-butyl ether under nitrogen for several hours until all starting material had disappeared (TLC), the spirolactone **25a** was formed as an equimolar mixture of epimers. However, under these conditions the isolated yield of **25a** was low (15–20%) and no other organometallic products were identified. Incorporation of triphenylphosphine into the reaction mixture led to the formation of spirolactone **25b**, in which the phosphine ligand has been incorporated, together with substantial amounts of **24b**, corresponding to CO/PPh_3 ligand exchange on **24a**. Interestingly, heating **24b** under these conditions did not produce any of the cyclized compound **25b**, inferring that ligand exchange occurs subsequent to the C–C bond-forming step during the cyclization.

Owing to the requirement for fairly high temperature (no reaction occurs in refluxing toluene) and noting the fairly rapid incorporation of triphenylphosphine ligand into product, we supposed that the reaction mechanism involved loss of CO ligand, followed by a reincorporation of CO (or PPh_3) after the cyclization (see later). Since these particular couplings were not conducted in a closed vessel, one reason for the poor yield would be a lack of free CO in the reaction milieu. Therefore **24a** was heated in di-*n*-butyl ether under a balloon (or bubbler) of carbon monoxide gas, whereupon the spirolactone **25a** was produced in 88% isolated yield, again as an equimolar mixture of diastereomers. These epimers were readily separated by preparative TLC, and X-ray crystallography on one of them[10] revealed that C–C bond for-

mation occurs syn to the $Fe(CO)_3$ moiety, as indicated in the structure.

We next turned our attention to the more highly substituted unsaturated esters **24c–i**, the butenyl ester **24j**, and the propargylic esters **24k** and **24l**. The results of successful reactions are summarized in Table I, from which it is observed that thermal cyclization of the allylic esters is limited to the simpler derivatives. For example, the crotyl ester **24c** gave no spirolactone **25c** on heating, but a combination of photochemical and mild thermal conditions gave **25c**, albeit in rather poor yield (entry 4). On the other hand, methallyl ester **24d** gave a low yield of spirolactone **25d** under thermal conditions, but no cyclization occurred under photochemical conditions (entries 5 and 6). The 3-butenyl ester **24e** was not problematic and gave **25e** in 89% yield under thermal reaction conditions. More highly substituted allyl esters **24f–i** as well as the 4-butenyl and propargylic esters completely failed to cyclize under both thermal and photochemical conditions.

Next we investigated the thermal coupling reactions of a series of allyl amides **26**, prepared from **23** in analogous fashion ((i), oxalyl chloride, CH_2Cl_2; (ii) amine). Trial experiments with the simple monoallyl amide were not encouraging, so all subsequent



(10) Preliminary communications of part of this work: (a) Pearson, A. J.; Zettler, M. W.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1987**, 264. (b) Pearson, A. J.; Zettler, M. W. *J. Chem. Soc., Chem. Commun.* **1987**, 1233.

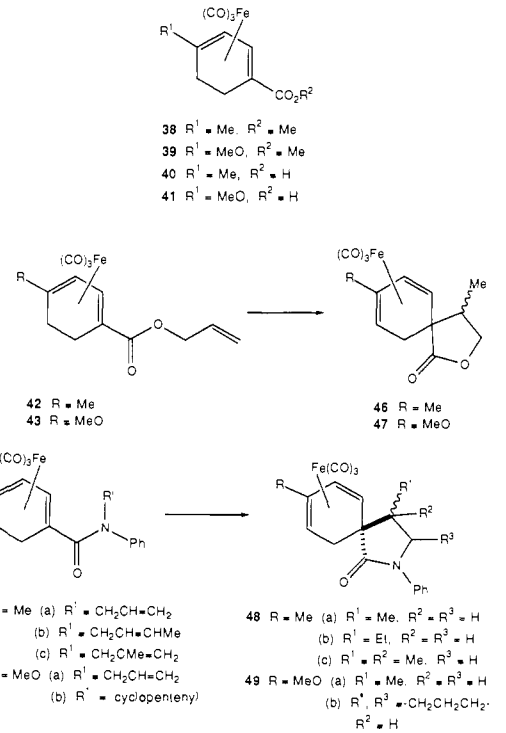
Table II. Thermal Cyclization Reactions of Allylic Amide Derivatives **26** and **28–32**[a]

entry	substrate	reaction time, h	product (yield, %)
1	**26a**	6.5	**27a** (84)
2	**26b**	6.5	**27b** (88)
3	**26c**	6.5	**27c** (90)
4	**26d**	7	**27d** (80)
5	**28**	8	**33** (40)
6	**29a**	6.5	**34a** (94)
7	**29b**	6.5	**34b** (87)
8	**30**	6.5	**35** (85)
9	**31**	8	**36**
10	**32**	8	**37** (58)

[a] All reactions run in di-*n*-butyl ether at reflux temperature and under a CO atmosphere.

runs were conducted with N-substituted allyl amides. For convenience, most experiments utilized *N*-phenyl amide derivatives, two runs being conducted with *N*-benzyl amides in order to demonstrate that a removable group can be used. Table II summarizes the results of studies for the conversion of **26** to spirolactams **27**. It became apparent that these reactions are much more facile than the corresponding ester cyclizations, usually giving higher yield in a shorter reaction time. This observation prompted us to examine various cyclopentenyl derivatives **28–31** and cyclohexenyl amide **32**, which gave high yields of cyclized compounds, each as an equimolar mixture of diastereomers (except **29**). Disappointingly, the exocyclic methylene group in compound **31** was isomerized under these conditions to give **36** as the sole product, no cyclization being observed for this material. Compared with the corresponding esters, these cycloalkene derivatives all gave very impressive results.

The scope of this unique cyclization reaction was further examined with regard to substitution on the complexed diene and the nature of the olefinic side chain. The dihydro-*p*-toluic and -*p*-anisic ester[11] derivatives **38** and **39** were readily prepared.



Saponification of these esters to the corresponding carboxylic acids proved somewhat troublesome compared with hydrolysis of the unsubstituted ester derivative **13**. Low yields (30–40%) of **40** and **41** were eventually obtained by acidic hydrolysis of the ester

(11) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 495.

Table III. Scope of the Diene–Fe(CO)$_3$/Alkene Coupling Reaction Using Substituted Diene Complexes, Allylic Ether Side Chain Derivatives, and Butenyl Ketone Derivatives

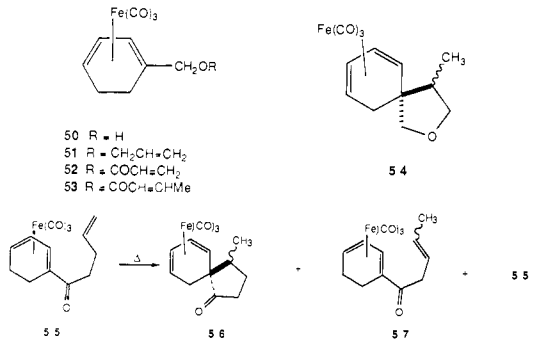
entry	substrate	reaction time,[a] h	product (yield, %)
1	**42**	12	**46** (88)
2	**43**	12	**47** (48)
3	**44a**	9	**48a** (84)
4	**44b**	9	**48b** (75)
5	**44c**	9	**48c** (88)
6	**45a**	9	**49a** (57)
7	**45b**	9	**49b** (trace)
8	**51**	12	**54** (40)
9	**55**	12	**56** (11) + **57**

[a] All reactions run in di-*n*-butyl ether at reflux temperature and under a CO atmosphere.

carbonyl group, the substituent effect being transmitted through the diene–Fe(CO)$_3$ moiety. This was also apparent in the subsequent conversions of **40** and **41** to the allylic esters and amides; formation of the acid chloride required longer reaction times, and lower yields were recorded for the final conversion to ester and amide derivatives.

Cyclization of the ester and amide derivatives **42–45** was carried out as for the earlier examples. Again, in cases where diastereomeric products are possible, both isomers were formed in equal amounts. In all tested cases of simple allylic ester or amide substrates, cyclization proceeded smoothly to give good yields of spirolactones **46** and **47** or spirolactams **48** and **49**. Use of the cyclopentenyl amide derivative **45b** was disappointing, giving only a trace of spirolactam **49b** after a 9-h reaction period. Prolonged refluxing gave no improvement, leading to substantial decomposition of starting material, and so this was not pursued further. The results of this study are summarized in Table III.

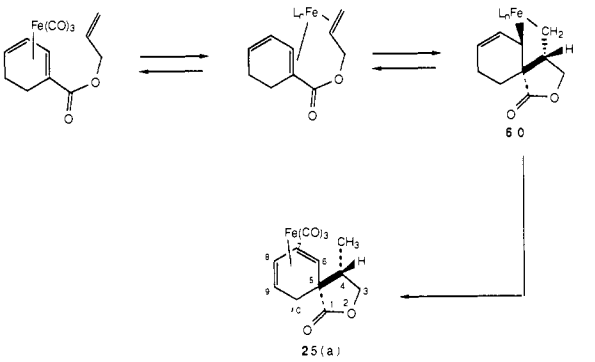
We also examined the cyclization of allylic ether derivative **51**, as well as the acrylate and crotonate derivatives **52** and **53**. These



were readily prepared from the alcohol **50**, which was itself obtained by reduction of the ester **13** using diisobutylaluminum hydride (this material had been prepared earlier by Birch and Williamson[6b] via borane reduction of the carboxylic acid **23**; it may be noted that attempts to reduce esters or acids with the lithium aluminum hydride in the presence of the diene–Fe(CO)$_3$ group results in substantial decomposition of the organometallic complex, presumably due to hydride attack at the carbonyl ligands). While cyclization of allyl ether **51** proceeded reasonably well, giving **54** in 40% yield, esters **52** and **53** were recovered unchanged after heating in refluxing di-*n*-butyl ether. Thus, while cyclization occurs for esters and amides having the electron-withdrawing carbonyl group attached to the diene–Fe(CO)$_3$ unit, the reaction is suppressed when an electron-poor alkene partner is used. (This might also be a result of geometric requirements of the transition state that are not met when the olefinic partner is of a planar nature as in **52** and **53**.)

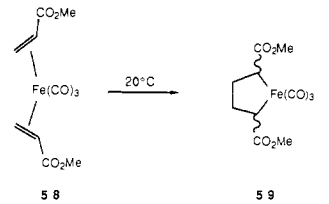
Finally the all-carbon version of the spirocyclization reaction was studied with butenyl ketone **55**, prepared by reaction of butenylmagnesium bromide with the acid chloride generated from **23** (see above). When **55** was heated in refluxing di-*n*-butyl ether, the spiroketone **56** was formed in low yield (11%). A mixture of unreacted **55** and the conjugated enone derivative **57** was also

Scheme I. Partial Mechanism of Diene–Fe(CO)$_3$/Alkene Coupling, Illustrating the Intermediacy of Ferracyclopentane Derivatives (Ligand Environment of the Metal Unspecified)



isolated (69% combined). The formation of **57**, which undergoes no further reaction on heating, represents a problem for the spirocyclization reaction. Nevertheless, the formation of the spiro[4.5]decane skeleton, which is present in a large group of monoterpene natural products,[12] is a feasible process with this technique, although we have not attempted to refine the procedure to give better yields at this stage.

(2) Mechanistic Implications and Control of the Stereochemical Course of Spirocyclization. As noted in the preceding discussion, whenever the spirocyclization leads to the formation of two new centers of chirality, an equimolar mixture of diastereomers is produced. Since X-ray analysis[10a] of one of the epimers of product **25a** shows that coupling of the diene and alkene moieties occurs cis to the Fe(CO)$_3$, the implied mechanism involves coordination of the pendant alkene to the metal, followed by formation of a metallacyclopentane derivative. This is supported by Green's observations on the formation of complexes such as **18** and mechanistic studies by Kerber and co-workers[13] on related reactions. It is also well-known that bis(methyl acrylate)iron tricarbonyl (**58**) undergoes conversion to the metallacyclopentane **59** on warming to room temperature.[14] A partial mechanism of the cyclization process is given in Scheme I.



From a consideration of the type of mechanism shown in Scheme I, we were convinced that the cyclization intermediate **60** should have the stereochemistry depicted. Completion of the cyclization process should lead to a single diastereomer of **25a** as indicated in Scheme I. Formation of the C(4)-epimeric spirolactone requires a fused ferracyclopentane intermediate **61**, which is highly strained (see Figure 1). An alternative way of depicting the diastereomers of **25a** is shown in Figure 2, and such diastereomers could result from a single product **25a** by a well-precedented rearrangement[15] of the cyclohexadiene–Fe(CO)$_3$ unit, as suggested in Figure 2. With this in mind, we carried out the experiments now described in order to test this simple mechanistic idea and to determine whether the stereochemical outcome of the reaction could be controlled.

If the cyclization reaction itself is stereospecific, then use of optically pure allylic ester **24a** or amide **26a** should give spirolactone (spirolactam) in which the absolute stereochemistry at

(12) Review: Marshall, J. A.; Brady, S. F.; Andersen, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283.
(13) Kerber, R. C.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1976**, *110*, 345.
(14) Grevels, F. W.; Schulz, D.; Koerner von Gustorf, E. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 534.
(15) Alper, H.; LePort, P. C.; Wolfe, S. *J. Am. Chem. Soc.* **1969**, *91*, 7553. Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63.

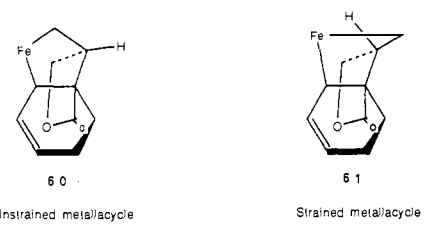


Figure 1. Comparison of diastereomeric ferracyclopentane intermediates **60** and **61**.

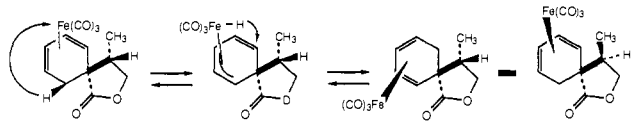
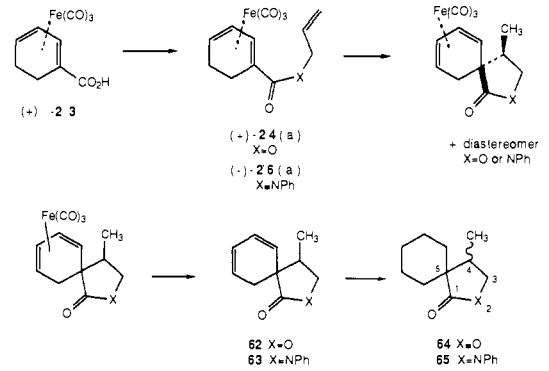


Figure 2. Diastereomer interconversion via cyclohexadiene–$Fe(CO)_3$ rearrangement.

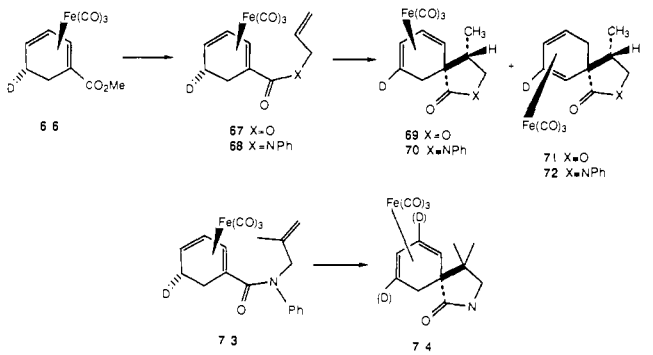
C(4) is fixed. This was tested as follows. Enantiomerically pure acid (+)-**23** was prepared by optical resolution according to the method of Birch and co-workers[16] and converted to allylic ester or amide **24** or **26** as described above. That no racemization



occurred during this conversion was established by NMR methods (chiral lanthanide shift reagent). Exposure of each substrate to thermal cyclization conditions afforded the expected epimeric mixture of products. Treatment of the mixture with trimethylamine *N*-oxide gave diene **62** or **63**, each of which was hydrogenated to give **64** or **65**, respectively.

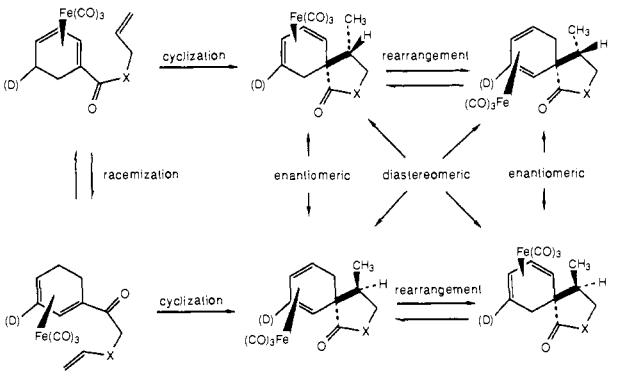
Both spirocyclic compounds **64** and **65** were optically active. Optical purity was determined by NMR spectroscopy in the presence of (+)-tris[3-(heptafluorobutyryl)camphorato]europium(III), and both products showed ca. 40% enantiomeric excess. Since C(4) is the only asymmetric center in these molecules, the results imply that the stereochemistry at this center is (partially) fixed during the cyclization. This result was confirmed by using deuterium-labeled complexes as follows.

Treatment of the (cyclohexadienyl)iron complex **14** with sodium borodeuteride gave the labeled complex **66**, containing >95%



(16) Birch, A. J.; Bandara, B. M. R. *Tetrahedron Lett.* **1980**, 2981.
(17) Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1101.

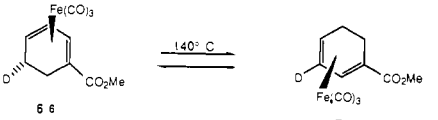
Scheme II. Combined Cyclization and Competing Racemization and Rearrangement of Diene–$Fe(CO)_3$ Complexes



deuterium (by NMR and mass spectrometry). This was converted to the deuterium-labeled ester and amide derivatives **67** and **68** and each was cyclized as before. Separation of diastereomers by preparative TLC, followed by ^1H NMR analysis, allowed determination of the position of the deuterium label in each diastereomer. From this study, it was found that diastereomers **69** and **70** contained ca. 75% deuterium at the terminal diene position indicated, while **71** and **72** contained ca. 75% deuterium at the inner diene position. The stereochemistry of each diastereomer has been established by X-ray crystallography.[10a] In confirmation of this result, cyclization of the deuterium-labeled methallyl amide **73** gave **74** as one diastereomer in which the deuterium label was equally distributed between the terminal and inner diene positions as indicated in the structure. In fact, this result also confirms that the diastereomers are those in which the stereochemistry at C(5) is the same while that at C(4) differs, rather than the alternative having fixed C(4) stereochemistry with cyclization occurring cis and trans to the metal (see also conversion of **26c** to **27c**).

These results, and those using enantiomerically pure complexes, are consistent with the sequence of events shown in Scheme II. *Stereospecific* cyclization competes with racemization of the starting material, accounting for partial loss of optical purity at C(4) of the spirocycle, as well as partial randomization of the deuterium label. Subsequent to cyclization, facile rearrangement of the diene–$Fe(CO)_3$ unit, as discussed earlier, leads to the observed mixture of diastereomers. From the results of enantiomeric excess for **64** and **65** and deuterium labeling, the rate of cyclization is approximately twice the rate of racemization.

We had not anticipated that racemization of the ester and amide complexes by diene–$Fe(CO)_3$ rearrangement would proceed so rapidly under nonacidic thermal conditions. Consequently, this was confirmed by using optically pure methyl ester derivative (−)-**13**, as well as deuterium-labeled compound **66**. Under typical

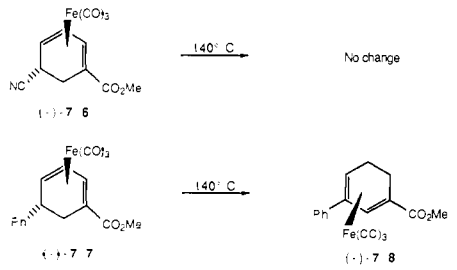


cyclization reaction conditions (140 °C, Bu_2O, 8 h), complete racemization of (−)-**13** and equilibration of **66** to give an equimolar mixture of **66** and **75** occurred, thus confirming that precyclization diene rearrangement may accompany the earlier reactions.[18]

With this information in hand, we examined the possibility of suppressing the racemization by attaching substituents to the cyclohexadiene ring. Conversion of optically pure (−)-**14** to

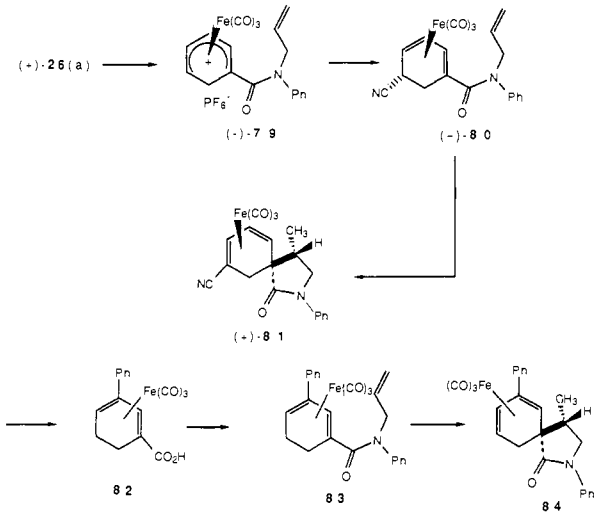
(18) The clean isomerization of **66** and racemization of (−)-**13** is puzzling in that only very minor amounts of other rearrangement products, e.g., tricarbonyl[2-(methoxycarbonyl)cyclohexadiene]iron, are detectable in the product, especially in view of the fact[6b] that this particular complex can be prepared by reaction of 2-(methoxycarbonyl)cyclohexadiene with $Fe(CO)_5$ in refluxing di-*n*-butyl ether (24–44-h reaction time) with very little contamination by other complexes. We have no explanation for these rather strange results.

complexes (−)-**76** and (−)-**77** was readily accomplished. Subjection



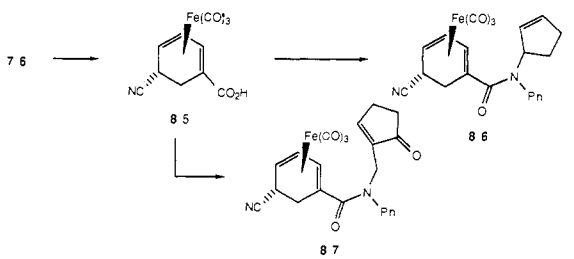
of (−)-**76** to the cyclization conditions led to recovery of this material with *no rearrangement* and *no loss of optical purity*, while thermal treatment of (−)-**11** ($[\alpha]_D = -117°$) led to *complete rearrangement* to give **78** ($[\alpha]_D = -18.5°$).

Presumably these observations reflect the thermodynamic stability of the isomeric complexes that can be formed by diene–Fe(CO)$_3$ rearrangement and/or the relative facility of hydrogen transfer from the diene ligand to iron during the rearrangement. Such effects indicated a means of controlling stereochemistry during the spirocyclization reaction. Hydride abstraction from the amide complex (+)-**26a** afforded the dienyl complex (−)-**79**, which was converted to complex (+)-**80**. Cy-



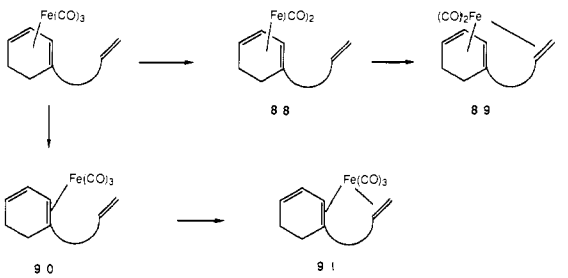
clization of this compound gave a single product, (+)-**81**, in optically pure form (by NMR). Phenyl-substituted allyl amide complex *rac*-**83** was obtained from rearranged ester **78** by hydrolysis to acid **82** and sequential treatment of this compound with oxalyl chloride and *N*-allylaniline (these reactions proceed much more slowly than with the simple unsubstituted carboxylic acid derivatives). Again, cyclization of **83** occurred stereospecifically to give **84**.

Thus, the spirocyclization reaction can be carried out with complete stereochemical control in the above cases, although application of this technique to the more interesting cyclizations has proved troublesome. For example, hydride abstraction from the cyclopentenyl amide derivatives **28** and **30** was unsuccessful. Cyano-substituted amide derivatives **86** and **87** were therefore



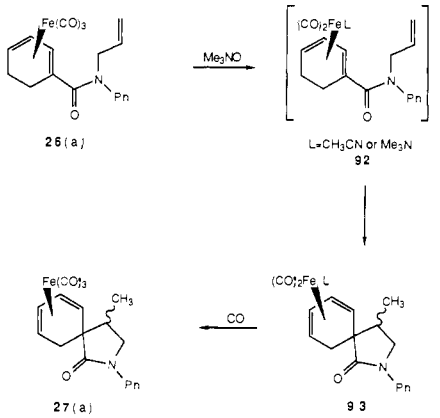
prepared from the cyano-substituted methyl ester *rac*-**76** by the following sequence: (i) selective hydrolysis of ester with ethanethiol/aluminum chloride; (ii) sequential treatment of carboxylic acid **85** with oxalyl chloride and the appropriate cyclopentenyl amine derivative. So far, attempts to effect thermal cyclization of **86** and **87** have failed, and since the cyano substituent on these molecules is of rather limited value as a functional group for studies in, e.g., trichothecene synthesis, these cyclizations were not further pursued.

(3) A Probe of CO Ligand Dissociation Using Trimethylamine *N*-Oxide. As mentioned earlier and outlined in Scheme I, the diene–Fe(CO)$_3$/alkene coupling reaction appears to involve prior coordination of the pendant alkene to the metal. This requires dissociation of one ligand from the iron, which could be carbon monoxide or one-half of the diene, giving 16-electron complexes **88** or **90**, respectively. Each of these could incorporate the



pendant alkene into the iron coordination sphere, giving **89** or **91**, either of which could lead to diene/alkene coupling. Trimethylamine *N*-oxide is known[19] to cause selective disengagement of CO ligand, and this was examined as a means of effecting the cyclization.

An acetonitrile solution of *N*-allyl-*N*-phenyl amide complex **26a**



was treated with 1.7 equiv of trimethylamine *N*-oxide to selectively displace a carbon monoxide ligand. The reaction was monitored by infrared spectroscopy, and after 15 min, no tricarbonyl complex remained. Rather, CH_3CN (or Me_3N) replaced the lost CO ligand as evidenced by a shift of the remaining iron carbonyl bands to lower wavenumber, indicating the presence of an electron-donating ligand as in complex **92**. Upon gentle warming (50 °C), lactam formation occurred as evidenced by the appearance of a lactam carbonyl at 1700 cm^{-1}, with concomitant reduction in intensity of amide carbonyl at 1630 cm^{-1}, indicating conversion of **92** to **93**.

In addition, the reaction was run in deuterated acetonitrile and followed by ^{1}H NMR. The resulting spectra were complicated by peak broadening due to small amounts of paramagnetic decomposition product. However, after several hours at room temperature, two methyl doublets appeared at 1.1 and 0.9 ppm, indicating the presence of a spirolactam. The reaction was monitored for an additional 24 h and showed continual growth of methyl doublets. Interestingly, the intensity of the two doublets increased at different rates to finally give a 50:50 mixture of products, suggesting some type of equilibrium exists between the

(19) Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun.* **1979**, 277.

two epimers even under these relatively mild conditions. Attempts to isolate spirolactam **93** were unsuccessful, apparently due to instability of the acetonitrile (or trimethylamine) substituted metal moiety. However, displacement by carbon monoxide (benzene at 45 °C) allowed isolation of spirolactam **27a**. Although the isolated yield of **27a** by this method (65%) is not as good as the thermal procedure, this experiment provides evidence that CO loss initiates the coupling reaction and also indicates the possibility for performing these conversions under milder conditions.

Conclusions

Under thermal conditions, a variety of olefinic groups can be coupled intramolecularly with diene–$Fe(CO)_3$ complexes to generate spirocyclic products. The reaction can be made to proceed stereospecifically by using appropriate substituents on the diene–$Fe(CO)_3$ unit, and a range of allylic amide derivatives undergo the cyclization readily to give highly functionalized products. There is some potential for applying this technique to the synthesis of trichothecenes such as verrucarol or calonectrin, but this will require the development of milder reaction conditions in order to avoid diastereomer formation and rearrangement of the allyl amide group. The reaction appears to require loss of CO ligand, to allow coordination of the pendant alkene to iron. This so-formed intermediate undergoes coupling of the olefinic groups, eventually leading to the spirocyclic product. This new reaction overcomes a number of problems associated with the preparation of electrophilic dienyl iron complexes and promises to lead to C–C bond-forming methods that complement the well-established reaction of dienyl iron complexes with carbon nucleophiles.

Experimental Section

General. All spirocyclization reactions were performed under a carbon monoxide atmosphere in a flame-dried, single-neck, round-bottom flask unless otherwise noted. All other chemical reactions were performed under a dry, oxygen-free, inert atmosphere (nitrogen or argon passed through activated molecular sieves and Ridox columns) in flame-dried glass vessels. Aldrich Gold Label (99+%, sure-seal bottle) di-*n*-butyl ether was used without further purification for all thermal spirocyclization reactions. Solvents used in all other reactions were freshly distilled under dry nitrogen as follows: THF, DME, and benzene from Na/benzophenone; CH_2Cl_2 and CH_3CN from CaH_2; Et_2O from $LiAlH_4$. Reagent-grade Bu_2O was filtered through basic alumina and purged with nitrogen for use in complexation reactions. All solutions used in chromatography were purified in-house by distillation of commercially available materials. Deviations from any of the above practices are detailed in the Experimental Section under individual compounds. Residual solvent was removed from oils after chromatography by exposing a film of the material to high vacuum (10^{-3} mmHg) for 16–24 h.

Infrared spectra were obtained on a Perkin-Elmer 1420 spectrophotometer and were referenced to polystyrene at 1601 cm^{-1}. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz. The samples were referenced to tetramethylsilane at 0.0 ppm. Elemental analyses were obtained through Galbraith Laboratories, Inc., Knoxville, TN. Mass spectral analyses were performed either at the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln or in-house on a Kratos MS25A instrument. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at room temperature. Preparative thin-layer chromatography (PLC) was performed on commercially available UNIPLATE 20 cm × 20 cm plates (0.5 mm) or on similarly proportioned plates (1.0-mm layer) prepared in-house with Kieselgel 60 PF_{254} silica gel.

General Procedure for the Preparation of Allylic Esters and Amides. In a clean, single-neck, round-bottom flask, the appropriate carboxylic acid derivative was dissolved in freshly distilled methylene chloride under argon. Two equivalents of oxalyl chloride was added via syringe, and the solution was stirred at room temperature 3–6 h (conversion to acid chloride can be monitored by IR), after which the solvent and excess oxalyl chloride were removed in vacuo with a rotary evaporator (bath temperature = 30 °C). The tan, viscous oil was maintained under vacuum (2 mmHg) for 5–10 min and was then dissolved in freshly distilled benzene. Pyridine (2 molar equiv) and the appropriate alcohol or amine (2 molar equiv) were added via syringe, and the reaction mixture was stirred at room temperature for 16–24 h (reaction can be monitored by TLC). The product mixture was diluted with diethyl ether, washed with H_2O, saturated aqueous Na_2CO_3, and 2 N HCl, dried over $MgSO_4$, concentrated, and subjected to flash chromatography or preparative TLC (20% EtOAc/hexane unless otherwise noted) to afford the desired racemic (unless otherwise noted) allyl ester or allyl amide in 70–95% yield, usually as a viscous yellow oil. Deviations from this procedure are noted in the experimental data for specific compounds.

General Procedure for the Thermally Induced Spirocyclization Reaction. The appropriate allyl ester or allyl amide complex (100 mg) was dissolved in di-*n*-butyl ether (10 mL) in a clean, flame-dried, single-neck, round-bottom flask under argon. The solution was purged with CO for 1 min, after which it was refluxed with magnetic stirring for 6–12 h (specific reflux times are given for each compound). It was then cooled to room temperature, diluted with diethyl ether, and filtered through Celite. Concentration followed by preparative TLC (20% EtOAc/Hex) yielded a racemic (unless otherwise noted) 1:1 epimeric mixture of spirolactones or spirolactams that could be separated by preparative TLC using multiple-elution techniques.

Tricarbonyl(allyl 1–4-η-cyclohexa-1,3-dienecarboxylate)iron (24a). Acid **23** (2.0 g, 7.6 mmol) was treated with oxalyl chloride (15 mmol, 1.92 g), pyridine (15 mmol, 1.23 mL), and allyl alcohol (15 mmol, 0.87 g) as described above to afford 1.8 g (6 mmol, 80%) of allyl ester **24a** as a yellow oil after flash chromatography. IR (CCl_4) ν_{max} 2060, 1985, 1710, 1650 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.07 (1 H, d, J = 5.6 Hz, H2), 5.94 (1 H, m, H9), 5.37 (1 H, dd, J = 5.8, 4.4 Hz, H3), 5.32 (1 H, dd, $J_{11,10(trans)}$ = 17.3 Hz, $J_{11,9}$ = 1.4 Hz, H11), 5.22 (1 H, dd, $J_{11,10(cis)}$ = 10.4 Hz, $J_{11,9}$ = 1.4 Hz, H11), 4.68 and 4.54 (1 H each, ddt each, J_{gem} = 13.4 Hz, $J_{9,10}$ = 5.6 Hz, $J_{9,11(cis)}$ = $J_{9,11(trans)}$ = 1.4 Hz, H9), 3.38 (1 H, m H4), 2.21 (1 H, ddd, J_{gem} = 14.6 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 11.7 Hz, $J_{6\text{-endo},5\text{-exo}}$ = 2.4 Hz, H6), 1.93 (1 H, m, H5-endo), 1.70 (1 H, m, H5-exo), 1.45 (1 H, ddd, J_{gem} = 14.6 Hz, $J_{6\text{-exo},5\text{-exo}}$ = 8.3 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 3.4 Hz, H6-endo). HRMS Calcd for $C_{11}H_{12}O_4Fe$ (M − 2CO): 276.0075. Found: 276.0088; m/e (%) 276 (1), 248 (30), 220 (100), 164 (0.4).

Tricarbonyl(*N*-allyl-*N*-phenyl-1–4-η-cyclohexa-1,3-dienecarboxamide)iron (26a). Acid **23** (1.0 g, 3.8 mmol) was treated with oxalyl chloride (7.5 mmol, 0.66 mL), pyridine (7.5 mmol, 0.61 mL), and *N*-allylaniline (freshly distilled, 7.5 mmol, 1.1 mL) as described to yield 1.37 g (95%) of desired amide **26a** as a yellow viscous oil after flash chromatography. (Note: when *N*-allylaniline is prepared in-house, careful distillation of the product is necessary to avoid contamination by aniline.) IR (CCl_4) ν_{max} 2020, 1985, 1630, 1595 cm^{-1}. ^1H NMR (benzene-d_6, 50 °C) δ 7.1 (5 H, m, Ph), 6.0 (1 H, m, H10), 5.34 (1 H, d, $J_{2,3}$ = 4.4 Hz, H2), 4.9 (2 H, m, H11), 4.4 (1 H, dd, J_{gem} = 14.5 Hz, $J_{9,10}$ = 5.9 Hz, H9), 4.3 (1 H, dd, $J_{3,4}$ = 6.0 Hz, $J_{3,2}$ = 5.0 Hz, H3), 4.1 (1 H, dd, J_{gem} = 14.5, $J_{9,10}$ = 6.9 Hz, H9), 2.7 (1 H, m, H4), 2.1 (1 H, m, H6-endo), 1.6 (1 H, m, H5-endo), 1.2 (2 H, m, H5-exo and H6-exo). HRMS Calcd for $C_{18}H_{17}O_3NFe$ (M − CO): 351.0552. Found: 351.0560; m/e (%) 351 (1.6), 323 (13), 295 (66), 239 (21), 105 (100).

Tricarbonyl(*N*-cyclopent-2-en-1-yl-*N*-phenyl-1–4-η-cyclohexa-1,3-dienecarboxamide)iron (28). Acid **23** (550 mg, 2.1 mmol) was treated with oxalyl chloride (4.2 mmol, 0.363 mL), pyridine (4.2 mmol, 0.34 mL), and *N*-(cyclopent-2-en-1-yl)aniline (4.2 mmol, 660 mg) as described. (Note: the benzene solution of acid chloride, pyridine, and the amine was refluxed 24 h, cooled, and worked up as usual to afford 675 mg (79%) of the desired product (**28**) as a mixture of diastereomers (1:1) after flash chromatography.) Modified flash chromatography allows the separation of the two diastereomers (15% EtOAc/Hex, 8-in. column of flash silica gel, gentle pressure). IR (CCl_4) ν_{max} 2030, 1980, 1625 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.4–7.1 (5 H, m, Ph), 5.7 (2 H, m, vinyl), 5.6 (2 H, m, CHN and H2), 5.0 (1 H, br t, J = 5.5 Hz, H3), 3.2 (1 H, m, H4), 2.3–1.3 (8 H, series of multiplets, $4CH_2$). The other diastereomer showed the following distinguishable resonances: 5.7 (3 H, m, vinyl and CHN). HRMS Calcd for $C_{19}H_{19}ONFe$ (M − 3CO): 321.0830. Found: 321.0809; m/e (%) 377 (65), 349 (100), 321 (25), 265 (75).

Tricarbonyl[*N*-((cyclopent-1-enyl)methyl)-*N*-phenyl-1–4-η-cyclohexa-1,3-dienecarboxamide]iron (29a). Acid **23** (152 mg, 0.58 mmol) was treated with oxalyl chloride (1.1 mmol, 0.10 mL), pyridine (1.1 mmol, 0.089 mL), and *N*-((cyclopent-1-enyl)methyl)aniline (50 mg, 0.29 mmol) as described to give 47 mg (38.7%) of desired amide **29a** as a viscous yellow oil after flash chromatography. (Note: better yield (78%) was obtained when the acid chloride and amine were refluxed for 16 h and/or 1 mol % of 4-(dimethylamino)pyridine was added.) IR (CCl_4) ν_{max} 2025, 1985, 1975, 1640 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.45–7.2 (5 H, m, Ph), 5.4 (2 H, m, H2 and vinyl), 4.97 (1 H, br t, J = 5.5 Hz, H3), 4.5 (1 H, d, J_{gem} = 15.1 Hz, H9a), 4.25 (1 H, d, J_{gem} = 15.1 Hz, H9b), 3.2 (1 H, m, H4), 2.3–1.3 (10 H, m, $5CH_2$). HRMS Calcd for $C_{21}H_{21}O_3NFe$ (M − CO) 391.0870. Found: 391.0847; m/e (%) 391 (0.7), 363 (50.5), 335 (100), 279 (22).

Tricarbonyl[*N*-((5-oxocyclopentenyl)methyl)-*N*-phenyl-1–4-η-cyclohexa-1,3-dienecarboxamide]iron (30). Acid **23** (71 mg, 0.27 mmol) was treated with oxalyl chloride (0.53 mmol, 0.047 mL), pyridine (0.27 mmol, 0.022 mL), and *N*-((5-oxocyclopentenyl)methyl)aniline (0.27 mmol, 50 mg) as described in the general procedure to give 98.2 mg (84%) of the desired amide **30** after flash chromatography as a yellow solid, mp

127–129 °C. IR (CCl_4) ν_{max} 2020, 1980, 1700, 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.6 (1 H, br s, vinyl), 7.5–7.3 (5 H, m, Ph), 5.3 (1 H, d, $J_{2,3}$ = 4.5 Hz, H2), 4.9 (1 H, br t, J = 5.5 Hz, H3), 4.4 (2 H, CH_2N), 3.2 (1 H, m, H4), 2.5 (2 H, m), 2.3 (2 H, m), 2.0 (1 H, m, H6-endo), 1.8 (1 H, m, H5-endo), 1.6 (1 H, m, H5-exo), 1.3 (1 H, m, H6-exo). Mass spectrum, *m/e* 405, 377, 349, 321, 225, 77.

Tricarbonyl(6–9-η-1-oxo-4-methyl-2-oxaspiro[4.5]deca-6,8-diene)iron (25a). Allyl ester **24a** (100 mg, 0.5 mmol) was refluxed in Bu_2O under a CO atmosphere for 12 h to afford spirolactone **25a** in 88% yield (88 mg) after preparative TLC. IR (CCl_4) ν_{max} 2025, 1970, 1770 cm^{-1}. Epimer 1 (4*R*,5*S*,6*R*,9*R*): ^{1}H NMR ($CDCl_3$) δ 5.5 (2 H, m, H7 and H8), 4.2 (1 H, dd, J_{gem} = 9.2 Hz, $J_{3,4(cis)}$ = 6.2 Hz, H3), 3.9 (1 H, m, H3′), 3.3 (1 H, m, H9), 2.7 (1 H, dd, $J_{6,7}$ = 6.3 Hz, $J_{6,8}$ = 1.4 Hz, H6), 2.2 (1 H, m, H4), 2.1–1.8 (2 H, m, H10), 1.2 (3 H, d, J = 7.0 Hz, CH_3). Epimer 2 (4*S*,5*S*,6*R*,9*R*): mp 141 °C. ^{1}H NMR ($CDCl_3$) δ 5.3 (2 H, m, H7 and H8), 4.52 (1 H, dd, J_{gem} = 9.2 Hz, $J_{3,4(cis)}$ = 5.5 Hz, H3), 3.9 (1 H, m, H3′), 3.4 (1 H, m, H9), 2.96 (1 H, dd, $J_{6,7}$ = 6.2 Hz, $J_{6,8}$ = 1.3 Hz, H6), 2.45 (1 H, m, H4), 2.1–1.8 (2 H, m, H10), 1.0 (3 H, d, J = 7.3 Hz, CH_3). Anal. Calcd for $C_{13}H_{12}O_5Fe$: C, 51.36; H, 3.94. Found: C, 51.35; H, 3.97.

Dicarbonyl(triphenylphosphine)(6–9-η-1-oxo-4-methyl-2-oxaspiro-[4.5]deca-6,8-diene)iron (25b). Allyl ester **24a** (300 mg, 0.98 mmol) and triphenylphosphine (1.1 mol, 286 mg) were refluxed in 10 mL of Bu_2O (argon atmosphere) for 24 h to afford 45 mg (15%) of spirolactone **25b** after PLC along with the triphenylphosphine-substituted allyl ester **24b**. IR (CCl_4) ν_{max} 1980, 1925, 1770 cm^{-1}. ^{1}H NMR ($CDCl_3$) produced a spectrum where broadening of all signals occurred. Methyl doublets could be seen for both epimers at 1.08 and 0.9 ppm, respectively. Mass spectrum, *m/e* (%) 510 (7.4), 482 (10.2), 442 (11.5), 252 (20), 183 (30).

Dicarbonyl(triphenylphosphine)(allyl 1–4-η-cyclohexa-1,3-dienecarboxylate)iron (24b). Major product from above-attempted spirocyclization reaction. IR ν_{max} (CCl_4) 1990, 1940, 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.7–7.3 (15 H, m, PPh_3), 6.0 (2 H, m, H2 and H10), 5.4 (1 H, dd, J = 16, 1 Hz, H11a), 5.2 (1 H, dd, J = 8, 1 Hz, H11b), 4.7 (4 H, m, H3, H4, H9a, H9b), 2.2–1.8 (4 H, m, H5 and H6).

Tricarbonyl(6–9-η-1-oxo-4-ethyl-2-oxaspiro[4.5]deca-6,8-diene)iron (25c). Crotyl ester **34c** (100 mg, 3 mmol) was dissolved in 10 mL of freshly distilled benzene in a clean, flame-dried, 20-mL, three-neck, round-bottom flask fitted with a reflux condenser and CO balloon. The solution was purged with CO gas for 60 s, after which it was exposed to a 250-W sunlamp for 8 h under a CO atmosphere (heat generated by lamp is sufficient to raise the solution to its boiling point). The solution was diluted with petroleum ether and filtered through Celite. Evaporation of solvent and PLC purification yielded the spirolactone **25c** as a pale yellow wax in 20% overall yield (40% based on recovered starting material) (20 mg, 0.6 mmol). IR (CCl_4) ν_{max} 2020, 1980, 1775 cm^{-1}. Epimer 1 (4*R*,5*S*,6*R*,9*R*): ^{1}H NMR ($CDCl_3$) δ 5.5 (2 H, m, H7 and H8), 4.2 (2 H, ABX, J_{AB} = 9.3 Hz, J_{AX} = 6 Hz, J_{BX} = 4.5 Hz, H3), 3.2 (1 H, m, H9), 2.7 (1 H, dd, J = 6.0, 1.5 Hz, H6), 2.1 (1 H, m, H4), 2.0–1.6 (2 H, m, H10-endo and -exo), 1.2 (2 H, m, H11), 0.9 (3 H, t, J = 7.0 Hz, CH_3). Epimer 2 (4*S*,5*S*,6*R*,9*R*): ^{1}H NMR ($CDCl_3$) δ 5.5 (1 H, br t, J = 5.4 Hz, H8), 5.3 (1 H, br t, J = 5.4 Hz, H7), 4.4 (1 H, dd, J_{gem} = 9.7 Hz, $J_{3,4}$ = 5.8 Hz, H3), 4.1 (1 H, dd, J_{gem} = 9.7 Hz, $J_{3,4}$ = 1.0 Hz, H3′), 3.3 (1 H, m, H9), 2.9 (1 H, dd, J = 6.2, 1.4 Hz, H6), 2.3 (1 H, m, H4), 2.0 (2 H, d, J = 3.2 Hz, H10-endo and -exo), 1.3 (2 H, m, CH_2), 0.8 (3 H, t, J = 7.0 Hz, CH_3). HRMS Calcd for $C_{14}H_{14}O_5Fe$ (M^+): 318.0190. Found: 318.0167; *m/e* (%) 318 (2.4), 290 (50.1), 262 (38.5), 234 (100), 178 (34.4).

Tricarbonyl(6–9-η-1-oxo-4,4-dimethyl-2-oxaspiro[4.5]deca-6,8-diene)iron (25d). Methallyl ester **24d** (100 mg, 0.3 mmol) was refluxed in Bu_2O (as described) 10 h to afford spirolactone **25d** (15 mg, 21% based on starting material consumption of 71%) after PLC. IR (CCl_4) ν_{max} 2060, 1980, 1775 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.4 (1 H, m, H8), 5.2 (1 H, m, H7), 4.1 (1 H, d, J_{gem} = 9.0 Hz, H3), 3.8 (1 H, d, J_{gem} = 9.0 Hz, H3′), 3.4 (1 H, m, H9), 2.7 (1 H, dd, J = 6.3, 1.1 Hz, H6), 2.0 (1 H, dd, J = 14, 1.0 Hz, H10-endo), 1.7 (1 H, dd, J = 14, 3 Hz, H10-exo), 1.1 (3 H, s, CH_3), 0.9 (3 H, s, CH_3).

Tricarbonyl(6–9-η-1-oxo-2-phenyl-4-methyl-2-azaspiro[4.5]deca-6,8-diene)iron (27a). *N*-Allyl-*N*-phenyl amide complex **26a** (100 mg, 0.26 mmol) was refluxed according to the described procedure (reflux time = 5 h) to afford 84 mg (0.22 mmol, 88%) of desired spirolactam **27a** as a yellow viscous oil (1:1 mixture of epimers). IR (CCl_4) ν_{max} 2020, 1975, 1700 cm^{-1}. Epimer 1 (4*R*,5*S*,6*R*,9*R*): ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m, Ph), 5.5 (2 H, m, H7 and H8), 3.8 (1 H, dd, J_{gem} = 9.7 Hz, $J_{3,4}$ = 6.7 Hz, H3), 3.4 (1 H, dd, J_{gem} = 9.7 Hz, $J_{3',4}$ = 5.3 Hz, H3′), 3.2 (1 H, m, H9), 2.3 (1 H, dd, J = 6.3, 1.6 Hz, H6), 2.2 (1 H, m, H4), 2.0 (1 H, dd, J = 15, 2.3 Hz, H10-endo), 1.8 (1 H, dd, J = 15, 3.1 Hz, H10-exo), 1.1 (3 H, d, J = 6.9 Hz, CH_3). Epimer 2 (4*S*,5*S*,6*R*,9*R*): ^{1}H NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m, Ph), 5.5 (1 H, br t, J = 6.0 Hz, H8), 5.3 (1 H, br t, J = 6.0 Hz, H7), 4.1 (1 H, dd, J_{gem} = 10.0 Hz, $J_{3,4}$ = 6.1 Hz, H3), 3.4 (1 H, d, J_{gem} = 10.0 Hz, H3′), 3.3 (1 H, m, H9), 3.0 (1 H, dd, $J_{6,7}$ = 6.3 Hz, $J_{6,8}$ = 1.3 Hz, H6), 2.4 (1 H, m, H4), 2.0 (2 H, d, J = 3 Hz, H10), 1.0 (3 H, d, J = 7.1 Hz, CH_3). HRMS Calcd for $C_{19}H_{17}O_4NFe$ (M^+): 379.0506. Found: 379.0510; *m/e* (%) 379 (2), 351 (63), 323 (15), 295 (100), 239 (4).

Tricarbonyl(3-oxo-2-phenylspiro[2-azabicyclo[3.3.0]octane-4,1′-[2,4]-cyclohexadiene])iron (33). Amide **28** (14 mg) was heated according to the above procedure (reflux time = 6 h) to give the spirolactam **33** in 38% yield (5.3 mg) along with decomplexed spirolactam (3.0 mg, 33%). IR (CCl_4) ν_{max} 2020, 1980, 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (5 H, m, Ph), 5.5 (1 H, H4′), 5.3 (1 H, br t, J = 5.5 Hz, H3′), 4.7 (1 H, br t, J = 5.3 Hz, H1), 3.4 (1 H, m, H5′), 2.9 (1 H, d, $J_{6,7}$ = 6 Hz, H2′), 2.6 (1 H, m, H8), 2.4–1.0 (8 H, series of multiplets, H6, H6′, H7, and H8). HRMS Calcd for $C_{21}H_{19}O_4NFe$ (M^+): 405.0665. Found: 405.0665; *m/e* (%) 405 (2), 377 (46), 349 (2.7), 321 (100), 265 (1).

Tricarbonyl(7–10-η-1-oxo-13-phenyl-13-azadispiro[4.0.5.3]tetradeca-7,9-diene)iron (34a). Amide **29a** (19 mg, 0.045 mmol) was heated according to the general procedure (reflux time = 6.5 h) to afford 17.9 mg (94%) of pure spirolactam **34a** as a yellow waxy solid. IR (CCl_4) ν_{max} 2020, 1975, 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.6–7.0 (5 H, m, Ph), 5.4 (1 H, br t, J = 5.2 Hz, H9), 5.17 (1 H, br t, J = 5.9 Hz, H8), 3.65 (1 H, d, J_{gem} = 9.4 Hz, H14), 3.45 (1 H, m, H10), 3.25 (1 H, d, J_{gem} = 9.5 Hz, H14′), 2.9 (1 H, d, $J_{7,8}$ = 6.3 Hz, H7), 2.0–1.2 (10 H, series of multiplets, H11-endo and -exo, 4CH_2). HRMS Calcd for $C_{22}H_{22}O_4NFe$ (M + H): 420.0891. Found: 420.0903; *m/e* (%) 420 (80), 391 (90), 363 (20), 335 (100).

Tricarbonyl(1,12-dioxo-13-phenyl-13-azadispiro[4.0.5.3]tetradeca-7,9-diene)iron (35). Allylic amide **30** (12 mg, 0.028 mmol) was heated according to the general procedure (reflux time = 6 h) to give 4.7 mg of the desired spirolactam **35** after PLC (85% yield based on consumed starting material of 5.5 mg) as a yellow solid, mp 87 °C. IR (CCl_4) ν_{max} 2030, 1980, 1740, 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.5–7.1 (5 H, m, Ph), 5.5 (1 H, m, H9), 5.2 (1 H, m, H8), 4.1 (1 H, m, H14 for one diastereomer), 3.7 (1 H, d, J_{gem} = 10.3 Hz, H14), 3.5 (1 H, d, J_{gem} = 10.3 Hz, H14′ of one diastereomer), 3.3 (3 H, m, H14′ of one diastereomer, and H7, H10), 2.8 (1 H, d, $J_{7,8}$ = 5.1 Hz, H7 for one diastereomer), 2.5–1.3 (8 H, methylenes). HRMS Calcd for $C_{22}H_{20}O_5NFe$ (M + H): 434.0695. Found: 434.0689; *m/e* (%) 434 (0.5), 405 (0.1), 377 (41), 349 (100), 293 (1).

Tricarbonyl(4-methyl-1-carboxycyclohexa-1,3-diene)iron (40). The corresponding methyl ester (100 mg, 0.34 mmol) was refluxed in 15% aqueous H_2SO_4 for 24 h, after which the solution was extracted twice with ether. The ethereal layers were combined and washed with H_2O, followed by extraction with saturated Na_2CO_3 solution (2 × 10 mL). The sodium carbonate extracts were combined and acidified to pH = 1 with 2 N HCl. The acidic solution was then extracted with ether. The resulting ethereal layer was washed with water, dried over $MgSO_4$, and concentrated to afford 38 mg (40%) of a yellow crystalline solid, mp (decomposed at 159 °C). IR (CCl_4) ν_{max} 2020, 1990, 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.9 (1 H, d, $J_{2,3}$ = 4.5 Hz, H2), 5.3 (1 H, d, $J_{3,2}$ = 4.5 Hz, H3), 2.3 (2 H, m, methylene), 1.7 (3 H, s, CH_3), 1.5 (2 H, m, methylene).

Tricarbonyl(allyl 1–4-η-4-methylcyclohexa-1,3-dienecarboxylate)iron (42). Carboxylic acid **40** (200 mg, 0.83 mmol) was treated with oxalyl chloride (1.65 mmol, 0.144 mL), pyridine (1.65 mmol, 0.133 L), and allyl alcohol (1.65 mmol, 0.112 mL) as described in the general procedure. (Note: acid chloride formation required 5–6 h; the acid chloride formation can be monitored by IR (acid chloride band at 1785 cm^{-1})) to afford 230 mg (90%) of the desired ester **42** as a yellow oil after flash chromatography. IR (CCl_4) ν_{max} 2025, 1980, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.88 (1 H, m, vinyl), 5.86 (1 H, d, $J_{2,3}$ = 4.5 Hz, H2), 5.3–5.2 (3 H, m, H3, vinyl), 4.6 (2 H, m, H9), 2.2 (1 H, m, H6-endo), 2.0 (1 H, m, H5-endo), 1.6 (3 H, s, CH_3), 1.6–1.5 (2 H, m, H6-exo and H5-exo). HRMS Calcd for $C_{12}H_{14}O_3Fe$ (M − 2CO): 262.0300. Found: 262.0289; *m/e* (%) 318 (0.3), 290 (0.7), 262 (28), 234 (100).

Tricarbonyl(*N*-allyl-*N*-phenyl-1–4-η-4-methylcyclohexa-1,3-diene-1-carboxamide)iron (44a). Carboxylic acid **40** (200 mg, 0.83 mmol) was treated with oxalyl chloride (1.65 mmol, 0.144 mL), pyridine (1.54 mmol, 0.133 mL), and *N*-allylaniline (1.65 mmol, 0.224 mL) as described above. (Note: acid chloride formation requires 5–6 h; the acid chloride formation can be monitored by IR (acid chloride band at 1785 cm^{-1})) to afford the desired allyl amide **44a** in 80% yield (326 mg) as a viscous yellow oil after flash chromatography. IR (CCl_4) ν_{max} 2020, 1975, 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (5 H, m, Ph), 5.9 (1 H, m, vinyl), 5.3 (1 H, d, $J_{2,3}$ = 4.6 Hz, H2), 5.0 (2 H, m, vinyl), 4.9 (1 H, d, $J_{3,2}$ = 4.4 Hz, H3), 4.5 (1 H, dd, J_{gem} = 14.6 Hz, $J_{9,10}$ = 5.8 Hz, H9a), 4.1 (1 H, dd, J = 14.6, 6.8 Hz, H9b), 2.1–1.6 (2 H, m, H6-endo and H5-endo), 1.5 (3 H, s, CH_3), 1.6–1.3 (2 H, m, H5-exo and H6-exo). HRMS Calcd for $C_{18}H_{19}O_2NFe$ (M − 2CO): 337.0781. Found: 337.0757; *m/e* (%) 337 (3), 309 (11), 253 (27), 121 (58), 119 (100).

Tricarbonyl(1–4-η-allyl 4-methoxycyclohexa-1,3-dienecarboxylate)iron (43). Acid **41** (52 mg, 0.18 mmol) was treated with oxalyl chloride (0.35 mmol, 0.031 mL), pyridine (0.35 mmol, 0.029 mL), and allyl alcohol (0.35 mmol, 0.024 mL) as described. (Note: formation of acid chloride requires 6 h with gentle heating) to give 15.8 mg (30%) of allyl ester **43** as a yellow oil along with recovered starting material. IR (CCl_4) ν_{max} 2020, 1980, 1710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.9 (2 H, m, H2 and vinyl), 5.3 (3 H, m, H3, vinyl), 4.6 (2 H, m, H9), 3.5 (3 H, s, MeO), 2.4–2.1 (2 H, m, H6-endo and H5-endo), 1.8 (1 H, m, H5-exo), 1.6 (1 H, m, H6-exo). HRMS Calcd for $C_{11}H_{14}O_6Fe$ (M^+): 334.0139. Found: 334.0168; *m/e* (%) 334 (1), 306 (7), 278 (27), 250 (100).

Tricarbonyl(*N*-allyl-*N*-phenyl-4-methoxycyclohexa-1,3-dienecarboxamide)iron (45a). Acid **41** (40 mg, 0.136 mmol) was treated with oxalyl chloride (0.27 mmol, 0.024 mL), pyridine (0.27 mmol, 0.022 mL), and *N*-allylaniline (0.27 mmol, 0.037 mL) as described above to yield 17 mg (31%) of desired allyl amide **45a** as a viscous yellow oil after PLC. IR (CCl_4) ν_{max} 2020, 1980, 1640 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m, Ph), 5.9 (1 H, m, vinyl), 5.0 (4 H, m, H2, H3, vinyl), 4.4 (1 H, dd, J_{gem} = 14.6 Hz, $J_{9,10}$ = 5.9 Hz, H9), 4.1 (1 H, dd, J_{gem} = 14.6 Hz, $J_{9',10}$ = 6.8 Hz, H9′), 3.4 (3 H, s, MeO), 2.3–1.9 (2 H, m, H6-endo and H5-endo), 1.7 (1 H, m, H5-exo), 1.5 (1 H, m, H6-exo). HRMS Calcd for $C_{20}H_{20}O_5NFe$ (M + H): 410.0672. Found: 410.0702; *m/e* (%) 410 (1.5), 381 (0.1), 353 (22), 325 (39), 269 (30), 137 (97).

Tricarbonyl(6–9-η-1-oxo-2-phenyl-4-methyl-8-methyl-2-azaspiro[4.5]deca-6,8-diene)iron (48a). 4-Methyl-substituted allyl amide **44a** (29.8 mg) was refluxed as described (reflux time = 8.5 h) to give 27 mg of methyl-substituted spirolactam **48a** (79%, 1:1 mixture of epimers) after PLC as a yellow solid. IR (CCl_4) ν_{max} 2020, 1970, 1710 cm^{-1}. Epimer 1 (4*R*,5*S*,6*R*,8*S*,9*R*): ^1H NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m, Ph), 5.3 (1 H, dd, $J_{7,6}$ = 6.5 Hz, $J_{7,9}$ = 1.0 Hz, H7), 3.7 (1 H, dd, J_{gem} = 9.6 Hz, $J_{3,4(cis)}$ = 6.8 Hz, H3), 3.4 (1 H, dd, J_{gem} = 9.6 Hz, $J_{3',4}$ = 5.6 Hz, H3′), 3.2 (1 H, m, H9), 2.6 (1 H, d, $J_{6,7}$ = 6.7 Hz, H6), 2.3 (1 H, m, H4), 2.15 (3 H, s, CH_3), 2.0 (2 H, m, H10-endo and -exo), 1.0 (3 H, d, J = 7.0 Hz, CH_3). Epimer 2 (4*S*,5*S*,6*R*,8*S*,9*R*): ^1H NMR ($CDCl_3$) δ 7.6 (5 H, m, Ph), 5.2 (1 H, dd, H7), 4.2 (1 H, dd, J_{gem} = 9.4 Hz, $J_{3',4}$ = 6.4 Hz, H3′), 3.5 (overlapping, 1 H, d, J_{gem} = 9.1 Hz, H3, and 1 H, m, H9), 2.8 (1 H, d, $J_{6,7}$ = 6.3 Hz, H6), 2.2 (1 H, m, H4), 2.1 (3 H, s, CH_3), 2.0 (2 H, d, J = 3.0 Hz, H10-endo and -exo), 1.2 (3 H, d, J = 7.1 Hz, CH_3). HRMS Calcd for $C_{20}H_{19}O_4NFe$ (M^+): 393.0569. Found: 393.0566; *m/e* (%) 393 (0.4), 365 (45), 309 (100).

Tricarbonyl[(hydroxymethyl)-1–4-η-cyclohexa-1,3-diene]iron (50). Diisobutylaluminum hydride (16 equiv, 57.6 mmol, 11.68 mL of a 1.0 M solution in hexanes) was added to a THF solution of tricarbonyl(1-carbomethoxycyclohexa-1,3-diene)iron (1.0 g, 3.6 mmol) in 20 mL of THF at −78 °C. The solution was stirred 2 h, the dry ice–acetone bath was removed and the solution was allowed to stir 16 h at room temperature. The solution was quenched (caution, exothermic; use water bath cooling) by slow addition of H_2O, stirred for 30 min, diluted with ether, and filtered through Celite. The ethereal layer was separated, washed with H_2O, dried over $MgSO_4$, concentrated, and flash chromatographed to yield 900 mg (100%) of pure alcohol **50** as a yellow-orange solid, mp 63–65 °C (lit.[6b] mp 63–64 °C). IR (CCl_4) ν_{max} 3610, 2020, 1980 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.4 (1 H, d, $J_{2,3}$ = 4.0 Hz, H2), 5.1 (1 H, dd, $J_{3,4}$ = 6.35, $J_{3,2}$ = 4.0 Hz, H3), 3.8 (2 H, s, CH_2OH), 3.2 (1 H, m, H4), 1.8–1.6 (4 H, m, H6-endo and -exo, H5-endo and -exo).

Tricarbonyl(1–4-η-((allyloxy)methyl)cyclohexa-1,3-diene)iron (51). Tricarbonyl[1-(hydroxymethyl)cyclohexa-1,3-diene]iron (**50**) (500 mg, 0.002 mmol) was added to a stirring suspension of NaH (1.2 equiv, 0.0024 mol, 57.6 mg) in THF at 0 °C. The solution was stirred for 30 min, after which allyl bromide (freshly distilled, 1.2 equiv, 0.0024 mol, 0.21 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. After residual NaH was destroyed with a few drops of EtOH, the mixture was diluted with ether and filtered through Celite. After the solvent was evaporated, the product was subjected to flash chromatography to give pure allyl ether **51** in 78% yield (450 mg) as a yellow oil. IR (CCl_4) ν_{max} 2015, 1965 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.9 (1 H, m, vinyl), 5.4–5.1 (4 H, m, H2, H3, vinyl), 3.9 (2 H, m, CH_2), 3.7 (1 H, d, $J_{7a,7b}$ = 10.7 Hz, H7a), 3.5 (1 H, d, $J_{7b,7a}$ = 10.7 Hz, H7b), 3.1 (1 H, m, H4), 1.8–1.5 (4 H, series of multiplets, H6-endo and -exo, and H5-endo and -exo).

Tricarbonyl(6–9-η-4-methyl-2-oxaspiro[4.5]deca-6,8-diene)iron (54). Allylic ether **51** (10 mg) was refluxed according to the general procedure to yield 4.0 mg of desired spiroether complex (40%) **54** along with 5.2 mg of starting material and rearranged starting material (pendant olefin isomerization). IR (CCl_4) ν_{max} 2020, 1970 cm^{-1}. The complex was isolated as an inseparable mixture of diastereomers and is reported as such, differentiating between diastereomers when possible. ^1H NMR ($CDCl_3$) δ 5.3 (4 H, m, H7 and H8 for both epimers, A and B), 4.2 (1 H, dd, H3 (A)), 3.9 (1 H, dd, J_{gem} = 8 Hz, $J_{3,4}$ = 5 Hz, H3 (B)), 3.5 (5 H, d + m, d: 2 H, J = 8 Hz, 1 H (A), m: 1 H, H9 (A)), 2.0 (1 H, dd, H6 (A)), 1.8 (1 H, d, H6 (B)), 2.1–1.4 (6 H, series of multiplets, H10-endo and -exo (A + B), H4 (A + B)), 1.1 (3 H, d, J = 7.0 Hz, CH_3 (A)), 0.9 (3 H, d, J = 7.0 Hz, CH_3 (B)). HRMS Calcd for $C_{13}H_{14}O_4Fe$ (M^+): 190.1241. Found: 290.0225; *m/e* (%) 290 (1.2), 262 (29), 234 (33), 206 (55), 149 (100).

Tricarbonyl[1-(1-oxo-4-pentenyl)cyclohexa-1,3-diene]iron (55). Acid **23** (100 mg, 30.38 mmol) was dissolved in 2 mL of CH_2Cl_2. Oxalyl chloride (0.066 mL, 0.75 mmol) was added, and the solution was stirred for 3 h. In a separate flask, Mg turnings (11 mg, 0.45 mmol) and butenyl bromide (0.45 mmol, 0.046 mL) were allowed to react in THF to generate the Grignard reagent. After 0.5 h, the Grignard reagent was added to a solution of CuI (0.23 mmol, 0.44 mg) in THF (3 mL) at 0 °C. This solution was stirred for 15 min, after which a THF solution of the newly formed acid chloride (CH_2Cl_2 and excess oxalyl chloride removed as previously described) was added via syringe. The solution was slowly warmed to room temperature and stirred for 16 h. The solution was quenched with saturated aqueous NH_4Cl and extracted with ether. The ethereal layer was washed with saturated Na_2CO_3 solution, H_2O, and 2 N HCl, dried over $MgSO_4$, and concentrated. Flash chromatography afforded 82 mg (71%) of the desired ketone. IR 2020, 1990, 1705 cm^{-1}. ^1H NMR δ 6.0 (1 H, d, $J_{2,3}$ = 4.4 Hz, H2), 5.8 (1 H, m, H10), 5.3 (1 H, br t, J = 5.5 Hz, H3), 5.0 (2 H, m, H11), 4.1 (2 H, m, H8), 3.4 (1 H, m, H4), 2.4 (2 H, dt, J = 6.7 Hz, H9), 2.2 (1 H, m, 6-endo), 1.9 (1 H, m, 5-endo), 1.6 (1 H, m, 5-exo), 1.4 (1 H, m, 6-exo).

Tricarbonyl(6–9-η-2-oxo-4-methylspiro[4.5]deca-6,8-diene)iron (56). Butenyl ketone derivative **55** (8.7 mg, 0.029 mmol) was heated according to the general procedure to give 1.0 mg (11%) of the desired spiroketone **56** along with 6.0 mg (69%) of recovered starting material and crotyl ketone derivative from rearrangement of the pendant olefin. IR (CCl_4) ν_{max} 2030, 1990, 1720 cm^{-1}. Identifiable NMR resonances are as follows: δ 3.2 (1 H, m, H9), 3.0 (1 H, d, H6), 2.7 (d, H6 for second epimer), 1.1 (d, J = 7 Hz, CH_3 for one diastereomer).

1-Oxo-4-methyl-2-oxaspiro[4.5]deca-6,8-diene (62). The epimeric mixture of optically active spirolactones **25a** generated from optically pure allyl ester complex ($[\alpha]^{25}_D$ −136°) (43.9 mg, 0.09 mmol) was dissolved in 5 mL of benzene and treated with 23 equiv of Me_3NO (2.11 mmol, 158 mg). The solution was stirred at 40 °C for 1 h, after which it was diluted with ether, filtered through Celite, washed with H_2O, and concentrated. (Note: The diene was isolated and characterized, but it was generally used crude to avoid fractionation of diastereomers.) The spirolactones were isolated as a mixture of diastereomers and are presented as such: IR (CCl_4) ν_{max} 1760 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.2 (2 H, m, H8), 5.9 (4 H, m, H7 and H9), 5.5 (2 H, 2d, $J_{6,7}$ = 8.9 Hz, H6), 4.3 (2 H, m, H3), 3.8 (2 H, m, H3), 2.9 (1 H, d, J = 18.2 Hz, H10), 2.5 (1 H, d, J = 15.0 Hz, H10), 2.4–2.1 (4 H, 2 × H10 and 2 × H4), 1.0 (6 H, 2d, J = 6.9 Hz, CH_3).

1-Oxo-4-methyl-2-oxaspiro[4.5]decane (64). The crude demetalated dienes **62** were dissolved in a 1:1 mixture of benzene and MeOH, and the solution was purged with argon. Pd–C (5 mol %) was added and the solution was then purged with hydrogen. The mixture was stirred 28 h under a H_2 atmosphere (H_2-filled balloon) and then diluted with ether, filtered through Celite, washed with H_2O, dried, and concentrated to give the optically active, hydrogenated spiro compound **64** in 93% yield (23.8 mg for both steps) as a colorless oil. $[\alpha]^{25}_D$ −21.25°, 40% ee by NMR. IR (CCl_4) ν_{max} 1760 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.3 (1 H, dd, J_{gem} = 9.0 Hz, $J_{3,4}$ = 6.5 Hz, H3), 3.8 (1 H, dd, J_{gem} = 9.0 Hz, $J_{3',4}$ = 4.9 Hz, H3′), 2.3 (1 H, m, H4), 1.9–1.1 (10 H, m, H6–H10), 1.0 (3 H, d, J = 7.0 Hz, CH_3). HRMS Calcd for $C_{10}H_{17}O_2$ (M + H): 169.1214. Found: 169.1232; *m/e* (%) 169 (100), 123 (20).

1-Oxo-2-phenyl-4-methyl-2-azaspiro[4.5]decane (65). The epimeric mixture of spirolactams, derived from the simple allyl amide complex, was treated in the same way as the spirolactones above to give the hydrogenated lactam **65** in 93% overall yield. IR (CCl_4) ν_{max} 1700 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.6–7.0 (5 H, m, Ph), 3.8 (1 H, dd, J_{gem} = 9.6 Hz, $J_{3,4}$ = 6.7 Hz, H3), 3.2 (1 H, dd, J_{gem} = 9.6 Hz, $J_{3',4}$ = 3.6 Hz, H3′), 2.3 (1 H, m, H4), 1.7–1.2 (10 H, m, H6–H10), 1.0 (3 H, d, J = 7.0 Hz, CH_3). NMR–CSS: ca. 35% ee. H3 doublet splits into two doublets.

Tricarbonyl(1–3-η-carbomethoxy-5-*exo*-deuteriocyclohexa-1,3-diene)iron (66). Sodium borodeuteride (0.25 mmol, 10.6 mg) was added in one portion to a solution of tricarbonyl(η^5-1-carbomethoxycyclohexadienyl)iron hexafluorophosphate (**14**) (100 mg, 0.23 mmol) in dry acetonitrile (5 mL), and the mixture was stirred at room temperature 16 h (long reaction time due to low solubility of $NaBD_4$). The solution was quenched with H_2O, diluted with ether, and separated. The ethereal layer was washed with H_2O, dried over $MgSO_4$, and concentrated to give 59.5 mg (93%) of desired deuterated ester **66** after flash chromatography. IR (CCl_4) ν_{max} 2030, 1985, 1710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.0 (1 H, d, $J_{2,3}$ = 4.3 Hz, H2), 5.3 (1 H, dd, $J_{3,4}$ = 6.4 Hz, $J_{3,2}$ = 4.3 Hz, H3), 3.7 (3 H, s, CO_2Me), 3.3 (1 H, br t, H4 (compared to complicated multiplet in normal spectrum), 2.2 (1 H, br t, H_6-endo (compared to ddd

in normal spectrum)), 1.9 (1 H, m, H5-endo (compared to tt in normal spectrum)), 1.4 (1 H, br dd, H6-exo (compared to ddd in normal spectrum)); missing resonance at 1.6 ppm shows deuterium incorporation into 5-exo position. HRMS Calcd for $C_{11}H_9DO_5Fe$ (M^+): 278.9940. Found: 278.9938; *m/e* (%) 279 (5), 251 (36), 223 (73). No $C_{11}H_{10}O_5Fe$ was detected in the mass spectrum.

Tricarbonyl(1–4-η-carboxy-5-*exo*-deuteriocyclohexa-1,3-diene)iron. A solution of tricarbonyl(1-carbomethoxy-5-deuteriocyclohexa-1,3-diene)-iron (**66**) in MeOH (5 mL) containing KOH (30% solution, 1.5 mL) was stirred at room temperature 16 h. The solution was acidified to pH = 1 with 2 N HCl, poured into ether, and separated. The ethereal layer was washed with H_2O (2 × 50 mL), followed by saturated Na_2CO_3 solution (2 × 50 mL). The sodium carbonate washings were combined and reacidified to pH = 1 with 2 N HCl, poured into ether, and separated. The ethereal layer was then washed with H_2O, dried over $MgSO_4$, and concentrated to afford the acid complex 5-deuterio-**23** as yellow crystals (270 mg, 1.02 mmol, 85%). IR (CCl_4) ν_{max} 2030, 1990, 1670 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.0 (1 H, d, $J_{2,3}$ = 4.4 Hz, H2), 5.4 (1 H, dd, $J_{3,4}$ = 6.4 Hz, $J_{3,2}$ = 4.4 Hz, H3), 3.4 (1 H, m, H4), 2.2 (1 H, dd, J_{gem} = 14.4 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 12.0 Hz, H6-endo (compared to ddd in nondeuterated compound)), 1.9 (1 H, br d, H5-endo (compared to dd)), 1.4 (1 H, dd, J_{gem} = 14.5 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 2.9 Hz, H6-exo (compared to ddd)); missing resonance at 1.6 ppm indicates D labeling. Mass spectrum *m/e* (%) 265 (30), 237 (10), 209 (20), 153 (10), 106 (100); Calcd for $C_{10}H_7DO_5Fe$ (M^+): 264.9783. Found: (M^+) 264.9785. No peak corresponding to $C_{10}H_8O_5Fe$ was detected in the mass spectrum.

Tricarbonyl(allyl 1–4-η-deuteriocyclohexa-1,3-dienecarboxylate)iron (67). The deuterated acid from above (58 mg, 0.22 mmol) was treated with oxalyl chloride (0.44 mmol, 0.038 mL), pyridine (0.44 mmol, 0.018 mL), and allyl alcohol (0.44 mmol, 0.015 mL) as described earlier to afford the desired 5-deuterio allyl ester complex **67** as a yellow oil (57 mg, 85%) after chromatography. IR (CCl_4) ν_{max} 2020, 1980, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.0 (1 H, d, $J_{2,3}$ = 4.4 Hz, H2), 5.8 (1 H, m, vinyl), 5.3 (3 H, m, H3 and vinyl), 4.6 (2 H, m, H9), 3.3 (1 H, m, H4), 2.2 (1 H, dd, J_{gem} = 14.4 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 12.0 Hz, H6-endo (compared to ddd)), 1.9 (1 H, br d, H5-endo (compared to br dd)), 1.4 (1 H, dd, J_{gem} = 14.4 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 2.9 Hz, H6-exo (compared to ddd)); missing resonance at 1.6 ppm.

Tricarbonyl(*N*-allyl-*N*-phenyl-1–4-η-5-*exo*-deuteriocyclohexa-1,3-dienecarboxamide)iron (68). The 5-deuterio acid (53.1 mg, 0.21 mmol) was treated with oxalyl chloride (0.42 mmol, 0.036 mL), pyridine (0.42 mmol, 0.032 mL), and *N*-allylaniline (0.42 mmol, 0.056 mL) as described above to yield 75.8 mg (95%) of desired amide **68** as a yellow viscous oil after chromatography. IR (CCl_4) ν_{max} 2020, 1980, 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (5 H, m, Ph), 5.9 (1 H, m, vinyl), 5.4 (1 H, dd, $J_{2,3}$ = 4.4 Hz, $J_{2,4}$ = 0.9 Hz, H2), 5.0 (3 H, m, H3 and vinyl), 4.4 (1 H, dd, J = 14.6, 5.9 Hz, H9a), 4.1 (1 H, dd, J = 14.6, 6.7 Hz, H9), 3.2 (1 H, m, H4 (simplified multiplet)), 2.1 (1 H, dd, J_{gem} = 13.9 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 12.0 Hz, H6-endo (compared to ddd)), 1.9 (1 H, br m, H5-endo (compared to br dd)), 1.4 (1 H, m, H6-exo (compared to ddd); missing proton at 1.6 ppm. HRMS Calcd for $C_{17}H_{16}DNO_2Fe$ (M − 2CO): 324.0671. Found: 324.0671; *m/e* (%) 324 (19), 296 (100), 240 (12).

Tricarbonyl(*N*-methylallyl-*N*-phenyl-1–4-η-5-*exo*-deuteriocyclohexa-1,3-dienecarboxamide)iron (73). The 5-deuterio acid (50 mg, 0.18 mmol) was treated with oxalyl chloride (0.36 mmol, 0.033 mL), pyridine (0.36 mmol), 0.029 mL), and *N*-methylallylaniline (0.36 mmol, 54 mg) as described to afford 62.1 mg (86.6%) of desired deuterium-labeled methallyl amide **73** as a yellow viscous oil after flash chromatography. IR (CCl_4) ν_{max} 2025, 1980, 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.4–7.2 (5 H, m, Ph), 5.4 (1 H, d, $J_{2,3}$ = 4.5 Hz, H2), 5.0 (1 H, dd, J = 6.4, 4.5 Hz, H3), 4.8 and 4.7 (2 H, 2s, vinyl), 4.4 (1 H, d, J_{gem} = 15 Hz, H9a), 4.2 (1 H, d, J_{gem} = 15 Hz, H9b), 3.2 (1 H, m, H4 (less complicated)), 2.1 (1 H, dd, J = 14, 2.4 Hz, H6-endo (compared to ddd)), 1.9 (1 H, br m, H5-endo), 1.7 (3 H, s, CH_3), 1.3 (1 H, dd, J = 14, 3.5 Hz, H6-exo (compared to ddd)); missing resonance at 1.6 ppm. HRMS Calcd for $C_{19}H_{18}DNO_3Fe$ (M − CO): 366.0777. Found: 366.0778; *m/e* (%) 366 (0.7), 338 (19), 310 (100).

Tricarbonyl(6–9-η-1-oxo-4-methyl-9-deuterio-2-oxaspiro[4.5]deca-6,8-diene)iron (69) and Tricarbonyl(6–9-η-1-oxo-4-methyl-7-deuterio-2-oxaspiro[4.5]deca-6,8-diene)iron (71). Deuterated allyl ester **67** (16 mg, 0.05 mmol) was refluxed according to the general procedure (reflux time = 11 h) to yield 14.0 mg (87.5%) of deuterium-labeled spirolactones **69** and **71** after PLC. IR (CCl_4) ν_{max} 2020, 1980, 1770 cm^{-1}. ^{1}H NMR ($CDCl_3$) for compound **69**: δ 5.5 (2 H, m, H7 and H8 (simplified)), 4.2 (1 H, dd, J_{gem} = 9.2 Hz, $J_{3,4}$ = 6.2 Hz, H3), 3.9 (1 H, dd, J_{gem} = 9.2 Hz, $J_{3',4}$ = 4.9 Hz, H3'), 2.7 (1 H, dd, $J_{6,7}$ = 6.4 Hz, $J_{6,8}$ = 1.4 Hz, H6), 2.2 (1 H, m, H4), 2.1 (1 H, d, J_{gem} = 15.0 Hz, H10-endo (compared to dd)), 1.9 (1 H, d, J_{gem} = 15.0 Hz, H10-exo (compared to dd)), 1.15 (3 H, d, J = 7.1 Hz, CH_3). The resonance at 2.1 ppm (outer diene (C9)) shows ca. 70% reduction in intensity compared to **25a**. ^{1}H NMR ($CDCl_3$) for compound **71**: δ 5.5 (1 H, d, $J_{8,9}$ = 6.8 Hz, H8), 4.5 (1 H, dd, J_{gem} = 9.2 Hz, $J_{3',4}$ = 5.7 Hz, H3'), 3.9 (1 H, d, J_{gem} = 9.2 Hz, H3), 3.4 (1 H, dt, J = 6.6, 2.9 Hz, H9 (compared to complex multiplet)), 2.9 (1 H, s, H6 (compared to d)), 2.3 (1 H, m, H4), 1.9 (2 H, m, H10-endo and H10-exo), 1.0 (3 H, d, J = 7.3 Hz, CH_3). The resonance at 5.3 ppm (inner diene (C7)) showed 70% intensity reduction. HRMS Calcd for $C_{12}H_{11}DO_4Fe$ (M − CO): 277.0147. Found: 277.0142; *m/e* (%) 277 (62), 249 (43), 221 (100).

Tricarbonyl(6–9-η-1-oxo-4-methyl-9-deuterio-2-azaspiro[4.5]deca-6,8-diene)iron (70) and Tricarbonyl(6–9-η-1-oxo-4-methyl-7-deuterio-2-azaspiro[4.5]deca-6,8-diene)iron (72). Deuterium-labeled allyl amide **68** (29 mg, 0.076 mmol) was refluxed according to the general procedure to give 26.1 mg (90%) of deuterium-labeled spirolactams after PLC. IR (CCl_4) ν_{max} 2020, 1980, 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) for compound **70**: δ 7.6–7.1 (5 H, m, Ph), 5.5 (2 H, m, H7 and H8 (simplified)), 3.8 (1 H, dd, J_{gem} = 9.8 Hz, $J_{3,4}$ = 6.8 Hz, H_3), 3.4 (1 H, dd, J_{gem} = 9.8 Hz, $J_{3',4}$ = 5.3 Hz, H3β), 2.8 (1 H, dd, $J_{6,7}$ = 6.3 Hz, $J_{6,8}$ = 1.6 Hz, H6), 2.2 (1 H, m, H4), 2.0 (1 H, d, J_{gem} = 15.0 Hz, H10-endo (compared to dd)), 1.9 (1 H, d, J_{gem} = 15.0 Hz, H10-exo (compared to dd)), 1.2 (3 H, d, J = 7.0 Hz, CH_3). Reduced intensity (ca. 70% reduction) for the resonance at 3.2 ppm (outer diene (C9)). ^{1}H NMR ($CDCl_3$) for compound **72**: δ 7.6–7.1 (5 H, m, Ph), 5.5 (1 H, dd, $J_{8,9}$ = 6.5 Hz, $J_{8,6}$ = 1.3 Hz, H8), 4.2 (1 H, dd, J_{gem} = 10.0 Hz, $J_{3',4}$ = 6.2 Hz, H3'), 3.4 (2 H, m + d; m: 1 H, H9; d: J_{gem} = 10.0 Hz, H3), 3.0 (1 H, d, $J_{6,8}$ = 1.3 Hz, H6 (compared to dd)), 2.4 (1 H, m, H4), 2.0 (2 H, d, J = 2.9 Hz, H10-endo and H10-exo), 1.0 (3 H, d, J = 7.1 Hz, CH_3). Reduced intensity for the resonance at 5.3 ppm (inner diene (C7)). HRMS Calcd for $C_{19}H_{16}DNO_4Fe$ (M^+): 380.0569. Found: 380.0566; *m/e* (%) 380 (1), 352 (56), 324 (20), 296 (100), 240 (15).

Tricarbonyl(6–9-η-1-oxo-4,4-dimethyl-9-deuterio-2-azaspiro[4.5]deca-6,8-diene)iron and Tricarbonyl(6–9-η-1-oxo-4,4-dimethyl-7-deuterio-2-oxaspiro[4.5]deca-6,8-diene)iron (74). Deuterium-labeled methallyl amide **73** (20 mg, 0.051 mmol) was refluxed according to the general procedure to yield 18.4 mg (0.045 mmol, 92%) of deuterium-labeled spirolactam **74** after PLC. ^{1}H NMR showed 0.5 deuterium atom on the outer diene (C9) and 0.5 deuterium atom on the inner diene (C7). Inner diene resonances at δ 5.5 and 5.2 integrate 1:1 (H8 and H7) for complex **27c**. Here they integrate 1.5:1, signifying deuterium at C7 as shown. A similar situation obtains for H6 and H9. HRMS Calcd for $C_{19}H_{18}DNO_3Fe$ (M − CO): 366.0777. Found: 366.0778; *m/e* (%) 366 (1), 338 (19), 310 (100).

(−)-Tricarbonyl(1–4-η-1-carbomethoxy-5-cyanocyclohexa-1,3-diene)-iron (76). Procedure 1. Optically pure tricarbonyl(1-carbomethoxy-cyclohexadienyl)iron hexafluorophosphate (**14**) ($[\alpha]^{25}_D$ −49.2°, 50 mg, 0.12 mmol) was dissolved in 5 mL of CH_3CN and treated with NaCN (7.0 mg, 0.142 mmol) dissolved in 0.5 mL of water. The solution was stirred overnight, diluted with ether, and filtered through a Celite–neutral alumina pad. The ethereal solution was washed with H_2O, dried over $MgSO_4$, and concentrated to give after flash chromatography optically pure nitrile **76** as a viscous yellow oil (28 mg, 78%) ($[\alpha]^{25}_D$ −78°, acetone, *c* 1.5). **Procedure 2.**[20] Five molar equivalents (5.93 mmol, 0.790 mL) of trimethylsilyl cyanide was added to a stirring solution of (−)-**14** (500 mg, 1.19 mmol) in CH_3CN (10 mL) at room temperature. The solution turned from yellow to orange and after 3 h the reaction was complete. The reaction was quenched with H_2O, and the solution turned dark green. This solution was extracted with ether (2 × 20 mL) to afford a yellow ethereal solution, which was dried over $MgSO_4$ and filtered through Celite impregnated with 10 g of neutral alumina to give after concentration and flash chromatography 281 mg (78%) of the pure cyano-substituted ester **76** as a yellow viscous oil. IR (CCl_4) ν_{max} 2220, 2020, 1990, 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.2 (1 H, d, $J_{2,3}$ = 4.4 Hz, H2), 5.5 (1 H, dd, $J_{3,4}$ = 5.9 Hz, $J_{3,2}$ = 4.8 Hz, H3), 3.7 (3 H, s, CO_2Me), 3.2 (1 H, m, H4), 3.0 (1 H, dt, J ≈ 11.8, 3.6 Hz, H5-endo), 2.5 (1 H, dd, J_{gem} = 15.6 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 11.8 Hz, H6-endo), 1.8 (1 H, dd, J_{gem} = 15.6 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 3.5 Hz, H6-exo). HRMS Calcd for $C_{12}H_9O_5NFe$ (M^+): 303.9849. Found: 303.9870; *m/e* (%) 303 (0.36), 277 (100), 249 (27), 221 (0.6), 192 (6).

(−)-Tricarbonyl(1–4-η-1-carbomethoxy-5-*exo*-phenylcyclohexa-1,3-diene)iron (77). Cuprous iodide (0.03375 g, 0.1178 mmol) was dissolved in THF and cooled to 0 °C. Phenyllithium in ether (2.0 equiv, 0.356 mmol) was added dropwise until dissolution of the CuI was complete. The solution was cooled to −78 °C and 75 mg (0.178 mmol) of solid

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(−)-**14** was admitted at once. The solution was stirred for 25 min, after which time all the complex had dissolved. The solution was then poured into a beaker containing ether and saturated NH_4Cl solution and stirred 15 min. The ethereal layer was washed with H_2O, dried ($MgSO_4$), and evaporated. Flash chromatography gave **77** (80.9 mg) in 96.4% yield as a yellow oil. ($[\alpha]^{24}_D$ −117°, acetone, *c* 1). IR (CCl_4) ν_{max} 2025, 1980, 1705 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.3–7.1 (5 H, Ph), 6.62 (1 H, d, $J_{2,3}$ = 4.3 Hz, H2), 5.5 (1 H, dd, $J_{3,4}$ = 6.3 Hz, $J_{3,2}$ = 4.4 Hz, H3), 3.7 (3 H, s, CO_2Me), 3.5 (1 H, dt, *J* = 11.4, 3.7 Hz, H5-endo), 3.3 (1 H, m, H4), 2.8 (1 H, dd, J_{gem} = 15.4 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 12.2 Hz, H6-endo), 1.5 (1 H, dd, J_{gem} = 15.4 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 4.3 Hz, H6-exo). HRMS Calcd $C_{17}H_{14}O_5Fe$ (M^+): 354.0190. Found: 354.0194; *m/e* (%) 354 (10), 326 (38), 298 (40), 270 (20), 210 (100).

(−)-**Tricarbonyl(1–4-η-carbomethoxy-3-phenylcyclohexa-1,3-diene)iron (78).** Optically pure **77** (100 mg, 0.28 mmol) was heated according to the general ring-closure procedure (reflux time = 6 h) to afford the rearranged 3-phenyl-substituted carbomethoxy derivative **78** in 83% yield (83 mg) after flash chromatography as a yellow viscous oil ($[\alpha]^{25}_D$ −18.5°). IR (CCl_4) ν_{max} 2030, 1995, 1710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.6–7.2 (5 H, m, Ph), 6.4 (1 H, s, H2), 3.9 (1 H, m, H4), 3.7 (3 H, s, CO_2Me), 2.2–1.4 (4 H, series of multiplets, H6 and H5). HRMS Calcd for $C_{17}H_{14}O_4Fe$ (M^+): 354.0190. Found: 354.0176; *m/e* (%) 354 (14), 326 (38), 298 (48.5), 270 (26), 214 (35), 210 (100).

(−)-**Tricarbonyl[(*N*-allyl-*N*-phenylcarbamoyl)-1–5-η-cyclohexa-1,3-dienylium]iron Hexafluorophosphate (79).** In a clean, flame-dried, three-neck, round-bottom flask a methylene chloride solution (10 mL) of the optically pure *N*-allyl-*N*-phenyl amide complex (+)-**26a** (123 mg, 0.36 mmol, $[\alpha]^{25}_D$ +136, acetone, *c* 3) was treated with triphenylmethyl hexafluorophosphate (170 mg, 0.44 mmol), and the solution was stirred 16 h. The tan solution was poured into a beaker containing 150 mL of stirred wet ether to allow the precipitation of the hydride abstraction product. The solution was filtered through a Büchner funnel, and the precipitate was washed thoroughly with ether. Reprecipitation from dichloromethane/ether twice following a similar procedure gave 167 mg (89%) of the desired salt **79** as a pale yellow powder ($[\alpha]^{25}_D$ −90.6°, acetone, *c* 1). IR (CCl_4) ν_{max} 2110, 2065, 1995, 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.4 (5 H, m, Ph), 7.0 (1 H, br t, *J* = 5.3 Hz, H3), 6.2 (1 H, d, *J* = 5.8 Hz, H2), 5.8 (1 H, m, vinyl), 5.6 (1 H, br t, *J* = 5.3 Hz, H4), 5.1 (2 H, vinyl), 4.5 (1 H, dd, *J* = 15.2, 5.2 Hz, H9), 4.1 (1 H, t, H5), 2.6 (1 H, dd, *J* = 15, 6.5 Hz, H6-endo), 0.6 (1 H, d, *J* = 15 Hz, H6-exo). Anal. Calcd for $C_{19}H_{16}O_4NFePF_6$: C, 43.63; H, 3.16; N, 2.68. Found: C, 43.78; H, 3.26; N, 2.58.

(+)-**Tricarbonyl(*N*-allyl-*N*-phenyl-1–4-η-5-*exo*-cyanocyclohexa-1,3-dienecarboxamide)iron (80).** Optically pure **79** (150 mg, 2.87×10^{-4} mol) was added to a clean, flame-dried, three-neck, round-bottom flask fitted with an N_2 bubbler and rubber septa and dissolved into CH_3CN (5 mL) under an inert atmosphere. To the stirring solution was added NaCN (1.1 equiv, 15.75 mg, 3.25×10^{-4} mol) in water (0.1 mL) at room temperature. The reaction was monitored by IR and after 3 h was complete. The product mixture was diluted with H_2O and Et_2O and transferred to a separatory funnel. The ethereal layer was removed, washed with water, dried over $MgSO_4$, and concentrated. Flash chromatography afforded the desired amide **80** in 87% yield (96.9 mg) ($[\alpha]^{25}_D$ +9.4°, acetone, *c* 3). IR (CCl_4) ν_{max} 2220, 2030, 1990, 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.5–7.1 (5 H, m, Ph), 5.9 (1 H, m, vinyl), 5.4 (1 H, d, $J_{2,3}$ = 4.9 Hz, H2), 5.1 (3 H, m, vinyl and H3), 4.7–4.1 (2 H, m, H9), 3.0 (1 H, m, H4), 2.6 (1 H, dd, J_{gem} = 15 Hz, $J_{6\text{-endo},5\text{-endo}}$ = 7.2 Hz, H6-endo), 2.1 (1 H, dd, $J_{5\text{-endo},6\text{-endo}}$ = 7.2 Hz, $J_{5\text{-endo},4}$ = 1.3 Hz, H5-endo), 1.7 (1 H, dd, J_{gem} = 15 Hz, $J_{6\text{-exo},5\text{-endo}}$ = 3.5 Hz, H6-exo). HRMS Calcd for $C_{17}H_{16}ON_2Fe$ (M − 3CO): 320.0609. Found: 320.0614; *m/e* (%) 320 (4), 237 (2.5), 105 (100).

(+)-(**4*S*,5*S*,6*R*,9*S***)-**Tricarbonyl(6–9-η-1-oxo-2-phenyl-4-methyl-9-cyano-2-azaspiro[4.5]deca-6,8-diene)iron (81).** The optically pure cyano-substituted allyl amide complex (+)-**80** (16 mg, 0.04 mmol) was refluxed according to the general procedure (reflux time = 6.5 h) to yield cyano-substituted spirolactam **81** in 84% yield (13.4 mg) as a yellow viscous oil after PLC ($[\alpha]^{25}_D$ +96.7°, acetone, *c* 1). IR (CCl_4) ν_{max} 2205, 2025, 1995, 1700 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.6–7.1 (5 H, m, phenyl), 5.9 (1 H, d, $J_{8,7}$ = 4.0 Hz, H8), 5.6 (1 H, dd, $J_{7,6}$ = 6.8 Hz, $J_{7,8}$ = 4.0 Hz, H7), 3.9 (1 H, dd, J_{gem} = 9.9 Hz, $J_{3,4}$ = 6.5 Hz, H3), 3.4 (1 H, dd, J_{gem} = 9.9 Hz, $J_{3',4}$ = 4.4 Hz, H3′), 3.0 (1 H, dd, $J_{6,7}$ = 6.8 Hz, $J_{6,8}$ = 1.0 Hz, H6), 2.3 (1 H, m, H4), 2.0 (1 H, d, J_{gem} = 14.5 Hz, H10-endo), 1.9 (1 H, d, J_{gem} = 14.5 Hz, H10-exo), 1.3 (3 H, d, *J* = 7.0 Hz, CH_3). HRMS Calcd for $C_{20}H_{16}O_3N_2Fe$ (M^+): 404.0459. Found: 404.0488; *m/e* (%) 404 (0.7), 376 (6.3), 348 (7), 320 (100), 264 (8).

Tricarbonyl(1–4-η-*N*-allyl-*N*-phenyl-3-phenylcyclohexa-1,3-dienecarboxamide)iron (83). 3-Phenyl-substituted acid **82** from the hydrolysis of **78** (48 mg, 0.14 mmol) was treated with oxalyl chloride (0.282 mmol, 0.025 mL), pyridine (0.282 mmol, 0.011 mL), and *N*-allylaniline (0.282 mmol, 0.019 mL) as described above (formation of the acid chloride required 6 h) to give 56.7 mg (89%) of the desired 3-phenyl-substituted allyl amide **83** as a yellow viscous oil after flash chromatography. IR (CCl_4) ν_{max} 2020, 1985, 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.5–7.2 (10 H, m, 2Ph), 6.0 (1 H, s, H2), 5.9 (1 H, m, vinyl), 5.1 (2 H, m, vinyl), 4.5 (1 H, dd, J_{gem} = 14.5 Hz, $J_{9,10}$ = 6.0 Hz, H9), 4.1 (1 H, dd, J_{gem} = 14.6 Hz, $J_{9',10}$ = 6.8 Hz, H9′), 3.7 (1 H, d, $J_{4,2}$ = 1.8 Hz, H4), 2.0–1.2 (4 H, H6-endo and -exo, H5-endo and -exo). HRMS Calcd for $C_{23}H_{21}O_2NFe$ (M − 2CO): 399.0913. Found: 399.0925; *m/e* (%) 399 (0.3), 371 (6.7), 313 (41), 153 (100).

Tricarbonyl(6–9-η-1-oxo-4-methyl-7-phenyl-2-azaspiro[4.5]deca-6,8-diene)iron (84). 3-Phenyl-substituted allylic amide **83** (16.3 mg, 0.036 mmol) was heated according to the general procedure (reflux time = 8 h) to afford 13.6 mg (84%) of the desired 7-phenyl-substituted spirolactam **84** after PLC. IR (CCl_4) ν_{max} 2040, 1970, 1700 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.6–7.2 (10 H, m, 2Ph), 5.8 (1 H, d, $J_{8,9}$ = 6.4 Hz, H8), 3.8 (1 H, dd, J_{gem} = 9.8 Hz, $J_{3,4}$ = 6.6 Hz, H3), 3.5 (1 H, dd, J_{gem} = 9.8 Hz, $J_{3',4}$ = 4.6 Hz, H3′), 3.2 (2 H, d + m, d: 1 H, $J_{6,8}$ = 1.6 Hz, H6; m: 1 H, H9), 2.3 (1 H, m, H4), 2.1 (1 H, dd, J_{gem} = 15.0 Hz, $J_{10\text{-endo},9}$ = 1.7 Hz, H10-endo), 1.9 (1 H, dd, J_{gem} = 15.0 Hz, $J_{10\text{-exo},9}$ = 3.0 Hz, H10-exo), 1.3 (3 H, d, *J* = 7.0 Hz, CH_3). HRMS Calcd for $C_{24}H_{21}O_3NFe$ (M − CO): 427.0870. Found: 427.0860; *m/e* (%) 427 (3.8), 399 (4.8), 371 (100), 315 (17).

Me_3NO-Inititated Spirocyclization Reaction. *N*-Allyl-*N*-phenyl amide complex **26a** was dissolved in freshly distilled CH_3CN under an inert atmosphere. Dry Me_3NO (1.7 equiv) was added and the reaction was stirred at room temperature and monitored by IR. After 15 min, carbonyl bands at 2220 and 1995 cm^{-1} (starting material $Fe(CO)_3$) were replaced by new carbonyl bands at 1980 and 1915 cm^{-1}, indicating the disappearance of $Fe(CO)_3$ species and the presence of newly formed $Fe(CO)_2L$ complex (L = Me_3N or CH_3CN). The solution was then warmed to 55 °C and the reaction was monitored by IR to completion (8 h). Infrared spectroscopy recorded the slow formation of the desired spirolactam signal at 1700 cm^{-1} and concomitant reduction in amide signal at 1630 cm^{-1}. The spectra also showed *no* new formation of diene–*Fe(CO)*$_3$ species during the course of the reaction. Once complete, the solvent was removed in vacuo and replaced with freshly distilled benzene. Carbon monoxide was bubbled into the product mixture for 6 h, after which the solution was filtered through Celite and concentrated. The desired spirolactam ($Fe(CO)_3$) complex **27a** was isolated in 65% yield along with decomplexed spirolactam and decomplexed starting material.

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Supplementary Material Available: Details of preparation and characterization of compounds **24c–k**, **25e**, **26b–d**, **27b–d**, **29b**, **31**, **32**, **34b**, **37**, **44b,c**, **46**, **47**, **48b,c**, **52**, **53**, **85**, **86**, **87**, and all aminocyclopentene derivatives, as well as details of experiments using optically pure complexes (19 pages). Ordering information is given on any current masthead page.