through Celite and the filtrate was concentrated to give the lactam **9** (0.16 g, 96%): IR γ_{max} (CCl_4) 1745 (CO_2CH_3), 1710 (NC=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.2 (1 H, m, NCH), 3.7 (3 H, s, CO_2CH_3), 2.8 (2 H, unsym d, J = 6 Hz, CH_2C=O); ^{13}C NMR ($CDCl_3$) δ 174.25, 172.37, 62.89, 52.04, 41.78, 40.02, 36.25, 27.48, 26.12; exact mass calcd for $C_9H_{13}NO_3$ 183.0892, found 183.0895 (M^+).

Reduction of Lactam Ester 9. To a solution of **9** (0.1 g, 0.55 mmol) in anhydrous THF (5 mL) was added lithium aluminium hydride (0.06 g, 1.5 mmol), and the system was heated under reflux for 18 h. Then, we added successively, water (60 μL), 15% aqueous sodium hydroxide (60 μL), and water (180 μL). Evaporation of volatiles left a residue which was leached with ether and the resulting solution was dried ($MgSO_4$). Evaporation and purification on alumina gave **1** (0.07 g, 92%) as a yellow oil: picrate mp 188–189 °C (lit.[11] mp 188–189 °C).

Registry No. (±)-**1**, 18929-90-3; **6**, 94500-38-6; (±)-**7** (isomer 1), 94500-39-7; (±)-**7** (isomer 2), 94500-40-0; **8**, 56783-09-6; (±)-**9**, 93264-55-2; *N*-acetylpyrrolidine, 4030-18-6; methyl oxalate, 553-90-2.

Model Reactions for Sterically Controlled Syntheses of Cyclohex-2-enones with 4,4- or 5,5-Quaternary Centers: A Direct Chiral Synthesis of 4-Allyl-4-cyanocyclohex-2-enone from the Anion of (+)-Tricarbonyl(5-cyano-2-methoxycyclohexa-1,3-diene)iron

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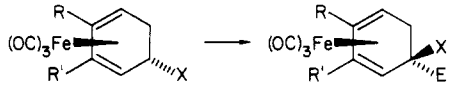
The temporary π-attachment of complexed transition metals to olefinic double bonds results in forms of activation and steric control (lateral control) in organic synthesis differing from those achievable by classical functional groups attached by σ-bonds to the skeleton of a molecule (endogenous control). In particular, steric[1] and chiral[2] formations of new bonds can be directed.

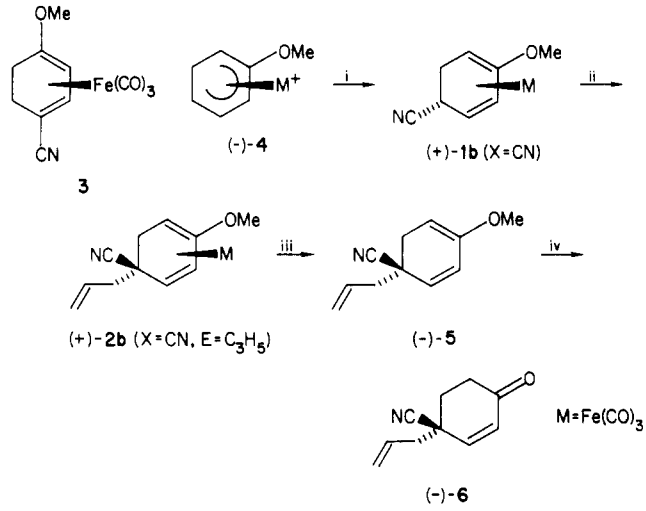
A new type of synthetic capability provided here is the stereospecific protonation of some (cyclohexadienyl)Fe(CO)$_3$ anions or alkylation of these to produce a quaternary center. In these derivatives formation of the carbanion is permitted in the classical manner by endogenous activation due to CN, SO_2Ar, or CO_2Me (eq 1).[3,4] The steric



(1)

1a, R=R'=H
b, R=OMe; R'=H
c, R=H; R'=OMe

Scheme I[a]



[a] (i) KCN; (ii) LDA, C_3H_5Br; (iii) Me_3NO, $(Me)_2NCOMe$, 70 °C, 0.5 h; (iv) Amberlyst (H^+) Resin, Et_2O, 45 min.

effect of a bulky complexing group such as Fe(CO)$_3$ on one face of the molecule is similar to that already demonstrated for the reduction of a carbonyl[1,5] and for the reactions of related cyclohexadienyl cations.[1] A new feature is that regiospecific electrophilic attack is achieved (Table I) in the same situation as that defined by the position of initial nucleophilic attack of cyanide on the substituted cation complex.

The expected[6] α (exo) direction of attack for carbon electrophiles is supported in this series by the identity of the product of methylation of **1a** (X = CO_2Me) with the known[7] compound **2a** (E = Me, X = CO_2Me, entry 6). The kinetic products of α (exo) protonation or deuteration of the anions correspondingly have the CN β (endo) to the Fe(CO)$_3$, as supported by NMR spectra[8] and nonidentity with the α-isomer. This is a novel method of forming these β-isomers in steric purity following initial 5-β (endo) hydrogen removal from the 5α-CN precursor.

In the 2-OMe series (b; X = CN, entries 8 and 9) partial isomerization occurs to form the more stable complex **3**, which itself is resistant to proton loss under the conditions of reaction. Nevertheless, the process remains a useful one, producing in this series, as shown below, 4,4-disubstituted cyclohex-2-enones. The isomerization side reaction is apparently restricted to the 2-OMe derivatives since no similar reaction is observed in the related 3-OMe structures (compare entries 8 and 11).

It is significant that when the anion derived from **1b** (X = CN) is reacted at −70 °C with benzaldehyde, an immediate color change from red to yellow is seen and the

(1) Birch, A. J.; Bandara, B. M. R.; Chamberlain, K.; Chauncy, B.; Dahler, P.; Day, A. I.; Jenkins, I. D.; Kelly, L. F.; Khor, T. C.; Kretschmer, G.; Liepa, A. J.; Narula, A. S.; Raverty, W. D.; Rizzardo, E.; Sell, C.; Stephenson, G. R.; Thompson, D. J.; Williamson, D. H. *Tetrahedron* **1981**, *37*, Woodward Special Issue, 289.

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

(3) An entirely different set of processes operate when the complex without the activating group (e.g., **1a**, X = H) is treated with lithium bases, see: M. F. Semmelhack, M. F.; Harndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15 and references therein.

(4) A case can be made for relating this process to the phosphonium salt analogue reported by Lewis (e.g., **1a**, X = Ph_3P^+). However, the products of the reaction are structurally different and also the Wittig procedure described is limited to aldehydes. Hackett, P.; Johnson, B. F. G.; Lewis, J.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 1247.

(5) Barton, D. H. R.; Patin, H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 829. Lee, C. C.; Demchuk, D. J.; Gill, N. S.; Sutherland, R. G. *J. Organomet. Chem.* **1983**, *247*, 71.

(6) The direction of attack was expected to be the same as that observed in the related cyclohexadienyliron cation series (ref 1). There is some evidence to suggest that electrophiles approach the cycloheptatrienyliron anion from the exo direction (Moll, M.; Wurstl, P.; Behrens, H.; Merbach, P. *Z. Naturforsch.* **1978**, *33B*, 1304), while tricarbonylcyclohexadienylmanganese anion reacts with methyl iodide to give endo-methylated derivatives (Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989). In the present series α-attack of the electrophile is supported by correlation with a known compound (ref 7) and by comparison of physical and spectral properties of **2b** (E = Me, X = CN) with its reported C-5 epimer (Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 339).

(7) Bandara, B. M. R.; Birch, A. J.; Chauncy, B.; Kelly, L. F. *J. Organomet. Chem.* **1981**, *208*, C31.

(8) Bandara, B. M. R.; Birch, A. J.; Raverty, W. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1745.

0022-3263/85/1950-0712$01.50/0

Table I

entry	starting materials[a]	X	electrophile	product	yield, %
1	1a/LDA	CN	H_2O or ^2H_2O	2a, X = CN; E = H or ^2H	85
2	1a/LDA	CN	MeI	2a, X = CN; E = Me	68
3	1a/LDA	CN	CH_2=$CHCH_2Br$	2a, X = CN; E = C_3H_5	70
4	1a/LDA	CN	PhCHO	2a, X = CN; E = CH(OH)Ph	63[c]
5	1a/LDA	CN	CH_2=CHCN	2a, X = CN; E = CH_2CH_2CN	25
6	1a/LDA	CO_2Me	MeI	2a, X = CO_2Me; E = Me	66
7	1a/BuLi/TMEDA	SO_2-p-Tol	MeI	2a, X = SO_2-p-Tol; E = Me	82
8	1b/LDA	CN	MeI	2b, X = CN; E = Me	55[d]
9	1b/LDA	CN	CH_2=$CHCH_2Br$	2b, X = CN; E = C_3H_5	56[d]
10	1b/LDA	CN	PhCHO	2b, X = CN; E = CH(OH)Ph	65[e]
11	1c/LDA	CN	MeI	2c, X = CN; E = Me	66
12	1c/LDA	CN	PhCHO	2c, X = CN; E = CH(OH)Ph	58[f]

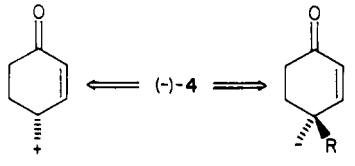
[a] 1.1 equiv of base/THF/−70 °C, 0.5 h; then electrophile −70 °C to room temperature. [b] ca. 10–15% starting material generally recovered. [c] 2:1 mixture of diastereomers (separated). [d] ca. 35% 3 isolated. [e] 1:1 mixture of diastereomers (^1H NMR). [f] 4:1 mixture of diastereomers (separated).

isomerization product 3 is not formed (entry 10). However, when the same anion is treated with MeI (entry 8), a color change only occurs upon warming the mixture from −70 °C to room temperature. In this latter case complex 3 is also formed. Diisopropylamine, present from the initial exchange between the complex and LDA, may be the proton source necessary for the isomerization side reaction since treatment of the anion from **1b** (X = CN) with diisopropylamine results in complete conversion of starting complex into 3.

The 3-OMe series **1c** similarly produces 5,5-disubstituted cyclohex-2-enones. The precursor cation (see Experimental Section) in this case is symmetrical, so a resolved center cannot be formed unless there is a further substituent to render the complex asymmetric.

The synthetic importance of the reactions is that they result in a quaternary carbon (which is optically active if the original complex was resolved) carrying two functional groups attached to a specifically substituted cyclohexadiene ring. In particular, the 2-OMe series **1b** gives rise, after removal of $Fe(CO)_3$ and hydrolysis, to 4,4-disubstituted cyclohex-2-enones. For example, introduction of allyl into optically pure[9] (−)-4 using allyl bromide resulted, after removal of $Fe(CO)_3$ with Me_3NO and mild acid treatment, in the cyclohex-2-enone 6 of the absolute configuration shown (Scheme I).[10]

That the analogous cation procedure based on 4 is synthetically equivalent to the availability of cyclohex-2-enones with a chiral 4-cation (e.g., 7) for bond formation



7 8

has been noted.[1] This procedure provides a similar 4-anion equivalent 8 in the set with R = CN, SO_2Ar, or CO_2R'.[11] It also provides from **1c** the synthetic equivalent of a set of cyclohex-2-enone 5-anions.

The sequence complements the widely used synthetic alkylations of the carbanions from dihydrobenzoic acids, shown to occur adjacent to CO_2H.[12] That process is not chiral, and unlike the present one, is based on Birch reduction of benzoic acids, which prohibits the presence of oxygen para to CO_2H and therefore the direct production of carboxylic analogues of 6. The present procedure depends on the initial reduction of benzenes providing a wide range of possible complexes.

Experimental Section

General Methods. All chromatographic separations were performed on Merck silica gel (At. 7734) using 15% ethyl acetate in hexane as solvent system. Optical rotations were obtained for 0.1% solutions in chloroform and ^1H NMR spectra were recorded for deuteriochloroform solutions. Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl. Ether refers to diethyl ether.

Preparation of Starting Materials. The nitriles **1a** (X = CN) and **1b** (X = CN) were prepared in yields substantially improved over existing procedures. Details are given below for tricarbonyl(1α-cyano-3-methoxycyclohexa-2,4-diene)iron (1c; X = CN). The ester **1a** (X = CO_2Me) was prepared according to the published method.[13]

Tricarbonyl(1α-cyano-3-methoxycyclohexa-2,4-diene)iron (1c; X = CN). An aqueous solution of potassium cyanide (1 g in 2–3 mL) was added dropwise to a solution of tricarbonyl(3-methoxycyclohexadienyl)iron hexafluorophosphate[14] (4 g) in acetonitrile (30 mL) at 0 °C. After 15 min the solution was diluted with ether (60 mL) and poured into H_2O. Extractive workup with ether gave a yellow solid which was purified by chromatography, 94%; mp 45–46 °C; NMR 5.21 (dd, J = 7, 2 Hz, 1 H), 3.68 (s, 3 H), 3.35 (m, 1 H), 2.95 (m, 1 H), 2.7 (m, 1 H), 1.9 (m, 2 H); IR 2230, 2055, 1990; MS, m/e (relative intensity) 275 (M, 9), 247 (24), 219 (20), 191 (21), 164 (100). Anal. Calcd for $C_{11}H_9FeNO_4$: C, 48.04; H, 3.30; Fe, 20.30; N, 5.08. Found: C, 47.83; H, 3.33; Fe, 20.03; N, 5.11.

Tricarbonyl[1α-[[(4-methylphenyl)sulfonyl]oxy]cyclohexa-2,4-diene]iron (1a; X = SO_2-p-C_6H_4Me). Addition of sodium p-toluenesulfinate (3 g) to a stirred solution of tricarbonylcyclohexadienyliron hexafluorophosphate (5 g in 50 mL of acetonitrile) caused a color change from orange to yellow. After 15 min the IR spectrum showed only neutral complex. The solution was poured into H_2O and extracted with ether. Workup and then chromatography gave the pure sulfone, 96%; mp 141–142 °C; NMR 7.7 (d, J = 8 Hz, 2 H), 7.3 (d, J = 8 Hz, 2 H), 5.45 (m, 2 H), 3.5 (m, 1 H), 3.1 (m, 1 H), 2.85 (m, 1 H), 2.43 (s, 3 H), 2.1 (m, 2 H); IR 2060, 1990; MS, m/e (relative intensity) 374 (M, 0), 290 (5), 219 (62), 212 (66), 135 (100). Anal. Calcd for $C_{16}H_{14}FeO_5S$: C, 51.36; H, 3.77; Fe, 14.92; S, 8.57. Found: C, 51.15; H, 3.70; Fe, 14.62; S, 8.35.

General Alkylation Procedure. To a stirred solution of LDA (1.1 mmol) in THF (8 mL) at −70 °C was added, dropwise via

(9) Bandara, B. M. R.; Birch, A. J.; Kelly, L. F.; Khor, T. C. *Tetrahedron Lett.* **1983**, *24*, 2491.
(10) For an alternative approach to optically active 4,4-disubstituted cyclohex-2-enones, see: Otani, G.; Yamada, S. *Chem. Pharm. Bull.* **1973**, *210*, 2125 (and references therein).
(11) For a summary of other approaches, see: Kinney, W. A.; Grouse, G. D.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4986.
(12) Birch, A. J. *J. Chem. Soc.* **1950**, 1551.
(13) Nametkin, N. S.; Tyurin, V. D.; Slupchin'sky, M.; Al-laddaui, M. N. *J. Organomet. Chem.* **1978**, *154*, 289.
(14) Birch, A. J.; Kelly, L. F.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1006. Kelly, L. F.; Dahler, P.; Narula, A. S.; Birch, A. J. *Tetrahedron Lett.* **1981**, *22*, 1433.

syringe, a THF solution of the appropriate nitrile **1a–c** (X = CN) or the ester **1a** (X = CO_2Me) (1 mmol in 5 mL) to produce a deep-red solution. After stirring 30 min, an excess of electrophile was added, and the solution was allowed to warm to room temperature. (In the case of benzaldehyde the red color was quenched immediately and so only sufficient was added to produce a yellow solution.) The pale yellow/orange solution was poured into H_2O containing 5 mL of dilute HCl and extracted with ether. Workup and chromatography gave the materials in the yields listed in Table I.

Tricarbonyl(1β-cyano-1α-methylcyclohexa-2,4-diene)iron (2a; X = CN, E = Me): mp 56–58 °C (hexane); NMR 5.4 (m, 2 H), 3.1 (m, 2 H), 2.45 (dd, J = 16, 4 Hz, 1 H), 1.75 (dd, J = 16, 2 Hz, 1 H), 1.37 (s, 3 H); IR 2245, 2060, 1995; MS, m/e (relative intensity) 259 (M, 4), 231 (12), 203 (13), 175 (15), 147 (100). Anal. Calcd for $C_{11}H_9FeNO_3$: C, 51.0; H, 3.5; N, 5.41; Fe, 21.56. Found: C, 51.29; H, 3.52; N, 5.33, Fe, 21.36.

Tricarbonyl[1β-cyano-1α-(2-propenyl)cyclohexa-2,4-diene]iron (2a; X = CN, E = C_3H_5): mp 64–66 °C; NMR 5.95–5.6 and 5.5–5.0 (m, 5 H), 3.1 (m, 2 H), 2.22 (m, 3 H), 1.82 (dd, J = 16, 2 Hz, 1 H); IR 2240, 2065, 1990; MS, m/e (relative intensity) 285 (M^+, 6), 257 (14), 229 (30), 201 (37), 173 (100). Anal. Calcd for $C_{13}H_{11}FeNO_3$: C, 54.78; H, 3.89; Fe, 19.59; N, 4.91. Found: C, 55.02; H, 3.74; Fe, 19.26; N, 4.71.

Tricarbonyl[1β-cyano-1α-(phenylhydroxymethyl)cyclohexa-2,4-diene]iron (2a; X = CN, E = $CH(OH)C_6H_5$). First diastereomer (minor), oil, MNR 7.3 (m, 5 H), 5.3 (m, 2 H), 4.26 (s, 1 H), 3.15 (m, 2 H after D_2O exchange), 2.04 (m, 2 H); second diastereomer (major), oil, NMR 7.4 (m, 5 H), 5.3 (m, 2 H), 4.02 (s, 1 H), 3.12 (m, 1 H), 2.35 (m, 3 H), 2.1 (br, 1 H, exchanges with D_2O); IR 2240, 2060, 2000; MS, m/e (relative intensity) 351 (M, 2), 323 (5), 295 (5), 267 (17), 134 (70), 78 (100); exact mass calcd for $C_{14}H_{13}FeNO$ (M – 3CO) 267.0347, found 267.0332.

Tricarbonyl[1β-cyano-1α-(2-cyanoethyl)cyclohexa-2,4-diene]iron (2a; X = CN, E = CH_2CH_2CN): NMR 5.4 (m, 2 H), 3.1 (m, 2 H), 2.5 (m, 3 H), 1.85 (m, 3 H); IR 2245, 2065, 2000; MS, m/e (relative intensity) 298 (M, 4), 270 (10), 242 (24), 214 (100); exact mass calcd for $C_{10}H_{10}FeN_2$ (M – 3CO) 214.0193, found 214.0180.

Tricarbonyl[1β-(methoxycarbonyl)-1α-methylcyclohexa-2,4-diene]iron (2a; X = CO_2Me; E = Me). This product was identical with that reported.[7]

Tricarbonyl(1β-cyano-1α-methyl-4-methoxycyclohexa-2,4-diene)iron (2b; X = CN, E = Me) and Tricarbonyl(1-cyano-4-methoxycyclohexa-1,3-diene)iron (3). Chromatographic separation required two passes. **2b** (X = CN, E = Me); mp 91–92 °C (hexane); NMR 5.03 (dd, J = 6, 2 Hz, 1 H), 3.66 (s, 3 H), 3.32 (m, 1 H), 2.72 (d, J = 6 Hz, 1 H), 2.44 (dd, J = 16 4 Hz, 1 H), 1.85 (br d, J = 16 Hz, 1 H), 1.36 (s, 3 H); IR 2245, 2065, 1995; MS, m/e (relative intensity) 289 (M, 7), 261 (15), 233 (25), 178 (100). Anal. Calcd for $C_{12}H_{11}FeNO_4$; C, 49.86; H, 3.84; Fe 19.32; N, 4.85. Found: C, 49.46; H, 3.80; Fe, 18.92; N, 4.87. **3**: mp 72–73 °C; NMR 5.44 (d, J = 6 Hz, 1 H), 5.3 (d, J = 6 Hz, 1 H), 3.5 (s, 3 H), 2.4 (m, 1 H), 1.88 (m, 3 H); IR 2235, 2060, 1990; MS, m/e (relative intensity) 275 (M, 7), 247 (15), 219 (46), 192 (100), 190 (97). Anal. Calcd for $C_{11}H_9Fe_2NO_4$: C, 48.04; H, 3.3; N, 5.09; Fe, 20.30. Found: C, 48.18; H, 3.49; Fe, 20.75; N, 5.16.

Tricarbonyl[1β-cyano-1α-(2-propenyl)-4-methoxycyclohexadiene]iron (2b; X = CN, E = C_3H_5): oil; NMR 5.96–5.6 and 5.3–5.0 (m, 4 H), 3.64 (s, 3 H), 3.3 (m, 1 H), 2.7 (d, J = 6 Hz, 1 H), 2.3 (m, 3 H), 1.88 (dd, J = 16, 2 Hz, 1 H); IR 2240, 2060, 1990; MS, m/e (relative intensity) 315 (M, 6), 287 (21), 259 (28), 231 (100); exact mass calcd for $C_{11}H_{13}FeNO$ (M – 3CO) 231.0346, found 231.0335. Complex **3** (32%) was also isolated.

Tricarbonyl[1β-cyano-1α-(phenylhydroxymethyl)-4-methoxycyclohexa-2,4-diene]iron (2b; X = CN, E = $CH(OH)C_6H_5$). Obtained as a 1:1 mixture of diastereomers: mp 103–115 °C (hexane); NMR 7.3 (m, 2 × 5 H), 4.95 (dd, J = 6, 2 Hz, 2 × 1 H), 4.55 (s, 1 H), 4.02 (s, 1 H), 3.58 (s, 2 × 3 H), 3.26 (m, 2 × 2 H), 2.32 (m, 2 × 1 H), 2.04 (m, 2 × 1 H); IR 2240, 2055, 1985; MS, m/e (relative intensity) 381 (M, O), 297 (2), 276 (5), 247 (12), 220 (24), 191 (18), 164 (100). Anal. Calcd for $C_{18}H_{15}FeNO_5$: C, 56.72; H, 3.97; Fe, 14.65; N, 3.65. Found: C, 56.43; H, 4.02; Fe, 14.77; N, 3.85.

Tricarbonyl(1β-cyano-1α-methyl-3-methoxycyclohexa-2,4-diene)iron (2c; X = CN, E = Me): mp 85–87 °C; NMR 5.18 (dd, J = 6, 2 Hz, 1 H), 3.66 (s, 3 H), 3.38 (d, J = 2 Hz, 1 H), 2.64 (m, 1 H), 2.3 (dd, J = 16, 4 Hz, 1 H), 1.65 (dd, J = 16, 2 Hz, 1 H), 1.43 (s, 3 H); IR 2240, 2060, 1995; MS, m/e (relative intensity) 284 (M, 6), 261 (13), 233 (16), 205 (22), 188 (69), 123 (100). Anal. Calcd for $C_{12}H_{11}FeNO_4$: C, 49.86; H, 3.84; Fe, 19.32; N, 4.85. Found: C, 49.57; H, 3.85; Fe, 19.76; N, 5.03.

Tricarbonyl[1β-cyano-1α-(phenylhydroxymethyl)-3-methoxycyclohexa-2,4-diene]iron (2c; X = CN, E = $CH(OH)C_6H_5$). First diastereomer (minor), oil, NMR 7.36 (m, 5 H), 5.08 (dd, J = 6, 2 Hz, 1 H), 4.42 (s, 1 H), 3.66 (s, 3 H), 3.46 (d, J = 2 Hz, 1 H), 2.56 (m, 2 H), 1.96 (m, 2 H); second diastereomer (major), oil, NMR 7.4 (m, 5 H), 5.12 (dd, J = 6, 2 Hz, 1 H), 4.15 (s, 1 H), 3.64 (s, 3 H), 2.82 (d, J = 2 Hz, 1 H), 2.68 (m, 2 H), 2.2 (m, 2 H); IR 2240, 2055, 1990; MS, m/e (relative intensity) 381 (M, O), 353 (5), 325 (15), 297 (40), 207 (100). Anal. Calcd for $C_{18}H_{15}FeNO_5$: C, 56.72; H, 3.97; Fe, 14.65; N, 3.67. Found: C, 56.82; H, 4.13; Fe, 14.34; N, 3.82.

Tricarbonyl[1β-[[(4-methylphenyl)sulfonyl]oxy]-1α-methylcyclohexa-2,4-diene]iron (2a; X = SO_2-p-C_6H_4Me, E = Me). A solution of sulfone **1a** (X = SO_2-p-C_6H_4Me) (1 mmol) in THF (5 mL) was added dropwise to a stirred solution of n-butyllithium (1.1 mmol) and tetramethylethylenediamine (1.1 mmol) in THF (8 mL) at –70 °C. After 30 min methyl iodide (1 mL) was added and the mixture was then allowed to warm to room temperature. Workup as described for the LDA reactions gave the product: mp 112–114 °C (MeOH); NMR 7.72 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz, 1 H), 5.3 (m, 2 H), 3.28 (m, 1 H), 2.8 (m, 3 H), 2.24 (s, 3 H), 1.68 (dd, J = 16, 2 Hz, 1 H), 1.30 (s, 3 H); IR 2055, 1985; MS, m/e (relative intensity) 388 (M, O), 360 (1), 332 (15), 304 (7), 226 (20), 212 (100). Anal. Calcd for $C_{17}H_{16}FeO_5S$: C, 52.60; H, 4.15; Fe, 14.39; S, 8.26. Found: C, 53.00; H, 4.39; Fe, 14.57; S, 8.16.

(1*R*)-4-Oxo-1-(2-propenyl)cyclohex-2-enecarbonitrile (6). Fully resolved[9] (–)-2-methoxy salt **4** (0.47 g) was converted to nitrile **1b** (X = CN), $[\alpha]_{589}$ +177°, and allylated to give **2b** (X = CN, E = C_3H_5), $[\alpha]_{589}$ +66°, by the methods just described. Pure **3**, $[\alpha]_{589}$ –127°, was isolated (36%) from the alkylation step by chromatography. A solution of (+)-nitrile **2b** (X = CN, E = C_3H_5) (0.16 g) in dimethylacetamide (5 mL) was heated at 75 °C for 15 min in the presence of trimethylamine N-oxide dihydrate (1 g). The mixture was allowed to cool in the oil bath and then diluted with ether (15 mL), filtered through Celite, and extracted to give crude diene **5**. This material was substantially pure according to TLC and NMR [6.0–5.64 and 5.3–5.05 (m, 5 H), 4.62 (m, 1 H), 3.56 (s, 3 H), 2.5 (m, 4 H)] and had $[\alpha]_{589}$ –82°. The crude material (0.08 g) was treated directly with Amberlyst 15 Resin (H^+ form, Rohm and Haas) in ether (0.5 g in 5 mL) at room temperature during 45 min. After filtration through Celite and evaporation, the compound was purified by chromatography to provide enone **6** as a pale yellow oil (0.067 g, 91%): NMR 6.7 (dd, J = 10, 1 Hz, 1 H), 5.1 (d, J = 10 Hz, 1 H), 6.0–5.7 and 5.4–4.5 (m, 3 H), 2.7–1.9 (m, 6 H); IR 2230, 1690; MS, m/e (relative intensity) 161 (M. 100), 133 (15), 100 (19), 99 (26), 91 (30), 65 (33); $[\alpha]_{589}$ –73°; exact mass calcd for $C_{10}H_{11}NO$ 161.0841, found 161.0840.

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Registry No. **1a** (X = SO_2-p-C_6H_4Me), 94570-57-7; **1a** (X = CN), 67180-14-7; **1a** (X = CO_2Me), 78684-58-9; (+)-**1b** (X = CN), 94667-94-4; **1c** (X = CN), 94667-93-3; **2a** (X = CN, E = H), 94667-95-5; **2a** (X = CN, E = Me), 94570-58-8; **2a** (X = CN, E = $CH_2CH{=}CH_2$), 94570-59-9; **2a** (X = CN, E = CH(OH)Ph) (isomer 1), 94570-60-2; **2a** (X = CN, E = CH(OH)Ph) (isomer 2), 94667-96-6; **2a** (X = CN, E = CH_2CH_2CN), 94570-61-3; **2a** (X = CO_2Me, E = Me), 78641-79-9; **2a** (X = SO_2-p-C_6H_4Me, E = Me), 94570-62-4; **2b** (X = CN, E = Me), 94667-97-7; (+)-**2b** (X = CN, E = $CH_2CH{=}CH_2$), 94596-66-4; **2b** (X = CN, E = CH(OH)Ph) (isomer 1), 94570-63-5; **2b** (X = CN, E = CH(OH)Ph) (isomer 2), 94667-98-8; **2c** (X = CN, E = Me), 94570-64-6; **2c** (X = CN, E = CH(OH)Ph) (isomer 1), 94570-65-7; **2c** (X = CN, E = CH(OH)Ph) (isomer 2), 94667-99-9; **3**, 12307-38-9; (–)-**4**, 79120-66-4; (*S*)-(–)-**5**, 94537-94-7; (*R*)-(–)-**6**, 94537-95-8; H_2O, 7732-18-5; MeI, 74-88-4; $CH_2{=}CHCH_2Br$, 106-95-6; PhCHO, 100-52-7; $CH_2{=}CHCN$, 107-13-1; tricarbonyl(3-methoxy-2,4-cyclohexadienyl)iron hexafluorophosphate, 74883-20-8.