($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 1.66–1.73 (m, 4 H), 2.32–2.65 (m, 6 H), 9.08 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 51.40; H, 8.81.

6-(Ethylthio)hexanoic acid (16): colorless oil; bp 124 °C (1.8 mm); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 1.30–1.88 (m, 6 H), 2.32–2.64 (m, 6 H), 10.10 (br s, 1 H). Anal. Calcd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15. Found: C, 54.35; H, 8.93.

4-(n-Propylthio)butyric acid (17): colorless oil; bp 115–116 °C (1.5 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1235 cm^{-1}; NMR ($CDCl_3$) δ 0.99 (t, J = 6.8 Hz, 3 H), 1.60 (sextet, J = 6.8 Hz, 2 H), 1.91 (quintet, J = 6.8 Hz, 2 H), 2.50 (t, J = 6.8 Hz, 4 H), 2.57 (t, J = 6.8 Hz, 2 H), 11.08 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 52.06; H, 8.90.

4-(Isopropylthio)butyric acid (18): colorless oil; bp 110–112 °C (1.8 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, J = 6.7 Hz, 6 H), 1.91 (quintet, J = 7.5 Hz, 2 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.60 (t, J = 7.5 Hz, 2 H), 2.93 (septet, J = 6.7 Hz, 1 H), 11.23 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 51.98; H, 8.44.

4-(Isobutylthio)butyric acid (19): colorless oil; bp 120–121 °C (1.7 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1235 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (d, J = 6.3 Hz, 6 H), 1.65–2.05 (m, 3 H), 2.36–2.63 (m, 6 H), 11.39 (br s, 1 H). Anal. Calcd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15. Found: C, 54.57; H, 9.33.

3-(Phenylthio)propionic acid (22): colorless needles; mp 56.0–56.5 °C (from petroleum ether) (lit.[3d] mp 59–60 °C); IR ($CHCl_3$) 3600–2300, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.66 (AA', 2 H, CH_2Cl_2), 3.15 (BB', 2 H, SCH_2) 7.18–7.41 (m, 5 H), 8.50 (br s, 1 H, CO_2H), mass spectrum, m/e 182 (M^+).

4-(Phenylthio)butyric acid (23): colorless needles; mp 66.0–67.0 °C (from petroleum ether–dichloromethane); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (quintet, J = 7.0 Hz, 2 H), 2.46 (t, J = 7.0 Hz, 2 H), 2.98 (t, J = 7.0 Hz, 2 H), 7.04–7.56 (5 H, aromatic). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16. Found: C, 61.35; H, 5.94.

4-(Phenylthio)-2,2-diphenylbutyric acid (24): colorless prisms; mp 173–174 °C (from petroleum ether–dichloromethane); IR ($CHCl_3$) 3600–2400, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.73 (s, A_2B_2, 4 H), 7.00–7.28 (m, 5 H, aromatic), 7.31 (s, 10 H, aromatic). Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79. Found: C, 75.52; H, 5.74.

***cis*-2-[(Phenylthio)methyl]cyclohexanecarboxylic acid (25)**: colorless prisms; mp 65–66 °C (from petroleum ether–dichloromethane; IR (NaCl, neat) 3600–2400, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.20 (9 H), 2.50–3.30 (3 H), 6.80–7.55 (m, 5 H, aromatic); high-resolution mass spectrum, calcd for $C_{14}H_{18}O_2S$ (M^+) m/e 250.103, found m/e 250.102.

5-(Phenylthio)valeric acid (26): mp 61–62 °C (from n-hexane–ether); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.61–1.81 (m, 4 H), 2.37 (br t, J = 7.5 Hz, 2 H), 2.93 (br t, J = 7.5 Hz 2 H), 7.00–7.50 (5 H, aromatic). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.79; H, 6.81.

[1-[2-(Phenylthio)ethyl]cyclopentyl]acetic acid (27): colorless oil; IR (NaCl, neat) 3600–2400, 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.20–2.00 (10 H), 2.33 (s, 2 H, CH_2CO_2H), 2.73–3.10 (m, 2 H, CH_2SPh), 7.00–7.40 (m, 5 H, aromatic), 11.2 (br s, 1 H, CO_2H); high-resolution mass spectrum, calcd for $C_{15}H_{20}O_2S$ (M^+) m/e 264.118, found m/e 264.121.

Thianthrene[17] (D): colorless needles; mp 153–156 °C (from acetone); IR (KBr) 1440, 760, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.09–7.26 (m, 4 H), 7.36–7.53 (m, 4 H). Anal. Calcd for $C_{12}H_8S_2$: C, 66.68; H, 3.73. Found: C, 66.63; H, 3.66.

Methyl 4-(Ethylthio)-2,2-diphenylbutyrate (28). The acid 11 was methylated with diazomethane (in either solution) as usual to give the methyl ester **28** (98%, after purification by SiO_2 column chromatography): colorless prisms; mp 51.5–52.0 °C (from methanol); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, J = 7.3 Hz, 3 H), 2.12–2.76 (m, 6 H), 3.69 (s, 3 H), 7.27 (br s, 10 H, aromatic). Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.54; H, 6.99.

Methyl 2,2-Diphenylbutyrate (29). To a solution of the ester **28** (232 mg, 0.74 mmol) in 95% EtOH (10 mL) was added Raney nickel (3.24 g). After being refluxed for 15 h, the reaction mixture was treated as usual to give **29** (166 mg, 88.8%), which was purified by microdistillation: colorless oil; bp 126–128 °C (1.8 mm); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.75 (t, J = 7.3 Hz, 3 H), 2.43 (q, J = 7.3 Hz, 2 H), 3.67 (s, 3 H), 7.27 (br s, 10 H, aromatic). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.41; H, 6.88.

Registry No. 1, 57-57-8; 2, 616-45-5; 3, 956-89-8; 4, 108-29-2; 5, 104-67-6; 6, 87-41-2; 7, 542-28-9; 8, 502-44-3; 9, 7244-82-8; 10, 71057-15-3; 11, 71057-16-4; 12, 71057-17-5; 13, 71057-18-6; 14, 79313-52-3; 15, 71057-19-7; 16, 71057-20-0; 17, 79313-53-4; 18, 79313-54-5; 19, 79313-55-6; 20, 79389-25-6; 21, 27579-18-6; 22, 5219-65-8; 23, 17742-51-7; 24, 77734-57-7; 25, 79313-56-7; 26, 17742-53-9; 27, 77754-88-2; 28, 79313-57-8; 29, 79328-68-0; thianthrene, 92-85-3; EtSH, 75-08-1; n-PrSH, 107-03-9; i-PrSH, 75-33-2; i-BuSH, 513-44-0; PhSH, 108-98-5; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3.

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Organometallic Complexes in Organic Synthesis. 15. Absolute Configurations of Some Simply Substituted Tricarbonyliron Complexes

Arthur J. Birch,* Warwick D. Raverty, and G. Richard Stephenson

Research School of Chemistry, Australian National University, Canberra, ACT 2600, Australia

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Unsymmetrically substituted tricarbonyl(η-cyclohexadiene)iron(0) complexes have a molecular center of chirality. Stereospecific reactions of the derived tricarbonyl(η-cyclohexadienyl)iron(1+) salts have been used to direct the formation of new chiral centers at carbon and so to define absolute configurations of key complexes by chemical correlation with the terpenes cryptone and phellandrene. Further interconversions in the series have determined the configurations of a number of simply substituted tricarbonyliron complexes which have potential for application in asymmetric organic synthesis.

Complexation by transition metals can confer on an organic compound reactivity properties which differ markedly from those expected for the functional groups of the free ligand. Stabilization[1] of cationic species in such cases activates the ligand toward nucleophilic attack in a fashion that is independent[2] of the need for classical cationoid substituents, though the position and nature of substituents is still of importance if regioselectivity is to

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0022-3263/81/1946-5166$01.25/0

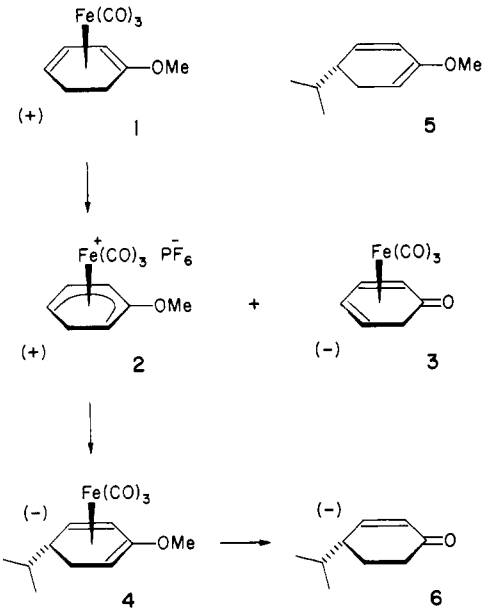
be ensured.[3] Although these properties have been used sporadically in specific cases, only recently have the general implications of the application of transition metals to provide lateral control of reactivity been examined.[2] The approach is distinct from conventional organic synthesis which achieves regio- and stereocontrol by manipulations of endogenous functional groups which may, ideally, be similar to those needed in the final product.

Work with racemic compounds has served to delineate the properties of tricarbonyliron complexes to a degree which permits rational synthetic design.[4] The utility of the concept of lateral control[2] of reactivity is apparent in the current application[4f,5] of the method to problems in organic synthesis. The stereospecific alkylation reactions of tricarbonyl(η^5-cyclohexadienyl)iron(1+) salts are of particular interest due to their ability[6] to direct the formation of a new chiral center. Substituents introduced on the face opposite to the metal are denoted α while those on the same face are termed β substituents.[2] A new asymmetric center so formed will be fully resolved, if a fully resolved salt is employed. Decomplexation removes the original chiral center to leave only the new one. If the absolute configuration of the initial salt is known, that of the new center is also known because of the stereospecificity involved. This indicates a new approach to asymmetric synthesis. Providing resolution is possible and the absolute configuration can be determined, this sequence can lead from an optically inactive prochiral molecule, via a metal-stabilized cation, to a synthetic product with a resolved chiral center at carbon. Related synthetic sequences could in theory be carried out by using electrophilic reagents and resolved neutral complexes, providing steric control of the reaction is maintained, but this possibility has not yet been examined.

For employment of such strategies it is necessary to know how to prepare resolved complexes, to determine absolute configurations of key intermediates, and to ascertain whether the interconversions of optically active transition-metal complexes result in any racemization of products.

The determination of the absolute configurations of a series of tricarbonyliron complexes was accomplished as follows. Both (+) and (−) isomers of several simple diene complexes have been prepared by asymmetric complexation[7] although not in completely resolved states. Fully resolved complexes have been obtained in some cases by resolution of diastereomers.[8] We report here determinations of the absolute configurations, as related to the optical rotations, of some simple cyclohexadiene complexes of types basic to synthetic requirements. Alkylation of tricarbonyl(η^5-cyclohexadienyl)iron(1+) salts was employed to generate a new chiral center at carbon. The substituents at this position in the ligand were chosen to allow simple correlation with terpenes of known absolute configuration, after removal of the metal. Since the alkylation reactions are stereospecific and the stereochemical relationship between the new center produced and the directing chirality of the metal complex is well understood,[4a,9] this serves to define the absolute configurations of the complexes. Optically pure material is not necessary for this determination; the samples used were of low enantiomeric excess, obtained by induction of asymmetry during complexation.[7] Part of this investigation has been the subject of a preliminary communication.[10] Work is in progress[8b] on methods for obtaining a series of fully resolved complexes for synthetic application.

Scheme I



Results

Chemical Correlation of (1*S*)-(+)-Tricarbonyl-[(1,2,3,4-η)-1-methoxy-1,3-cyclohexadiene]iron(0) (1) with (*R*)-(−)-Cryptone. Conversion of the (+) isomer of 1 ($[\alpha]_D$ +8.3°) to the 2-methoxy salt 2 ($[\alpha]_D$ +4.8°) was performed by the usual procedure.[11] As expected, the dienone complex 3 ($[\alpha]_D$ −34°) was the major product. The magnitude of rotation of 2 obtained by this means indicates an enantiomeric excess of approximately 4%. (Fully resolved 2 has $[\alpha]_D$ ca. +116°[8b]). Alkylation of 2 with diisopropylcadmium at −10 °C gave 4 ($[\alpha]_D$ −5.1°) in 55% yield after chromatography. The product was identified as the 5α isomer by examination of the ^{1}H NMR spectrum which indicated the presence of a single stereoisomer. Alkylations of tricarbonyl(η^5-cyclohexadienyl)iron(1+) salts have been shown[9d] to result in specific α substitution relative to the metal. Removal of the tricarbonyliron group from 4 with trimethylamine *N*-oxide in dimethylacetamide gave the free ligand 5 which was hydrolyzed without prior purification by mild acid treatment to give the enone 6 in 49% yield from 4. Partial racemization occurred at this

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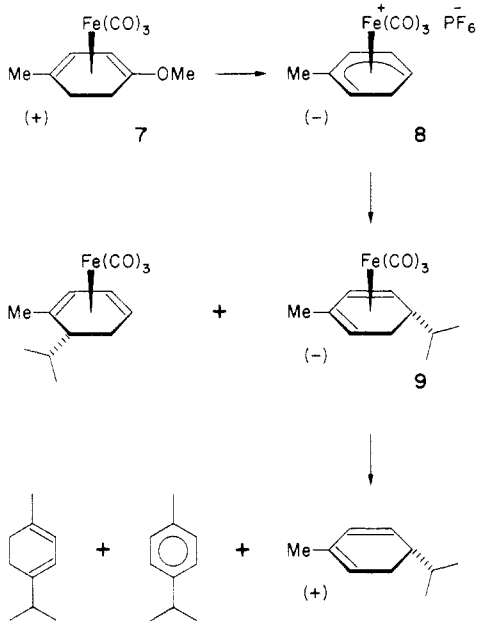
Scheme II

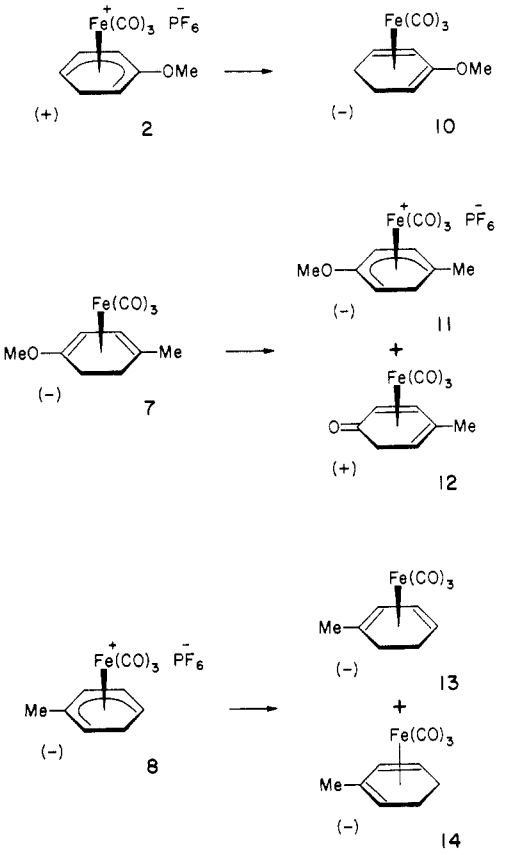


step. Comparison of ORD spectra with that of an authentic specimen of (*R*)-(−)-cryptone indicated the absolute configurations of the series of methoxydiene complexes shown in Scheme I.

Chemical Correlation of (1*S*,4*R*)-(+)-Tricarbonyl-[(1,2,3,4-η)-1-methoxy-4-methyl-1,3-cyclohexadiene]-iron(0) (7) with (*S*)-(+)-"α"-Phellandrene. Treatment of the (+) isomer of 7 ($[\alpha]_D$ +12.6°) with concentrated H_2SO_4 by the normal procedure[12] gave the 2-methyl salt 8 ($[\alpha]_D$ −2.5°). Close examination of the ^1H and ^{13}C NMR spectrum of this material revealed the presence of a trace of the 1-methyl isomer. This was removed by deprotonation with triethylamine. The pure salt 8 was recovered with unchanged rotation. In this case alkylation with diisopropylcadmium gave a 78% yield of a mixture of regioisomers corresponding to addition at C-1 and C-5.[9d] Separation on silver nitrate impregnated silica afforded a pure sample of 9 ($[\alpha]_D$ −1.2°) which was identified by comparison with the enantiomer of 9 [($[\alpha]_D$ +11.9°) obtained by direct complexation[9a,13] of (*R*)-(−)-"α"-phellandrene. The ORD spectra of the two antipodes of 9 determine the absolute configurations of the series of methyl-substituted complexes drawn in Scheme II. The magnitudes of rotation indicate an enantiomeric excess of about 10% for the sample obtained by alkylation. No evidence of the known[13c] β isomer of 9 could be detected in the crude product from the alkylation of 8, confirming the stereospecificity of the reaction.[9d] Removal of the tricarbonyliron group from 9 gave a product containing (*S*)-(+)-"α"-phellandrene, "α"-terpinene, and *p*-cymene, of which the first is the only chiral constituent. The ORD of this mixture agreed with the assignments of absolute configuration made above.

Absolute Configurations of Complexes Derived from (1*S*)-(+)-Tricarbonyl[(1,2,3,4-η)-1-methoxy-1,3-cyclohexadiene]iron(0) (1). The preparation of the (−) isomer of 6 from the (+) isomer of 1 also defines the absolute configurations of the products 2–4. The (−) isomer of 4 has the 2*S*,5*R* configuration. Thus the (+) isomer of the salt 2 has the 2*S* configuration, the (−) isomer of the dienone complex 3 has the 2*S* configuration, and the (+) isomer of the 1-methoxy diene complex 1 has the 1*S* configuration. The absolute configuration of the (−) isomer of tricarbonyl[(1,2,3,4-η)-2-methoxy-1,3-cyclohexadiene]-iron(0) (**10**) was shown to be 2*S* by reduction of the (2*S*)-(+) isomer of 2 by sodium borohydride in acetonitrile.

Scheme III



Absolute Configurations of Complexes Derived from (1*S*,4*R*)-(+)-Tricarbonyl[(1,2,3,4-η)-1-methoxy-4-methyl-1,3-cyclohexadiene]iron(0) (7). The interconversion of 7 and 9 indicates the absolute configuration of the intermediate salt 8. The (−) isomer of 9 has the 2*R*,5*S* configuration. Thus the (−) isomer of 8 has the 2*R* configuration and the (+) isomer of 7 is 1*S*,4*R*. Treatment of the (1*R*,4*S*)-(−) isomer of 7 ($[\alpha]_D$ −52°) with triphenylmethylium tetrafluoroborate in CH_2Cl_2 at −5 °C gave the expected[9a,14] products. The (−) isomer of the 2-methoxy-5-methyl salt 11 ($[\alpha]_D$ −73°) obtained in this way must thus be the 2*R*,5*S* isomer, while the (+) isomer of the dienone complex 12 ($[\alpha]_D$ +219°) is 2*R*,4*S* (Scheme III). The value for the enantiomeric excess of 7 ($[\alpha]_D$ +12.6°) calculated above indicates the compounds used for this determination had a higher enantiomeric excess of about 41%. The configurations of the 1- and 2-methyl-1,3-cyclohexadiene complexes (13 and 14, respectively) were determined by borohydride reduction of the (2*R*)-(−) isomer of 8 ($[\alpha]_D$ −2.5°). Conditions were chosen to give a roughly equal mixture of 13 and 14 since a practical method of selective reduction of 8 could not be found.[3] The mixture of regioisomers was separated by chromatography on silver nitrate impregnated silica, and ORD spectra of pure samples of both regioisomers indi-

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cated a (−) sign of rotation. This corresponds to the 1*R* configuration of **13** and the 2*R* configuration of **14**. Knowledge of the absolute configuration of **13** has permitted the determination[8a] of the absolute configuration of the resolved carboxylic acid complex (1*S*)-(+)-tricarbonyl[(1,2,3,4-η)-1-carboxy-1,3-cyclohexadiene]iron(0). The enantiomeric excess of **13** deduced from this correlation agrees well with the value obtained by interconversion with **9**. This result indicates that direct complexation of "α"-phellandrene proceeds without significant racemization.

Interconversion of the (2*R*)-(−)-Tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron(1+) (2) and (2*S*)-(+)-Tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron(1+) (8) Salts. The assignment of the absolute configurations of the complexes **2** and **8** depend on independent correlations. The interconversion of the two salts was performed and supported the assignments of the two series of compounds. Alkylation of the (2*R*)-(−) isomer of **2** ($[\alpha]_D$ −10.7°) with lithium dimethylcuprate was performed by addition of a solution of **2** in CH_3CN to a solution of the cuprate reagent in tetrahydrofuran at −45 °C. This method is superior to the published[15] procedure; (2*R*,5*R*)-(+)-tricarbonyl[(1,2,3,4-η)-2-methoxy-5-methyl-1,3-cyclohexadiene]iron(0) (**15**; $[\alpha]_D$ +11.7°) was obtained in 75% yield. Treatment of this complex with concentrated H_2SO_4 in the usual way gave the (+) isomer of **8** contaminated by a small amount of tricarbonyl[(1,2,3,4,5-η)-1-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate. The enantiomeric excess of **8** ($[\alpha]_D$ +0.6°) obtained by this route was approximately 2%, compared to 9% for the starting material **2**. The partial racemization indicated by this observation presumably occurs during the conversion of **15** to **8**. The α stereochemistry of alkylation of **2** is further attested by this sequence since the migration of the site of coordination in **15** requires the presence of β-hydrogens at C-5 and C-6. Compounds with β-alkyl substituents cannot rearrange in this fashion.[2,16]

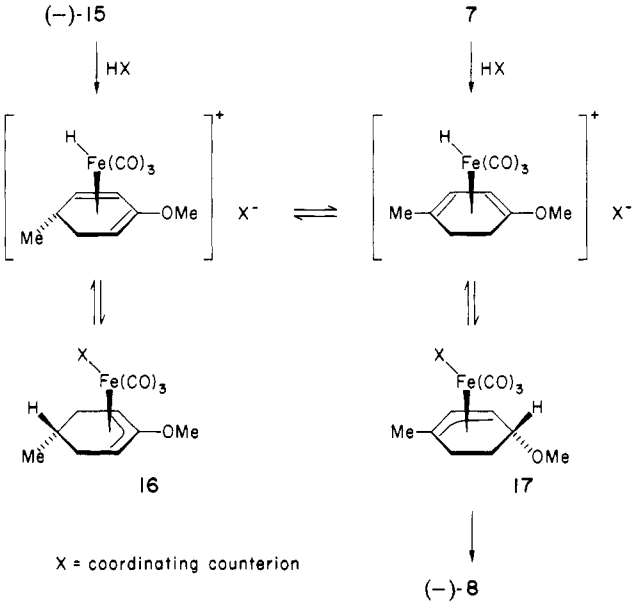
Discussion

Interconversions of optically active transition-metal π complexes such as those described above modify a molecular center of chirality by changing the nature and position of coordination of metal to the organic ligand. The metal serves to distinguish the two faces of an otherwise planar, prochiral ligand, a distinction which persists throughout a series of transformations. Thus, unless complete racemization is encountered, the signs of rotation of the products can be related to absolute configuration, once that of one member of a series has been defined. When racemization occurs in such systems, the metal atom must lie on a plane of symmetry produced in a product, intermediate, or transition state.

Effect of Interconversions on the Configuration of the Molecular Chiral Center. Hydride abstraction and nucleophilic addition reactions of tricarbonyliron complexes are amenable to simple interpretation since, although the number of carbon atoms coordinated to the metal is altered, the stereochemistry of molecular center of chirality is left unchanged. There is no evidence for migration of the site of coordination relative to substituents on the ring when such reactions are performed under normal conditions, though at elevated temperatures, thermal rearrangements of neutral diene complexes have been observed.[17] In contrast, exposure of neutral complexes to acidic conditions is known to promote rearrangement[12] of the position of coordination. Protonation to form various η^3-allyl species has been demonstrated[18] in many cases. The precise natures of the species formed depend on whether the acid counterion is sufficiently nucleophilic to add to the metal. Deuterium incorporation studies[18a] implicate a η^3-allyl cationic intermediate which may account[18a] for the temperature dependence of the spectrum of protonation products. The equilibrium concentrations in such systems can also depend on the properties of the ligand and the nature and concentration of the acid.[18a,c] Hydrogen transfers between the metal and the ring are invoked[12] to explain the rearrangements of tricarbonyliron complexes in strong acids. Thus the treatment of methoxy diene complexes with concentrated H_2SO_4 proceeds[12] through a series of reversible steps until irreversible (under these conditions[19]) loss of methanol leads to the formation of the tricarbonyl(η-cyclohexadienyl)iron(1+) salt. One terminus of the dienyl system of the desired product is situated at the position originally bearing the methoxy substituent. Thus the configuration of an optically active product can be related to that of the starting material since pathways involving symmetrical intermediates may be discounted for this purpose. Racemization will occur, however, if such intermediates participate in the reaction.

Conversion of **15** to **8** was found to involve partial racemization, presumably via the formation of the symmetrical intermediate **16**. This reflects a competition between

Scheme IV[a]



[a] These structures are drawn to conform to the transformations indicated by other formulas; they have the opposite configurations to those described in the text.

(15) Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1101.
(16) (a) Birch, A. J. *Ciba Found. Symp.* **1978**, *53*, 194. (b) Birch, A. J.; Kretschmer, G., unpublished results.
(17) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63. Hine, K. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1976**, 1702.
(18) (a) Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296. (b) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. (c) Whitesides, T. H.; Arhart, R. W. *Ibid.* **1975**, *14*, 209. (d) Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5792. Brookhart, M.; Harris, D. L. *Inorg. Chem.* **1974**, *13*, 1540. Olah, G. A.; Liang, G.; Yu, S. H. *J. Org. Chem.* **1976**, *41*, 2227.
(19) Under mild acidic conditions addition of methanol to the salt is reversible: Hine, K. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1975**, 81. Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1977**, *127*, C22.

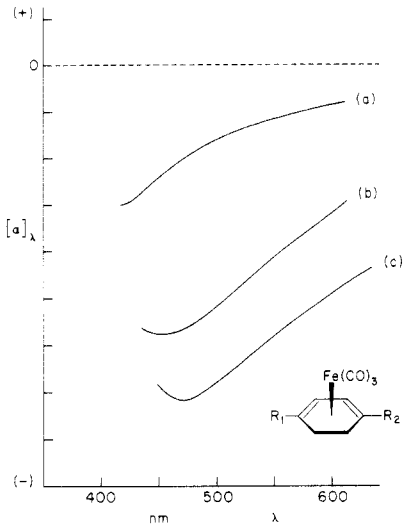


Figure 1. Units for the ordinate are indicated in brackets: (a) (1*R*)-(−)-**13**, R_1 = Me, R_2 = H [2°], ~10% ee; (b) (1*R*)-(−)-**1**, R_1 = OMe, R_2 = H [8°], ~10% ee; (c) (1*R*,4*S*)-(−)-**7**, R_1 = OMe, R_2 = Me [10°], ~40 ee.

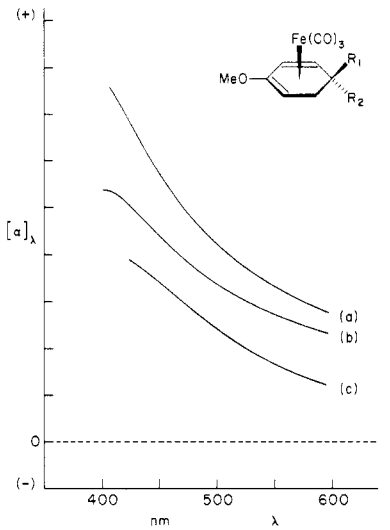


Figure 2. Units for the ordinate are indicated in brackets: (a) (1*S*,4*R*)-(+)-**6**, R_1 = Me, R_2 = $CH(CO_2Et)_2$ [15°], ~40% ee; (b) (2*R*,5*R*)-(+)-**15**, R_1 = H, R_2 = Me [5°], ~10% ee; (c) (2*R*)-(+)-**10**, R_1 = H, R_2 = H [1°], ~1% ee.

hydrogen transfer to the ring of **15** at C-1 and C-4 (Scheme IV). Protonation at C-1 and subsequent rearrangement by hydrogen transfers between the ring and metal to form **17** must compete effectively with protonation of **15** at C-4 as complete racemization would result if the converse were true. In the case of **7**, direct hydrogen transfer to form **17** is possible, and little racemization via rearrangement to **16** is anticipated. Although interconversions of the protonated intermediates are reversible, the reaction is driven by the consumption of **17** with the eventual irreversible formation of **8**, and it is doubtful if a true equilibrium is ever established. 1,2-Elimination of methanol appears to occur to a minor extent as evidenced by traces of the 1-methyl salt as noted above. Recovery of methoxy diene complexes from milder acidic conditions, where salt formation is prevented, results[6] in slow racemization.

Hydride abstraction from 1-methoxy diene complexes forms a mixture of 1- and 2-methoxy-substituted salts. The former is readily hydrolyzed, and this provides a convenient means of separation.[14] The hydrolysis proceeds by nucleophilic addition of water under reversible, mild-acid conditions. Only addition at C-1 leads to the formation of the dienone complexes **3** and **12** through hydrolysis of the resulting hemiacetal. Thus the ketone function of the product is formed at the carbon bearing the methoxy substituent in the starting material. This mechanism is supported by the position of the methyl group in the product **12**. Assignments of the absolute configurations of **3** and **12** by correlation with **1** and **7**, respectively, were made on this basis.

Application of the *R*–*S* Nomenclature to Tricarbonyliron π Complexes. The Cahn, Ingold, Prelog *R*–*S* nomenclature has been extended[20] to encompass compounds with molecular chirality. The *R*–*S* names given above have been derived by application of the procedures used to define names for analogous chiral ferrocene, tricarbonylchromium and -molybdenum complexes.[21] Unlike previous examples, these compounds may possess additional chiral centers in the ring coordinated to the metal. The principles, however, are the same. For this purpose

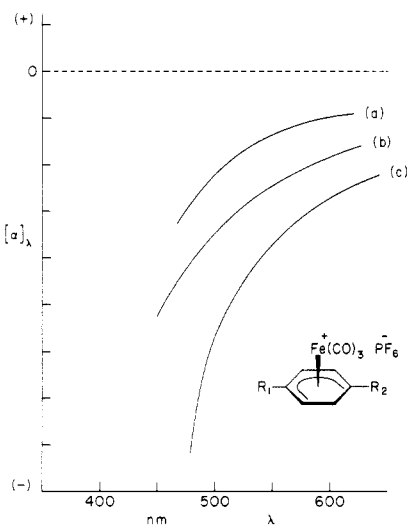


Figure 3. Units for the ordinate are indicated in brackets: (a) (2*R*)-(−)-**8**, R_1 = Me, R_2 = H [2.5°], ~10% ee; (b) (2*R*)-(−)-**2**, R_1 = OMe, R_2 = H [6°], ~10% ee; (c) (2*R*,5*S*)-(−)-**11**, R_1 = OMe, R_2 = Me [25°], ~40% ee.

each atom bound covalently to the metal is formally assigned[20,22] a metal–carbon single bond, regardless of the true nature of the bonding. (In the case of tricarbonyliron complexes, there may, in reality, be considerable differences between the nature of the bonding at the various carbons attached to the metal.) The priority of the substituents and hence the correct name for a given configuration may then be deduced in the normal way, each center being considered tetrahedrally substituted, irrespective of the actual geometries.

Relation of ORD Curves to Those of Optically Active Complexes Derived from Natural Products. The ORD curves depicted in Figures 1–3 are all of the simple type. The sign of rotation does not change with wavelength in the region examined and is thus sufficient to indicate the absolute configuration. The strong yellow absorbance of the complexes prevented observation of ORD curves in the ultraviolet region, and attempts to record CD curves were unsuccessful. It would be useful to be able to relate

(20) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(21) For examples, see: Klyne, W.; Buckingham, J. "Atlas of Stereochemistry", 2nd ed.; Chapman and Hall: London, 1978; Vol. 1, p 223.

(22) Schlögl, K. In *Top. Stereochem.*; **1967**, *1*, 39.

the sign of rotation to specific structural features of the complexes in order to allow absolute configurations to be inferred from rotation data alone. Although insufficient examples are available to draw firm conclusions at this stage, some interesting correlations do emerge. Comparisons with ORD curves of optically active complexes derived by direct complexation[13a] of optically active natural products further support these findings. In particular, it appears that the stereochemistry of the metal–ligand π-bonding system usually dominates the factors which contribute to the sign of rotation. The 5α and 5β stereoisomers of the complex **9**, (2*S*,5*R*)-(+)- and (2*S*,5*S*)-(+)-tricarbonyl[(1,2,3,4-η)-5-isopropyl-2-methyl-1,3-cyclohexadiene]iron(0), both show the same sign of rotation irrespective of the configuration at C-5. Indeed the 2*S* isomer of **14** is also the (+) isomer. While both 1- and 2-methyl-substituted complexes (**13** and **14**) are (1*S*)-(+) and (2*S*)-(+), respectively, the (+) isomers of methoxy-substituted complexes correspond to different configurations. The (+) isomers of **1** and **7** are both in the (1*S*) configuration. In contrast, the (2*R*)-methoxy-substituted complexes **4**, **10**, **15**, and (1*S*,4*R*)-(+)-tricarbonyl[dimethyl[(2,3,4,5-η)-4-methoxy-1-methyl-2,4-cyclohexadien-1-yl]propanedioate]iron(0)[6] [(2,3,4,5-η-4-methoxy-1-methyl-2,4-cyclohexadien-1-yl]propanedioate]iron(0)[6] prove to be the (+) isomers. The salts **2**, **8**, **11**, and (1*S*,4*S*)-(+)-tricarbonyl[(1,2,3,4,5-η)-1-isopropyl-4-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate[13a] have the *S* configuration of methyl or methoxy substituents for C-2 or C-4 and give positive rotations. The dienone complexes prepared to date typically possess anomalously large magnitudes of rotation. This suggests that the dienone system has chiroptical properties which far outweigh the contributions of other functionalities to the magnitude of rotation. The 2*S* isomers of **3**, **12**, and (2*S*,5*S*)-(−)-tricarbonyl[(2,3,4,5-η)-5-isopropyl-2-methyl-2,4-cyclohexadien-1-one]iron(0)[13a] all exhibit large negative rotations. The effects of the other substituents, however, as anticipated from the trends indicated above, would also lead to this sign of rotation.

Conclusion

The results of our work define for the first time in the tricarbonyl(η-cyclohexadiene)iron series the absolute configurations of a range of simply substituted complexes. These correlations also allow the efficiency of the asymmetric complexation procedure[7] to be assessed, and, since the absolute configurations of the products are now known, the way is clear to investigate the mechanism of the induction process by comparison of the configurations of the products and the inducing chiral centers. The discovery of conditions causing racemization of intermediate complexes provides a useful indication of reactions which must be avoided if tricarbonyliron complexes are to be employed in asymmetric synthesis. The assignment of absolute configurations permits the prediction of the configuration of new chirality in the products of alkylation reactions, and so allows rational application to the synthesis of specific asymmetric centers.

The principles underlying this approach apply equally to complexes of open-chain dienes and to a number of complexes with other metals and other ligands on the metal. Asymmetric synthesis using the separation[23] of diastereomers containing a tricarbonyl[η^6-arene)chromium(0) center and palladium-catalyzed intramolecular chirality-transfer reactions[24] have been reported, and we and other authors have indicated the potential extension of stereospecific reactions of complexes of iron,[5c,13a,16a,25] cobalt,[26] and palladium[27] to direct the asymmetric synthesis of chiral centers carbon.

Experimental Section

General Methods. Optical rotations were measured on a Bendix NPL automatic polarimeter 143C or on a Perkin-Elmer 241 polarimeter fitted with a 10-cm microcell. ORD spectra were recorded with a JASCO ORD/UV5 scanning polarimeter. Optically active diene complexes **1** and **7** were prepared by asymmetric induction during complexation;[6,7] a typical procedure has been published separately.[2] The experimental details for the preparation and alkylation of the optically active salt **8** are reported elsewhere.[2] All reactions involving tricarbonyliron complexes were performed under nitrogen. Rotation measurements were recorded at 22 °C.

Purification of (2*R*)-(−)-Tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron(1+) Hexafluorophosphate (8). To 0.167 g of the salt **8**, obtained from **7** by treatment with concentrated H_2SO_4, in 2 mL CH_3CN was added 2 drops of Et_3N. The solution darkened, and a brown precipitate began to form. After being stirred for 10 min, the mixture was filtered through Celite and evaporated to dryness. The residue was taken up in the minimum volume of CH_3CN, and the cloudy solution was filtered into 10 mL of ether. The resulting yellow precipitate was collected, washed with water and ether, and dried over KOH. Pure **8** (0.044 g, 26%) was recovered with unchanged $[\alpha]_D$.

(2*S*,5*R*)-(−)-Tricarbonyl[(1,2,3,4-η)-5-isopropyl-2-methoxy-1,3-cyclohexadiene]iron(0) (4). (1*S*)-(+)-Tricarbonyl-[(1,2,3,4-η]-1-methoxy-1,3-cyclohexadiene]iron(0) [**1**; 4.40 g, 17.6 mmol; $[\alpha]_D$ +8.3° (*c* 12, $CHCl_3$)] was treated with 6.8 g (20.6 mmol) of triphenylmethylium tetrafluoroborate in 60 mL of dry CH_2Cl_2 for 1.5 h at 20 °C. A normal workup[11] afforded 1.75 g (42%) of (2*S*)-(−)-tricarbonyl[(2,3,4,5-η)-2,4-cyclohexadien-1-one]iron(0) [**3**, $[\alpha]_D$ −34.4° (*c* 2, $CHCl_3$)] and 0.68 g (10%) of (2*S*)-(+)-tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate [**2**, $[\alpha]_D$ +4.8° (*c* 6, CH_3CN)], both indistinguishable by ^1H NMR from authentic samples of the racemic compounds.

A solution of diisopropylcadmium in tetrahydrofuran (20 mL, prepared from 0.29 g of Mg, 1.2 g of 2-chloropropane, and 0.92 g $CdCl_2$) was added dropwise to 0.68 g (1.73 mmol) of the salt **2** in CH_3CN (5 mL, distilled from CaH_2) at −10 °C. After being stirred for 2 min, the mixture was quenched with 10 mL of 10% NH_4Cl(aq) and worked up in the normal way.[9d] Column chromatography (silica; hexane/benzene, 9:1) and distillation under reduced pressure [50 °C (10^{-3} mmHg)] gave 0.28 g (55%) of the title compound **4** as a yellow oil: $[\alpha]_D$ −5.1° (*c* 9, $CHCl_3$); IR (neat) 2040, 1930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (3 H, d, J = 7 Hz, CH_3CH), 0.85 (3 H, d, J = 7 Hz, CH_3CH), 1.0–2.1 (4 H, m, H-5β, H-6α, H-6β, and CH_3CHCH_3), 2.69 (1 H, dd, J = 7, 3 Hz, H-4), 3.32 (1 H, m, H-1), 3.66 (3 H, s, CH_3O), 5.17 (1 H, dd, J = 7, 2.5 Hz, H-3). Anal. Calcd for $C_{13}H_{16}FeO_4$: C, 53.5; H, 5.5. Found: C, 53.7; H, 5.6.

Conversion of the Complex 4 to (*R*)-(−)-4-Isopropyl-2-cyclohexenone (Cryptone, 6). To 0.25 g (0.8 mmol) of **4** [$[\alpha]_D$ −5.1° (*c* 9, $CHCl_3$)] in 4 g of *N*,*N*-dimethylacetamide was added 1.25 g of trimethylamine *N*-oxide dihydrate, and the suspension was stirred for 1 min in an oil bath at 75 °C. Gas was evolved, and the suspension turned red-brown. The mixture was removed from the heating bath, and stirring continued until gas evolution ceased (ca. 3 min) after which the mixture was warmed in the oil bath for 5 min, allowed to cool for 5 min, cooled on ice for 15 min, and finally filtered through Celite. The residue was washed with ether (5 × 20 mL), and the combined filtrates were washed with water (5 × 25 mL) and dried ($MgSO_4 \cdot 3H_2O$). The solvent

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(24) Trost, B. M.; Klun, T. P. *J. Org. Chem.* **1980**, *45*, 4256.

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

(27) Holton, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 8083.

was removed at 0 °C, giving 0.10 g of a pale yellow oil [$[\alpha]_D$ −5° (c 5, $CHCl_3$)], which displayed a ^1H NMR [($CDCl_3$) δ 0.94 (6 H, d, J = 7 Hz), 1.5–2.4 (4 H, m), 3.56 (3 H, s), 4.64 (1 H, m), 5.94 (2 H, m)] consistent with the expected product **5**. Earlier experiments had indicated this product to be unstable, and it was subjected to acid hydrolysis without purification.

The crude diene **5** (0.10 g) was dissolved in 5 mL of $CHCl_3$ and stirred with 0.06 g of oxalic acid and 0.2 mL of water absorbed on 2.0 g of silica gel (Merck) at 15 °C for 18 h. The mixture was filtered and the residue washed with $CHCl_3$ (5 × 1 mL). Solvent was removed from the combined filtrates at 0 °C, and the residue was distilled in a sealed tube at 60 °C (ca. 1 mmHg), giving 0.058 g (49% from **4**) of a colorless oil: $[\alpha]_D$ −2.9° (c 6, C_2H_5OH); ^1H NMR ($CDCl_3$) δ 0.94 (d, J = 7 Hz), 0.95 (d, J = 7 Hz), 1.6–2.7 (m), 5.95 (dd, J = 10, 3 Hz), 6.85 (dd, J = 10, 2 Hz), indistinguishable from that of an authentic sample of (*R*)-(−)-cryptone. The semicarbazone melting point was 195–197 °C [lit.[28] mp 195–196.5 °C (*R,S*)].

Conversion of the Complex 9 to (*S*)-(+)-5-Isopropyl-2-methyl-1,3-cyclohexadiene ("α"-Phellandrene). To 0.14 g (0.5 mmol) of **9** [$[\alpha]_D$ +1.2° (c 13, $CHCl_3$)] in 1.4 mL of *N,N*-dimethylacetamide was added 0.7 g of trimethylamine *N*-oxide dihydrate, and the suspension was stirred for 1 min in an oil bath at 75 °C. The mixture was removed from the heating bath and stirred until gas evolution had ceased (ca. 3 min) after which heating was resumed for 1 min. The brown suspension was chilled and filtered through Celite, and the residue was washed with pentane (3 × 10 mL). The yellow filtrate was washed with water (5 × 10 mL), dried (K_2CO_3), and concentrated. The crude product was transferred to a distillation tube and the solvent removed with a gentle stream of nitrogen. Distillation was performed in a sealed tube at ca. 0.1 mmHg; the receiver was cooled with liquid nitrogen, and 0.04 g of a colorless oil [α +0.012° (c 3.48, l = 0.1, $CHCl_3$)] was collected. This product was identified by ^1H NMR and GLC as a mixture of "α"-phellandrene, 1-isopropyl-4-methylbenzene (*p*-cymene), and 1-isopropyl-4-methyl-1,3-cyclohexadiene ("α"-terpinene) containing *ca.* 50% "α"-phellandrene. The mixture was obtained in 48% yield.

Removal of the tricarbonyliron group by the method of Thompson[29] was also investigated. To 0.12 g of **9** was added 4 mL of a saturated solution of $CuCl_2 \cdot 2H_2O$ in C_2H_5OH. After being stirred at room temperature for 1 h, the dark mixture was poured into 40 mL of ether, filtered through Celite, washed with water (4 × 10 mL), and dried (K_2CO_2). Removal of solvent and distillation as before gave a similar mixture of terpenes with a lower proportion of "α"-phellandrene.

(2*S*)-(−)-Tricarbonyl[(1,2,3,4-η)-2-methoxy-1,3-cyclohexadiene]iron(0) (10). To a solution of 0.08 g (0.2 mmol) of the 2-methoxy salt **2** [$[\alpha]_D$ +1.0° (c 8, CH_3CN)] in 3 mL of CH_3CN was added 0.05 g (excess) of $NaBH_4$ in one portion. After being stirred at room temperature for 5 min the mixture became lighter in color, was filtered through Celite, and was evaporated under reduced pressure. The residue was extracted with 15 mL of pentane in four portions. The extracts were filtered through silica, washed with brine (10 mL), dried, and evaporated to give 0.036 g of the known[14] **10** [$[\alpha]_D$ −1.3° (c 3.5, $CHCl_3$)] as the sole product in 67% yield.

Hydride Abstraction from (1*R*,4*S*)-(−)-Tricarbonyl[(1,2,3,4-η)-1-methoxy-4-methyl-1,3-cyclohexadiene]iron(0) (7). To 1.53 g (5.8 mmol) of **7** [$[\alpha]_D$ −52° (c 5, $CHCl_3$)] in 2 mL of CH_2Cl_2 was added 1.92 g (5.8 mmol) of triphenylmethylium tetrafluoroborate dissolved in 20 mL of CH_2Cl_2 at −5 °C. After being stirred for 1.5 h, the mixture was concentrated to ca. 5 mL under vacuum, and 80 mL of ether was added. The yellow precipitate was collected, hydrolyzed, and extracted with ether in the usual way.[9a] Addition of NH_4PF_6 to the aqueous fraction caused 1.0 g (42%) of (2*R*,5*S*)-(−)-tricarbonyl[(1,2,3,4,5-η)-2-methoxy-5-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate [**11**, $[\alpha]_D$ −73° (c 10, CH_3CN)] to precipitate as a fine yellow powder. (2*R*,4*S*)-(+)-Tricarbonyl[(2,3,4,5-η)-4-methyl-2,4-cyclohexadien-1-one]iron(0) [**12**, $[\alpha]_D$ +219° (c 0.2, $CHCl_3$)] was obtained from the ether fraction by preparative TLC (silica, ether) as a fairly unstable yellow oil (0.2 g, 14%). The ^1H NMR spectra of both products agreed with data for the racemic compounds.

(1*R*)-(−)-Tricarbonyl[(1,2,3,4-η)-1-methyl-1,3-cyclohexadiene]iron(0) (13) and (2*R*)-(−)-Tricarbonyl[(1,2,3,4-η)-2-methyl-1,3-cyclohexadiene]iron(0) (14). To a solution of 0.65 g (1.7 mmol) of (2*R*)-(−)-tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate[2] [8, $[\alpha]_D$ −2.5° (c 9, CH_3CH)] in 14 mL of CH_3CN was added in one portion of 0.19 g of $NaBH_4$ at −5 °C. After being stirred for 10 min, the mixture was filtered and evaporated, and the residue was extracted with pentane (3 × 15 mL). The extracts were filtered through a pad of alumina and evaporated to give 0.33 g (81%) of a yellow oil which was identified by ^1H NMR and GLC comparison[3] with authentic racemic material[9a] as a roughly 1:1 mixture of **13** and **14**. Separation was achieved by chromatography in a darkened room on 150 g of silver nitrate impregnated silica (30%) eluted with ca. 5 L dry distilled hexane. A pure (GLC) sample (0.06 g) of **14** [$[\alpha]_D$ −1.7° (c = 7, $CHCl_3$)] was eluted first followed by a mixture of **13** and **14**. Elution with hexane was continued until no further **14** could be detected in the eluant. A pure (GLC) sample (0.02 g) of **13** [$[\alpha]_D$ −1.5° (c 3, $CHCl_3$)] was washed from the column with benzene.

(2*R*,5*R*)-(+)-Tricarbonyl[(1,2,3,4-η)-2-methoxy-5-methyl-1,3-cyclohexadiene]iron(0) (15). A cooled solution of 0.1 g (0.25 mmol) of (2*R*)-(−)-tricarbonyl[(1,2,3,4,5-η)-2-methoxy-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate [**2**, $[\alpha]_D$ −10.7° (c 9, CH_3CN)] in 1 mL of CH_3CN was added to a solution of $LiMe_2Cu$ (prepared at −5 °C from 0.07 g dry CuI suspended in 1 mL of tetrahydrofuran and 1 mL of a 1.4 M solution of MeLi in ether) at −45 °C. The flask and syringe were washed with 1 mL of tetrahydrofuran which was added to the mixture. After the mixture was stirred vigorously at −45 °C for 2 min, the reaction was quenched by addition of 20 mL of iced 5% HCl(aq) and extracted with ether (2 × 20 mL). The extracts were washed with water (10 mL) and brine (2 × 10 mL), dried over $MgSO_4 \cdot 3H_2O$, and filtered through a pad of silica. Evaporation under reduced pressure gave 0.05 g of a yellow oil [$[\alpha]_D$ +11.7° (c = 4, $CHCl_3$)] which was identified as the title product **15** (75% yield) by comparison with the published[15] ^1H NMR data for the racemic compound.

Conversion of the Complex 15 to (2*S*)-(+)-Tricarbonyl[(1,2,3,4,5-η)-2-methyl-2,4-cyclohexadien-1-yl]iron(1+) Hexafluorophosphate (8). To 0.04 g of neat **15** [$[\alpha]_D$ +11.7° (c = 4, $CHCl_3$)] at 5 °C was added four drops of concentrated H_2SO_4 from a pipet. The resulting dark paste was mixed thoroughly with a Teflon spatula for 10 min. After trituration with 0.5 mL ether, addition of 3 drops of saturated NH_4PF_6(aq) caused immediate formation of a yellow precipitate which was collected by filtration, washed with water and ether, and dried over KOH pellets at 10^{-3} mmHg. The product (0.03 g, 53% crude yield) was identified as the salt **8** contaminated by a small proportion (5–10%) of tricarbonyl[(1,2,3,4,5-η)-1-methyl-2,4-cyclohexadien-1-yl]iron(1+) hexafluorophosphate. The sign of rotation of this material [$[\alpha]_D$ +0.6° (c 3, CH_3CN)] agrees with that expected for the absolute configurations assigned above.

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Registry No. (1*R*)-**1**, 74242-50-5; (1*S*)-**1**, 74242-90-3; (2*R*)-**2**, 79120-66-4; (2*S*)-**2**, 76704-83-1; (2*S*)-**3**, 74242-52-7; (2*S*,5*R*)-**4**, 79171-32-7; **5**, 76640-26-1; (*R*)-**6**, 2158-59-0; (1*S*,4*R*)-**7**, 74242-47-0; (1*R*,4*S*)-**7**, 74242-51-6; (2*R*)-**8**, 76740-63-1; (2*S*)-**8**, 79120-68-6; (2*R*,5*S*) **9**, 76683-58-4; (2*S*)-**10**, 79120-69-7; (2*R*)-**10**, 74242-48-1; (2*R*,5*S*)-**11**, 78379-31-4; (2*R*,4*S*)-**12**, 79120-70-0; (1*R*)-**13**, 75765-31-0; (2*R*)-**14**, 75765-32-1; (2*R*,5*R*)-**15**, 79120-71-1; 2-chloropropane, 75-29-6; (*R*)-(−)-cryptone semicarbazone, 79120-25-5; (*S*)-(+)-5-isopropyl-2-methyl-1,3-cyclohexadiene, 2243-33-6.

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