environment approach used above for the assignment of ^1H NMR spectra of isomers of homonuclear substituted compounds, in principle, can be extended to the spectra of the heteronuclear compounds $D^{H}{}_1D^{Fp}{}_3$ and $D^{Co}{}_1D^{Fp}{}_3$[1] (Figure 3).

In order to predict the ^1H NMR spectra of these compounds and assign the isomers, it is necessary to know the relative through-bond shielding effect of the two metallic substituents and the relative through-space shielding effect of the two metallic substituents and of CH_3.

The following limiting cases yield to analysis: (1) If the through-bond shielding effect is the same for both metallic silicon substituents, but their through-space shielding effects are different, a single cluster of peaks is expected in the methyl region. (2) If the through-space effect is the same for the two substituents but the through-bond effect is different, two symmetrical clusters of peaks are expected. (3) If both through-bond and through-space effects of the two substituents are different, two unsymmetrical clusters of peaks are expected.

The spectrum of a partially-substituted $D^{H}{}_{4-n}D^{Fp}{}_n$ (n = 3.1) (Figure 3a) shows the presence of two clusters of peaks in the methyl region in the ratio 3:1. The spectrum illustrates the limiting case 3 above, where the through-bond shielding effect of the Si–H (at right) is clearly different from the effect of the Fp group (at left). The cyclopentadienyl region is very complex and cannot be assigned, but the total number of peaks does not exceed 18, as expected. The spectrum of $D^{Co}{}_1D^{Fp}{}_3$ (Figure 3b) shows only one group of peaks in the methyl region illustrating the first limiting case above where the through-bond effects of Fp and $Co(CO)_4$ are roughly the same, but their through-space effects are different. The model predicts 14 peaks for CH_3–Si–Fp groups and six peaks for CH_3–Si–Co when only the compound $D^{Co}{}_1D^{Fp}{}_3$ is present. The observed spectrum of $D^{Co}{}_1D^{Fp}{}_3$ shows 20 peaks in the methyl region. The assignment of these peaks is impossible because the precise shielding effects of each substituent are unknown. The model also predicts 12 peaks in the cyclopentadienyl region. The spectrum shows only 11 peaks, but it seems reasonable to assume that the large central peak results from the overlap of two peaks. The assignments of the ^1H NMR spectrum of isomers of $D^{Co}{}_1D^{Fp}{}_3$ could be possible by means of a partial separation of these isomers as used successfully for $D^{Fp}{}_4$. This was not attempted due to the difficulty involved in preparing a large enough sample of pure $D^{Co}{}_1D^{Fp}{}_3$.

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Registry No. $D_3{}^{H}$(I), 89887-17-2; $D_3{}^{Ph}$(I), 3424-57-5; $D_3{}^{Br}$(I), 89887-18-3; $D_3{}^{H}$(II), 89887-19-4; $D_3{}^{Ph}$(II), 6138-53-0; $D_3{}^{Br}$(II), 89887-20-7; $D_4{}^{H}$(I), 89887-21-8; $D_4{}^{Ph}$(I), 4885-37-4; $D_4{}^{Br}$(I), 89887-22-9; $D_4{}^{Co}$(I), 89885-87-0; $D_4{}^{Fp}$(I), 89887-14-9; $D_4{}^{H}$(II), 89887-23-0; $D_4{}^{Ph}$(II), 5131-04-4; $D_4{}^{Br}$(II), 89887-24-1; $D_4{}^{Co}$(II), 89885-88-1; $D_4{}^{Fp}$(II), 89887-15-0; $D_4{}^{H}$(III), 89887-25-2; $D_4{}^{Ph}$(III), 15331-54-1; $D_4{}^{Br}$(III), 89887-26-3; $D_4{}^{Co}$(III), 89887-16-1; $D_4{}^{Fp}$(III), 89885-89-2; $D_4{}^{H}$(IV), 89887-27-4; $D_4{}^{Ph}$(IV), 4885-39-6; $D_4{}^{Br}$(IV), 89887-28-5; $D_4{}^{Co}$(IV), 89885-90-5; $D_4{}^{Fp}$(IV), 89885-91-6; $D_5{}^{H}$(I), 89887-29-6; $D_5{}^{H}$(II), 89887-30-9; $D_5{}^{H}$(III), 89887-31-0; $D_5{}^{Co}$(III), 89885-92-7; $D_5{}^{H}$(IV), 89887-32-1; $D_5{}^{Co}$(IV), 89885-93-8.

Chirality Transfer in the Coordination Sphere of Iron

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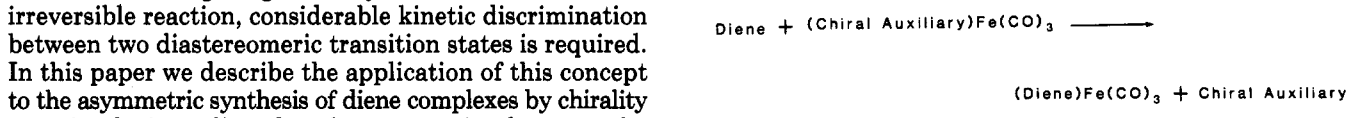
Transfer of chirality between a chiral donor complex and an unsymmetrical diene ligand gives rise to optically active tricarbonyliron complexes with enantiomeric excesses as high as 40%.

To achieve a high degree of asymmetric induction in an irreversible reaction, considerable kinetic discrimination between two diastereomeric transition states is required. In this paper we describe the application of this concept to the asymmetric synthesis of diene complexes by chirality transfer during a ligand exchange reaction between the metal complex of a chiral auxiliary and a prochiral diene (Scheme I). Our results indicate a much higher degree of asymmetric induction than is obtained[2] when a chiral auxiliary is directly attached to the ligand, as is anticipated because of the more intimate involvement of the chiral component when linked within the coordination sphere of the metal.

Scheme I



In view of the synthetic utility[3] of enone complexes as a source of the tricarbonyliron group in ligand exchange reactions, we selected a range of chiral enone complexes as donors for this study. Reports have indicated that

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Table I. Chirality Transfer in the Formation of Complex 7a

chiral donor	temp, °C	time, h	yield, %	$[\alpha]_D$, deg	abs conf	ee, %
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	80	19[a]	22	−42	1*R*,4*S*	33
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	40	19[b]	9	−49	1*R*,4*S*	39
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	65	88[a]	26	−54	1*R*,4*S*	43
(+)-pulegone	110	6[c]	58	+4	1*S*,4*R*	3
(+)-pulegone	80	90[a]	48	+6	1*S*,4*R*	5
(+)-pulegone	40	270[b]	79	+13	1*S*,4*R*	10
(+)-pinocarvone	40	18[b]	40	−1	1*R*,4*S*	1
(−)-myrtenal	80	19[a]	0			
(+)-3-methylenecamphor	80	19[a]	0			
(+)-3-benzylidenecamphor	40	90[a]	13	−4	1*R*,4*S*	3
(−)-cholest-4-ene-3,6-dione	70	70[a]	0			

[a] In benzene. [b] In petroleum ether. [c] In toluene.

Table II. Chirality Transfer in the Formation of Complex 7b

chiral donor	temp, °C	time, h	yield, %	$[\alpha]_D$, deg	abs conf	ee, %
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	80	17[a]	10	−29	1*R*	14
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	60	110[a]	26	−37	1*R*	18
(+)-pulegone	80	18[a]	83	+15	1*S*	7
(+)-pulegone	40	240[b]	27	+9	1*S*	4
(−)-cholest-4-ene-3,6-dione	80	70[a]	3	+1.5	1*S*	1

[a] In benzene. [b] In petroleum ether.

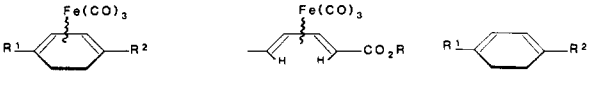
remarkable regioselectivity is attainable[4] in reactions involving transfer of tricarbonyliron from benzylideneacetone to one of several isomeric ligands present in the reaction mixture, although no attempt had previously been made to achieve an enantioselective method of complexation in this way. The preparations of optically active enone complexes of pulegone (**1**) and pinocarvone (**2**) have been described by Koerner von Gustorf et al.,[5] and our preliminary results of asymmetric induction experiments using (+)-pulegone and (−)-3β-(acetyloxy)pregna-5,16-dien-20-one (**3**) as chiral donors have been reported.[6]

Results

Formation of the Chiral Donor Complexes. Donor complexes were generated in situ either photochemically from $Fe(CO)_5$ or thermally from $Fe_2(CO)_9$, from a range of optically active enones. Either preparation results in the presence of $Fe(CO)_5$ in the crude product used for ligand exchange, but, at the temperatures employed, direct complexation of the diene by $Fe(CO)_5$ cannot occur, so formation of racemic material in this way does not complicate the analysis of the results. The thermal method was found to be more reliable and was used for the reactions reported below. Our initial studies[6] with pulegone and 3β-(acetyloxy)pregna-5,16-dien-20-one indicated, however, that similar results can be obtained photochemically. Isolation of the donor complexes was attempted only in the case of pulegone where the presence of two stable, epimeric tricarbonyliron complexes was expected.[5] Comparison of NMR resonances of the enone complexes with those obtained from the crude reaction mixture indicated that the two isomers were present in roughly equal amounts. The thermal stability of the enone complexes produced varied considerably. Complexes of pinocarvone, 3-methylenecamphor (**4**), and myrtenal were particularly unstable, and in such cases, the photochemical method of preparation may prove superior.

The Ligand Exchange Reaction. A solution of the 1,3-diene was added, under nitrogen, to the crude donor complex, and the mixture was heated until ligand exchange was complete. The product was isolated by chromatography and distillation and optical rotations were measured on analytically pure samples. At moderate temperatures, at which the best optical yields were achieved, the rate of the exchange reaction was slow and long reaction times were necessary to obtain satisfactory chemical yields. The yield was also highly dependent on the enone used. In cases where the enone was too unstable, excessive thermal decomposition prevented effective ligand exchange. A critical balance was needed between the stereochemical interactions required for a high asymmetric induction and undue steric crowding that can render the complex too unstable to be of use. Thus the more stable complex of 3-benzylidenecamphor (**5**) proved to be a better donor than that of 3-methylenecamphor, but pinocarvone, which gave a still better chemical yield, was unsatisfactory because of the low degree of asymmetric induction achieved. In the cases of the two most effective donors, (−)-3β-(acetyloxy)pregna-5,16-dien-20-one (**3**) and (−)-cholest-4-ene-3,6-dione (**6**), the chiral auxilliaries were recovered by crystallization from the crude product.

Optical Purity and Absolute Configurations of Products. The chemical correlations of the products **7a** and **7b** with phellandrene and cryptone have been reported[7] elsewhere, and the complex **7c** is available[8] in optically pure form by direct complexation of limonene.



7 a: R^1 = OMe, R^2 = Me
b: R^1 = OMe, R^2 = H
c: R^1 = $CHMe_2$, R^2 = Me

8 a: R = Me
b: R = H

9 a: R^1 = OMe, R^2 = Me
b: R^1 = OMe, R^2 = H

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Table III. Chirality Transfer in the Formation of Complex 7c

chiral donor	temp, °C	time, h	yield, %	$[\alpha]_D$, deg	abs conf	ee, %
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	65	112[a]	21	−6	1*S*,4*S*	43

[a] In benzene.

Table IV. Chirality Transfer in the Formation of Complex 8a

chiral donor	temp, °C	time, h	yield, %	$[\alpha]_D$, deg	ee, %
(−)-3β-(acetyloxy)pregna-5,16-dien-20-one	80	19[a]	16	+28	14
(+)-pulegone	40	300[b]	38	+7	4
(+)-pulegone	80	19[a]	27	+14	7
(−)-myrtenal	69	19[a]	0		
(−)-cholest-4-ene-3,6-dione	80	19[a]	49	−38	19

[a] In benzene. [b] In petroleum ether.

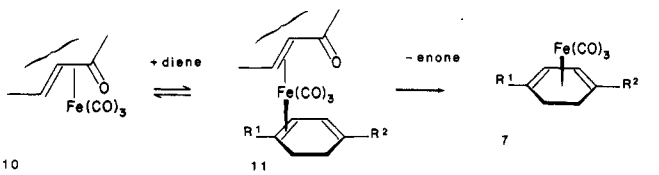
The optical purity and absolute configurations of the products from the ligand exchange reaction were determined from the magnitude and sign of specific rotation measurements, respectively. The absolute configuration of the ester **8a** has not been determined. However, the resolution[9] of the tricarbonyliron complex of sorbic acid and esterification of the product has led to an estimate[10] of $[\alpha]_{578}$ as 205° for the fully resolved complex **8a**; optical yields reported here were calculated from this value.

Variation of Diene and Donor Ligand Employed. The degree of chirality transfer was measured for a range of dienes and chiral auxilliaries. The results are summarized in the Tables I–IV. It is clear from these results that the donor complex which gives the highest optical yield depends on the nature of the diene used. This is unfortunate for synthetic purposes since optimization would need to be repeated for each substrate. The best inductions for cyclic dienes were given by (−)-3β-(acetyloxy)-pregna-5,16-dien-20-one (**3**), but (−)-cholest-4-ene-3,6-dione (**6**), which was ineffective as a donor for the cyclic dienes used, was the best donor for the acyclic diene. The degree of induction was also sensitive to the substituents on the diene. The presence of a methyl group in the diene **9a** resulted in a higher optical yield than was obtained with the diene **9b**, and the best chirality transfer occurred in cases in which both termini of the diene were substituted.

Discussion

In a reaction of this type, chirality transfer takes place between an auxiliary, with chiral centers at carbon, and a prochiral diene. The product has planar chirality, and the degree of asymmetric induction depends on the selectivity achieved between the two enantiofaces of the diene during complexation. A number of kinetic investigations of the exchange reactions of olefinic ligands have been reported.[11] Frequently a competition is observed between a dissociative pathway, in which the metal–ligand bond is broken to form a coordinatively unsaturated intermediate that then reacts with an incoming ligand, and an associative pathway, in which the incoming ligand participates in breaking the metal–ligand bond, though in some cases only one of these processes operates. In the most recent kinetic investigation of the displacement of benzylideneacetone by dienes, contributions from both the dissociative and associative processes were required[12] to account fully for the rate data obtained, though the latter process was considered to proceed by a mechanism that predominantly involved bond breaking in the approach to the transition state.

Scheme II



The ligand exchange can be regarded as a stepwise process, in which the enone ligand is displaced via a bis(olefin) complex, **11**, in which only one olefinic linkage of the diene is bound to the metal (Scheme II). This intermediate **11** may either revert to the starting material **10**, by loss of the diene ligand, or may lose the enone to form the diene complex **7**. This later process would leave the stereochemistry of the metal complex unchanged, since while changing from η^2 to η^4 bonding the metal remains bound to the same face of the diene. The absolute configuration of the product **7** is determined during the initial approach of the diene to form the intermediate **11**.

Conclusion

The following criteria appear necessary if substantial chirality transfer is to occur. The chiral donor must not otherwise be chemically modified during complexation, and the complex formed must possess reasonable thermal stability yet must be sufficiently labile to undergo ligand exchange in mild conditions. Since the selectivity observed for the preferential formation of one enantiomer during ligand exchange must reflect the differing steric interactions between the chiral donor and the diene ligand in the transition states of competing reaction paths and since the steric interactions increase when there is crowding in the transition state, the presence of bulky substituents should lead to greater selectivity. A balance must be struck, however, since excessively bulky ligands cause either the thermal instability of the donor complex or a failure to form the diene complex due to complete blocking of the ligand transfer process. Ideally, a chiral donor should possess a structure that interferes with only one of the

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competing pathways and so gives good selectivity for one enantiomer.

The results presented here have a wider significance. They provide an example of a chirality transfer reaction that is mediated by coordination to a metal center. The outcome is unusual since the isolation of stable metal diene complexes as products allows direct investigation of the stereochemistry of the process.

Experimental Section

General Methods. Optical rotations were measured in chloroform at 22 °C on a Bendix N.P.L. 143C automatic polarimeter or on a Perkin-Elmer 241 polarimeter fitted with a 10-cm microcell. ^{1}H NMR spectra were recorded at 100 MHz with a JEOL JNM-MH-100 or a Varian Associates H.A. 100 spectrometer, and ^{13}C NMR spectra were recorded at 15.04 MHz with a JEOL JNM FX 60 spectrometer. Tetramethylsilane or benzene were used as internal references. IR spectra were measured with a Perkin-Elmer 257 spectrometer. Petroleum ether refers to the fraction of bp 40–60 °C. (+)-Pulegone and (−)-myrtenal were purchased from Aldrich Chemical Co. Ltd and were used without purification. α-Terpinene was purchased from Fluka A.G. (−)-Cholest-4-en-3,6-dione,[13] (+)-3-methylenecamphor,[14] and (+)-3-benzylidenecamphor[15] were prepared by literature procedures. All reactions involving tricarbonyliron complexes were performed with degassed solvents under nitrogen.

Preparation of Methoxy-1,3-cyclohexadienes. A solution of 10 g (91 mmol) of 1-methoxy-1,4-cyclohexadiene was heated under reflux with 0.3 g (0.8 mmol) of chlorotris(triphenylphosphine)rhodium in ethanol-free chloroform for 3 h. Evaporation and filtration through basic alumina with benzene gave a 3:2 mixture (by ^{1}H NMR) of 1,3- and 1,4-dienes as a pale yellow oil. 1-Methoxy-4-methyl-1,3-cyclohexadiene was obtained similarly as a 10:3 mixture with the 1,4-diene. These equilibrium mixtures were used without separation or further purification; the yields reported are based on the proportion of the mixture present as the 1,3-diene, since 1,4-dienes have been shown to be inert to the reaction conditions used for ligand exchange.[4b]

General Procedure for Chirality Transfer Using 3β-(Acetyloxy)pregna-5,16-dien-20-one. A solution of 3β-(acetyloxy)pregna-5,16-dien-20-one [$[\alpha]_D$ −39° (*c* 5)] in petroleum ether or benzene was added to a slight excess of $Fe_2(CO)_9$, warmed gently to ca. 40 °C, and then heated for 5 h. The $Fe_2(CO)_9$ was consumed. After filtration through Celite under nitrogen, the solvent was evaporated and the diene was added in the appropriate solvent for ligand exchange. After being heated as indicated in Tables I–IV, the mixture was cooled, filtered through Celite, and evaporated. The steroid was recovered (30–82%) from the residue by crystallization from hexane, and the filtrate was reduced in volume and chromatographed to isolate the diene complex. The complex was distilled (10^{-3} mmHg, 40–60 °C, Kugelrohr) to give products that were analytically pure.

Isolation of Diene Complexes after Ligand Exchange. The following conditions were used to isolate the diene complexes: **Tricarbonyl[(1–4-η)-1-methoxy-4-methyl-1,3-cyclohexadiene]iron(0)** was chromatographed on silica eluted with benzene/hexane (1:1, v/v). **Tricarbonyl[(1–4-η)-1-methoxy-1,3-cyclohexadiene]iron(0)** was separated by chromatography on silica eluted with benzene/hexane (1:1, v/v) from a small quantity of the 2-methoxy isomer which was also formed in the reaction. **Tricarbonyl[(1-4-η)-1-isopropyl-4-methyl-1,3-cyclohexadiene]iron(0)** was chromatographed on silica eluted with hexane. **Tricarbonyl[methyl (2–5-η)-2,4-hexadienoate]iron(0)** was chromatographed on silica eluted with benzene. Typically, between 0.5 and 2 g of products were obtained from reactions employing efficient chiral donors. The yields of these reactions are indicated in Tables I–IV.

General Procedure for Chirality Transfer Using Cholest-4-ene-3,6-dione. (−)-Cholest-4-ene-3,6-dione, mp 124–125 °C [lit.[13] mp 124–126 °C] and $[\alpha]_D$ −42.5° (*c* 1), was treated as described above for 3β-(acetyloxy)pregna-5,16-dien-20-one. After evaporation the steroid was recovered by crystallization from methanol, and the filtrate was concentrated and chromatographed to isolate the diene complex.

General Procedure for Chirality Transfer Using Pulegone. (+)-Pulegone [$[\alpha]_D$ +22° (neat)] was treated as described above for 3β-(acetyloxy)pregna-5,16-dien-20-one. The crude product was distilled at 10^{-3} mmHg (Kugelrohr), and the two fractions obtained were chromatographed separately. The diene complexes were redistilled.

Preparation of (+)-Pinocarvone. Pinocarvone was prepared by selenium dioxide oxidation of β-pinene using a combination of literature procedures.[16] The coproduct myrtenal was separated by selective hydrolysis[16b] of the bisulfite addition compounds by additions of sodium carbonate during steam distillation. Sodium hydroxide was added to the residue. (+)-Pinocarvone {$[\alpha]_D$ +66° (*c* 2) [lit.[17] $[\alpha]_D$ +60° (*c* 1)]} was isolated by prolonged steam distillation and redistilled {bp 39–40 °C (at 0.2 mmHg) [lit.[16a] bp 48–49 °C (at 1.5 mmHg)]}.

Chirality Transfer Using Pinocarvone. Irradiation[5] of a mixture of 3 g (22 mmol) of (+)-pinocarvone and 5 g (25 mmol) of $Fe(CO)_5$ in 320 mL of benzene gave a deep orange-red solution that was filtered through Celite under nitrogen. The reaction mixture was unusually sensitive to both air and heat, temperatures above 40 °C resulting in rapid darkening and deposition of a black solid. Removal of solvent at 30 °C afforded a deep red oil. Attempts to obtain a crystalline product by trituration or distillation were unsuccessful, and the oil was used without further purification. Reaction with 2 g (16 mmol) of the diene **9a** was performed by heating in 50 mL of petroleum ether at 40 °C for 18 h. The complex **7a** (1.68 g, 40%) was isolated in the same way as is described above for pulegone. Attempts to prepare the tricarbonyliron complex of pinocarvone thermally using $Fe_2(CO)_9$ were unsuccessful.

Chirality Transfer Using 3-Benzylidenecamphor. 3-Benzylidenecamphor was recrystallized from ethanol as colorless needles, mp 97–98 °C (lit.[15] 97 °C) [$[\alpha]_D$ +404° (*c* 1, benzene) (lit.[15] $[\alpha]_D$ +412°; lit.[18] $[\alpha]_D$ +406°)]. The reaction was performed as described above for pulegone, except that in this case the donor complex was formed by stirring at room temperature for 24 h; attempted reaction with $Fe_2(CO)_9$ at 60 °C resulted in decomposition of the product.

Attempted Chirality Transfer Using Myrtenal. Reaction of (−)-myrtenal with $Fe_2(CO)_9$ was attempted by using the method employed for pulegone. A black solution was obtained. After addition of methyl 2,4-hexadienoate or the diene **9a** in benzene and stirring at 69 °C for 19 h, the reaction was worked up in the usual way. No tricarbonyliron complexes were obtained.

Attempted Chirality Transfer Using 3-Methylenecamphor. 3-Methylenecamphor [$[\alpha]_D$ +119.5° (*c* 1.5) (lit.[14] $[\alpha]_D$ +142°; lit.[19] $[\alpha]_D$ +127°)] was obtained by distillation {bp 81°C (at 0.7 mmHg) [lit.[19] 82–84° (at 10 mmHg)]} using a spinning-band column. Reaction with $Fe_2(CO)_9$ was attempted by the method employed for pulegone. A dark red solution was obtained. After addition of the diene, the reaction mixture was heated for 19 h and worked up in the usual way. No tricarbonyliron complexes were obtained.

Isolation of Tricarbonyliron Complexes[4] of Pulegone. A solution of 4 g (26 mmol) of (+)-pulegone [$[\alpha]_D$ +22°, (neat)] in 100 mL of petroleum ether was added to 11 g (30 mmol) of $Fe_2(CO)_9$ and heated gently at reflux for 5 h. The deep red solution was filtered through Celite, concentrated to 10 mL, and chilled to −78 °C. A dark red liquid was decanted from a red precipitate that was recrystallized from pentane at −78 °C as dark red needles (0.84 g, 11%): ^{1}H NMR (C_6D_6) δ 0.89 and 0.93 (3 H, d, J = 6 Hz, and d, J 6 Hz, CH_3-7), 1.39 and 1.42 (3 H, s and s, CH_3-9), 1.55 and 1.57 (3 H, s and s, CH_3 10), 2.0–2.6 (7 H, m, H-1, H-2, H-5, H-6); ^{13}C NMR (C_6D_6) δ 21.5, 26.0, 26.4, 26.9, 30.1, 30.4,

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31.6, 38.2, 39.6, 68.8, and 69.8 (C-8), 99.1 and 99.5 (C-4), 144.2 and 145.8 (C-3). The NMR spectra clearly indicated the presence of roughly equal amounts of the two expected[5] isomers. A small portion was sublimed at 35 °C (at 10^{-3} mmHg) as orange needles: IR (cyclohexane) 2051, 1991 1965 cm^{-1}, (Nujol) 1074, 1030, 940, 921, 879 cm^{-1}; m/z 292 (1%, M^+), 264, 137, 123, 109, 95, 82, 81, 67. Anal. Calcd for $C_{13}H_{14}O_4Fe$: C, 53.4; H, 5.5. Found: C, 53.3; H, 5.6.

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Registry No. 1, 89-82-7; 2, 34413-88-2; 3, 979-02-2; 4, 16161-84-5; 5, 36065-09-5; 6, 984-84-9; 7a (isomer 1), 74242-51-6; 7a (isomer 2), 74242-47-0; 7b (isomer 1), 74242-50-5; 7b (isomer 2), 74242-90-3; 7c (isomer 1), 90129-93-4; 7c (isomer 2), 90129-94-5; 8a (isomer 1), 74219-69-5; 8a (isomer 2), 90129-95-6; 9a, 20023-36-3; 9b, 2886-59-1; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; (−)-myrtenal, 564-94-3; 1-methoxy-1,4-cyclohexadiene, 2886-59-1; chlorotris(triphenylphosphine)rhodium, 14694-95-2; 1-methoxy-4-methyl-1,4-cyclohexadiene, 20023-36-3; β-pinene, 127-91-3; methyl 2,4-hexadienoate, 1515-80-6; ((+)-pulegone)tricarbonyliron (isomer 1), 90129-96-7; ((+)-pulegone)tricarbonyliron (isomer 2), 90129-97-8.

An Electrochemical Study of the Reduction of Mono- and Bis(iron) Cyclophane Complexes

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The electrochemical reduction of six $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-cyclophane})]^+PF_6^-$ and four $\{[(\eta^5\text{-}C_5H_5)Fe]_2(\text{cyclophane})\}^{2+}(PF_6)_2^{2-}$ complexes were studied in several aprotic solvents by cyclic voltammetry, polarography, chronoamperometry, and coulometry. The mono(iron) complexes reduce in two one-electron steps (+/0/−) separated by 0.6–0.8 V. The neutral radical complexes are less stable than other CpFe(arene) radicals. Ease of reduction and stability of the neutral radicals seems to depend on the extent of overlap of metal and ligand orbitals. The bis(iron) complexes reduce in two one-electron steps (2+/+/0) separated by 0.15–0.25 V, depending on cyclophane structure and solvent. This is interpreted as sequential reduction of each iron with the extent of the Fe–Fe interaction affecting the potential separation. Decomposition of the reduced mono- and bis(iron) complexes proceeds by loss of the cyclophane followed by disproportionation of the $CpFe^I$ fragment to ferrocene and Fe(0).

The chemical and electrochemical reductions of the mixed-sandwich cations $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6R_6)]^+$ have been extensively studied,[2–9] and a variety of the corresponding CpFe(arene) neutral radicals have been shown to be quite stable.[5–9] Under the proper conditions, though, they may undergo dimerization or other radical reactions.

Initial polarographic investigations[3] of these compounds in acetonitrile established that the complexes underwent two one-electron reductions; only the first was found to be reversible. Shortly thereafter, the nominally Fe(I) neutral radical was isolated.[4] The potential of the first reduction varied with the substituents on the arene ring and ranged from −1.0 to −1.5 V vs. SCE. Because the stability of the radical depended upon the solvent, displacement of the arene was assumed to be the pathway of decomposition to ferrocene and free arene.

More recently the reactivity of these radicals and their second one-electron reduction have been extensively investigated. Nesmeyanov et al.[5] reported electrochemical detection of a significant lifetime for [CpFe(naphthalene)]$^-$, and El Murr[6] reported cyclic voltammetry studies showing that the second reduction of CpFe(benzene)$^{0/-}$ is chemically reversible in THF. In the presence of electrophiles, the anions suffer attack at the arene to form neutral cyclohexadienyl complexes.

Astruc and co-workers[7–9] investigated in detail the redox chemistry of the complexes $[(\eta^5\text{-}C_5H_{5-m}R_m)Fe(\eta^6\text{-}C_6H_{6-n}R_n)]^+$ (R = Me, Et; m = 0–5; n = 0–6). The stability of the generally persistent radicals, as well as reaction pathway, depended on alkyl substitution. In aprotic solvents dimerization of some of the radicals occurred through the arene ring; others underwent loss of the arene followed by disproportionation to ferrocene.[7,9] Because of the stability and low redox potential (−1.6 to −1.9 V vs. SCE in aqueous 0.1 M LiOH),[8] these 19-electron complexes make useful reducing agents.[8,9]

Hendrickson et al.[10] investigated the electrochemistry of a variety of novel $[(CpFe)_2(\text{arene})]^{2+}$ complexes in which each CpFe fragment is bonded to different centers in

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