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Synthesis of Novel Chiral Cyclopentadienes: Synthesis of Chiral Iron Complexes and the Crystal Structures of [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$SnCl$_3$] and [(η^5-C$_5$(Me)$_4$C(H)(CH$_3$)(C$_2$H$_5$))Fe(CO)-(η^4-diphenylbutadiene)]$^+$[BF$_4$]$^-$

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Two new functionalized tetramethylcyclopentadiene (FTMCP) ligands are described: optically active (1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)-ethane **(2)** and racemic 1-methyl-1-(2,3,4,5-TMCP)propane **(3)**. These ligands were used to synthesize cationic diene complexes [(η^5-FTMCP)Fe(CO)(η^4-diene)]$^+$[BF$_4$]$^-$ (diene = diphenylbutadiene **(11)**, methyl hexa-2,4-dienoate **(10)**). The absolute configuration of the ligand **2** was determined from the crystal structure of complex [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)-ethane)Fe(CO)$_2$SnCl$_3$] **(8)**.

Introduction

Despite the widespread use of the pentamethylcyclopentadienyl (PMCP) ligand in transition-metal chemistry, there have been comparatively few studies describing the synthesis and use of functionalized tetramethylcyclopentadiene (FTMCP) ligands. Recently, however, interest has been generated in these types of ligands for use in asymmetric synthesis, catalysis, inorganic polymers, and as heterodifunctional ligands.[1−8] A recent review by Halterman[9] gives an overview of chiral cyclopentadienes and their uses in organometallic chemistry.

A comprehensive range of FTMCP ligands can be synthesized by adopting procedures developed for synthesizing PMCP. Feitler and Whitesides[10] included a synthesis for 1-ethyl-2,3,4,5-tetramethylcyclopentadiene (1-Et-2,3,4,5-TMCP) in their examination of synthetic routes to PMCP. The use of 2,3,4,5-tetramethylcyclopent-2-enone enolate and pentamethylfulvene as precursors to FTMCP ligands was explored by Mintz and co-workers.[11−13] The electrophilic allylation of enolyzable 1,3-dicarbonyl compounds and successive acid-catalyzed cyclization can also be used to prepare tetra- and pentaalkylated cyclopentadienyl ketones and carboxylic acids.[14] Cesarotti et al.[1,15,16] reported the synthesis of chiral 1-menthyl-2,3,4,5-tetramethylcyclopentadiene, with lithium tetramethylcyclopentadienide as the starting material. Phosphine-substituted FTMCP ligands can also be synthesized by this route.[17]

Perhaps the most practical and efficient route to FTMCP ligands is that of Threlkel and Bercaw,[18] which is based on the reaction of 2-butenyllithium with esters. By adapting the above synthesis and using an optically active ester,[19] Dormond synthesized an optically pure pentaalkylcyclopentadiene, 1-phenyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane.[20] Conversion of the ligand to its lithium salt by reaction with *n*-butyllithium and subsequent reaction with TiCl$_4$ yielded a titanyl complex in >99% ee. The optically pure dimeric molybdenum complex [(C$_5$(CH$_3$)$_4$C*(H)(Ph)(C$_2$H$_5$))Mo(CO)$_3$]$_2$ was also described.

In this report we describe the effective synthesis of a new optically active FTMCP ligand using the 2-butenyllithium/ester procedure of Threlkel and Bercaw, but which employs the relatively inexpensive optically active ester of naproxen (ethyl (6-methoxy-α-methyl-2-naphthalenyl)acetate).

The synthesis of cationic iron diene complexes [(η^5-PMCP)Fe(CO)(η^4-diene)]$^+$ in high yield[21−24] has previ-

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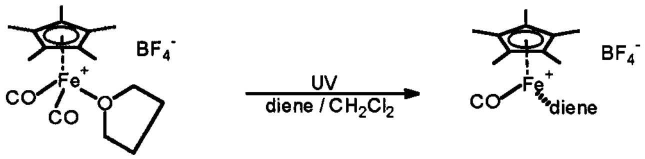

Figure 1. Synthesis of cationic diene complexes of iron.

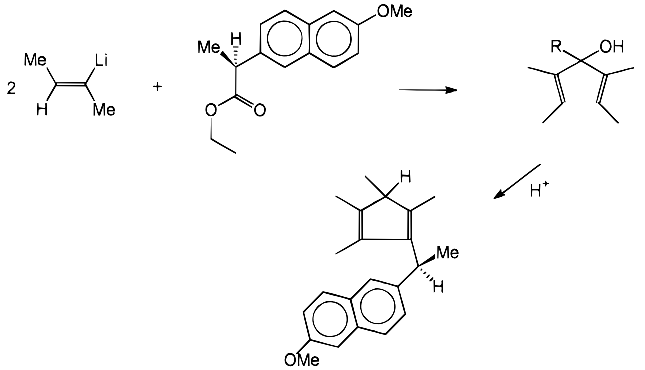

Figure 2. Synthesis of (1*S*)-(−)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane.

ously been reported by this laboratory (Figure 1). Here we describe the effect of introducing a chiral group on the cyclopentadienyl ring. The reaction of these new cationic diene complexes with nucleophiles is also examined.

Results and Discussion

Ligand Synthesis. The reaction of 2-butenyllithium with the optically pure (2*S*)-(+)-2-(6-methoxynaphthalenyl)ethyl propionate (**1**; the ethyl ester of Naproxen) proceeds in a straightforward manner yielding the optically active (1*S*)-(−)-1-(6-methoxynaphthaleneyl-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane **(2)** in 60% yield (Figure 2). However, close attention to detail and absolutely anhydrous conditions are necessary for optimum yield. The product **2** is a mixture of isomers which differ in the position of the hydrogen atom attached to the cyclopentadienyl ring. Because of the large number of isomers ^{1}H NMR spectra were very complex and characterization of the product using NMR was not possible. Analytically pure **(2)** exhibited an optical rotation of $[\alpha]_D{}^{20} = -66°$ ($c = 1$, CHCl$_3$). This is opposite in sign to the starting ester **1**; however, this does not necessarily indicate inversion since the sodium salt of the parent naproxen also has a negative rotation and yet maintains the same absolute configuration. The ligand **2** is air-stable when pure and can be stored at room temperature for months without any sign of decomposition.

The synthesis of the racemic 1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane **(3)** was achieved by the reaction of 2-butyllithium with 2,3,4,5-tetramethylcyclopent-2-enone in anhydrous pentane followed by acid hydrolysis. The crude product is a viscous oil which can be purified either by column chromatography or by vacuum distillation at low temperature (<60 °C). The ligand, **3**, was not characterized but was reacted directly with Fe(CO)$_5$ to yield the dimer [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)Fe(CO)$_2$]$_2$ **(5)**, which was fully characterized. Complex **5** was also characterised crystallographically.[26]

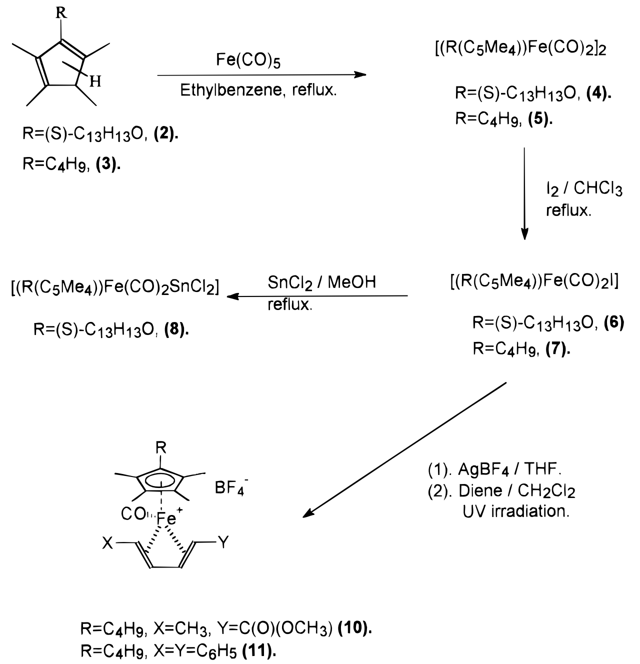

Figure 3. Synthesis of iron carbonyl complexes using FTMCP ligands.

Synthesis of Iron Complexes. Synthesis of the dimers [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$]$_2$ **(4)** and [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)-propane)Fe(CO)$_2$]$_2$ **(5)** was carried out by reacting the appropriate ligand **2** or **3** with Fe(CO)$_5$ in ethylbenzene under reflux under an inert atmosphere (Figure 3). This is a modification of the procedure of King et al.[25] and has also been used successfully in this laboratory for the synthesis of the [(PMCP)Fe(CO)$_2$]$_2$ dimer. The reaction times required for **2** and **3** are only slightly longer than that required for the reaction of PMCP with Fe(CO)$_5$ (22 h vs 16 h).[21,22] The dimers crystallized from the reaction mixture, and the crude products were converted to the dicarbonyl iodides **(6, 7)** without further purification. The dimers are stable in the solid form but decompose in solution when exposed to the atmosphere. The iodides, being air-stable, were easier to purify than the dimers. Excessive heating of the iodide [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$I] **(6)** was found to result in racemization, which was discovered when the crystal structure of the iodide **6** was solved in a centric space group.[26] The very dark colors of the dimers and iodides made direct determination of their optical rotation by conventional polarimetry impossible. For this reason the iodide **6** was converted to the SnCl$_3$ derivative (η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$SnCl$_3$ **(8)**, which was lighter in color and more crystalline. The overall yield of **8** was 64%, obtained as analytically pure crystals. All the crystals had the same morphology, and

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Table 1. Comparison of ^{13}C NMR Spectra (ppm) for Iron Carbonyl Complexes

	4[a]	**5**	**6**	**7**	**10**[a]	**11**[a]
C(3−7)	102.1	104.02	99.4	100.3	105.7/105.3	102.98
	100.27	98.32	98.6	97.56	102.7/102.3	99.2
	100	97.83	97.5	97.12	101/99.4	98.5
	99.53	97.63	92.32	96.3	98.7/98	94.75
	96.84	96.81		94.28	97.8/98.4	94.37
C(8)	35.65	31.45	36.3	32.14	32.2/32	32.05
C(13)	22.43	20.0	22.2	20.63	19/18.6	18.3
C(9−12)	11.69	10.06	12.1	11.33	10.3	9.34
	8.74	9.11	10.9	11.07	9.9	8.83
	8.29	7.97	10.6	10.57	9.4	
	(1:1:2)	(1:1:2)	10.0	10.19	9.3	

[a] **4**, **10**, and **11** were recorded in $CDCl_3$, all others in CS_2.

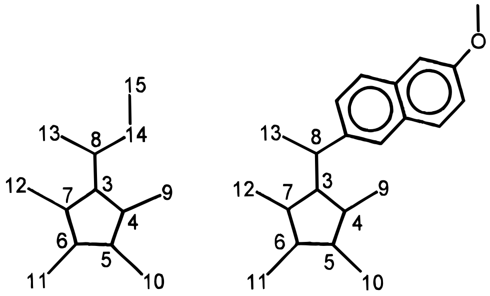

Figure 4. Labeling scheme for NMR spectra of the FTMCP complexes.

one of these was used for the structure determination. Optical rotation measurements using solutions of these crystals gave $[\alpha]_D^{20} = -31 \pm 2°$, $c = 1$, $CHCl_3$. The crystal structure of **8**, (Figure 6) determined the absolute structure and showed that the configuration at the chiral center (*S*) was retained. Unfortunately it was not possible to obtain good-quality NMR spectra of this compound. The carbonyl bands for **8** are at 2026 and 1986 cm^{-1} in dichloromethane solution, which compares to 1974 and 1923 cm^{-1} for [(PMCP)Fe(CO)$_2$Sn(Ph)$_3$].[27] The large difference is due to the stronger electron-withdrawing effect of the $SnCl_3$ group. A similar result has been reported for the Cp analogues [(Cp)Fe(CO)$_2$-Sn(Cl)$_3$] and [(Cp)Fe(CO)$_2$Sn(Ph)$_3$], the values for which are 2048, 2008 and 2048, 2008 cm^{-1}, respectively.[28]

The primary features of the NMR spectra of the dimers and the iodide complexes are the signals due to the pentasubstituted cyclopentadienyl ligand. The introduction of a chiral substituent (whether racemic or resolved) lowers the symmetry of the Cp ring, therefore, separate signals are observed in the proton spectrum for each of the four methyl groups. In the ^{13}C spectra individual signals for the five ring carbons and the four attached methyl groups are also seen. The ^{13}C results are summarized in Table 1.

For complexes with the η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl) ethane ligand the naphthyl ring induces a downfield shift of ~4 ppm of the signal of the chiral carbon C(8) in the ^{13}C spectra of complexes **4** and **6** because of its greater electron-withdrawing effect Figure 4. The effect is reduced at C(13) (the methyl group attached to C(8)) but is still an appreciable 2 ppm. The effect of the naphthyl ring on the position of individual ring carbons is not easily ascertained because it is not possible to establish conclusively the correct assignment for the ring carbons.

The synthesis of the cationic diene complex [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)-Fe(CO)(η^4-methyl hexa-2,4-dienoate)]$^+$[BF$_4$]$^-$ **(10)** was based on Reger and Coleman's method for Cp complexes,[29] which was adapted in this laboratory[20−24] for the synthesis of PMCP cationic diene complexes. A shorter route was employed for the synthesis of [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)-Fe(CO)(diphenylbutadiene)]$^+$[BF$_4$]$^-$ **(11)** in which the dimer **5** was reacted directly with $AgBF_4$ in THF to generate the THF cation [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)Fe(CO)$_2$(THF)]$^+$[BF$_4$]$^-$ **(9)**. Subsequent irradiation of this THF-substituted cation with diphenylbutadiene in dichloromethane for 46 h yielded the cationic diene **11**. This procedure eliminates the need to synthesize and purify the dicarbonyl iodide complex **7**.

The cationic diene complex **10** was isolated as a mixture of diastereoisomers (four isomers are possible: $R_{Cp}R_{Fe}$, $R_{Cp}S_{Fe}$, $S_{Cp}S_{Fe}$, and $S_{Cp}R_{Fe}$), because the methyl hexa-2,4-dienoate ligand can bond to the iron in two different orientations relative to the FTMCP ligand. All attempts at separating the diastereoisomers (even partially) by multiple recrystallization failed. The proton NMR spectra of the cationic diene complexes were poorly resolved due to slight contamination with traces of paramagnetic impurities which could not be removed, even after 5−10 recrystallizations. ^{13}C NMR spectra were resolved, however, and it is possible to see that the methyl hexa-2,4-dienoate ligand in complex **10** is bound to the iron atom in both possible orientations to yield a mixture of isomers in equal proportions. The NMR spectra do not show all the peaks for the four possible isomers because the $R_{Cp}R_{Fe}$ and $S_{Cp}S_{Fe}$ isomers are enantiomers, as are the $R_{Cp}S_{Fe}$, $S_{Cp}R_{Fe}$ pair. Therefore, NMR will only show two sets of signals, and these are given in Table 1. If the methyl hexa-2,4-dienoate ligand had bound to the iron atom in complex **10** in only one orientation, then the NMR spectra would only show a single set of resonances for the cyclopentadienyl ring carbons C(3−7); however, this is not the case. Two resonances are observed for each of the diene carbons C(2A) and C(5A) in ^{13}C NMR spectra of complex **10**.

Attempts to prepare analogous cationic diene complexes using the η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane ligand **2** have not been successful due to difficulties in separation and purification of the reaction products.

Nucleophilic attack at the coordinated η^4-diene of **10** with sodium methoxide in methanol yields the neutral red oil **12** as the only product, (Figure 5). The complex **12** decomposes slowly when exposed to the atmosphere, and accurate microanalytical data could not be obtained. Characterization of the product by NMR and IR spectroscopy (and comparison with the PMCP analogue, which had been fully characterized previously in this laboratory[23]) showed it to be the η^3-allyl complex [(η^5-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)-Fe(CO)(η^3-$C_8H_{13}O_3$)] **(12)**, isolated as a mixture of diastereoisomers. It was not possible to separate the various diastereoisomers. As in the case of the PMCP analogue, nucleophilic attack takes place at the terminal

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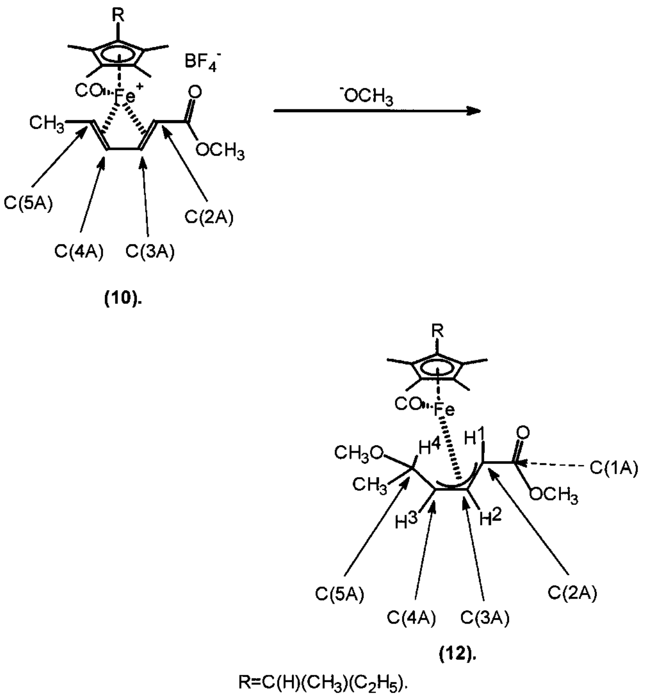

Figure 5. Nucleophilic attack on cationic diene **10** showing the atom labels of the η^4-diene ligand for NMR spectra.

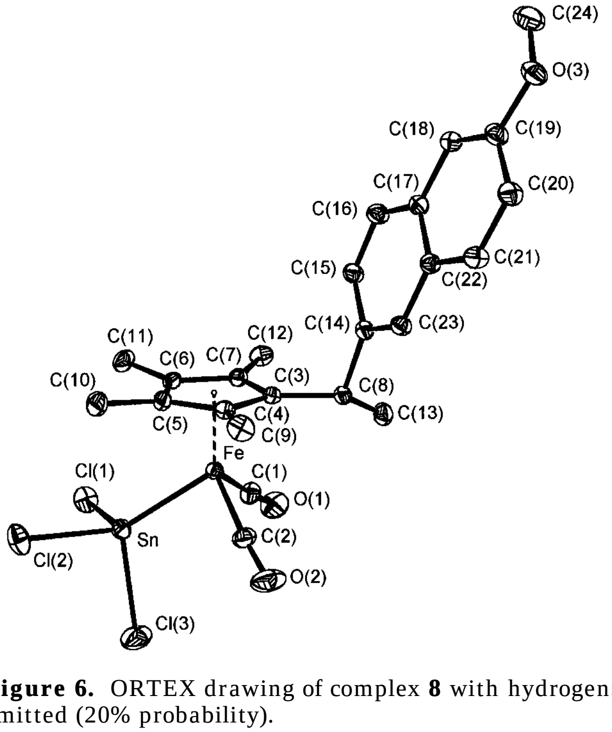

Figure 6. ORTEX drawing of complex **8** with hydrogens omitted (20% probability).

carbon C(5A) of the η^4-diene. Nucleophilic attack is directed to the C(5A) carbon by a combination of the directing effect of the carbomethoxy group and relief of steric strain.[23] The ^{1}H and ^{13}C NMR spectra of **12** are complex and indicate the presence of two sets of diastereoisomers. The diene carbons C(2A−5A) all show two resonances, which confirms that the diene ligand is bound to the iron in both possible orientations in a 1:1 ratio. It is clear that the chiral substituent on the cyclopentadienyl ring does not control the coordination of the η^4-diene in the formation of **10**.

Table 2. Selected Bond Lengths (Å) for [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$SnCl$_3$] (8)

Sn(1)−Cl(3)	2.371(2)	C(3)−C(4)	1.436(5)
Sn(1)−Cl(2)	2.375(2)	C(3)−C(7)	1.438(4)
Sn(1)−Cl(1)	2.3908(12)	C(3)−C(8)	1.505(5)
Sn(1)−Fe(1)	2.4698(6)	C(4)−C(5)	1.422(5)
Fe(1)−C(2)	1.778(4)	C(4)−C(9)	1.510(5)
Fe(1)−C(1)	1.784(4)	C(5)−C(6)	1.419(6)
Fe(1)−C(3)	2.094(3)	C(5)−C(10)	1.495(6)
Fe(1)−C(4)	2.104(4)	C(6)−C(7)	1.455(5)
Fe(1)−C(7)	2.113(4)	C(6)−C(11)	1.509(5)
Fe(1)−C(6)	2.122(3)	C(7)−C(12)	1.494(5)
Fe(1)−C(5)	2.128(4)	C(8)−C(14)	1.518(5)
O(1)−C(1)	1.131(6)	C(8)−C(13)	1.521(6)
O(2)−C(2)	1.141(6)		

Table 3. Selected Bond Angles (deg) for [(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)Fe(CO)$_2$SnCl$_3$] (8)

Cl(3)−Sn(1)−Cl(2)	96.42(8)	C(5)−C(4)−C(9)	126.0(4)
Cl(3)−Sn(1)−Cl(1)	100.29(7)	C(3)−C(4)−C(9)	124.7(4)
Cl(2)−Sn(1)−Cl(1)	97.58(5)	C(9)−C(4)−Fe(1)	128.7(3)
Cl(3)−Sn(1)−Fe(1)	115.34(5)	C(6)−C(5)−C(10)	126.4(4)
Cl(2)−Sn(1)−Fe(1)	126.17(4)	C(4)−C(5)−C(10)	125.5(4)
Cl(1)−Sn(1)−Fe(1)	116.34(4)	C(10)−C(5)−Fe(1)	131.7(3)
C(2)−Fe(1)−C(1)	94.1(2)	C(5)−C(6)−C(11)	126.7(4)
C(2)−Fe(1)−C(3)	101.5(2)	C(7)−C(6)−C(11)	124.1(4)
C(1)−Fe(1)−C(3)	104.1(2)	C(11)−C(6)−Fe(1)	130.7(3)
C(2)−Fe(1)−Sn(1)	92.4(2)	C(3)−C(7)−C(12)	130.0(3)
C(1)−Fe(1)−Sn(1)	88.6(2)	C(6)−C(7)−C(12)	123.1(3)
O(1)−C(1)−Fe(1)	176.0(5)	C(12)−C(7)−Fe(1)	129.0(3)
O(2)−C(2)−Fe(1)	175.3(5)	C(3)−C(8)−C(14)	110.2(3)
C(4)−C(3)−C(8)	122.0(3)	C(3)−C(8)−C(13)	117.3(3)
C(7)−C(3)−C(8)	130.0(3)	C(14)−C(8)−C(13)	110.8(3)
C(8)−C(3)−Fe(1)	128.9(2)		

Description of Structures. The structure of the tin derivative **8** is similar to the structures of the Cp analogues that have been reported by Greene et al.[30−34] Table 4 gives a comparison of bond lengths and angles between **8** and two of its Cp analogues. The Fe−Sn bond lengths are virtually identical, while the tin−chloride bonds are slightly longer in complex **8**. In addition the iron−FTMCP carbon bond lengths are longer than those for the Cp compound. This is expected, as the increased steric pressure of the five substituents would force the ring farther away from the iron atom. Also evident is the *trans* influence of the CO ligands, with the two Fe−Cp bonds trans to the carbonyls being longer than the other three by ~0.01−0.03 Å.

The Sn atom is in a distorted-tetrahedral environment with Cl−Sn−Cl angles of 96−100° and Cl−Sn−Fe angles in the range 115−126° (Table 2). Curiously, one of the Sn−Cl bonds is slightly longer than the other two in both complex **8** and CpFe(CO)$_2$·SnCl$_3$ (Table 3). This effect is not present in the CpFe(CO)$_2$SnBr$_3$ complex.

The structure of **11** is shown in Figure 7. The high value of the *R* index in the structure of the cationic diene complex [(η^5-C$_5$(Me)$_4$C(H)(CH$_3$)(C$_2$H$_5$))Fe(CO)(diphenylbutadiene)]$^+$[BF$_4$]$^-$ **(11)** is probably due to the problems associated with the disordered BF$_4^-$ anion. The four fluorines were each disordered over two sites (with occupancies of 70% and 30%), which generated distorted cubic geometry about the boron. However, despite these problems the standard deviations of the bond lengths and angles in the cation are quite good.

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Table 4. Comparison of Bond Lengths and Bond Angles for Complex 8 and Two Cp Analogues

bond lengths (Å) and angles (deg)	8	$CpFe(CO)_2 \cdot SnCl_3$[32]	$CpFe(CO)_2 \cdot SnBr_3$[34]
Fe−Sn	2.4698(6)	2.467(1)	2.462(2)
Fe−C(1)	1.784(4)	1.785(6)	1.768(12)
Fe−C(2)	1.778(4)	1.785(6)	1.747(13)
Sn−X	Cl(1) = 2.3908(12) Cl(2) = 2.375(2) Cl(3) = 2.371(2)	Cl(1) = 2.373(2) Cl(2) = 2.350(2) Cl(3) = 2.358(2)	Br(1) = 2.505(2) Br(2) = 2.491(2) Br(3) = 2.508(2)
Fe−C(ring)	C(3) = 2.094(3) C(4) = 2.104(4) C(5) = 2.128(4) C(6) = 2.122(3) C(7) = 2.113(4)	C(3) = 2.088(7) C(4) = 2.109(6) C(5) = 2.089(7) C(6) = 2.086(6) C(7) = 2.087(6)	C(3) = 2.08(1) C(4) = 2.09(2) C(5) = 2.07(2) C(6) = 2.11(1) C(7) = 2.09(2)
Sn−Fe−C(1)	88.6(2)	90.0(2)	92.0(4)
Sn−Fe−C(2)	92.4(2)	91.1(2)	88.5(4)
C(1)−Fe−C(2)	94.1(2)	94.9(3)	96.0(6)

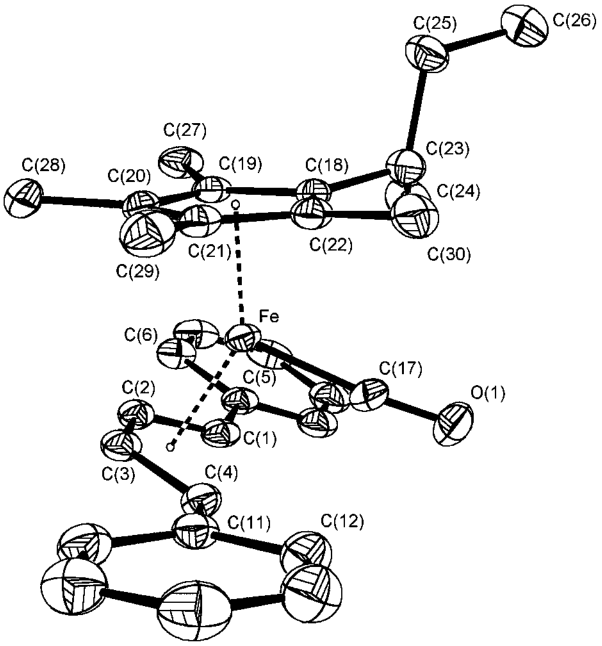

Figure 7. ORTEX drawing of complex **11**.

Table 5. Selected Bond Lengths (Å) for 11

Fe(1)−C(17)	1.776(5)	C(5)−C(6)	1.422(7)
Fe(1)−C(3)	2.064(5)	C(11)−C(12)	1.398(7)
Fe(1)−C(2)	2.072(4)	C(18)−C(19)	1.424(6)
Fe(1)−C(22)	2.083(5)	C(18)−C(22)	1.445(7)
Fe(1)−C(18)	2.098(4)	C(18)−C(23)	1.498(7)
Fe(1)−C(19)	2.121(4)	C(19)−C(20)	1.414(7)
Fe(1)−C(21)	2.128(5)	C(19)−C(27)	1.506(7)
Fe(1)−C(20)	2.133(4)	C(20)−C(21)	1.422(6)
Fe(1)−C(4)	2.258(5)	C(20)−C(28)	1.494(7)
Fe(1)−C(1)	2.282(4)	C(21)−C(22)	1.414(7)
O(1)−C(17)	1.139(6)	C(21)−C(29)	1.482(7)
C(1)−C(2)	1.390(7)	C(22)−C(30)	1.509(6)
C(1)−C(5)	1.453(7)	C(23)−C(24)	1.503(8)
C(2)−C(3)	1.401(7)	C(23)−C(25)	1.522(7)
C(3)−C(4)	1.397(6)	C(25)−C(26)	1.498(9)
C(4)−C(11)	1.477(7)		

Table 6. Selected Bond Angles (deg) for 11

C(17)−Fe(1)−C(3)	114.8(2)	C(1)−C(2)−Fe(1)	79.8(3)
C(17)−Fe(1)−C(2)	113.9(2)	C(3)−C(2)−Fe(1)	69.9(3)
C(3)−Fe(1)−C(2)	39.6(2)	C(4)−C(3)−C(2)	123.3(5)
C(17)−Fe(1)−C(22)	87.5(2)	C(4)−C(3)−Fe(1)	78.9(3)
C(17)−Fe(1)−C(18)	87.6(2)	C(2)−C(3)−Fe(1)	70.5(3)
C(17)−Fe(1)−C(4)	82.7(2)	C(3)−C(4)−Fe(1)	63.8(3)
C(3)−Fe(1)−C(4)	37.4(2)	O(1)−C(17)−Fe(1)	174.2(5)
C(2)−Fe(1)−C(4)	69.1(2)	C(19)−C(18)−C(23)	129.3(4)
C(17)−Fe(1)−C(1)	81.2(2)	C(22)−C(18)−C(23)	123.5(4)
C(3)−Fe(1)−C(1)	68.3(2)	C(18)−C(23)−C(24)	118.0(5)
C(2)−Fe(1)−C(1)	36.8(2)	C(18)−C(23)−C(25)	108.2(5)
C(4)−Fe(1)−C(1)	79.8(2)	C(24)−C(23)−C(25)	114.3(5)
C(2)−C(1)−Fe(1)	63.3(2)	C(26)−C(25)−C(23)	112.5(6)
C(1)−C(2)−C(3)	122.4(4)		

The structure shows that **11** crystallized in an *exo* configuration with the CO ligand lying symmetrically out of the face of the coordinated diene. The coordination geometry is approximately distorted tetrahedral if the Cp ring and carbonyl ligands occupy a single site each and the diene ligand is bidentate. The $C(H)(CH_3)(C_2H_5)$ substituent of the ring is oriented *syn* to the carbonyl ligand with the ethyl group of the chiral substituent pointing up above the plane of the Cp ring. The methyl and hydrogen attached to C(23) are therefore directed downward below the plane to minimize steric strain. The bond lengths Fe−C(22) (2.083(5) Å) and Fe−C(18) (2.098(4) Å) (see Table 5) are the shortest of the Fe−ring carbon bonds. When viewed from above the plane of the Cp ring, the CO group is staggered with respect to the ring substituents attached to C(22) and to C(18). As in the previous structure (of complex **8**) it seems that the *trans* influence of the carbonyl ligand dominates over the steric effect of the $C(H)(CH_3)(C_2H_5)$ substituent, causing the *trans* iron−Cp ring bonds to be lengthened. A similar effect is also visible in the structure of $[(\eta^5\text{-PMCP})Fe(CO)(\text{methyl hexa-2,4-dienoate})]^+[BF_4]^-$,[23] where the Fe−C(10) bond length is also short (2.106(14) Å).

As observed in the structure of $[(\eta^5\text{-PMCP})Fe(CO)(\text{methyl hexa-2,4-dienoate})]^+[BF_4]^-$,[23] the inner carbons of the η^4-diene unit of **11** have Fe−C bonds that are shorter than the outer ones, but in this case by a larger margin (~0.19 Å vs ~0.15 Å).

Materials and Procedures

All reactions were carried out under an atmosphere of dry nitrogen or argon, using glassware that was dried for several hours at 150 °C, before assembly under a stream of nitrogen while still hot. All solvents were dried by standard methods.

Iron pentacarbonyl, 2-chlorobutane, and 2-bromo-2-butene were obtained from Aldrich and used without further purification. Naproxen was supplied by Roche Ireland Ltd. and used as supplied.

^1H and ^{13}C NMR spectra were recorded on JEOL JNM-GX 270 and EX 90 FT NMR spectrometers. Microanalyses were carried on a Perkin-Elmer 2400 CHN analyzer in the UCG microanalytical laboratory. Optical rotation measurements were made on a Perkin-Elmer 241 polarimeter. IR spectra were recorded on Perkin-Elmer 983G and 1600FT-IR spectrometers. Spectra of liquid samples were taken as films and those of solids in dichloromethane solution.

X-ray Structure Determination. The structures was solved by direct methods (SHELX86[35]) and refined by full-

Table 7. Crystallographic Data and Structure Refinement Details for Complexes 8 and 11

empirical formula	$C_{30}H_{35}BF_4FeO$	$C_{24}H_{25}Cl_3FeO_3Sn$
fw	554.24	642.33
cryst size, mm	0.34 × 0.29 × 0.41	0.33 × 0.27 × 0.38
temp, K	293(2)	293(2)
wavelength, Å	0.710 69	0.710 69
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
unit cell dimens	$a = 9.527(2)$ Å, $\alpha = 102.97(2)°$, $b = 11.383(2)$ Å, $\beta = 96.67(2)°$, $c = 14.345(2)$ Å, $\gamma = 112.48(2)°$	$a = 12.3200(10)$ Å, $b = 14.1150(10)$ Å, $c = 15.002(2)$ Å
V, Å^3	1365.1(4))	2608.8(4)
Z	2	4
density (calcd), Mg/m^3	1.348	1.635
abs coeff, mm^{-1}	0.601	1.843
$F(000)$	580	1280
θ range for data collection, deg	2.02−31.97	2.14−39.95
index ranges	$0 \le h \le 10, -12 \le k \le 12, -14 \le l \le 14$	$0 \le h \le 22, 0 \le k \le 25, 0 \le l \le 27$
no. of rflns collected	6991	9046
no. of indep rflns	6446 (R(int) = 0.0151)	8761 (R(int) = 0.0311)
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	6446/0/372	8761/0/291
Goodness of fit on F^2 [39]	0.919	0.965
final R indices ($I > 2\sigma(I)$)	R1 = 0.0805, wR2 = 0.1915	R1 = 0.0470, wR2 = 0.1303
R indices (all data)	R1 = 0.1764, wR2 = 0.2242	R1 = 0.0848, wR2 = 0.1450
largest diff peak and hole, e Å^{-3}	1.073 and −0.694	1.608 and −0.905
abs structure param		−0.070(25)

matrix least squares using SHELXL-93.[36] The data were collected on an Enraf-Nonius CAD4 diffractometer. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions with common thermal parameters. The non-hydrogen atoms were refined ansiotropically. All calculations were carried out on a VAX 6610 computer. The ORTEX[37] program was used to obtain the drawings. The Flack parameter was used to establish the absolute structure of complex **8**.

Preparation of (2*S*)-(+)-2-(6-Methoxynaphthalenyl)ethyl Propionate (1). A 50 g amount of 6-methoxy-α-methyl-2-naphthaleneacetic acid (Naproxen; $[\alpha]_D^{20} = +66.1°$, $c = 1$, $CHCl_3$) was dissolved in 250 cm^3 of dry, deoxygenated ethanol, and after the addition of 2.64 g of H_2SO_4 the mixture was refluxed under nitrogen for 5−6 h. The solution was then cooled to room temperature slowly, during which time the ester precipitated. The precipitate was filtered and then recrystallized from hot methanol to yield a white crystalline product, which was dried under high vacuum before use. The ester as used had an optical rotation of $[\alpha]_D^{20} = +50°$ ($c = 1$, $CHCl_3$).

(1*S*)-(−)-1-(6-Methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane (2). A 2.1 g (0.30 mol) amount of 0.5 mm lithium wire was placed directly into a dry 1 L (three-necked) flask under an argon atmosphere; 300 cm^3 of anhydrous ether was then added. Under argon the reflux condenser and pressure-equalizing dropping funnel containing 20 g (0.148 mol) of deoxygenated 2-bromo-2-butene were fitted. After the reaction vessel was purged once more with argon, 2−3 cm^3 of the halide was added all at once to initiate the reaction. Once the mixture had begun to reflux gently, the remainder of the halide was added dropwise at a rate which maintained a gentle reflux. After complete addition of the halide, the reaction mixture was stirred for an additional 1 h.

A 19.35 g (0.075 mol) amount of the ester **1** was dissolved in the minimum amount of anhydrous diethyl ether (250 cm^3), deoxygenated and added dropwise to the lithium reagent with constant stirring. The resulting pale green solution was then poured carefully onto 200 cm^3 of saturated aqueous NH_4Cl, the ether layer was separated, and the pH of the aqueous layer adjusted to pH ~9 with HCl. The aqueous layer was then extracted with three portions of ether, and the combined ether layers were dried over Na_2SO_4. After filtration the yellow solution was concentrated by rotary evaporation.

The concentrate was dissolved in 30 cm^3 of diethyl ether, 1.3 g of *p*-toluenesulphonic acid was added, and the mixture was refluxed under argon for 10 min and then stirred at room temperature for another 10 min before the solution was poured onto a solution of 0.7 g of Na_2CO_3 in saturated aqueous $NaHCO_3$ (80 cm^3). The aqueous layer was extracted three times with ether, and the combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the ether a waxy solid was obtained, which after double-recrystallization from hot methanol was dried under vacuum to give 14.0 g (60.8%) of the ligand as a pale beige powder. $[\alpha]_D^{20} = -66°$ ($c = 1$, $CHCl_3$). Anal. Calcd for $C_{22}H_{26}O$: C, 86.27; H, 8.50. Found: C, 86.44; H, 8.74.

1-Methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane (3). This was prepared by the reaction of 2-butyllithium with 2,3,4,5-tetramethylcyclopent-2-enone.

2-Butyllithium from 5.0 g (0.35 mol) of lithium wire and 32.41 g (0.35 mol) of 2-chlorobutane was added dropwise to 30.0 g (0.2174 mol) of 2,3,4,5-tetramethylcyclopent-2-enone dissolved in 500 cm^3 of pentane at 0 °C. After stirring at 0 °C for 15 h 2-propanol was added to destroy any remaining 2-butyllithium.

The yellow solution was then poured onto 600 cm^3 of water (which had been acidified with 1 mL of HCl (concentrated) and stirred for 2 h. The organic layer was separated, washed with 3 × 50 cm^3 aliquots of saturated NaCl solution, and dried over Na_2SO_4. Removal of solvent in vacuo gave a yellow oil, which was chromatographed on neutral alumina using hexane as eluant and evaporated to give crude **3** (28 g, 72%).

Bis(*μ*-carbonyl)dicarbonylbis(η^5-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)diiron (4). A 5.0 g (16.34 mmol) amount of (1*S*)-(−)-1-(6-methoxynaphthalene)-1-(2,3,4,5-tetramethylcyclopentadiene)ethane **(2)** and 9.6 g (49 mmol) of $Fe(CO)_5$ were heated under reflux in ethylbenzene for 22 h; this solution was cooled to room temperature, filtered, and extracted with toluene. The solvent was removed by slow evaporation to give the red-purple solid **4** (6.28 g, 92%). It was not, however, possible to obtain an analytically pure sample. IR (CH_2Cl_2 solution): ν(MC−O) 1926, 1748 cm^{-1}. ^{1}H NMR (90 MHz, CS_2/TMS): δ 7.6−6.8

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(39) R indices: $R1 = [\sum||F_o| - |F_c||]/\sum|F_o|$ (based on F); $wR2 = [[\sum_w(|F_o{}^2 - F_c{}^2|)^2]/[\sum_w(F_o{}^2)^2]]^{1/2}$ (based on F^2), $w = 1/[(\sigma F_o)^2 + (0.1P)^2]$. Goodness of fit $= [\sum_w(F_o{}^2 - F_c{}^2)^2/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

(multiplet, 6H, naphthyl protons); 4.3 (quartet, 1H, C(8)−*H*); 3.82 (s, 3H, OCH_3); 1.96 (s, 3H, vinyl Me); 1.84 (doublet, C(8)−CH_3); 1.79 (s, vinyl Me; this peak is coincident with half of the doublet peak for the methyl group on the chiral center C(8)−CH_3); 1.30 (s, 3H, vinyl Me); 1.24 (s, 3H, vinyl Me). ^{13}C NMR (22.4 MHz, $CDCl_3$/TMS): δ 157.41/140.64/133.1/129.21/128.97/127.06/126.85/125.42/118.71/105.64 (C(14−23) naphthyl ring carbons); 102.1/100.27/100/99.53/96.84 (C(3−7), cyclopentadienyl carbons); 55.28 (C(24), OCH_3); 35.65 (C(8)); 22.43 (C(13)); 11.69/8.74/8.29 (1:1:2, C(9−12), methyl's of TMCP). No ^{13}CO resonances were observed.

Bis(*μ*-carbonyl)dicarbonylbis(*η*^{5}-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)diiron (5). **3** (10.0 g) and $Fe(CO)_5$ (32.9 g) were used to give **5** by the method used for **4** (11.79 g, 73%). The high solubility of this dimer in hydrocarbon made recrystallization difficult, and it was used without further purification. Analytically pure crystals were grown by slow evaporation from a dichloromethane solution using a stream of nitrogen gas. Anal. Calcd for $C_{30}H_{42}O_4Fe_2$: C, 62.32; H, 7.27. Found: C, 62.45; H, 7.60. IR (CH_2Cl_2 solution): ν(MC−O): 1920, 1748 cm^{-1}. ^{1}H NMR (270 MHz, CS_2/TMS): δ 2.53 (multiplet, 1H, C(8)-*H*); 1.70 (s, 3H, vinyl Me); 1.56 (s, 3H, vinyl Me); 1.48 (s, 3H, vinyl Me); 1.34 (s, 3H, vinyl Me); 1.327 (doublet, 3H, C(8)−CH_3); 0.945 (triplet, 3H, C(8)−CH_2CH_3). The CH_2 signal (C(8)-C$H_2$$CH_3$) is broad and coincident with the vinyl methyl peaks (∼1.6 ppm).

^{13}C NMR (67.8 MHz, CS_2/TMS): δ 104.02/98.32/97.83/97.63/96.81 (C(3−7)); 31.45 (C(8)); 30.05 (C(14)); 20.0 (C(13)); 13.16 (C(15)); 10.06/9.11/7.97, (1:1:2, C(9−12), methyls of TMCP). No ^{13}CO resonances were observed.

(*η*^{5}-(1*S*)-1-(6-Methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)iron Dicarbonyl Iodide (6). A 4.0 g (4.8 mmol) amount of dimer **4** and 2.44 g (9.6 mmol) of iodine in 15 cm^3 of dry, degassed chloroform were refluxed with constant stirring for 30 min; this solution was cooled to room temperature and washed with a sodium thiosulfate solution (3 g in 10 cm^3 of water). The organic layer was separated, washed with water, and dried over Na_2SO_4. The crude material was chromatographed on a neutral alumina column using chloroform as eluant. On evaporation to dryness 4.35 g (83%) of **6** was obtained as a dark brown solid. Anal. Calcd for $C_{24}H_{25}O_3FeI$: C, 52.96; H, 4.60. Found: C, 52.92; H, 4.65. IR (CH_2Cl_2 solution): ν(CO): 2019, 1972 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$/TMS): δ 7.55−6.96 (multiplet, 6H, naphthyl ring protons); 3.95 (quartet, 1H, C(8)−*H*); 3.83 (s, 3H, OCH_3); 2.14 (s, 3H, vinyl Me); 1.99 (s, 3H, vinyl Me); 1.95 (s, 3H, vinyl Me); 1.85 (s, 3H, vinyl Me); 1.77 (doublet, 3H, C(8)−CH_3). ^{13}C NMR (67.8 MHz, CS_2/TMS): δ 215.2/215 (C≡O); 157.3/138.31/128.7/128.5/127/126.1/125/119.1/105.2 (C(14−23)); 99.4/98.6/97.5/92.32 (C(3−7)); 54.5 (C(24), OCH_3); 36.3 (C(8)); 22.2 (C(13)); 12.1, 10.9, 10.6, 10.0 (C(9−12), methyls on TMCP).

(*η*^{5}-1-Methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)iron Dicarbonyl Iodide (7). **7** was prepared by the method used for **6** in 73% yield and isolated as a black brown solid. Anal. Calcd for $C_{15}H_{21}O_2FeI$: C, 43.3; H, 5.05. Found: C, 43.373; H, 5.074. IR (CH_2Cl_2 solution): ν(MC−O) 2020, 1978 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$/TMS): δ 2.29 (w multiplet, 1H, C(8)−*H*); 2.02 (s, 3H, vinyl Me); 1.99 (s, 3H, vinyl Me); 1.96 (s, 3H, vinyl Me); 1.944 (s, 3H, vinyl Me); 1.57 (multiplet, 2H, C(8)−C$H_2$$CH_3$); 1.294 (doublet, J = 7.15 Hz, 3H, C(8)−CH_3); 0.932 (triplet, J = 7.32 Hz, 3H, C(8)−CH_2CH_3). ^{13}C NMR (67.8 MHz, CS_2/TMS) δ 215.2 (C≡O); 100.03/97.56/97.12/96.3/94.28 (C(3−7)); 32.14 (C(8)); 30.18 (C(14)); 20.63 (C(13)); 12.91 (C(15)); 11.33/11.07/10.57/10.19 (C(9−12)).

(*η*^{5}-(1*S*)-1-(6-methoxynaphthalenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane)$Fe(CO)_2SnCl_3$ (8). A 1.0 g (1.84 mmol) amount of the iodide **6** and 0.687 g (3.68 mmol) of anhydrous stannous chloride were refluxed in 20 cm^3 of dry methanol under nitrogen for 4 days until complete reaction had occurred. The reaction mixture was cooled to room temperature and then extracted into dichloromethane. The solution was filtered and repeatedly recrystallized from dichloromethane/petroleum ether (60−80 °C) by slow evaporation until analytically pure yellow-green crystals were obtained (0.75 g, 63.4% yield based on **6**). The crystals, one of which was used for X-ray crystallography, gave an optical rotation of $[\alpha]_D^{20} = -31 \pm 2°$ (c = 1, $CHCl_3$). Anal. Calcd for $C_{24}H_{25}O_2Cl_3FeSn$: C, 44.88; H, 3.92. Found: C, 44.35; H, 4.11. IR (CH_2Cl_2 solution): ν(MC−O) 2026, 1986 cm^{-1}.

[(*η*^{5}-$C_5(CH_3)_4C(H)(CH_3)(C_2H_5)$)Fe(CO)(methylhexa-2,4-dienoate)]$^+$[BF_4]$^-$(10). A 2.22 g (5.34 mmol) amount of the iodide **7** and 1.04 g of $AgBF_4$ were added to 30 cm^3 of freshly distilled THF under nitrogen and then stirred for 3 h (in the dark). The solvent was removed in vacuo, and the THF cation **9** (ν(MC−O) 2045, 1997 cm^{-1} (CH_2Cl_2 solution)) was extracted into 50 cm^3 of dry dichloromethane and the extract filtered through Celite to remove any silver residue. The solution was transferred to a 100 cm^3 three-necked flask equipped with a reflux condenser. The solution was deoxygenated, 3.28 g of methylhexa-2,4-dienoate was added, and the mixture was irradiated with a 125 W medium-pressure Hg lamp with constant stirring for 18 h, at which stage IR spectra showed that complete reaction had occurred. The mixture was filtered, concentrated to ∼5 cm^3, and treated with diethyl ether to precipitate the cation as an orange powder. Recrystallizations from dichloromethane/hexane gave **10** (1.86 g, 69%) as a beige powder. Anal. Calcd for $C_{21}H_{31}O_3BF_4Fe$: C, 53.20; H, 6.545. Found: C, 53.23; H, 6.69. IR (CH_2Cl_2 solution): ν(MC−O) 2023 cm^{-1}. IR (Nujol mull): 2021 (s), 1708 (s), 1315 (s), 1192 (s), 1062 (s), 1034 (s), 764 (vw), 721 (s) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$/TMS): δ 6.21 (broad multiplet, 1H, (H(2) or H(3)); 5.97 (broad multiplet, 1H, H(2) or H(3)); 3.7 (s, 3H, OCH_3); 2.69 (broad multiplet, 1H, H(4)); 2.40 (broad multiplet, 1H, H(1)); 2.20−1.6 (broad mass of peaks, vinyl methyls, C(8)−*H* and C(8)−CH_2), 1.4 (pair of doublets, $J(CH_3-H(4)) = 6$ Hz, (C(8)−CH_3); 1 (broad multiplet, 3H, C(8)−CH_2CH_3). ^{13}C NMR (67.8 MHz, $CDCl_3$/TMS): δ 220.76 (C≡O); 145.34 (C=O); 105.7/105.3/102.7/102.3/101/99.4/98.7/98/97.8/96.4 (C(3−7)); 93 (C(4A), C(3A)); 92.3/91.9 (C(5A)); 82.8/82.5 (C(2A)); 52.8/52.4 (C(OCH_3)); 32.2/32 (C(8)); 29.1 (C(14)); 19/18.6 (C(13)); 17/16.7 (CH_3 of methylhexa-2,4-dienoate); 13/12.6 (C(15)); 10.3/9.9/9.4/9.3 (C(9−12)).

[(*η*^{5}-$C_5(CH_3)_4C(H)(CH_3)(C_2H_5)$)Fe(CO)(diphenylbutadiene)]$^+$[BF_4]$^-$(11). A 2.22 g (3.84 mmol) amount of the dimer **5** and 1.04 g of $AgBF_4$ were added to 20 cm^3 of THF, and the mixture was stirred for 3 h under nitrogen. A 5.32 g amount of diphenylbutadiene was added and the solution irradiated for 46 h. The cation was isolated as a red-brown microcrystalline solid (1.38 g, 32.6%). Crystals suitable for X-ray analysis were grown by slow evaporation from a dichloromethane solution under a nitrogen atmosphere. Anal. Calcd for $C_{30}H_{35}OBF_4Fe$: C, 65.02; H, 6.32. Found: C, 65.16; H, 6.37. IR (CH_2Cl_2 solution): ν(MC−O): 1997 cm^{-1}. IR (Nujol mull): 1994 (s), 1708 (s), 1062 (s), 1034 (s), 771 (vw), 764 (w), 722 (vw), 699 (w) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$/TMS (resolution poor)): δ 7.41−7.26 (10H, phenyl rings); 6.44 (broad doublet, J = 10.11 Hz, 2H, H(2), H(3)); 3.04 (broad doublet, J = 10.6 Hz, 2H, H(1), H(4)); 2.07−1 (broad group of peaks, 15H, vinyl methyls, C(8)−*H* and C(8)−CH_2); 0.9 (multiplet, 3H, C(8)−CH_3); 0.8 (multiplet, 3H, C(8)−CH_2CH_3). ^{13}C NMR (67.8 MHz, $CDCl_3$/TMS): δ 222.56 (C≡O); 137.4−126 (phenyl rings); 102.98/99.2/98.5/94.75/94.37 (C(3−7)); 83.87 (C(3A,4A)); 79.1/78.9 (C(2A,5A); 32.05 (C(8)); 28.76 (C(14)); 18.13 (C(13)); 12.5 (C(15)); 9.34, 8.83 (C(9−12)).

Reaction of [(*η*^{5}-$C_5(CH_3)_4C(H)(CH_3)(C_2H_5)$)Fe(CO)(methylhexa-2,4-dienoate)]$^+$[BF_4]$^-$ with Sodium Methoxide. A 0.10 g amount of sodium metal was dissolved in 20 cm^3 of dry, degassed methanol under nitrogen, the solution was cooled to 0 °C, and 0.1g of **10** was added. The solution was stirred for 5 min before addition of 20 cm^3 of distilled water at 0 °C. The reaction mixture was extracted into diethyl ether (80 cm^3), dried over Na_2SO_4, filtered, and evaporated to a red oil. The product **12** ((*η*^{5}-1-methyl-1-(2,3,4,5-tetramethylcyclopentadienyl)propane)Fe(CO)(η^3-$C_8H_{13}O_3$)) was then sublimed onto a cold finger to give 0.08 g as a red viscous oil. IR (CH_2Cl_2 solution): ν(MC−O) 1931 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$/TMS): δ 4.6 (dd, 1H, *J*(H(1)−H(2)) = 10 Hz, *J*(H(2)−H(3)) = 8.2 Hz, H(2)); 3.67 (s, 3H, OCH_3); 3.14 (s, 3H, OCH_3); 2.70 (dd, 1H, *J*(H(3)−H(4)) = 10 Hz, *J*(H(2)−H(3)) = 8.2 Hz, H(3)); 2.37/2.60 (pair of multiplets, 1H, C(8)−*H*); 1.91 (pair, 3H, vinyl methyls); 1.61 (pair, 3H, vinyl methyls); 1.59 (doublet, 1H, *J*(H(1)−H(2)) ≈ 10 Hz, H(1)); 1.53 (pair, 3H, vinyl methyls); 1.45 (s, 3H, vinyl methyls); 1.26/1.42 (pair of doublets, 3H, *J* = 7.15 Hz, C(8)−CH_3); 1.29 (doublet, 3H, *J*(CH_3−H(4)) = 6.05 Hz, CH_3 bonded to C(5A); 0.95 (pair of 1:2:1 triplets, 3H, *J* = 7.32 Hz, C(8)−CH_2CH_3). ^{13}C NMR (67.8 MHz, $CDCl_3$/TMS): δ 224.11/224.08 ($C\equiv O$); 175.7 ($C{=}O$); 100/92.1/91.8/91.3/91.1/89.9 (C(3−7)); 83.6/83.5 (C(3A)); 79.28/79.25 (C(2A)); 64.08/63.97 (C(4A)); 55.76 (OCH_3 at C(5A)); 50.9 (OCH_3); 41.37/41.24 (C(5A)); 32.4/32.3 (C(8)); 30.1/29.8 (C(14)); 22.1/22.07/20.54/19.81 (CH_3 bonded to C(5A) and C(13)); 13.2/12.77 (C(15)); 10.78/10.57/10.2/9.97/8.99/8.94/8.74/8.42 (C(9−12)).

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Supporting Information Available: Tables giving crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **8** and **11** (15 pages). Ordering information is given on any current masthead page.

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