Stereocontrolled Double Functionalization of (Cyclohexadiene)- and (Cycloheptadiene)iron Complexes via Oxidative Cyclization Techniques

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Oxidative cyclization of primary alcohol groups onto diene–$Fe(CO)_2L$ systems in six- and seven-membered rings has been investigated by using a variety of oxidizing agents and various substituents on the diene. The product cyclic ethers, e.g., complexes **6**, **17**, and **18**, are readily opened on treatment with tetrafluoroboric acid in the presence of acetic anhydride to give stereospecifically substituted dienyl–$Fe(CO)_2L$ complexes **7** and **16**. Nucleophilic addition to these latter complexes occurs stereo- and regiospecifically, allowing access to cis 1,2-disubstitution in the six-membered ring and cis 1,3-disubstitution in the seven-membered ring.

Introduction

Stereocontrol during carbon–carbon bond formation is an important requirement for the construction of a variety of natural product types, one of the most noteworthy being macrolide antibiotics.[1] As part of a general investigation into the use of an $Fe(CO)_2L$ moiety to control stereochemistry during the attachment of substituents to six- and seven-membered rings, we undertook the studies described in this paper, to test the use of oxidative cyclization techniques for accomplishing double functionalization of diene–$Fe(CO)_2L$ complexes.[2] The general principle of double activation is shown in Figure 1, where it is seen that the organometallic group can be used to effect introduction of vicinal substituents cis in the six-membered ring[3] and substituents with a cis 1,3-relationship in the seven-membered ring.[4,5] The level of stereocontrol is particularly attractive for the latter ring size, which is more difficult to manipulate with standard organic chemical techniques.[6] While we have previously demonstrated controlled introduction of certain substituents with familiar techniques of hydride abstraction/nucleophile addition (e.g., conversion of **1** to **2**), we have sought more general methodology applicable in cases where hydride abstraction using triphenylmethyl cation is suppressed by, e.g., steric factors. The result of this study is described in this paper.

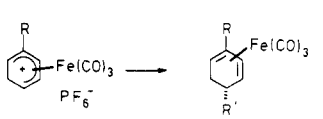
Results and Discussion

(a) Double Functionalization of Cyclohexadiene Complexes. It has been previously established[7] that cyclohexadiene–$Fe(CO)_3$ complexes carrying 5-exo substituents (as in, e.g., structure **4**) do not readily undergo hydride transfer to the triphenylmethyl cation, due to steric hindrance. An exception is a series of trimethylsilyl diene complexes[8] (e.g., **4d**) for which hydride abstraction proceeds smoothly, indicating a very profound influence of the silicon substituent. Consequently, conversion of complexes **4** to dienyl complexes generally requires an indirect approach[2] as previously described for related systems, and this section describes a routine investigation into the scope of this technique.

Table I. Oxidative Cyclization Reactions of Complexes 5a and 5b under Various Reaction Conditions

entry	reactant	conditns	product	yield %
1	**5a**	MnO_2/benzene	**6a**	17
2	**5b**	MnO_2/benzene	**6b**	40
3	**5a**	MnO_2/CH_2Cl_2	**6a**	17
4	**5a**	TTFA/EtOH	**6a**	21
5	**5b**	TTFA/EtOH	**6b**	86
6	**5a**	DDQ/CH_2Cl_2	**6a**	42
7	**5b**	DDQ/CH_2Cl_2	**6b**	50
8	**5a**	$Pb(OAc)_4$/benzene	**6a**	32
9	**5b**	$Pb(OAc)_4$/benzene	**6b**	35

It was previously assumed that reaction of dienyl–$Fe(CO)_3$ complexes **3** with "hard" enolates does not proceed satisfactorily, and attachment of the CH_2CO_2Me group to the ring has generally been accomplished by using indirect methods, e.g., via the (phenylsulfonyl)acetate derivatives.[9] While this works well for small-scale reactions, we found the required desulfonylation (Na/Hg amalgam) to give, e.g., **4b** to be low-yielding on a preparative scale (>1.0 g, ca. 50% yields were recorded in this laboratory). We now report that the direct introduction of CH_2CO_2Me substituent is accomplished in very good yield, on a preparative scale, by reaction of complexes **3a**, **3b**, or **3c** with methyl lithioacetate. In this way, the requisite diene complexes **4a–c** were obtained. In contrast, reaction of



3 (a) R = CH_3; (b) R = OCH_3; (c) R = H

4 (a) R = CH_3, R' = $CH_2CO_2CH_3$; (b) R = OCH_3, R' = $CH_2CO_2CH_3$; (c) R = H, R' = $CH_2CO_2CH_3$; (d) R = $SiMe_3$, R' = CH_3

5 (a) R = CH_3, R' = CH_2CH_2OH; (b) R = OCH_3, R' = CH_2CH_2OH

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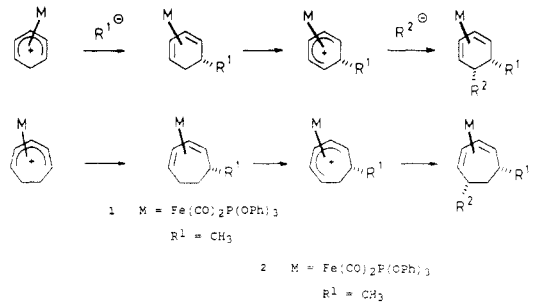
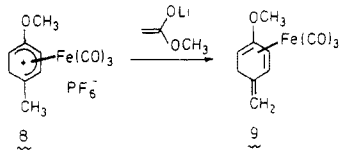


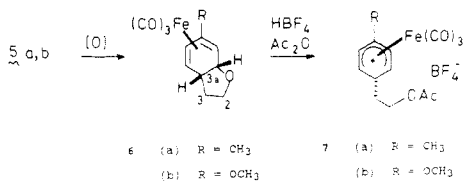
Figure 1. General principle of double activation of diene–Fe(CO)$_2$L complexes illustrating 1,2- and 1,3-stereocontrol.

complex **8** with methyl lithioacetate under identical conditions gave only the η^4-triene complex **9** by deprotonation of the methyl group. Therefore, provided appropriate



dienyl complexes are chosen, it is highly probable that direct alkylation with a range of lithium enolates can be accomplished.

Treatment of complexes **4a–c** with Ph_3CPF_6 gave no dienyl–Fe(CO)$_3$ salts, as expected. Reduction of the ester group of **4a** or **4b** to primary alcohol was therefore effected in the usual way, giving complexes **5a** or **5b**, respectively. The oxidative cyclization of these alcohols to ethers **6** was examined by using various reagents, summarized in Table I. In most cases low to moderate yields of cyclization product were obtained. The methoxy-substituted derivative **5b** gave consistently high yields (86%) of **6b** on treatment with thallium(III) trifluoroacetate, while the best yield of complex **6a** (42%) was obtained by using a previously unreported procedure (DDQ, CH_2Cl_2, Table I, entry 6). The stereochemistry of the cyclized products was assigned by analogy with previous studies.[2,3] The mechanism of this reaction is not yet known, and future studies will attempt to address this issue. Conversion of **6a** and **6b** to the 6-substituted cyclohexadienyl–Fe(CO)$_3$ complexes **7** was accomplished by treatment with tetrafluoroboric acid in acetic anhydride/dichloromethane. Again, higher yields were recorded for the more electron-rich complex **7b**, and it should be noted from a practical point of view that less satisfactory results were obtained by using HPF_6. With complexes **7** in hand, attention was focussed on their reactions with carbon nucleophiles.



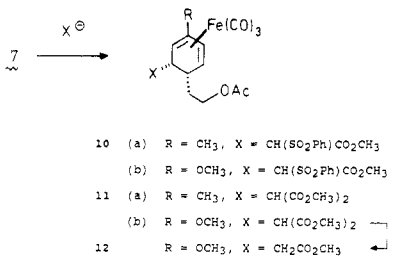
Best results of carbon–carbon bond formation were obtained by using stabilized enolate nucleophiles, to give complexes **10** and **11**, as summarized in Table II. The stereochemistry of the second nucleophile addition has been previously established as trans to the Fe(CO)$_3$ group and was not further studied here.[3,8] In this case reactions of **7** with $LiCH_2CO_2Me$ were completely unsuccessful and resulted in the production of aromatic material which was not further characterized. A small degree of diastereoselectivity during reactions of **7** with $NaCH(SO_2Ph)CO_2Me$ was observed, presumably due to steric factors, since no

Table II. Nucleophile Additions to Complexes 7a and 7b

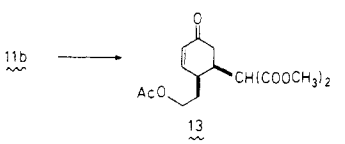
complex	nucleophile	product	yield, %
7a	$NaCH(SO_2Ph)CO_2Me$	**10a** (2:1)[a]	81
7b	$NaCH(SO_2Ph)CO_2Me$	**10b** (2:1)[a]	82
7a	$NaCH(CO_2Me)_2$	**11a**	80
7b	$NaCH(CO_2Me)_2$	**11b**	90

[a] Mixture of diastereomers obtained.

diastereoselectivity is observed during reaction of nonsubstituted dienyl–Fe(CO)$_3$ complexes with this nucleophile. Desulfonylation of the product complexes **10** was capricious and low-yielding, but decarbomethoxylation of the malonate adduct **11b** was found to give reasonable yields of the monoester **12**. These reactions are interesting, since they do show that a number of useful functional group transformations can be accomplished in the presence of the diene–Fe(CO)$_3$ system, *without diene rearrangement*.

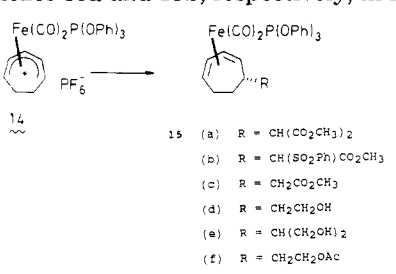


Removal of the Fe(CO)$_3$ group from complex **11b** using the amine oxide method[10] proceeded smoothly, and hydrolysis of the product dienol ether afforded the 4,5-disubstituted cyclohexenone **13**, having defined relative stereochemistry.



(b) Double Functionalization of Cycloheptadiene Complexes. Stereocontrolled attachment of carbon substituents onto the seven-membered ring using standard organic chemical methodology is more challenging than with the six-membered counterpart. While simple methyl-substituted cycloheptadieneiron complexes such as **1** undergo high-yielding hydride abstraction, this procedure is less successful when sterically demanding substituents are present.[11] Therefore, we have examined use of the above oxidative cyclization technique in this ring system.

The cycloheptadienyliron complex **14** did not undergo satisfactory reaction with $LiCH_2CO_2Me$, so indirect incorporation of the acetic ester side chain was utilized. As previously reported,[4] reaction of **14** with either dimethyl sodiomalonate or methyl (phenylsulfonyl)sodioacetate gave diene complexes **15a** and **15b**, respectively, in high yield.



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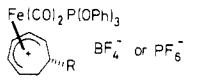
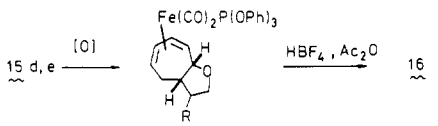
The sulfonylacetate derivative **15b** could be desulfonylated on a preparative scale to give monoester **15c** in excellent yield (cf. the poorer results with the earlier complexes). Interestingly, the diester complex **15a** could be decarbomethoxylated (NaCN, Me_2SO, 90–95 °C, 4 days) *without* decomposition or diene rearrangement. (This contrasts with the free diene obtained by decomplexation of **15a**, which is thermally labile and requires care during decarboxylation[4]). Reduction of **15c** to the primary alcohol **15d** proceeded cleanly. Similarly, diester **15a** was reduced to the diol **15e**. For a check of the applicability of hydride abstraction in these systems, the alcohol derivatives were protected as their acetates **15f** and **15g**. While the monoacetate **15f** underwent smooth hydride abstraction on treatment with trityl hexafluorophosphate, giving dienyl complex **16a** in 86% yield, the sterically encumbered diacetate **15g** was completely resistant to hydride abstraction.



16 (a) R = CH_2CH_2OAc
(b) R = $CH(CH_2OAc)_2$

Oxidative cyclization of **15d** and **15e** was examined by using several oxidizing agents. Fairly brief treatment of **15d** with manganese dioxide in refluent benzene gave the cyclic ether **17** in 90% yield, and this was converted to the dienyl salt **16a** on treatment with HBF_4 in acetic anhydride. Cyclization of the diol derivative **15e** proved to be

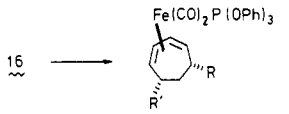


17 R = H
18 (a) R = CH_2OH
(b) R = CH_2OAc

more difficult. Reaction with MnO_2 in boiling benzene gave low yields of the desired product **18**, and this was not improved by using different solvents, reaction times, or temperatures. However, treatment of **15e** with DDQ in dichloromethane gave a single product in high yield, shown to be **18** by homonuclear decoupling NMR experiments. This compound was very sensitive to silica gel and alumina (neutral or basic) and was therefore only partially purified by rapid filtration through a short plug of basic alumina. Direct conversion of **18a** to the dienyl salt **16b** could not be accomplished (HBF_4/Ac_2O) so **18a** was protected as its acetate **18b**, which was smoothly converted to **16b** under the usual conditions. Thus, cycloheptadienyliron salts having quite bulky substitutents at C(6) can be prepared in good yield.

Attention was next directed at the reactions of **16a** and **16b** with carbon nucleophiles. Treatment of **16a** with excess lithium dimethylcuprate gave a single complex, **19a**, in 69% yield, showing unexpected loss of the acetyl group. Reaction with stabilized enolate nucleophiles proceeded in the expected manner to give complexes **19b–d** in very good yields. Similarly, complexes **19e–g** were obtained from the reaction of **16b** with nucleophiles; this time no deacylation was observed during reaction with Me_2CuLi. All of these reactions were regiospecific and stereospecific, as observed for the simpler complex **1**.[4]

In conclusion, stereo- and regiocontrolled double functionalization of cyclohexadiene– and cycloheptadiene–$Fe(CO)_2L$ complexes can be accomplished by using a variety of techniques. The oxidative cyclization procedure



19 (a) R = CH_2CH_2OH, R' = CH_3
(b) R = CH_2CH_2OAc, R' = $CH(CO_2CH_3)_2$
(c) R = CH_2CH_2OAc, R' = $CH(COCH_3)CO_2CH_3$
(d) R = CH_2CH_2OAc, R' = $CH(SO_2Ph)CO_2CH_3$
(e) R = $CH(CH_2OAc)_2$, R' = CH_3
(f) R = $CH(CH_2OAc)_2$, R' = $CH(CO_2CH_3)_2$
(g) R = $CH(CH_2OAc)_2$, R' = $CH(COCH_3)CO_2CH_3$

described here is most useful for those cases where direct hydride abstraction is suppressed by neighboring sterically demanding substituents.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1420, and ^1H NMR spectra were recorded at 200 MHz with a Varian XL-200 instrument. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Solvents were freshly distilled under nitrogen as follows: tetrahydrofuran (THF) from sodium and benzophenone; diethyl ether from lithium aluminum hydride; dichloromethane and acetonitrile from calcium hydride.

Tricarbonyl[methyl (2–5-η-4-methylcyclohexa-2,4-dienyl)acetate]iron (4a). To a stirred solution of lithium diisopropylamide [prepared from 0.64 g (6.3 mmol) of diisopropylamine and 2.4 mL of *n*-butyllithium (2.6 M in hexane)] in THF at −78 °C under nitrogen was added methyl acetate (0.54 g, 7.3 mmol). The mixture was stirred for 30 min, after which time the hexafluorophosphate salt **3a** (2 g, 5.3 mmol) was added in one portion. Stirring was continued at −78 °C for 30 min, and the reaction mixture was allowed to warm up to room temperature. The mixture was poured into water (50 mL) and extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), and evaporated in vacuo to yield the product **4a** (1.44 g, 89%; yellow oil) which was sufficiently pure for the next step: IR (ν_{max}, $CHCl_3$) 2040, 1975, 1730 cm^{-1}; NMR ($CDCl_3$) δ 5.18 (dd, J = 1.6, 6.3 Hz, 1 H, 3-H), 3.62 (s, 3 H, OCH_3), 3.01 (m, 1 H, 5-H), 2.89 (dd, J = 3.5, 6.2 Hz, 1 H, 2-H), 2.55–2.36 (m, 1 H, 1-H), 2.18–2.02 (m, 3 H, CH_2, endo-6-H), 2.07 (s, 3 H, CH_3), 1.28 (dt, J_t = 2.8, J_{gem} = 14.6 Hz, 1 H, exo-6-H); HRMS, found 306.0192 (M^+), calcd for $C_{13}H_{14}O_5Fe$ 306.0190.

Tricarbonyl[methyl (2–5-η-4-methoxycyclohexa-2,4-dienyl)acetate]iron (4b). The hexafluorophosphate complex **2a** (2 g, 5.1 mmol) was treated with the lithium enolate of methyl acetate in the above manner to yield compound **4b** (1.48 g, 90%) as a yellow oil, showing spectral data identical with that reported earlier:[9] IR (ν_{max}, $CHCl_3$) 2040, 1975, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.03 (dd, J = 2.2, 6.6 Hz, 1 H, 3-H), 3.63 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.28–3.24 (m, 1 H, 5-H), 2.66 (dd, J = 3.4, 6.4 Hz, 1 H, 2-H), 2.40–2.23 (m, 1 H, 1-H), 2.2–2.01 (m, 3 H, CH_2, endo-6-H), 1.19 (dt, J_t = 2.3, J_{gem} = 14.6 Hz, 1 H, exo-6-H); HRMS, found 322.0139 (M^+), calcd for $C_{13}H_{14}O_6Fe$ 322.0139.

Tricarbonyl(methyl 2–5-η-cyclohexa-2,4-dienylacetate]iron (4c). The hexafluorophosphate complex **3c** (0.5 g, 1.36 mmol) was treated with the lithium enolate of methyl acetate in the above manner to yield compound **4c** (0.3 g, 75%) as a yellow oil, showing spectral data identical with that reported earlier:[9] IR (ν_{max} $CHCl_3$) 2045, 1980, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37, 5.27 (2 t, J = 6.0 Hz, 2 H, 3-H, 4-H), 3.64 (s, 1 H, OCH_3), 3.10–2.96 (m, 2 H, 2-H, 5-H), 2.60–2.42 (m, 1 H, 1-H), 2.22–2.00 (m, 3 H, CH_2, endo-6-H), 1.32 (m, 1 H, exo-1-H).

Tricarbonyl[1–4-η-5-(2-hydroxyethyl)-2-methylcyclohexa-1,3-diene]iron (5a). To a stirred solution of the monoester **4a** (1.0 g, 3.3 mmol) in THF (20 ml) at −78 °C was added diisobutylaluminum hydride (4 equiv) in hexane. The mixture was stirred overnight and allowed to attain room temperature, after which time methanol (5 mL) and then water (5 mL) were added. Stirring was continued for 15 min, after which time ether (100 mL) was added, and the mixture was filtered through Celite. The organic extract was washed thoroughly with water, dried ($MgSO_4$), and evaporated to give the alcohol **5a** (0.78 g, 85%) as a yellow oil which was purified by flash chromatography: IR (ν_{max}, $CHCl_3$)

3620, 2040, 1970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (dd, J = 1.7, 6.4 Hz, 1 H, 3-H), 3.65–3.46 (m, 2 H, CH_2OH), 3.04–3.01 (m, 1 H, 5-H), 2.94 (dd, J = 3.4, 6.3 Hz, 1 H, 2-H), 2.18–1.95 (m, 2 H, 1-H, endo-6-H), 2.07 (s, 3 H, CH_3), 1.55–1.22 (m, 3 H, CH_2, exo-6-H), 1.16 (t, J = 5.3 Hz, 1 H, OH); HRMS, found 278.0242 (M^+), calcd for $C_{12}H_{14}O_4Fe$ 278.0242.

Tricarbonyl[1–4-η-5-(2-hydroxyethyl)-2-methoxycyclohexa-1,3-diene]iron (5b). The monoester complex **4b** (1.0 g, 3.1 mmol) was treated with diisobutylaluminum hydride (4 equiv) in the above manner and yielded compound **5b** (0.8 g, 88%) as a yellow oil: IR (ν_{max} $CHCl_3$) 3620, 2040, 1970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.06 (dd, J = 2.3, 6.6 Hz, 1 H, 3-H), 3.63 (s, 3 H, OMe), 3.54 (m, 2 H, CH_2OH), 3.30–3.26 (m, 1 H, 5-H), 2.70 (dd, J = 3.4, 6.5 Hz, 2-H), 2.06–1.99 (m, 2 H, 1-H, endo-6-H), 1.65 (t, J = 5.1 Hz, 1 H, OH), 1.51–1.38 (m, 3 H, CH_2, exo-6-H); HRMS, found 238.0287 (M^+ – 2CO), calcd for $C_{10}H_{14}O_3Fe$ 238.0292.

Oxidative Cyclization of Alcohol Complexes 5. (A) Using 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Tricarbonyl(4–7-η-6-methyl-2,3,3aβ,7aβ-tetrahydrobenzofuran)iron (6a). To a stirred solution of the alcohol complex **5a** (0.5 g, 1.8 mmol) in dry dichloromethane at room temperature was added DDQ (0.49 g, 2.2 mmol). The mixture was stirred under nitrogen for 3 h. TLC (30% EtOAc/hexane) after this time indicated disappearance of the starting material and formation of one, less polar compound. The mixture was quenched with triethylamine, poured into water, and then extracted with ether. Drying ($MgSO_4$) and concentration of the organic phase gave a yellow oil (**6a**) (0.21 g, 42%) which was purified by preparative TLC: IR: (ν_{max}, $CHCl_3$) 2050, 1980, 1450 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.43 (dd, J = 1.7, 6.4 Hz, 1 H, 5-H), 4.54 (dd, J = 4.0, 8.7 Hz 1 H, 7a-H), 3.72–3.52 (m, 2 H, 2-H)), 2.94 (dd, J = 1.7, 3.9 Hz, 1 H, 7-H), 2.70–2.88 (m, 2 H, 4-H, 3a-H), 2.18 (s, 3 H, CH_3), 1.93–1.29 (m, 2 H, 3-H); HRMS, found 276.0083 (M^+), calcd for $C_{12}H_{12}O_4Fe$ 276.0085. Anal. Calcd for $C_{12}H_{12}FeO_4$: C, 52.20; H, 4.38. Found: C, 51.74; H, 4.28.

Tricarbonyl(4–7-η-6-methoxy-2,3,3aβ,7aβ-tetrahydrobenzofuran)iron (6b): The alcohol complex **5b** (0.50 g, 1.7 mmol) was treated with DDQ in the above manner and yielded **6b** (0.25 g, 50%) as a yellow oil: IR: (ν_{max}, $CHCl_3$) 2050, 1980, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (dd, J = 1.9, 6.5 Hz, 1 H, 5-H), 4.56 (dd, J = 4.2, 8.6 Hz, 1 H, 7a-H), 3.71–3.53 (m, 2 H, 2-H), 3.68 (s, 3 H, OCH_3), 3.22 (dd, J = 2.3, 4.0 Hz, 1 H, 7-H), 2.74–2.57 (m, 2 H, 4-H, 3a-H), 1.87–1.16 (m, 2 H, 3-H). Anal. Calcd for $C_{12}H_{12}FeO_5$: C, 49.34: H, 4.14. Found: C, 49.23; H, 4.19.

(B) Using Manganese Dioxide in Benzene. Manganese dioxide (1.30 g, 0.018 mol) was heated at reflux temperature in benzene (50 mL) overnight by using a water separator. The mixture was cooled, and the alcohol complex **5a** (0.50 g, 1.8 mmol) in benzene was added. The mixture was boiled under N_2 for 3 h. The cooled mixture was filtered and evaporated to afford the product **6a** (0.09 g, 17%) as a yellow oil. The product was purified by preparative TLC.

The alcohol complex **3b** (0.50 g, 1.7 mmol) was treated with manganese dioxide in the above manner and yielded cyclized complex (0.2 g, 40%).

(C) Using Manganese Dioxide in Dichloromethane. Activated manganese dioxide (1.30 g, 0.018 mol) was added to a stirred solution of alcohol complex **5a** (0.50 g, 1.8 mmol) in dry dichloromethane. The mixture was refluxed for 3 h and then cooled. Filtration followed by evaporation gave a cyclized product (**6a**) (0.09 g, 17%).

(D) Using Thallium(III) Trifluoroacetate. The alcohol complex **5a** (0.5 g, 1.8 mmol) was dissolved in dry ethanol, and the stirred solution was cooled to −10 °C under nitrogen. Thallium(III) trifluoroacetate (3.64 g, 7.2 mmol) was added, and the mixture was stirred for 10 min, after which time solid sodium bicarbonate (1.5 g) was added. After being stirred for a further 30 min, the mixture was poured into ethyl acetate (30 mL) and filtered through a short column of alumina. The filtrate and washings were evaporated and subjected to preparative TLC to give a yellow oil product (**6a**) (0.10 g, 21%).

Likewise, reaction of alcohol complex **5b** (0.5 g, 1.7 mmol) with thallium(III) trifluoroacetate gave a cyclized complex (**6b**) (0.43 g, 86%).

(E) Using Lead Tetraacetate. To a stirred solution of the alcohol complex **5a** (0.5 g, 1.8 mmol) in dry benzene at room temperature was added lead tetraacetate (1.60 g, 3.6 mmol). The mixture was stirred under nitrogen for 30 min, then anhydrous $CaCO_3$ (0.5 g) was added, stirring was continued for 3 h at 50 °C, and the precipitate was removed by filtration and washed well with benzene. The combined benzene extracts were washed with water, dried over magnesium sulfate, and evaporated. The product **6a** was purified by preparative TLC (0.16 g, 32%).

Following the same procedure as above, alcohol complex **5b** (0.5 g, 1.7 mmol) gave cyclized compound **6b** (0.17 g, 35%) which was purified by preparative TLC.

Tricarbonyl[1–5-η-6-*exo*-(2-acetoxyethyl)-3-methylcyclohexa-1,3-dienylium]iron Tetrafluoroborate (7a). The complex **6a** (0.16 g, 0.58 mmol) was dissolved in dichloromethane (10 mL) and acetic anhydride (5 ml) and stirred at 0 °C while tetrafluoroboric acid (48%, 0.5 g, 5.7 mmol) was added dropwise. Stirring was continued for 30 min, after which time the product was precipitated by pouring the reaction mixture into ether. The dienylium complex was removed by filtration, washed with ether, and dried in vacuo to give **7a** (0.13 g, 55%) as a yellow solid: IR (ν_{max}, CH_2Cl_2) 2110, 2050, 1735 cm^{-1}; ^1H NMR (CD_3CN) δ 5.84 (d, J = 6.8 Hz, 2 H, 2-H, 4-H), 4.38 (t, J = 6.4 Hz, 2 H, CH_2OAc), 3.84 (t, J = 6.0 Hz, 2 H, 1-H, 5-H), 2.93 (quintet, J = 6.3 Hz, 1 H, 6-H), 2.68 (s, 3 H, CH_3), 1.9 (s, 3 H, OAc), 1.18 (q, J = 6.4 Hz, 2 H, CH_2). Anal. Calcd for $C_{14}H_{15}FeO_5BF_4$: C, 41.42; H, 3.72. Found: C, 41.77; H, 2.93.

Tricarbonyl[1–5-η-6-*exo*-(2-acetoxyethyl)-3-methoxycyclohexa-1,3-dienylium]iron Tetrafluoroborate (7b). Following the same procedure as above, complex **6b** (0.17 g, 0.58 mmol) gave a yellow solid (**7a**) (0.16 g, 0.38 mmol, 66% yield): IR (ν_{max}, CH_2Cl_2) 2100, 2050, 1730 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 6.01 (d, J = 7.2 Hz, 2 H, 2-H, 4-H), 4.23 (t, J = 6.4 Hz, 2 H, CH_2OAc), 4.16 (s, 3 H, OCH_3), 3.85 (t, J = 5.8 Hz, 2 H, 1-H, 5-H), 2.90 (quintet, J = 6.5 Hz, 1 H, 6-H), 2.0 (s, 3 H, OAc), 1.26–1.15 (m, 2 H, CH_2). Anal. Calcd for $C_{14}H_{15}FeO_6BF_4$: C, 39.85; H, 3.58. Found: C, 39.70; H, 3.20.

Tricarbonyl[methyl (2–5-η-6-(2-acetoxyethyl)-3-methylcyclohexa-2,4-dienyl)(phenylsulfonyl)acetate]iron (10a). To a stirred suspension of sodium hydride (0.007 g of 50% dispersion in mineral oil, washed under N_2 with pentane) in THF at 0 °C was added dropwise a solution of methyl (phenyl sulfonyl)acetate (0.03 g, 0.14 mmol) in THF, to give a suspension of methyl (phenylsulfonyl)sodioacetate. The iron complex **7a** (0.05 g, 0.12 mmol) was added as a solid in one portion, and stirring was continued until a clear solution was obtained (1 h). The solution was concentrated, poured into ether, and evaporated to give the diastereoisomeric mixture (2:1) of complex **10a** (0.05 g, 81%) as a yellow solid (mp 139–141 °C): IR (ν_{max}, $CHCl_3$) 2050, 1980, 1745, 1450, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.43 (m, 5 H, Ph), 5.20 (dd, J = 1.7, 5.9 Hz, 1 H, 4-H, minor diastereoisomer), 5.11 (dd, J = 1.7, 5.9 Hz, 1 H, 4-H, major diastereoisomer), 4.13–3.88 (m, 2 H, CH_2OAc), 3.85 (d, J = 3.2 Hz, 1 H), 3.60 (s, 3 H, OCH_3), 3.49 (s, 3 H, OCH_3), 3.24–3.15 (m, 1 H, 1-H), 3.00 (t, J = 1.7 Hz, 1 H, 2-H), 2.83 (dd, J = 4.0, 6.0 Hz, 1 H, 5-H), 2.17–1.96 (m, 1 H, 6-H), 1.94, 1.90 (2 s, 6 H, CH_3, OAc), 1.75–0.83 (m, 2 H); HRMS, found 476.0600 (M^+ – 2CO), calcd for $C_{21}H_{24}O_9SFe$ 476.0599. Anal. Calcd for $C_{23}H_{24}FeO_9S$: C, 51.89; H, 4.54. Found: C, 51.45; H, 4.35.

Tricarbonyl[methyl (2–5-η-6-(2-acetoxyethyl)-3-methoxycyclohexadienyl)(phenylsulfonyl)acetate]iron (10b). Following the same procedure as above, the salt **7b** (0.05 g, 0.12 mmol) gave the diastereoisomeric mixture (2:1) of complex **10b** (0.05 g, 82%) as a yellow solid (mp 93–95 °C): IR (ν_{max}, $CHCl_3$) 2060, 1980, 1745, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93–7.49 (m, 5 H, Ph), 5.13 (dd, J = 2.1, 6.4 Hz, 1 H, 4-H, minor diastereoisomer), 5.04 (dd, J = 2.1, 6.4 Hz, 1 H, 4-H, major diastereoisomer), 4.23–3.98 (m, 2 H, CH_2OAc), 3.95 (d, J = 3.4 Hz, 1 H), 3.06 (s, 3 H, OCH_3), 3.39 (t, J = 2.1 Hz, 1 H, 2-H), 3.23 (m, 1 H, 1-H), 2.70 (dd, J = 4.1, 6.4 Hz, 1 H, 5-H), 2.22–2.09 (m, 1 H, 6-H), 2.04 (s, 3 H, OAc), 1.86–0.90 (m, 2 H). Anal. Calcd for $C_{23}H_{24}FeO_{10}S$: C, 50.38; H, 4.41. Found: C, 50.15; H, 4.82.

Tricarbonyl[dimethyl (2–5-η-6-(2-acetoxyethyl)-3-methylcyclohexa-2,4-dienyl)malonate]iron (11a). To a stirred suspension of sodium hydride (0.007 g of 50% dispersion in mineral oil, washed under N_2 with pentane) in THF at 0 °C was added dropwise a solution of dimethyl malonate (0.02 g, 0.14 mmol) in THF, to give a suspension of dimethyl sodiomalonate.

The iron salt **7a** (0.05 g, 0.12 mmol) was added as a solid in one portion, and stirring was continued until a clear solution was obtained (1 h). The solution was concentrated, poured into ether, and evaporated to give the pure diester complex **11a** (0.043 g, 80%) as a yellow solid (mp 65–66 °C): IR (ν_{max}, $CHCl_3$) 2050, 1960, 1730, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.23 (dd, J = 1.7, 6.1 Hz, 1 H, 4-H), 4.19 (ddd, ABXY, J = 4.7, 7.5, 12.2 Hz, 1 H, C*H*OAc), 4.00 (dt, ABX, J_t = 8.1, J_{AB} = 12.2 Hz, 1 H, C*H*OAc), 3.75 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.12–3.03 (m, 2 H), 2.96 (dd, J = 3.8, 6.1 Hz, 1 H, 5-H), 2.71 (t, J = 1.7 Hz, 1 H, 2-H), 2.35–2.19 (m, 1 H, 6-H), 2.03, 2.04 (2 s, 3 H each, CH_3, OAc), 1.56–0.95 (m, 2 H). Anal. Calcd for $C_{19}H_{22}FeO_9$: C, 50.68; H, 4.93. Found: C, 50.83; H, 5.16.

Tricarbonyl[dimethyl (2–5-η-6-(2-acetoxyethyl)-3-methoxycyclohexa-2,4-dienyl)malonate]iron (11b). Following the same procedure as above, iron salt **7b** (0.05 g, 0.12 mmol) gave the diester complex **11b** (0.05 g, 90%) as a yellow solid (mp 111–112 °C): IR (ν_{max}, $CHCl_3$) 2060, 1980, 1735, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.07 (dd, J = 2.0, 6.3 Hz, 1 H, 4-H), 4.23 (ddd, ABXY, J = 4.7, 7.6, 12.4 Hz, 1 H, C*H*OAc), 4.01 (dt, ABX, J_t = 8.1, J_{AB} = 12.4 Hz, 1 H, C*H*OAc), 3.77 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3)$_2$, 3.60 (s, 3 H, OCH_3), 3.17 (d, J = 9.8 Hz, 1 H), 3.07–2.97 (m, 2 H, H-1, H-2), 2.73 (dd, J = 4.0, 6.3 Hz, 1 H, 5-H), 2.23–2.12 (m, 1 H, 6-H), 2.03 (s, 3 H, OAc), 1.54–0.94 (m, 2 H, CH_2); HRMS, found 410.0676 (M^+ – 2CO), calcd for $C_{17}H_{22}O_8Fe$ 410.0682. Anal. Calcd for $C_{19}H_{22}FeO_{10}$: C, 48.94; H, 4.76. Found: C, 49.24; H, 4.58.

Tricarbonyl[methyl [2–5-η-6-(2-acetoxyethyl)-3-methoxycyclohexa-2,4-dienyl)acetate]iron (12). Method A. The diester complex **11b** (0.12 g, 0.26 mmol) was dissolved in dry hexamethylphosphoramide (10 mL) and purged with nitrogen. Tetramethylammonium acetate (0.4 g) was added, and the stirred mixture was heated at 95–100 °C for 21 h. The cooled mixture was diluted with ether (50 mL) and the extract washed with 10% aqueous hydrochloric acid, water, and sodium bicarbonate solution, dried ($MgSO_4$), and evaporated to give **12** as a yellow solid (0.03 g, 31%): mp 105–107 °C (pentane–ether) after recrystallization; IR (ν_{max}, $CHCl_3$) 2060, 1980, 1735, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.05 (dd, J = 2.3, 6.4 Hz, 1 H, 4-H), 4.16 (ddd, ABXY, J = 5.0, 7.8, 11.0 Hz, 1 H, C*H*OAc), 4.0 (dt, ABX, J_t = 7.5, J_{AB} = 10.9 Hz, 1 H, C*H*OAc), 3.65 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3), 3.24 (t, J = 2.7 Hz, 1 H, 2-H), 2.67 (m, 2 H, 5-H, 1-H), 2.30 (dd, J = 6.4, 15.5 Hz, one of C*H*$_2$CO$_2$Me), 2.00 (s, 3 H, OAc), 2.13–1.93 (m, 2 H), 1.66–0.99 (m, 2 H); HRMS, found 352.0608 (M^+ – 2CO), calcd for $C_{15}H_{20}O_6Fe$ 352.0609.

Method B. The diester complex **11b** (0.4 g, 0.88 mmol), dimethyl sulfoxide (15 mL), water (2–3 drops), and sodium cyanide (0.13 g, 2.58 mmol) were placed in a 50-mL round-bottom flask equipped with magnetic stirrer and fitted with a condenser. The mixture was heated at 50–60 °C under N_2 overnight. After this time, the mixture was poured into 30 mL of ice water and the aqueous layer was saturated with NaCl. The monoester was extracted with 3 × 20 mL of ether, and the yellow ether extract was dried over magnesium sulfate and concentrated. The concentrated compound was purified by preparative TLC and dried under vacuum to yield **12** (0.05 g, 48%).

Dimethyl (2-(2-Acetoxyethyl)-5-oxo-3-cyclohexenyl]malonate (13). The diester complex **11b** (0.091 g, 0.2 mmol) was dissolved in benzene (20 mL) and added to anhydrous trimethylamine *N*-oxide (0.63 g, 44 equiv) in benzene (20 mL) at 50 °C and the mixture stirred. After 3 h IR spectroscopy indicated the disappearance of the metal carbonyl peak (2060 and 1980 cm^{-1}). The mixture was cooled and filtered through Celite, washing the Celite cake well with ether. The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent afforded the metal-free compound. The product was dissolved in methanol (20 mL) and the solution stirred at 0 °C while a solution of oxalic acid (0.08 g) in water was added. Stirring was continued for 1 h at 0 °C, and the mixture was poured into sodium bicarbonate solution and extracted with ether. Removal of solvent gave enone **13** (0.04 g, 68%) as a colorless oil: IR (ν_{max}, $CHCl_3$) 1740, 1680, 1620 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (dd, J = 5.8, 10.2 Hz, 1 H, 3-H), 6.1 (d, J = 10.8 Hz, 1 H, 4-H), 4.19 (t, J = 5.6 Hz, 2 H, C*H*$_2$OAc), 3.81 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.53 (d, J = 10.9 Hz, 1 H, 9-H), 3.17–3.01 (m, 1 H, 1-H), 2.78–2.70 (m, 1 H, 2-H), 2.44–2.31 (m, 2 H, 6-H), 2.10 (s, 3 H, OAc), 2.66–2.08 (m, 2 H, 7-H); HRMS, found 269.1020 (M^+ – C_2H_3O), calcd for $C_{13}H_{17}O_6$ 269.1025.

Dicarbonyl[methyl (2–5-η-cyclohepta-2,4-dienyl)-acetate](triphenyl phosphite)iron (15c). A. Desulfonylation. Treatment of **15b** (2.70 g, 3.70 mmol) with 6% Na/Hg using the procedure described above gave the monoester complex **15c** as a yellow solid (2.07 g, 95%) after column chromatography (silica gel, 50% EtOAc/hexane) and recrystallization (Et_2O) (complex decomposes before melting point attained): IR (ν_{max}, CCl_4) 1999, 1941, 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 15 H, P(OPh)$_3$), 4.62 (m, 2 H, 2-H, 3-H), 3.60 (s, 3 H, CO_2Me), 2.84 (m, 1 H, 4-H), 2.57 (m, 1 H, 1-H), 2.35 (m, 1 H, 5-H), 2.12 (m, 2 H, CH_2), 1.83 (m, 2 H, 7-H$_2$), 1.23 (m, 1 H, endo-6-H), 0.97 (qd, J = 11.8, 4.9 Hz, 1 H, exo-6-H); FD MS, m/z (relative intensity) 589 [M^+ + 1, 32], 588 [M^+, 100], Anal. Calcd for $C_{30}H_{29}FePO_7$: C, 61.24; H, 4.97. Found: C, 60.98; H, 4.75.

B. Decarboxylation. A solution of the diester complex **15a** (4.99 g, 7.72 mmol) was dissolved in degassed Me_2SO (200 mL). To it was added a solution containing H_2O (3 mL), Me_2SO (10 mL), and NaCN (1.18 g, 24.1 mmol). The resulting solution was immersed in an oil bath at 85–90 °C and was stirred for 4 days. The darkened solution was then allowed to cool to room temperature and added to a cold brine solution. The product was extracted with ether, washed with water, dried ($MgSO_4$), filtered, and evaporated. Following chromatographic purification, complex **15c** (3.0217 g, 66%) was obtained.

Dicarbonyl[1–4-η-5-(2-hydroxyethyl)cyclohepta-1,3-diene](triphenyl phosphite)iron (15d). To a solution of the monoester complex **15c** (1.29 g, 2.19 mmol) in THF (80 mL) at −78 °C was added DIBAL-H (8.8 mL, 1.0 M in hexane). The solution was stirred at −78 °C for 4 h and was then allowed to warm to room temperature overnight. The reaction was quenched by the addition of water (5 mL). The mixture was stirred for 30 min, and then ether was added. Following filtration through Celite, the filtrate was washed with water, dried ($MgSO_4$), filtered, and evaporated. A yellow oil (**15d**) (1.1686 g, 95%) resulted after chromatographic purification: IR (ν_{max}, CCl_4) 3632, 1995, 1941 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (m, 15 H, P(OPh)$_3$), 4.59 (m, 2 H, 2-H, 3-H), 3.55 (t, 2 H, J = 6.8 Hz, C*H*$_2$OH), 2.88 (m, 1 H, 4-H), 2.61 (m, 1 H, 1-H), 1.82 (m, 3 H, 5-H, 7-H$_2$), 1.57 (s, 1 H, OH), 1.34 (m, 2 H, CH_2), 1.11 (m, 1 H, endo-6-H), 0.73 (qd, 1 H, J_q = 12.5, J_d = 4.9 Hz, exo-6-H); FD MS, m/z (relative intensity) 561 [M^+ + 1, 32], 560 [M^+, 100].

Oxidative Cyclization of Complex 15d. A solution of the alcohol complex **15d** (0.264 g, 0.471 mmol) in benzene (10 mL) was refluxed with activated MnO_2 (1.47 g, 16.96 mmol) for 20 min. The mixture was cooled to room temperature, filtered through Celite, and evaporated. The yellow oil **17** (0.2370 g, 90%) was judged at least 95% pure by NMR and was used as such for the next step: IR (ν_{max}, CCl_4) 1997, 1945, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (m, 15 H, P(OPh)$_3$), 4.70 (m, 1 H, 3-H), 4.59 (m, 1 H, 2-H), 4.13 (dd, 1 H, J = 6.7, 3.0 Hz, 1 H, 5-H), 3.60 (m, 2 H, 8-H$_2$), 2.52 (m, 1 H, 1-H), 2.24 (td, J = 7.1, 3.0 Hz, 1 H, 4-H), 2.12 and 2.02 (2 m, 2 H, 7-H$_2$), 1.91 (m, 1 H, 6-H), 1.55 (m, 2 H, 9-H$_2$); FD MS, m/z (relative intensity) 559 [M^+ + 1, 37], 558 [M^+, 100].

Dicarbonyl[1–5-η-6-(2-acetoxyethyl)cycloheptadienyl]-(triphenyl phosphite)iron Tetrafluoroborate or Hexafluorophosphate (16a). A. From Complex 17. A solution of the cyclic ether complex **17** (0.219 g, 0.363 mmol) in CH_2Cl_2 (10 mL) and Ac_2O (0.74 mL) was stirred at 0 °C for 15 min. Tetrafluoroboric acid (0.19 mL, 48%) was added dropwise, and the solution was stirred at 0 °C for 2.5 h. Water was added, and the aqueous layer was removed and washed with CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was redissolved in CH_2Cl_2 and was added slowly to Et_2O. A yellow-orange solid (0.226 g, 90%) resulted.

B. From Complex 15f. Triphenylmethyl hexafluorophosphate (0.092 g, 0.236 mmol) was dissolved in CH_2Cl_2, the mixture was cooled to 0 °C, and the acetate complex **15f** (0.129 g, 0.215 mmol) was added. The solution was allowed to warm to room temperature, stirred for 3 h, and slowly added to Et_2O, forming an oil. The oil was washed thoroughly with Et_2O and dried under vacuum, giving a yellow-orange powder (**16a**) (0.137 g, 86%): IR (ν_{max}, CH_3CN) 2065, 2030, 1766, 1738 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.33 (m, 15 H, P(OPh)$_3$), 6.34 (t, 1 H, J = 6.1 Hz, 3-H), 6.19 (m,

1 H, 2-H), 5.83 (br t, 1 H, J = 6.1 Hz, 4-H), 4.92 (m, 1 H, 5-H), 4.64 (br t, 1 H, J = 6.2 Hz, 1-H), 3.99 (m, 2 H, CH_2OAc), 3.35 (m, 1 H, *endo*-6-H), 2.42 (m, 1 H, endo-7-H), 1.96 (s, 3 H, OAc), 1.64 and 1.36 (2 m, 2 H, CH_2), 0.99 (m, 1 H, exo-7-H). Anal. Calcd for $C_{31}H_{30}FeF_6O_7P_2$: C, 49.89; H, 4.05. Found: C, 50.11; H, 4.13.

Dicarbonyl[1–4-η-5-(2-acetoxyethyl)cyclohepta-1,3-diene](triphenyl phosphite)iron (15f). A solution of the alcohol complex **15d** (0.1531 g, 0.2732 mmol) in pyridine (15 mL) was stirred at room temperature with Ac_2O (0.056 mL). After 23 h, water (2 mL) was added and the solution was stirred for 30 min. The product was extracted with Et_2O, washed with dilute HCl, dried ($MgSO_4$), filtered, and evaporated. A yellow oil (**15f**) (0.1294 g, 79%) was obtained after chromatographic purification: IR (ν_{max}, CCl_4) 1996, 1942, 1742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 15 H, $P(OPh)_3$), 4.52 (m, 2 H, 2-H, 3-H), 3.91 (t, J = 6.9 Hz, 2 H, CH_2OAc), 2.78 (m, 1 H, 4-H), 2.49 (m, 1 H, 1-H), 1.92 (s, 3 H, OAc), 1.70 (m, 3 H, 5-H, 7-H_2), 1.34 (m, 2 H, CH_2CH_2OAc), 1.18 (br, d, J_{gem} = 12.6 Hz, 1 H, endo-6-H), 0.66 (qd, J = 12.6, 4.8 Hz, 1 H, exo-6-H); FD MS, m/z (relative intensity) 602 [M^+, 100]. Anal. Calcd for $C_{31}H_{31}FeO_7P$: C, 61.81; H, 5.19. Found: 61.98; H, 5.43.

Dicarbonyl[1–4-η-5-(2-hydroxyethyl)-7-methylcyclohepta-1,3-diene](triphenyl phosphite)iron (19a). Reaction of **16a** (0.093 g, 0.135 mmol) with Me_2CuLi as described previously gave the product **19a** as a yellow-orange oil (0.057 g, 69%) following chromatographic purification: IR (ν_{max}, CCl_4) 3616, 1994, 1940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 15 H, $P(OPh)_3$), 4.55 (m, 2 H, 2-H, 3-H), 3.54 (br dd, J = 6.7, 5.9 Hz, 2 H, CH_2OH), 1.86 (m, 2 H, 5-H, 7-H), 1.39 (m, 2 H, CH_2CH_2OH), 1.67 (1 H, OH), 0.81 (d, J = 6.8 Hz, 3 H, CH_3), 1.18 (br d, J_{gem} = 12.4 Hz, 1 H, endo-6-H), 0.38 (q, 1 H, J = 12.4 Hz, exo-6-H); FD MS, m/z 575 [M^+ + 1, 38], 574 [M^+, 100].

Dicarbonyl[dimethyl (2–5-η-6-(2-acetoxyethyl)cyclohepta-2,4-dienyl)malonate](triphenyl phosphite)iron (19b). Reaction of **16a** (0.104 g, 0.159 mmol) with $NaCH(CO_2CH_3)_2$ gave the product **19b** as a yellow oil (0.11 g, 86%) after chromatographic purification: IR (ν_{max}, CCl_4) 1997, 1944, 1737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (m, 15 H, $P(OPh)_3$), 4.54 (m, 2 H, 2-H, 3-H), 3.91 (t, 2 H, J = 6.7 Hz, CH_2OAc), 3.61 (s, 6 H, 2 CO_2CH_3), 3.09 (d, J = 6.4 Hz, 1 H, malonate CH), 2.54 (m, 2 H, 1-H, 4-H), 1.94 (s, 3 H, OAc), 1.85 (m, 2 H, 5-H, 7-H), 1.38 (CH_2, 2 H), 1.11 (br d, J_{gem} = 12.3 Hz, 1 H, endo-7-H), 0.62 (q, 1 H, J = 12.3 Hz, exo-7-H); FD MS, m/z (relative intensity) 733 [M^+ + 1, 30], 732 [M^+, 81]. Anal. Calcd for $C_{36}H_{37}FeO_{11}P$: C, 59.03; H, 5.09. Found: C, 58.67; H, 4.97.

Dicarbonyl[methyl (2–5-η-6-(2-acetoxyethyl)cyclohepta-2,4-dienyl)acetoacetate](triphenyl phosphite)iron (19c). Reaction of **16a** (0.1025 g, 0.1490 mmol) with $NaCH(CO_2CH_3)(COCH_3)$ gave the 1:1 mixture of diastereomers **19c** as a yellow oil (0.0861 g, 81%): IR (ν_{max}, CCl_4) 1997, 1944, 1739, 1717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 15 H, $P(OPh)_3$), 4.62 (m, 2 H, 2-H, 3-H), 3.98 (t, 2 H, J = 6.9 Hz, CH_2OAc), 3.68 and 3.66 (2 s, 3 H, CO_2CH_3 diastereomers), 3.18 and 3.14 (2 d, 1 H, J = 7.0 Hz, acetoacetate CH), 2.61 (m, 2 H, 1-H, 4-H), 2.19 and 2.15 (2 s, 3 H, $COCH_3$), 2.00 (s, 3 H, OAc), 1.94 (m, 2 H, 5-H, 7-H), 1.44 (m, 2 H, CH_2), 1.13 (br d, J_{gem} = 12.4 Hz, 1 H, endo-7-H), 0.60 (q, J = 12.4 Hz, exo-7-H); FD MS, m/z (relative intensity) 717 [M^+ + 1, 28], 716 [M^+, 69].

Dicarbonyl[methyl (2–5-η-6-(2-acetoxyethyl)cyclohepta-2,4-dienyl)(phenylsulfonyl)acetate](triphenyl phosphite)iron (19d). Reaction of **16a** (0.0856 g, 0.1244 mmol) with $NaCH(CO_2CH_3)(SO_2Ph)$ resulted in the 1:1 mixture of diastereomers **19d** as a yellow oil (0.0973 g, 96%): IR (ν_{max}, CCL_4) 1997, 1944, 1743 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41 (m, 5 H, SO_2Ph), 7.28 (m, 15 H, $P(OPh)_3$), 4.58 (m, 2 H, 2-H, 3-H), 3.96 (t, J = 6.8 Hz, 2 H, CH_2OAc), 3.63 and 3.60 (2 s, 3 H, CO_2CH_3), 3.07 (m, 1 H, sulfonyl acetate CH), 2.75 (m, 1 H, 1-H), 2.56 (m, 1 H, 4-H), 2.01 and 1.99 (2 s, 3 H, OAc), 1.81 (m, 2 H, 5-H, 7-H), 1.18 (m, 1 H, endo-7-H), 1.42 (m, 2 H, CH_2), 0.78 (q, J = 12.6 Hz, 1 H, exo-7-H); FD MS, m/z (relative intensity) 815 [M^+ + 1, 58], 814 [M^+, 100].

Dicarbonyl[1–4-η-5-(1,3-dihydroxy-2-propyl)cyclohepta-1,3-diene](triphenyl phosphite)iron (15e). A. To a solution of the diester complex **15a** (1.366 g, 2.114 mmol) in THF (80 mL) at −78 °C was added DIBAL-H (13.7 mL, 1.0 M in hexane). The mixture was stirred at −78 °C for 2 h and then was allowed to warm to room temperature and stirred overnight. Water (10 mL) was added; after 20 min, Et_2O was added and the mixture was filtered through Celite. The filtrate was washed with water, dried ($MgSO_4$), filtered, and evaporated. Following chromatographic purification, the complex **15e** was isolated as a yellow oil (1.0124 g, 83%).

B. To a solution of the diester complex **15a** (0.573 g, 0.887 mmol) in Et_2O (30 mL) at 0 °C was added $LiAlH_4$ (0.168 g, 4.433 mmol). The stirred suspension was allowed to warm to room temperature overnight. Water (5 mL) was added, the mixture was stirred for 15 min, and filtered through Celite, and the filtrate was washed, dried ($MgSO_4$), filtered, and evaporated. Purification by flash chromatography gave the complex **15e** as a yellow oil (0.37 g, 71%); IR (ν_{max}, CCl_4) 3621, 1995, 1940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 15 H, $P(OPh)_3$), 4.60 (m, 2 H, 2-H, 3-H), 3.66 (m, 4 H, CH_2OH), 2.83 (m, 1 H, 1-H), 2.51 (m, 1 H, 4-H), 2.22 (m, 1 H), 1.84 (m, 2 H, 7-H_2), 1.65 (s, 2 H, 2 OH), 1.61 (m, 1 H, 5-H), 1.12 (br d, 1 H, J_{gem} = 12.7 Hz, endo-6-H), 0.80 (qd, J = 12.7, 4.1 Hz, 1 H, exo-6-H); FD MS, m/z (relative intensity) 591 [M^+ + 1, 27], 590 [M^+, 100]. Anal. Calcd for $C_{30}H_{31}FeO_7P$: C, 61.03; H, 5.29. Found: C, 61.37; H, 5.43.

Oxidative Cyclization of Diol 15e. To a solution of the diol complex **15e** (0.485 g, 0.822 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added DDQ (0.243 g, 1.068 mmol). After the solution was stirred for 7.5 h, NEt_3 (1 mL) was added. The solution was stirred for 20 min and added to water, and the product was extracted with Et_2O, washed with water, dried ($MgSO_4$), filtered, and evaporated. The product **18a** was obtained as a yellow-orange oil (0.473 g, 97%). The complex decomposed on prolonged exposure to both silica gel and alumina, so purification was precluded: IR (ν_{max} CCl_4) 3626, 1997, 1943, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (m, 15 H, $P(OPh)_3$), 4.73 (m, 1 H, 6-H), 4.58 (m, 1 H, 7-H), 4.20 (dd, J = 6.9, 2.7 Hz, 1 H, 8a-H), 3.80 (t, 2 H, J = 8.9 Hz, CH_2OH), 3.42 (m, 2 H, CH_2O), 3.28 (br t, J = 9.1 Hz, 1 H, OH), 2.51 (m, 1 H, 3a-H), 2.29 (td, 1 H, J = 6.9, 1.9 Hz), 2.03 (m, 3 H), 1.57 (br m, 1 H); FD MS, m/z (relative intensity) 589 [M^+ + 1, 31], 588 [M^+, 100].

Acetylation of Complex 18a. A solution of the cyclic ether complex **18a** (0.149 g, 0.253 mmol) in pyridine (15 mL) at 0 °C was stirred with Ac_2O (0.052 mL, 0.507 mmol). The solution was allowed to warm to room temperature overnight. Water (1 mL) was added, the solution was stirred for 20 min, and the product was extracted with Et_2O, washed thoroughly with water, dried ($MgSO_4$), filtered, and evaporated. After chromatographic purification, the product **18b** was obtained as a yellow oil (0.133 g, 83%): IR (ν_{max}, CCl_4) 1999, 1947, 1747, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18 (m, 15 H, $P(OPh)_3$), 4.71 (m, 1 H, 6-H), 4.59 (m, 1 H, 7-H), 4.21 (dd, J = 6.9, 2.6 Hz, 1 H, 8a-H), 3.78 (3 H) and 3.38 (dd, J = 8.6, 5.5 Hz, 1 H, CH_2OAc and CH_2O), 2.52 (m, 1 H, 3a-H), 2.31 (m, 1 H), 2.09 (3 H, m), 1.93 (3 H, s, OAc), 1.59 (1 H, m); FD MS, m/z (relative intensity) 631 [M^+ + 1, 26], 630 [M^+, 100].

Dicarbonyl[1–5-η-6-(1,3-diacetoxy-2-propyl)cyclohepta-1,3-dienyl](triphenyl phosphite)iron Tetrafluoroborate (16b). The cyclic ether complex **18b** (0.127 g, 0.193 mmol) in CH_2Cl_2 (2 mL) was stirred with Ac_2O (0.40 mL) at 0 °C. Then, HBF_4 (0.10 mL, 48%) was added, the solution was allowed to warm slowly to room temperature, stirred for 4.5 h, added to water, and extracted with CH_2Cl_2 (10 mL), and the organic layer was separated, washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was dissolved in CH_2Cl_2 and added to Et_2O; a yellow-orange solid (**16b**) resulted (0.122 g, 83%): IR (ν_{max}, CH_3CN) 2065, 2030, 1742 cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.37 (15 H, m, $P(OPh)_3$), 6.37 (t, J = 6.0 Hz, 1 H, 3-H), 6.22 (m, 1 H, 2-H), 5.91 (br t, J = 6.0 Hz, 1 H, 4-H), 5.02 (m, 1 H, 5-H), 4.68 (m, 1 H, 1-H), 4.02 (m, 4 H, 2 CH_2OAc), 3.47 (m, 1 H, 6-H), 1.91 (m, 1 H), 2.44 (m, 1 H, endo-7-H), 2.04 (s, 3 H), 2.03 (s, 3 H), 1.02 (m, 1 H, exo-7). Anal. Calcd for $C_{34}H_{34}BF_4FeO_9P$: C, 53.72; H, 4.51. Found: C, 53.58; H, 4.66.

Dicarbonyl[1–4-η-5-(1,3-diacetoxy-2-propyl)cyclohepta-1,3-diene](triphenyl phosphite)iron (15g). A solution of the diol complex **15e** (0.356 g, 0.602 mmol) in pyridine (10 mL) was stirred with Ac_2O (0.14 mL, mmol) at room temperature for 36 h. Water (2 mL) was added, and the solution was stirred for 15 min. The product was extracted with Et_2O, washed with water, dried ($MgSO_4$), filtered, and evaporated. A yellow oil (**15g**) (0.363 g, 89%) was obtained after chromatographic purification: IR (ν_{max}, CCl_4) 1995, 1944, 1741 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (m, 15 H,

$P(OPh)_3$), 4.62 (m, 2 H, 2-H, 3-H), 4.01 (m, 4 H, 2 CH_2OAc), 2.83 (m, 1 H, 1-H), 2.50 (br t, J = 4.3 Hz, 1 H, 4-H), 2.01 (obscured m, 1 H, 5-H), 2.02 (s, 6 H, 2 OAc), 1.77 (m, 3 H), 1.18 (br d, J_{gem} = 12.8 Hz, 1 H, endo-6-H), 0.84 (qd, J = 12.8, 4.1 Hz, 1 H, exo-6-H); FD MS m/z (relative intensity) 675 [M^+ + 1, 32], 674 [M^+, 100]. Anal. Calcd for $C_{34}H_{35}FeO_9P$: C, 60.55; H, 5.23. Found: C, 60.94; H, 5.47.

Dicarbonyl[1–4-η-5-(1,3-diacetoxy-2-propyl)-7-methylcyclohepta-1,3-diene](triphenyl phosphite)iron (19e). Reaction of **16b** (0.072 g, 0.095 mmol) with Me_2CuLi gave the product **19e** as a pale yellow oil (0.048 g, 74%) after purification by PLC (50% EtOAc/hexane): IR (ν_{max}, CCl_4) 1997, 1945, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (m, 15 H, $P(OPh)_3$), 4.59 (m, 2 H, 2-H, 3-H), 4.08 (m, 4 H, 2 CH_2OAc), 2.61 (t, 1 H, J = 6.7 Hz, 4-H), 2.48 (m, 1 H, 1-H), 2.14 (m, 1 H, 5-H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.85 (m, 2 H), 1.09 (br d, J_{gem} = 12.6 Hz, 1 H, endo-6-H), 0.9 (d, J = 7 Hz, 3 H, CH_3), 0.47 (q, J = 12.6 Hz, 1 H, exo-6-H); FD MS, m/z (relative intensity) 689 [M^+ + 1, 36], 688 [M^+, 100].

Dicarbonyl[dimethyl (2–5-η-6-(1,3-diacetoxy-2-propyl)-cyclohepta-2,4-dienyl)malonate](triphenyl phosphite)iron (19f). Reaction of **16b** (0.066 g, 0.089 mmol) with $NaCH(CO_2CH_3)_2$ gave the complex **19f**, after purification by PLC (50% EtOAc/hexane) as a pale yellow oil (0.057 g, 82%): IR (ν_{max}, CCl_4) 2001, 1949, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27 (m, 15 H, $P(OPh)_3$), 4.63 (m, 2 H, 3-H, 4-H), 3.98 (m, 4 H, 2 CH_2OAc), 3.69 (s, 6 H, 2 CO_2CH_3), 3.16 (d, J = 6.5 Hz, 1 H, malonate CH), 2.58 (m, 3 H, 2-H, 5-H, 6-H), 2.15 (m, 1 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.84 (m, 1 H), 1.12 (br d, J_{gem} = 12.6 Hz, 1 H, endo-7-H), 0.78 (q, J = 12.6 Hz, 1 H, exo-7-H); FD MS, m/z (relative intensity) 805 [M^+ + 1, 7], 804 [M^+, 50], 674 [36], 310 [100]. Anal. Calcd for $C_{39}H_{41}FeO_{13}P$: C, 58.22; H, 5.14. Found: C, 58.57; H, 5.25.

Dicarbonyl[methyl (2–5-η-6-(1,3-diacetoxy-2-propyl)-cyclohepta-2,4-dienyl)acetoacetate](triphenyl phosphite)-iron (19g). Reaction of **16b** (0.056 g, 0.074 mmol) with $NaCH(CO_2CH_3)(COCH_3)$ gave the 1:1 mixture of diastereomers **19g** (0.031 g, 53%) as a pale yellow oil after purification by preparation TLC: IR (ν_{max} CCl_4) 2001, 1949, 1748, 1424 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (m, 15 H, $P(OPh)_3$), 4.62 (m, 2 H, 3-H, 4-H), 3.89 (m, 4 H, 2 CH_2OAc), 3.69 and 3.67 (2 s, 3 H, CO_2CH_3 diastereomers), 3.19 and 3.15 (2 d, 1 H, J = 6 Hz, acetoacetate CH), 2.57 (m, 3 H), 2.19 and 2.16 (2 s, 3 H, $COCH_3$ diastereomers), 2.02 (m, 1 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.83 (m, 1 H), 1.07 (br d, J_{gem} = 12.3 Hz, 1 H, endo-7-H), 0.69 (q, J = 12.3 Hz, 1 H, exo-7-H); FD MS, m/z (relative intensity) 788 [M^+, 50], 674 [78], 310, [100].

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Registry No. **3a**, 12307-12-9; **3b**, 51508-59-9; **3c**, 42535-11-5; **4a**, 103816-77-9; **4b**, 81857-48-9; **4c**, 87420-57-3; **5a**, 103834-73-7; **5b**, 103816-78-0; **6a**, 103816-79-1; **6b**, 103816-80-4; **7a**, 103816-82-6; **7b**, 103816-84-8; **10a** (isomer 1), 103816-85-9; **10a** (isomer 2), 103882-97-9; **10b** (isomer 1), 103816-86-0; **10b** (isomer 2), 103882-31-1; **11a**, 103834-74-8; **11b**, 103816-87-1; **12**, 103816-88-2; **13**, 103817-02-3; **15a**, 85939-52-2; **15b**, 85939-56-6; **15c**, 103816-89-3; **15d**, 103816-90-6; **15e**, 103816-91-7; **15f**, 103816-92-8; **15g**, 103834-75-9; **16a**$^+BF_4^-$, 103816-94-0; **16a**$^+PF_6^-$, 103882-32-2; **16b**, 103834-77-1; **17**, 103816-95-1; **18a**, 103816-96-2; **18b**, 103816-97-3; **19a**, 103816-98-4; **19b**, 103816-99-5; **19c** (isomer 1), 103817-00-1; **19c** (isomer 2), 103882-33-3; **19d** (isomer 1), 103817-01-2; **19d** (isomer 2), 103882-34-4; **19e**, 103834-78-2; **19f**, 103834-79-3; **19g** (isomer 1), 103834-80-6; **19g** (isomer 2), 103882-98-0; $NaCH(CO_2CH_3)(COCH_3)$, 34284-28-1; $NaCH(CO_2CH_3)_2$, 18424-76-5; methyl acetate, 79-20-9; diisobutylaluminum hydride, 1191-15-7; methyl (phenylsulfonyl)acetate, 34097-60-4; methyl (phenylsulfonyl)sodioacetate, 60729-65-9; dimethyl malonate, 108-59-8.

Catalytic Methods for the Synthesis of Oligosilazanes

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We have previously reported on the use of homogeneous catalysts [e.g., $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$] for the ring-opening oligomerization of octamethylcyclotetrasilazane. We now find that a variety of homogeneous and heterogeneous catalysts promote this reaction. We also observe that low pressures of hydrogen (1 atm) enhance transition-metal-catalyzed ring-opening oligomerization by up to 2 orders of magnitude. Furthermore, metal hydrides, which form under the reaction conditions, are equally active as catalysts in the absence of hydrogen. These results suggest that oligomerization catalysis proceeds via hydrogenation of Si–N bonds followed by reaction of an $-NH_2$ group with a metal-activated Si–H bond. To test this hypothesis, we have reacted a simple silazane, $HSiMe_2NHSiMe_2H$, with NH_3 using $Ru_3(CO)_{12}$ as a catalyst. We observe extremely rapid oligomerization, even at temperatures as low as 35 °C, with concomitant evolution of hydrogen. This reaction represents a new synthetic method for the oligomerization of silazane monomers, which does not require Si–N bond cleavage to precede Si–N bond formation, a fatal flaw in our original oligomerization process.

Introduction

The current search for silicon-containing polymers that can serve as precursors for the pyrolytic generation of silicon carbide (SiC)[1,2] and silicon nitride (Si_3N_4)[3,4] based ceramics has renewed interest in developing synthetic routes to silicon-based polymers. Present efforts center

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