tion[34] and the ^1H NMR (100 MHz) spectrum recorded. Sharp aldehydic resonances are not observed; however, a broad resonance centered at δ 9.06 was evident.

Purified PGH_2 (**1a**) (9 mg, 0.026 mmol) stored in dry $CDCl_3$ at −80 °C in a 5-mm NMR tube was concentrated to dryness at 5 °C[27] by blowing a small steady stream of argon onto the sample. pH 7.9 buffered D_2O (0.3 mL)[34] was added to the sample, and the solution was mixed thoroughly with shaking and sonication. The sample was placed into the probe of the XL-100 NMR spectrometer at room temperature, and the ^1H NMR spectrum was recorded in the FT mode 10 min after dissolution. The protic impurity from the solvent overlapped with the H-9 and H-11 bridgehead resonances of PGH_2 (**1a**) so monitoring of reaction progress based upon the disappearance of these resonances was not feasible. In addition, no resonances could be seen in the aldehyde region of the spectrum. Therefore, the sample was removed from the probe of the NMR spectrometer and allowed to stand at room temperature for 90 min.[35]

The contents of the NMR tube were transferred to a separatory funnel and acidified to pH 3 with 5% HCl. The aqueous layer was extracted with diethyl ether (5 × 8 mL), and the combined ether extracts were dried over anhydrous Na_2SO_4 (5 °C, 15 h). The ether was removed by rotary evaporation (20 °C, 20 min) and the last traces under high vacuum (20 °C, 0.03 mm). The residue was taken up in dry $CDCl_3$ and the ^1H NMR (100 MHz) spectrum recorded from which resonances centered at δ 9.67 (s, 1 H) and 9.53 (s, 1 H) were evident and were assigned to levuglandin LGE_2 (**3a**) and levuglandin LGD_2 (**2a**). The percent yield of **3a** and **2a** (22%) formed from decomposition of PGH_2 (**1a**) was determined by the cut and weigh method by dividing the weight of the aldehydic resonances at δ 9.67 and 9.53 by one-third the weight of the C-20 methyl resonance centered at δ 0.89 (t, 3 H) and multiplying by 100.

Reaction of Levulinaldehyde (2b) with Glycine Ethyl Ester. A solution (1.0 mL) was prepared volumetrically containing glycine ethyl ester (280 mg, 2.0 mmol, 2.0 M) in D_2O. Another solution (0.26 mL) was prepared volumetrically in a 5-mm NMR tube containing levulinaldehyde (**2b**) (52 mg, 0.52 mmol, 2.0 M) in D_2O. The latter solution was combined with an aliquot (0.25 mL) of the glycine ethyl ester solution. The contents of the NMR tube were mixed thoroughly by shaking and the ^1H NMR (60 MHz) spectrum of the solution was immediately recorded integrating the resonances at δ 10.08 (br t, 1 H), 6.38 (t, 1 H, J = 6 Hz), and 5.42 (t, 1 H, J = 6 Hz) which corresponded to signals for nonhydrated **2b**, an intermediate adduct between **2b** and glycine ethyl ester, and hydrated **2b**, respectively.[36] Next, the solution was slightly basified (pH 10) with dilute NH_4OH and extracted with chloroform (3 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and chromatographed on a preparative TLC plate (silica gel, 0.5 mm, one development with chloroform (containing 0.75% ethanol)). The pyrrole **24** (R_f 0.29–0.41) (17 mg, 0.104 mmol) was isolated in 20% yield. Spectral data for **24**: ^1H NMR ($CDCl_3$, 60 MHz) δ 6.55 (br t, 1 H), 6.08 (br t, 1 H, J = 3 Hz), 5.91 (br, 1 H), 4.54 (s, 2 H), 4.23 (q, 2 H, J = 7 Hz), 2.18 (br s, 3 H), 1.28 (t, 3 H, J = Hz). High-resolution mass spectrum (70 eV): measured mass (% intensity of base) 167.0638 (100.0), 166.0550 (4.9) ($M^+ - 1$), 139.0362 (1.2) ($M^+ - C_2H_4$), 94.0523 (37.7) ($C_5H_6NCH_2^+$).

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Registry No. 1a, 42935-17-1; **1b**, 279-35-6; **1d**, 88867-81-6; **1d$_6$**, 91712-40-2; **2a**, 91712-41-3; **2b**, 626-96-0; **2d**, 91712-42-4; **2d$_6$**, 91712-43-5; **3a**, 91712-44-6; **5b**, 26831-63-0; **5d**, 91712-45-7; **5d$_6$**, 91712-46-8; D_2, 7782-39-0.

(34) Sodium phosphate buffer, cf.: Colowick, S. P.; Kaplan, N. O., Eds. "Methods in Enzymology"; Academic Press: New York, 1955; Vol. 1, p 143.

(35) Decomposition of PGH_2 (**1a**) in aqueous media at room temperature is reported[5] to exhibit a $t_{1/2} \sim 20$ min. Therefore, to ensure complete decomposition of PGH_2, we allowed our sample to stand at room temperature for 90 min.

(36) Levulinaldehyde (**2b**) is ca. 50% hydrated in D_2O. However, in this particular experiment, the ratio of non-hydrated **2b** to the intermediate adduct remained at ca. 1:4 for 1 h at 35 °C whereas the resonance at δ 5.42 corresponding to hydrated **2b** was barely detectable.

Regio- and Stereocontrolled Functionalization of Cycloheptadiene Using Organoiron and Organoselenium Chemistry

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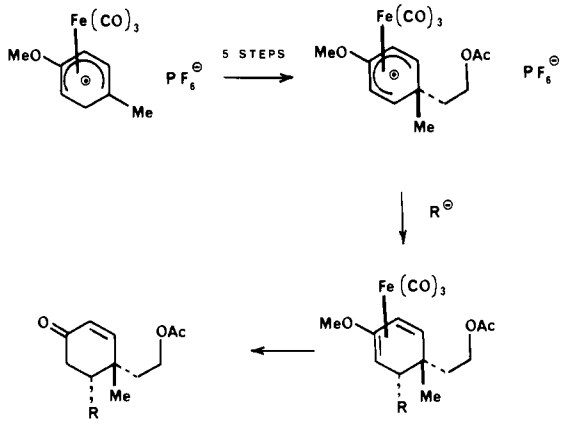
Abstract: Whereas the reactions of tricarbonylcycloheptadienyliron salts with nucleophiles generally occur in low yield giving mixtures of products, the corresponding dicarbonyl(triphenylphosphine) and dicarbonyl(triphenyl phosphite) complexes **8** give high yields of single adducts on reaction with a range of nucleophiles. The regioselectivity of nucleophile addition to **8** is strongly dependent on the nucleophile, "soft" nucleophiles attacking C-1, "hard" nucleophiles attacking C-2 of the dienyl ligand. The diene complexes **10** resulting from C-1 addition can be reactivated by hydride abstraction with $Ph_3C^+PF_6^-$, to give dienyl complexes **11**, which undergo a second nucleophile addition regio- and stereospecifically (trans to the $Fe(CO)_2L$ group). Decomplexation is easily accomplished, leading to cycloheptadienylacetic acid derivatives. Phenylselenolactonization of these compounds was accomplished, and the product allylic selenolactones could be subjected to oxidation accompanied by [2,3]-sigmatropic rearrangement of the intermediate selenoxides to give hydroxy lactones. Conformational analysis of substituted (cycloheptadiene)iron complexes and the lactone derivatives is reported.

The use of a transition-metal moiety to control the stereochemistry of consecutive carbon–carbon bond formations on an attached organic ligand offers a unique opportunity for attaining the synthesis of stereodefined organic molecules. We recently demonstrated[1] the efficacy of this method applied to the synthesis of cyclohexenone derivatives, summarized in Scheme I, in which cis stereochemistry is defined during the introduction of substituents at vicinal positions. However, stereocontrol in six- and five-membered rings using a variety of standard organic techniques is well established, so that these ring sizes are inappropriate for demonstrating the utility of the organometallic approach. On the other hand, the cycloheptane ring has received only scant attention[2]

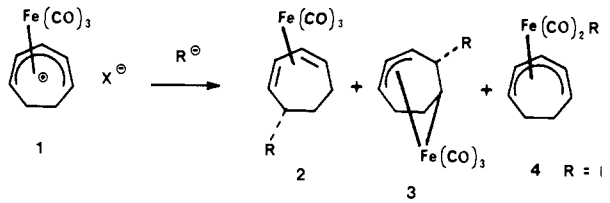
(1) Pearson, A. J.; Ong, C. W. *J. Org. Chem.* **1982**, *47*, 3780.

0002-7863/84/1506-6060$01.50/0

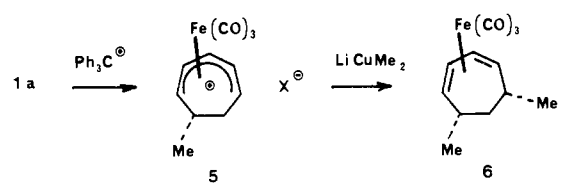
Scheme I



Scheme II



(a) R = Me
(b) R = n-Bu
(c) R = $CH(CO_2Me)_2$
(d) R = $CH(COMe)CO_2Me$
(e) R = $(\eta^4\text{-}C_7H_9)Fe(CO)_3$



as a building block for natural products synthesis and is commonly regarded as an awkward ring size, showing conformational effects that are not well understood.[3] Having established the rigid stereocontrol by a tricarbonyliron group attached to cyclohexadienyl cations, we considered that it would be very worthwhile to try and control the reactivity of related cycloheptadienyliron complexes with a view to preparing stereochemically defined cycloheptadiene derivatives.[4] A principal requirement of our study was that we be able to introduce substituents that carry functionality appropriate for further elaboration of the resultant unactivated diene using, for example, cyclofunctionalization techniques that have previously been established for monoalkenes. The most appropriate group of this purpose would be a CH_2CO_2H substituent.

Results and Discussion

(a) Reactivity of Cycloheptadienyliron Cations. We first examined some of the basic chemical aspects of tricarbonylcycloheptadienyliron tetrafluoroborate (**1**) and related cationic complexes. While **1** has previously been prepared in good yield from either cycloheptatriene or cycloheptadiene and shown to undergo reaction with simple nucleophiles such as cyanide, borohydride, and cyclopentadienyl anions,[5] these usually give mixtures of products of type **2** and **3**, often in poor yield. The ratios of these products appears to be dependent on the nucleophile and sometimes on reaction conditions, such as solvent, etc. A third mode of action is also noted in the case of iodide ion, which leads to the product **4** of overall attack at the metal with loss of CO ligand. We hoped that a more propitious choice of nucleophilic species might lead to high yield of either type of product, **2** or **3**.

Table I. Reactions of Dienyl Complexes **8a** and **8b** with Nucleophiles

complex	nucleophile	product(s)	9:10	yield, %
8a	NaCN	**9a**	100:0	91
8b	NaCN	**9b + 10b**	10:1	65
8b	NaSPh	**10c**	0:100	94
8b	$NaSC_6H_4$-*p*-NO_2	**10d**	0:100	91
8a	CH_3Li	**9e**	100:0	69
8a	$(CH_3)_2CuLi$	**10e**	0:100	quant
8b	CH_3Li	**9f**	100:0	94
8b	$(CH_3)_2CuLi$	**10f**	0:100	97
8a	*n*-C_4H_9Li	**9g** + triene	4:1[a]	65
8a	$(n\text{-}C_4H_9)_2CuLi$	**10g** + triene	8:1[a]	89
8b	*n*-C_4H_9Li	**9h + 10h**	9:1	92
8b	$(n\text{-}C_4H_9)_2CuLi$	**9h + 10h**	1:3	79
8a	C_6H_5Li	**9i**	100:0	91
8a	$(C_6H_5)_2CuLi$	**10i**	0:100	77
8b	C_6H_5Li	**9j**	100:0	77
8b	$(C_6H_5)_2CuLi$	**10j**	0:100	89
8a	CC≡CCMgCl	**9k + 10k**	10:1	72
8b	CC≡CCMgCl	**9l + 10l**	4:1	69
8a	$(CC{=}CC)_2CuMgCl$	**9m + 10m**	1:3	74
8b	$(CC{=}CC)_2CuMgCl$	**9n + 10n**	1:5	79
8a	C≡CCMgCl	**9o + 10o**	8:1	67
8a	$(C{=}CC)_2CuMgCl$	**9o + 10o**	1:2	63
8b	C≡CCMgCl	**9p + 10p**	6:1	61
8b	$(C{=}CC)_2CuMgCl$	**9p + 10p**	1:2	54
8a	$NaCH(CO_2CH_3)_2$	**10q**	0:100	quant
8b	$NaCH(CO_2CH_3)_2$	**10r**	0:100	quant
8a	$NaCH(CO_2CH_3)(COCH_3)$	**10s**	0:100	quant
8b	$NaCH(CO_2CH_3)(COCH_3)$	**10t**	0:100	quant
8a	$NaCH(SO_2Ph)(CO_2CH_3)$	**10u**	0:100	quant
8b	$NaCH(SO_2Ph)(CO_2CH_3)$	**10v**	0:100	75
8a	$NaCH(CN)(CO_2CH_3)$	**10w**	0:100	85
8b	$NaCH(CN)(CO_2CH_3)$	**10x**	0:100	81

[a] Ratio **9**: or **10**:triene.

As our starting point we chose to study the reaction between lithium dialkylcuprate reagents and complex **1**, since these have previously been shown to result in high-yielding alkylation of related tricarbonylcyclohexadienyliron hexafluorophosphate derivatives.[6] Similarly, alkyllithium reagents, when used in dichloromethane at low temperature,[7] but not when used in ethereal solvents, give high yield during alkylation of the six-membered ring counterparts. Treatment of complex **1** with dimethyl- and di-*n*-butylcuprate reagents resulted in poor yield of alkylated products of type **2** (R = Me, 20–25%, R = *n*-Bu, 23%). The corresponding organolithium reagents also gave low yields of multiple products. Several attempts were made to improve yields, but without success. Reaction of **1** with dimethyl sodiomalonate or methyl sodioacetoacetate gave the malonate adduct **2c** (R = $CH(CO_2Me)_2$) and the acetoacetate **2d** (R = $CH(COMe)CO_2Me$) in moderate but acceptable yields (56% and 67%, respectively), confirming a previous report on malonate anion addition,[5c] but the difficulties associated with direct alkylation indicated that a modification of the complex was necessary. Before embarking on any protracted approaches to such modification, though, we were interested in determining whether a second hydride abstraction/nucleophile addition sequence could be per-

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(6) Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1101; **1977**, *30*, 345.
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Table II. ^{1}H NMR Spectral Data for Substituted Diene–$Fe(CO)_2L$ Complexes[a]

complex	1-H, 4-H	2-H, 3-H	5-H	6α-H[b]	6β-H[b]	(7-H)$_2$	other
2a	3.07 (m), 2.86 (m)	5.28 (m)	1.97 (m)[c]	1.28 (m)	1.43 (m)	1.97 (m)[c]	0.95 (d, J = 6.7 Hz, Me)
2b	2.87 (m, 1-H), 3.04 (m, 4-H)	5.25 (m)	1.96 (m)[c]	0.89 (m)	1.35 (m)	1.96 (m)[c]	1.35 (m, 3 CH_2), 0.89 (t, CH_3)
2c	2.72 (m)	5.25 (m)	3.05 (d, J = 6.3 Hz)	1.33 (qd, $J_{5,6\alpha}$ = J_{gem} = $J_{6\alpha,7\beta}$ = 12.6, $J_{6\alpha,7\alpha}$ = 4.4 Hz)	1.32 (d, J_{gem} = 12.6 Hz)	2.06 (m)	3.75 (s, CO_2Me), 3.73 (s, CO_2Me), 3.26 (d, J = 6.3 Hz, malonate CH)
2d	2.69 (m)	5.28 (m)	3.05 (m)	1.05 (qd, J = 11.7, 3.1 Hz)	1.30 (m)	2.01 (m)	3.76, 3.72 (2 s, CO_2Me),[d] 3.31, 3.27 (2 x d, J = 8 Hz, CH), 2.23, 2.19 (2 s, COMe)
6	2.79 (m)	5.18 (m)	1.98 (m)[c]	1.19 (m)[c]	1.19 (m)[c]	1.98 (m)[c]	0.86 (d, J = 7 Hz, 2 Me)
7a	2.44 (m)	4.64 (m)	1.87 (m)	1.14 (m)	1.32 (m)	1.87 (m)	7.37 (PPh_3)
7b	2.82 (m)	4.61 (m)	1.75 (m)	1.06 (m)	1.26 (m)	1.75 (m)	7.24 ($P(OPh)_3$)
10c[e,f]	2.77 (m, $J_{1,2}$ = 7.0, J_{PH} = 2.8 Hz, 1-H), 3.37 (t, $J_{3,4}$ = J_{PH} = 6.3 Hz, 4-H)	4.47 (m, 2-H), 4.66 (m, 3-H)	3.78 (dd, J = 12.8, 3.4 Hz)	1.28 (qd, J = 12.8, 4 Hz)	1.62 (d, J = 12.8 Hz)	1.82 (m)	7.40 (2 H, dd, J = 8.0, 1.5 Hz, ortho Ar H), 7.02 (18 H, m, Ar H)
10d[e]	2.84 (m, 1-H), 3.08 (t, J = 6.3 Hz, 4-H)	4.57 (m)	3.74 (br d, J = 12.5 Hz)	1.21 (qd, J = 12.5, 4.5 Hz)	1.49 (br d, J = 12.5 Hz)	1.83 (m)	7.67 (2 H, d, J = 8.6 Hz, Ar H), 7.02 (17 H, m, Ar, H)
10e	2.42 (m), 2.24 (m)	4.62 (m)	1.96 (m)[c]	0.79 (qd, J = 11.8, 6.8 Hz)	1.28 (d, J = 11.8 Hz)	1.96 (m)[c]	7.37 (m, PPh_3), 0.79 (d, J = 6.7 Hz, Me)
10f	2.84 (m), 2.59 (t, J = 5.8 Hz)	4.57 (m)	1.79 (m)[c]	0.69 (qd, J = 12.4, 5.8 Hz)	1.19 (d, J = 12.4 Hz)	1.79 (m)[c]	7.35 (m, $P(OPh)_3$), 0.80 (d, J = 6.7 Hz, Me)
10g	2.33 (m), 2.20 (t, J = 6.8 Hz)	4.63 (m)	1.87 (m)[c]	0.81 (m)[c]	1.20 (m)[c]	1.87 (m)[c]	7.40 (m, PPh_3), 1.20 (m, 3 CH_2),[c] 0.81 (t, Me)[c]
10h	2.83 (m), 2.64 (t, J = 6 Hz)	4.58 (m)	1.83 (m)	0.67 (qd, J = 12.3, 4.1 Hz)	1.21 (m)[c]	1.68 (m)	7.26 (m, $P(OPh)_3$), 1.21 (m, 3 CH_2),[c] 0.85 (t, Me)
10i	2.39 (q, $J_{1,2}$ = $J_{1,7\alpha}$ = J_{PH} = 6.3 Hz, 1-H), 2.52 (m)	4.86 (m), 4.67 (dd, J = 6.3, 4.4 Hz, 2-H)	3.16 (br, d, J = 12.5 Hz)	1.27 (qd, J = 12.5, 4.6 Hz)	1.44 (d, J = 12.5 Hz)	2.03 (m)	7.41 (m, PPh_3), 7.18 (m, Ph)
10j	2.92 (m, 1-H),[c] 2.71 (m, 4-H)	4.74 (m)	2.92 (m)[c]	1.15 (qd, J = 12.0, 5.6 Hz)	1.26 (d, J = 12.0 Hz)	1.91 (m)	7.22 (m, $P(OPh)_3$, Ph)
10m	2.48 (m), 2.27 (m)	4.68 (m), 4.52 (m)	1.91 (m)[c]	0.86 (m)	1.27 (m)	1.91 (m)[c]	7.41 (m, PPh_3), 5.27 (m, 2 vinyl), 1.74 (m, CH_2), 1.60 (d, Me)
10n	2.84 (m), 2.67 (m)	4.59 (m)	1.76 (m)[c]	0.73 (m)	1.22 (m)	1.76 (m)[c]	7.26 (m, $P(OPh)_3$), 5.31 (m, vinyl), 1.76 (m, CH_2), 1.62 (d, J = 4.4 Hz, Me)
10o	2.18 (m)	4.62 (m)	1.84 (m)[c]	0.81 (qd, J = 11.7, 5.9 Hz)	1.30 (d, br, J = 11.7 Hz)	1.84 (m)[c]	7.42 (m, PPh_3), 5.68 (m, =CH), 4.89 (m, $=CH_2$), 1.60 (m, CH_2)
10p	2.83 (m), 2.65 (t, J = 6.8 Hz, 4-H)	4.58 (m)	1.77 (m)[c]	0.69 (qd, J = 12.7, 4.4 Hz)	1.29 (d, J = 12.7 Hz)	1.77 (m)[c]	7.26 (m, $P(OPh)_3$), 5.65 (m, =CH), 4.91 (m, $=CH_2$), 1.77 (m, CH_2)[c]
10q	2.58 (m), 2.18 (t, J = 5.9 Hz, 4-H)	4.62 (m)	2.77 (m)	1.04 (qd, J = 12.5, 5.6 Hz)	1.20 (d, J = 12.5 Hz)	1.98 (m)	7.36 (m, PPh_3), 3.65 (s, CO_2Me), 3.61 (s, CO_2Me), 3.14 (d, J = 7.1 Hz, CH)
10r	2.58 (m)	4.62 (m)	2.85 (m)	0.96 (qd, J = 12.0, 4.0 Hz)	1.20 (d, J = 12.0 Hz)	1.85 (m)	7.27 (m, $P(OPh)_3$), 3.67 (s, CO_2Me), 3.65 (s, CO_2Me), 3.14 (d, J = 6.8 Hz, CH)
10s[d]	2.51 (m)	4.65 (m)	2.79 (m)	0.91 (m)	1.24 (br d, J = 10.8 Hz)	1.92 (m)	7.34 (m, PPh_3), 3.66 and 3.63 (2 s, CO_2Me), 3.12 and 3.08 (2 d, J = 3.6 Hz, CH), 2.08 and 2.03 (2 s, COMe)
10t	2.41 (m, 1-H), 2.68 (m, 4-H)	4.62 (m)	2.85 (m)	0.91 (m)	1.19 (br d, J = 11.6 Hz)	1.83 (m)	4.26 (m, $P(OPh)_3$), 3.66 and 3.63 (2 s, CO_2CH_3), 3.12 and 3.08 (2 d, J = 8.6 Hz, CH), 2.19 and 2.13 (2 s, COMe)
10u[d,e]	2.36 (m, 1-H), 2.75 (t, 4-H), J = 5.4 Hz)	4.56 (m)	1.99 (m)	1.26 (m)[c]	1.26 (m)[c]	1.68 (m)	7.49 (m, Ph), 7.04 (m, PPh_3), 3.15 and 3.10 (2 s, CO_2CH_3), 3.23 (br d, CH)
10v[d]	2.66 (m)	4.41 (m, 2-H), 4.76 (m, 3-H)	1.66 (m)[c]	1.07 (m)	1.31 (m)	1.66 (m)[c]	7.36 (m, Ph), 7.02 (m, $P(OPh)_3$), 3.01 and 3.17 (2 s, CO_2CH_3), 2.97 (br d, CH)
10w[d]	2.46 (m, 1-H), 2.72 (m, 4-H)	4.81 (m)	2.01 (m)[c]	1.27 (m)	1.27 (m)	2.01 (m)[c]	7.44 (m, PPh_3), 3.71 and 3.68 (2 s, CO_2CH_3), 3.35 and 3.24 (2 d, J = 4.2 Hz, CH)

Table II (Continued)

complex	1-H, 4-H	2-H, 3-H	5-H	6α-H[b]	6β-H[b]	$(7\text{-H})_2$	other
12a	2.22 (m)	4.60 (m)	2.06 (m)[c]	0.43 (q, $J_{5,6\alpha} = J_{gem} = J_{6\alpha,7} =$ 12.4 Hz)	1.20 (br d, J_{gem} = 12.4 Hz)	2.06 (m)[c]	7.38 (m, PPh_3), 0.78 (d, J = 6.8 Hz, 2 CH_3)
12b	2.61 (m)	4.53 (m)	1.82 (m)[c]	0.34 (q, J = 12.4 Hz)	1.12 (br d, J = 12.4 Hz)	1.82 (m)[c]	7.26 (m, $P(OPh)_3$), 0.79 (d, J = 6.8 Hz, 2 CH_3)
12c	2.63 (m)	4.54 (m)	1.77 (m)	0.32 (q, J = 12.2 Hz)	1.12 (m)[c]	1.77 (m)	7.28 (m, $P(OPh)_3$), 1.16–1.06 (m, 3 CH_2)[c] 0.83 (m, 2 CH_3)
12d	2.72 (m)	4.69 (m)	2.98 (br d, J = 12.7 Hz)	0.84 (m)[c]	1.29 (m)	1.98 (m)	7.37 (m, $P(OPh)_3$, Ph), 0.87 (d, J = 7.6 Hz, CH_3)
12e	2.19 (m)	4.59 (m)	2.79 (m)	0.69 (q, J = 12.5 Hz)	1.20 (br d, J = 12.5 Hz)	2.19 (m)	7.35 (m, PPh_3), 3.65 and 3.61 (2 s, 2 CO_2CH_3), 3.11 (d, J = 7.0 Hz, CH), 0.81 (d, J = 6.8 Hz, CH_3)
12f	2.63 (m)	4.59 (m)	2.63 (m)	0.62 (q, J = 12.4 Hz)	1.14 (br d, J = 12.4 Hz)	1.90 (m)	7.26 (m, $P(OPh)_3$), 3.68 and 3.66 (2 s, 2 CO_2CH_3), 3.15 (d, J = 6.7 Hz, CH), 0.82 (d, J = 6.7 Hz, CH_3)
12g[d]	2.58 (m)	4.59 (m)	2.58 (m)	0.55 and 0.52 (2 q, J = 12.3 Hz)	1.08 (br d, J = 12.3 Hz)	2.18 (m)	7.28 (m, $P(OPh)_3$), 3.68 and 3.66 (2 s, CO_2CH_3), 3.17 and 3.13 (2 d, J = 8.0 Hz, CH), 2.20 and 2.15 (2 s, $COCH_3$), 0.81 (d, J = 6.7 Hz, CH_3)
12h[d,e]	2.54 (m)	4.56 (m)	2.18 (m)[c]	0.93 (q, J = 12.3 Hz)	1.57 (m)	2.18 (m)[c]	7.50 (m, Ph), 7.03 (m, PPh_3), 3.15 and 3.10 (2 s, CO_2CH_3), 3.22 (br d, J = 12 Hz, CH), 0.67 and 0.66 (2 d, J = 6.7 Hz, CH_3)[c]
12i[d,e]	2.48 (m, 1-H), 2.76 (m, 4-H)	4.36 (m, 2-H), 4.76 (m, 3-H)	1.77 (m)[c]	0.78 (q, J = 12.2 Hz)	1.16 (br d, J = 12.2 Hz)	1.77 (m)[c]	7.39 (m, Ph), 7.03 (m, $P(OPh)_3$), 3.22 and 3.19 (2 s, CO_2CH_3), 3.04 (br d, J = 13.1 Hz, CH), 0.60 and 0.55 (2 d, J = 6.9 Hz, CH_3)
12j	2.64 (m)[c]	4.60 (m)	2.64 (m)[c]	0.62 (q, J = 12.3 Hz)	1.20 (m)[c]	1.77 (m)	7.25 (m, $P(OPh)_3$), 3.72 and 3.67 (2 s, 2 CO_2CH_3), 3.16 (d, J = 6.3 Hz, CH), 1.20 (m, 3 CH_2)[c] 0.84 (t, CH_3)
12k	2.62 (m)	4.55 (m)	1.83 (m)[c]	0.34 (br q, J = 12.1 Hz)	1.15 (br d, J = 12.1 Hz)	1.83 (m)[c]	7.27 (m, $P(OPh)_3$), 5.65 (br m, =CH), 4.93 (m, $=CH_2$),[c] 1.83 (m, CH_2), 0.80 (d, J = 6.8 Hz, CH_3)

[a] All spectra run at 200 MHz in $CDCl_3$, using Me_4Si as internal reference, unless otherwise stated. [b] For description of multiplicity, see text. Assignment of couplings is listed for compound **2c**; all others follow the same pattern. [c] Overlapping or obscured peaks. [d] Equimolar mixture of diastereomers. [e] Measured in C_6D_6 solution. [f] Assignments based on decoupling experiments for all compounds. The following spin decoupling data is presented for complex **10c**, others being analogous. ^{31}P decoupling (13 600-Hz offset) resulted in simplification of all diene proton resonances: 3-H (δ 4.66) collapsed to dd, J = 5.6, 4.4 Hz; 2-H (δ 4.47) collapsed to dd, J = 6.5, 4.4 Hz (both showed fine coupling); 5-H remained unchanged; 4-H (δ 3.37) collapsed to a doublet, J = 6.6 Hz; the broad multiplet due to 1-H (δ 2.77) collapsed to a triplet, J = 6.5 Hz; no effect on 6-H and 7-H signals. ^1H decoupling experiments: irradiation at δ 1.6–1.8 caused collapse of 1-H (δ 2.77) to dd, $J_{1,2}$ = 6.5 Hz, collapse of 6α-H to d, J = 10.8 Hz, and collapse of 5-H (δ 3.78) to d, J = 10.8 Hz; irradiation of 6α-H caused collapse of 5-H (δ 3.78) to d, J = 3.4 Hz; irradiation of 3-H (δ 4.66) caused partial collapse of 2-H (δ 4.47) and collapse of 4-H (δ 3.37) to d, J = 6.1 Hz.

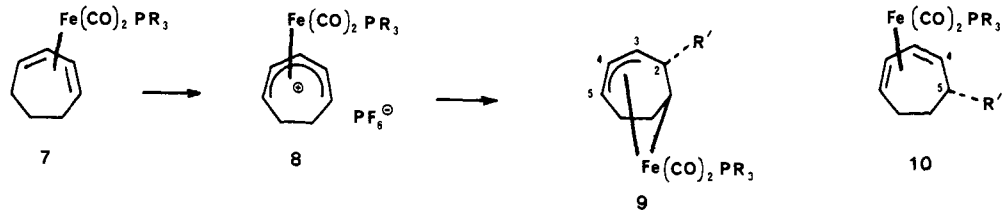
formed on the substituted complex **2a**, since our primary interest at this stage was in the application of the metal as a means of controlling relative stereochemistry. Accordingly, **2a** was treated with triphenylmethyl tetrafluoroborate, giving the substituted dienyl complex **5** in high yield. Reaction of this compound with lithium dimethylcuprate gave the dimethyl-substituted complex **6**, but again in low yield (18%) (Scheme II). The symmetrical nature of this molecule was confirmed by its NMR spectrum showing only one doublet corresponding to the two methyl groups. (NMR spectra are summarized in Table II.) Minor amounts of product from C-2 methylation were also observed in the NMR spectrum.

While these results indicated the feasibility of using the iron carbonyl group as a means of directing the stereochemistry of carbon–carbon bond formation at 1,3-positions in the seven-membered ring, there still remained the problem of low yields. In this respect, the observation that, during cuprate addition, there was obtained some of the known[5] dimer **2e**, together with large amounts of polar (TLC) material, was very useful, since we attributed the dimerization to electron-transfer processes, while the polar material *might* result from nucleophilic attack at a CO ligand. With this in mind it seemed appropriate to modify the ligand environment so as to increase electron density at the metal, thereby reducing the tendency for the complex to accept electrons and also deactivating the carbonyl ligands toward nucleophilic attack.

Since problems of low yield and mixed products have previously been encountered during the replacement of one CO ligand with phosphines or phosphites in tricarbonyl(cycloheptatriene)iron,[8] we decided to concentrate on the use of cycloheptadiene complexes. Treatment of tricarbonyl(cycloheptadiene)iron with either triphenylphosphine or triphenyl phosphite at elevated temperature gave high yields of the substituted derivatives **7a** and **7b** (Scheme III). During this work we found that the phosphine and phosphite complexes give very weak or no molecular ion in their electron impact (EI) mass spectra. This may be overcome by using field desorption (FD) techniques which give strong M^+ peaks; a few examples are given in the Experimental Section. Hydride abstraction from these complexes proceeded cleanly and in high yield to give the ether-insoluble dienyl salts **8a** and **8b**. The potential synthetic utility of these procedures is borne out by the fact that

(8) (a) Reckziegel, A.; Bigorgne, A. *J. Organomet. Chem.* **1965**, *3*, 341. (b) Chaudhari, F. M.; Pauson, P. L. *Ibid.* **1966**, *5*, 73.

Scheme III



(a) R = Ph
(b) R = OPh

(a) R = Ph, R' = CN
(b) R = OPh, R' = CN
(c) R = OPh, R' = SPh
(d) R = OPh, R' = $SC_6H_4NO_2$-p
(e) R = Ph, R' = Me
(f) R = OPh, R' = Me
(g) R = Ph, R' = n-Bu
(h) R = OPh, R' = n-Bu
(i) R = Ph, R' = Ph
(j) R = OPh, R' = Ph
(k) R = Ph, R' = $CHMeCH{:}CH_2$
(l) R = OPh, R' = $CHMeCH{:}CH_2$

(m) R = Ph, R' = $CH_2CH{:}CHMe$
(n) R = OPh, R' = $CH_2CH{:}CHMe$
(o) R = Ph, R' = $CH_2CH{:}CH_2$
(p) R = OPh, R' = $CH_2CH{:}CH_2$
(q) R = Ph, R' = $CH(CO_2Me)_2$
(r) R = OPh, R' = $CH(CO_2Me)_2$
(s) R = Ph, Ph, R' = $CH(CO{\cdot}Me)CO_2Me$
(t) R = OPh, R' = $CH(CO{\cdot}Me)CO_2Me$
(u) R = Ph, R' = $CH(SO_2Ph)CO_2Me$
(v) R = OPh, R' = $CH(SO_2Ph)CO_2Me$
(w) R = Ph, R' = $CH(CN)CO_2Me$
(x) R = OPh, R' = $CH(CN)CO_2Me$

they can be carried out easily on a scale of 150 g or more. With suitable quantities of these materials available, our attention was focused on their reactivity toward nucleophiles. Previous reports[5b] have dealt with the addition of cyanide and hydride (from BH_4^-) to the triphenylphosphine derivative **8a**, giving the product **9a** by attack at C-2, and these limited results have prompted the suggestion that C-1 and C-3 are deactivated due to the trans effect of the phosphine ligand, assuming a fixed conformation, leading us to anticipate that other nucleophiles would behave similarly. This is not the case, and the results of our study, summarized in Table I, clearly show the dependence of regioselectivity on the nature of the nucleophile and on the nature of ancillary ligands attached to the metal. Thus, we confirmed that CN^- adds exclusively to C-2 of **8a**, giving **9a**, and reaction with the triphenylphosphite complex **8b** gives an approximately 10:1 mixture of **9b** and **10b**. It is noteworthy that triphenylphosphine and triphenyl phosphite are poorer π-acceptor ligands than carbon monoxide[9] and that the tricarbonyliron complex gives a 78:22 mixture of C-2/C-1 adducts.[5] This is indicative of a correlation between π-acceptor strength of the ligand L (structure **8**) and regioselectivity of nucleophile addition. Turning our attention to thiophenoxide and p-nitrothiophenoxide nucleophiles, these give exclusively products of C-1 addition with **8b**. We have not examined reaction of these nucleophiles with the $Fe(CO)_3$ complex **1**. Since these results are of little consequence from the point of view of organic synthesis, attention has been directed at reactions of complexes **8** with organometallic nucleophiles and stabilized enolates. Reaction of **8a** and **8b** with organocuprate reagents resulted in predominant, in many cases exclusive, C-1 addition to give diene complexes **10**, while alkylation with the corresponding lithium or magnesium alkyls gave predominant C-2 addition to give type **9** complexes, all occurring in good to excellent yields (Table I). Different mechanistic pathways are available to cuprate and main-group organometallic reagents, and these results are most likely a consequence of initial formation of a carbon–copper bond followed by reductive elimination to give C–C bond formation during cuprate addition, as opposed to direct alkyl group transfer from the main-group derivatives.[10] This hypothesis is supported by our own observation that crotylmagnesium chloride gives products **9k** and **9l** from attack at the nonterminal position of the crotyl group, with effectual migration of the double bond, whereas the corresponding cuprate gave the terminal allyl alkylation products **10m** and **10n**.

The dienyl complexes also underwent very clean, high-yielding addition of stabilized enolates, $NaCH(CO_2Me)_2$, $NaCH(COMe)CO_2Me$, $NaCH(SO_2Ph)CO_2Me$, and $NaCH(CN)CO_2Me$, to give **10q–x** as the only observable products (NMR).

In summary, it can be seen that, using the appropriate nucleophile, either type of adduct **9** or **10** can be obtained in good yield (Table I).

At this point we should note the spectral characteristics of structural types **9** and **10**. While no significant differences could be observed in the IR and mass spectra of these compounds, it is known from previous studies that considerably different ^1H NMR patterns are associated with the two types of complexes.[5] Typically, a η^4-diene complex type **10** displays a two-proton multiplet at ca. δ 4.5 for 2-H and 3-H and a similar two-proton signal at ca. δ 2.4 for 1-H and 4-H. On the other hand, the σ-π-allyl complexes **9** give a set of three 1 H intensity peaks in the region of δ 4.2 = 3.0, corresponding to the π-allyl group, the proton on the σ-bonded carbon atom occurring at ca. δ 2.1 (examples are shown in Figure 1). The exact location of each π-allyl proton varies according to the nature of substituents attached to the hydrocarbon ligand, and also the type of ligand in the $Fe(CO)_2L$ moiety. Where possible, for each complex we carried out spin-decoupling experiments, allowing assignment of all peaks. Full NMR spectral data are given in Tables II and III, IR and mass spectra being included in the experimental section.

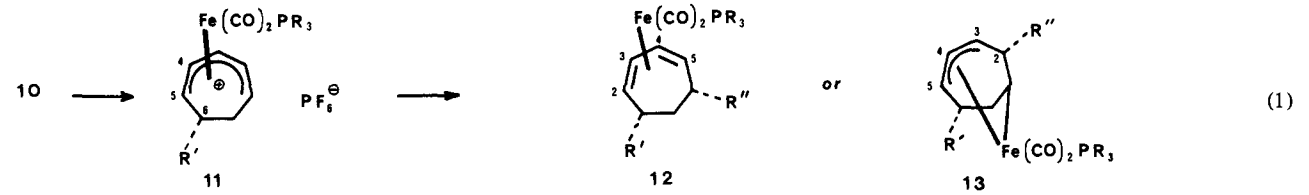
The question now arose whether we could introduce a second substituent onto the cycloheptadiene ring stereospecifically, regiospecifically, *and in high yield*. Hydride abstraction from the methyl-substituted derivatives **10e** and **10f** occurred without problem to give dienyl salts **11a** and **11b** (eq 1) in *overall* yields of 93–95% from dienyl salts **8a** and **8b**. The butyl-substituted complex **10h** reacted more sluggishly with Ph_3CPF_6, requiring prolonged treatment in boiling dichloromethane to give a 65% yield of **11c**. We shall return to this later. The alkyl-substituted dienyl salts thus obtained were submitted to a series of nucleophile additions, the results of which are summarized in Table IV. Both complexes **11a** and **11b** reacted with a series of alkylcuprate reagents to give disubstituted diene complexes **12** with high regioselectivity and in very high yields. The stereospecificity of the reaction was demonstrated by the observation of a *single* doublet (intensity 6 H) at ca. δ 0.8 in the 200-MHz ^1H NMR spectrum corresponding to both methyl groups of **12a** and **12b** (Figure 1) and the fact that the major product **12c** of Bu_2CuLi reaction with **11a** was identical in all respects with the product of Me_2CuLi reaction with **11c**. The second alkylation occurs cis to the already

(9) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 89.
(10) Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141. Blumenkopf, T. A.; Heathcock, C. H. *Ibid.* **1983**, *105*, 2354.

Table III. ^{1}H NMR Spectra of σ,π-Allyl-Fe(CO)$_2$L Complexes[a]

complex	1-H	2-H	3-H	4-H	5-H	6-H	7-H$_2$	other
9a	2.20 (m)	3.73 (m,[b] $J_{2,3}$ = 6.8 Hz)	4.11 (br t, $J_{2,3}$ = $J_{3,4}$ = 6.8 Hz)	3.94 (dd, $J_{3,4}$ = 6.8, $J_{4,3}$ = 9.4 Hz)	3.73 (m)[b]	2.01 (m)[b]	1.78 (m, 7β-H), 1.28 (d, 7α-H, J_{gem} = 10.6 Hz)	7.34 (m, PPh$_3$)
9b	2.19 (m)	3.62 (dd, $J_{2,3}$ = 6.8, $J_{1,2}$ = 8.9 Hz)	4.42 (m)[b]	4.42 (m)[b]	2.94 (t, $J_{4,5}$ = 6.5, $J_{5,6}$ = 6.5 Hz)	1.93 (m)	1.69 (m, 7β-H), 1.11 (br d, 7α-H, J_{gem} = 9.4 Hz)	7.27 (m, P(OPh)$_3$)
9c	1.93 (m)	2.88 (qt, J_q = 7.1, $J_{2,3}$ = 6.3 Hz)	4.00 (t, $J_{2,3}$ = $J_{3,4}$ = 6.3 Hz)	3.64 (m)[b]	3.64 (m)[b]	2.65 (m)	1.65 (m, 7β-H), 1.46 (m, 7α-H)	7.36 (m, PPh$_3$), 0.67 (d, J = 7.1 Hz, CH$_3$)
9f	2.11 (m)	2.58 (hextuplet, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 7.2 Hz)	4.23 (m)[b]	4.23 (m)[b]	3.27 (m)	1.61 (m)[b]	1.61[b] (m, 7β-H), 1.23 (m, 7α-H)	7.24 (m, P(OPh)$_3$), 0.54 (d, J = 7.2 Hz, CH$_3$)
9g	2.18 (m)	2.71 (quintet, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 7.7 Hz)	4.01 (t, $J_{2,3}$ = $J_{3,4}$ = J_{PH} = 7.7 Hz)	3.61 (m)[b]	3.61 (m)[b]	1.88 (m, 6β-H), 1.57 (m, 6α-H)[b]	1.57 (m, 7β-H),[b] 1.03 (m, 7α-H)	7.35 (m, PPh$_3$), 1.24 (m, 2 CH$_2$), 0.88 (m, CH$_2$CH$_3$)
9h	2.11 (m)	2.39 (quintet, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 6.9 Hz)	4.20 (m)[b]	4.20 (m)[b]	3.29 (m)[c]	1.66 (m)	1.47 (m, 7β-H), 1.28 (m, 7α-H)	7.27 (m, P(OPh)$_3$), 1.15 (m, 2 CH$_2$), 0.87 (m, CH$_2$CH$_3$)
9i	1.80 (m)	4.03 (m)[b]	4.17 (t, $J_{2,3}$ = $J_{3,4}$ = 7.5 Hz)	4.03 (m)[b]	3.79 (br t, J = 6 Hz)	1.80 (m)	1.06 (m)	7.39 (m, PPh$_3$), 7.16 (m, Ph)
9j	1.70 (m)[b]	3.86 (t, $J_{1,2}$ = $J_{2,3}$ = 7.9 Hz)	4.64 (q, $J_{2,3}$ = $J_{3,4}$ = J_{PH} = 7.9 Hz)	3.27 (t, $J_{3,4}$ = $J_{4,5}$ = 7.9 Hz)	4.22 (m)	1.70 (m)[b]	1.12 (m, 7β-H), 0.89 (m, 7α-H)	7.16 (m, P(OPh)$_3$)
9k	2.16 (m)	2.47 (q, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 7 Hz)	3.97 (m)	3.68 (m)[b]	3.68 (m)[b]	1.81 (m)	1.60 (m, 7β-H), 1.15 (m, 7α-H)	7.33 (m, PPh$_3$), 5.67 (br m, =CH), 4.93 (m, =CH$_2$), 1.81 (m, CH$_2$), 0.89 and 0.82 (2 d, J = 6.5 Hz, CH$_3$)
9l	2.14 (m)[b]	2.14 (m)[b]	4.34 (m)	4.21 (m)	3.27 (m)[c]	1.69 (m)	1.40 (m)	7.26 (m, P(OPh)$_3$), 5.51 (br m, =CH), 4.88 (m, =CH$_2$), 1.69 (m, CH$_2$), 0.76 and 0.72 (2 d, J = 7.1 Hz, CH$_3$)
9o	2.20 (m)	2.86 (quintet, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 7 Hz)	4.00 (br t, $J_{2,3}$ = $J_{3,4}$ = 7 Hz)	3.65 (m)[b]	3.65 (m)[b]	1.85 (m)	1.62 (m, 7β-H), 1.15 (m, 7α-H)	7.28 (m, PPh$_3$), 5.72 (br m, =CH), 4.94 (d, J = 11.7 Hz, =CH$_2$), 1.85 (m, CH$_2$)
9p	2.18 (m)	2.55 (quintet, $J_{1,2}$ = $J_{2,3}$ = $J_{2,2'}$ = 7 Hz)	4.26 (m)[b]	4.26 (m)[b]	3.30 (br t, J = 6 Hz)	1.69 (m)	1.44 (m, 7β-H), 1.32 (m, 7α-H)	7.26 (m, P(OPh)$_3$), 5.60 (br m, =CH, 4.88 (d, J = 12.3 Hz, =CH$_2$), 1.69 (m, CH$_2$)

[a] All spectra were measured in $CDCl_3$, with Me_4Si as internal reference. [b] Overlapping or obscured signals. [c] Signals observed as broadened triplet but accurate coupling constants were not accessible.



(1)

(a) R = Ph, R' = Me
(b) R = OPh, R' = Me
(c) R = OPh, R' = n-Bu

(a) R = Ph, R' = R" = Me
(b) R = OPh, R' = R" = Me
(c) R = OPh, R' = Me, R" = n-Bu
(d) R = OPh, R' = Me, R" = Ph
(e) R = Ph, R' = Me, R" = $CH(CO_2Me)_2$
(f) R = OPh, R' = Me, R" = $CH(CO_2Me)_2$

(g) R = OPh, R' = Me, R" = $CH(COMe)CO_2Me$
(h) R = Ph, R' = Me, R" = $CH(SO_2Ph)CO_2Me$
(i) R = OPh, R' = Me, R" = $CH(SO_2Ph)CO_2Me$
(j) R = OPh, R' = n-Bu, R" = $CH(CO_2Me)_2$
(k) R = OPh, R' = Me, R" = $CH_2CH{:}CH_2$

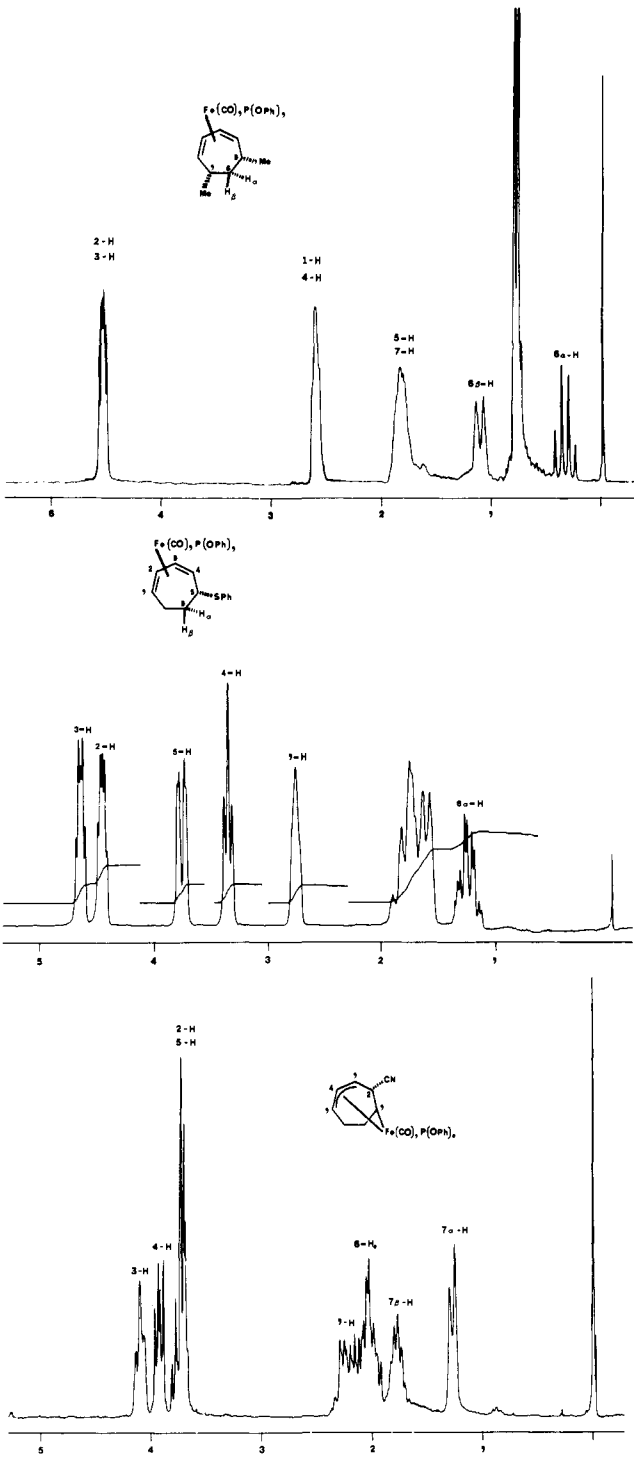


Figure 1. ^{1}H NMR (200-MHz) spectra of complexes **12b**, **10c**, and **9b** showing the δ 0–5.0 region. Spectra measured in $CDCl_3$ or C_6D_6 solution using Me_4Si as internal reference (see Tables II and III).

present substituent. Interestingly, reaction of **11a** and **11b** with alkyllithium and Grignard reagents gave products **12** of C-1 addition, contrasting with the same reaction of complexes **8**. On the other hand, the butyl-substituted complex **11c** gave a mixture of C-1 and C-2 adducts on reaction with methyllithium, in favor of the former, possibly indicating a delicate balance between steric and electronic effects (see later).

As expected, the methyl-substituted complexes **11a** and **11b** reacted with stabilized enolates, $NaCH(CO_2Me)_2$, $NaCH(COMe)CO_2Me$, $NaCH(SO_2Ph)CO_2Me$, and $NaCH(CN)CO_2Me$, to give the stereochemically defined disubstituted complexes **12a** and **12k** in very high yields. Similarly, the butyl-substituted derivative **11c** gave the diester complex **12j** in essentially quantitative yield on reaction with $NaCH(CO_2Me)_2$, indicating the potential generality of this strategy.

Table IV. Reactions of Dienyl Complexes **11a**, **11b**, and **11c** with Nucleophiles

complex	nucleophile	product(s)	yeild, %
11a	CH_3Li	**12a**	86
11a	$(CH_3)_2CuLi$	**12a**	83
11b	$(CH_3)_2CuLi$	**12b**	86
11b	CH_3Li	**12b**	74
11b	n-C_4H_9Li	**12c**	84
11b	$(n$-$C_4H_9)_2CuLi$	**12c**	63
11b	C_6H_5Li	**12d**	89
11b	$(C_6H_5)_2CuLi$	**12d**	75
11a	$NaCH(CO_2CH_3)_2$	**12e**	92
11b	$NaCH(CO_2CH_3)_2$	**12f**	97
11b	$NaCH(CO_2CH_3)(COCH_3)$	**12g**	88
11a	$NaCH(SO_2Ph)(CO_2CH_3)$	**12h**	83
11b	$NaCH(SO_2Ph)(CO_2CH_3)$	**12i**	91
11c	CH_3Li	**12c** + **13c**[a]	68
11c	$(CH_3)_2CuLi$	**12c**	50
11c	$NaCH(CO_2CH_3)_2$	**12j**	91
11b	C≡CCMgCl	**12k**	71
11b	$(C{\equiv}C)_2CuMgCl$	**12k**	60

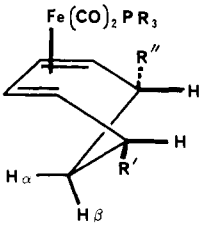
[a] 7:4 ratio.

The above results indicate that the regioselectivity of nucleophile addition to cycloheptadienyliron complexes is dependent on the nature of ancillary ligands attached to the metal, as well as the nature of the nucleophile, and in certain cases is influenced by substituents on the ring. While it is difficult at this stage to give hard and fast rules, or to completely rationalize the observations, we can put forward the following hypothesis. Complexes **1**, **8a**, **8b**, **11a**, and **11b** behave as ambident electrophiles; "soft" nucleophiles (highly polarizable with high-energy HOMO) attacking C-1, while "harder" nucleophiles (less polarizable, lower energy HOMO)[11] attack C-2. "Soft" nucleophiles, having HOMOs close in energy to the dienyl-$Fe(CO)_2L$ LUMO, will experience a strong orbital interaction. This interaction will become less important as the nucleophile HOMO energy becomes lower, and we might expect Coulombic interaction to become more important.[11,12] Such calculations as are available,[13] as well as carbon-13 NMR data,[14] indicate that C-2 and C-4 are the most positive dienyl positions, due to population of the (free) dienyl LUMO by synergistic interaction with the metal d orbitals. However, the relative magnitudes of coefficients in the complex LUMO are ambiguous,[15] since there are a number of orbitals that are close in energy and that compete for this assignment. It seems likely that the important orbital has large coefficients at C-1 and C-5; this speculation would lead to at least a partial rationalization of the above data. A problem arises in considering reactions of methyl-substituted dienyl complexes **11** since it is not clear to what extent nucleophile addition at C-2 is susceptible to steric retardation. The observation that products of C-1 addition undergo conformational flip (see next section), which is not allowed in the C-2 adducts, is indicative of the importance of nonbonded repulsions. Such interactions may well be responsible for disfavoring C-2 addition in complex **11b**, but the result of reaction **11c** with MeLi indicates a complex set of controlling factors.

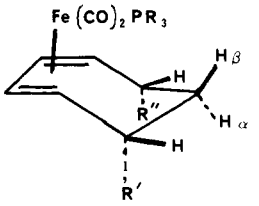
(b) Conformations of Substituted Cycloheptadiene Complexes: NMR Studies. During the preparation and characterization of the substituted η^4-diene complexes described above, we have observed characteristic ^{1}H NMR patterns (Table II) indicative of

(11) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223. Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1962**, 1062.
(12) Salem, L. *J. Am. Chem. Soc.* **1968**, *90*, 543, 553.
(13) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *107*, C40. Hoffmann, R.; Hofman, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.
(14) Birch, A. J.; Westermann, P. W.; Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1671.
(15) Hoffmann, R., personal communication. We are currently examining this problem in more detail (Eisenstein, O.; Butler, W.; Pearson, A. J. *Organometallics* **1984**, *3*, 1150.

a preference for boat conformation **14** over a chair conformation **15**. It may be noted at this stage that the diene–$Fe(CO)_2L$ unit



14



15

has the shape indicated, as obtained from X-ray studies of related cyclohexadiene complexes,[16] and that **14** and **15** are readily interconvertible by C–C bond rotations which *place no strain on the organometallic moiety*. We shall describe four examples here, but related complexes all behave similarly.

The NMR signals for protons attached to sp^3-hybridized carbon atoms of the diene ligand show no coupling to ligand phosphorus, as expected, in contrast to the long-range couplings from 1-H, 2-H, 3-H, or 4-H to phosphorus. This is exemplified by the decoupling data for complex **10c** given as a footnote for Table II.

We first noticed that complexes **12a** and **12b** both displayed a signal of intensity 1 H at unusually high field (δ 0.43 for **12a** and δ 0.34 for **12b**), which appeared as a 1:3:3:1 *quartet* in the ^1H NMR spectrum (see Figure 1). Spin-decoupling experiments confirmed that this was due to a proton at C-6 (coupled to 5-H and 7-H), and a consideration of conformations **14** and **15** conclusively showed it to be 6α-H, as follows. In **14**, 6α-H is expected to show large geminal coupling to 6β-H (observed ca. 12.2 Hz) and large (axial–axial) couplings to 5-H and 7-H (observed ca. 12.2 Hz) since the connecting dihedral angle is close to 180°. Coincidentally J_{gem}, $J_{5,6\alpha}$, and $J_{6\alpha,7}$ are all equal, so we observe a quartet. Conformation **15** would not show large coupling constants $J_{5,6}$ for either 6α-H or 6β-H. Examination of the ^1H NMR spectra of the monosubstituted complexes **10** supports this proposition. For example, spin-decoupling experiments allowed us to locate the 6α-H resonance at δ 1.25 for **10c** and δ 0.69 for **10f**, occurring as an apparent quartet of doublets (J_q = 12.5, J_d = ca. 4 Hz) for both compounds. The quartet pattern (J = 12.5 Hz) is again due to the equality of J_{gem}, $J_{5,6\alpha}$, and $J_{6\alpha,7}$, while the additional smaller coupling is due to the axial–equatorial $J_{6\alpha,7\alpha}$ (dihedral angle ca. 60°). The chairlike conformation **15** is not expected to give such large values of $J_{5,6\alpha}$ and $J_{6\alpha,7}$, since the corresponding dihedral angles are ca. 60°. Such patterns were *not* observed for the parent unsubstituted complexes **7a** and **7b**, so that these compounds appear to adopt the chair conformation **15**. Presumably, the relatively high-field position of the 6α-H resonance is due to the placing of this proton directly under the diene moiety in conformation **14**. This is in complete agreement with previous observations of unusually high-field resonance for a proton situated directly over the π-system in other complexes.[17] It is noteworthy that similar analysis of NMR spectra of substituted (η^3-cyclohexenyl)molybdenum complexes indicates a *chair* conformation for the six-membered ring, with the substituent axial.[18]

We anticipate that these hitherto unreported details will be of some significance regarding the chemical behavior of these complexes. Clearly, in the disubstituted complexes (R', R'' ≠ H) the adoption of boat conformation **15** relieves the pronounced 1,3-diaxial interaction between R^1 and R^2, as well as the interaction between these substituents and the diene moiety, but introduces a nonbonded interaction between 6α-H and the diene. In the case of monosubstituted derivatives **10**, there may be a more delicate balance between these effects, leading to easier interconversion of **14** and **15**. This offers a subtle explanation for the observed differences in rates of hydride abstraction from complexes **10a** and **10c**. For conformation **14**, we would expect negligible steric interaction between the substituent and the Ph_3C^+ cation as it approaches 7α-H (M-exo hydrides are always removed[19]), so the different reactivities of **10a** and **10c** indicate that a conformational flip is necessary before hydride abstraction will occur. This has two consequences: (1) the flip is likely to be less favorable for the butyl-substituted than for the methyl-substituted derivative, and (2) once in the chair conformation the now axial butyl group offers a greater degree of steric inhibition to Ph_3C^+ approach than does the methyl group. The suggestion that the chair conformation **15** is required for hydride abstraction and the fact that only exo hydrogens are removed is strongly indicative of a *stereoelectronic* effect during this reaction: the Fe–C-1 and C-7–H(α) bonds must be as near as possible to *antiperiplanar* for effective H^- departure. In a conformation such as **15** there is a pseudodiaxial relationship between these bonds, but in **14** the alignment is axial–equatorial. In this respect there is some analogy between this and the classical E2 elimination reaction of organic chemistry or even better the conversion of halohydrins to epoxides (a C–Fe bond is formed as H^- departs, with effective *inversion of configuration* at C-7 in **10**).

(c) Removal of the Metal and Cyclofunctionalization of the Product Dienes. Application of the above methodology to organic synthesis requires that we be able to (a) remove the metal from complexes **10** and **12** cleanly and in high yield and (b) further manipulate the liberated diene. It was with the latter requirement in mind that we chose to introduce functionalized substituents such as malonate, since a carboxylic acid residue is ideally suited for cyclofunctionalization, as exemplified by the broad range of lactonization procedures developed for monoalkene carboxylic acids.[20]

The complexes **10r**, **10v**, **12f**, and **12i** were readily demetalated by using a modification of the amine oxide method,[21] viz, the complex was treated with excess anhydrous trimethylamine *N*-oxide in dimethylacetamide at 55 °C for 36 h, giving the substituted cycloheptadiene derivatives **16** in 80–90% yield. Decarboxylation of the dienylmalonate derivatives **16a** and **16b** to give monoesters **16e** and **16f** was accomplished by the Krapcho procedure[22] (NaCN, wet Me_2SO, 70 °C, 36 h) although it was necessary to use a lower temperature with longer reaction time than usual, in order to avoid extensive diene rearrangement. Alternatively, the phenylsulfonyl ester derivatives **16c** and **16d** were desulfonylated by using sodium/mercury amalgam under milder conditions. The monoesters thus obtained were readily hydrolyzed to give carboxylic acids **16g** and **16h**, which could be submitted to an appropriate cyclofunctionalization procedure. For our initial studies in this area we chose phenylselenolactonization reactions of **16g** and **16h**, analogous to the well-established procedure for monoalkene derivatives.[20b] Treatment of **16g** with PhSeBr under appropriate conditions (1 equiv of PhSeBr, Et_3N, CH_2Cl_2, −72 °C, then −20 °C, 2 h) gave good yields of a mixture of three γ-lactones in approximate ratio 15:5:1, readily separated by preparative HPLC (eq 2). The major component was shown by 200-MHz ^1H NMR decoupling experiments to be the product **17a** of nonconjugate lactonization,[23] showing coupling constants ($J_{1,2}$ = 6.18, $J_{2,3}$ = 6.46 Hz) similar to those reported[24] for the iodolactone **20** and indicative of the conformation shown in which

(16) See, for example: Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 395. Pearson, A. J.; Mincione, E.; Chandler, M.; Raithby, P. R. *Ibid.* **1980**, 2774. Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 884.

(17) Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Friedrich, E. C. *J. Am. Chem. Soc.* **1954**, *87*, 3267.

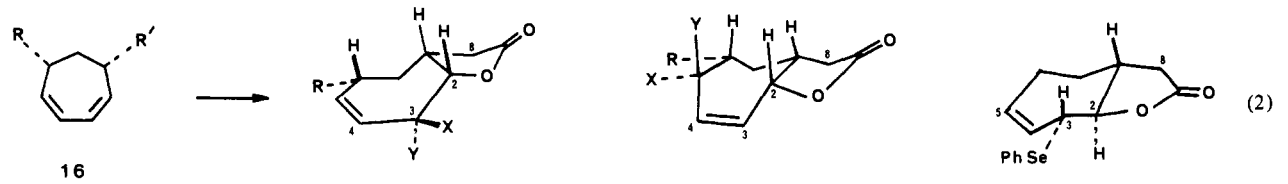
(18) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.

(19) Birch, A. J.; Chamberlain, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882. Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296.

(20) (a) See, for example: House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972; pp 441, 442. (b) Campos, M. de M.; Petragnani, N. *Tetrahedron Lett.* **1959**, *6*, 11; *Chem. Ber.* **1960**, *93*, 317. Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884. Clive, D. L. J.; Farina, V.; Singh, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2120. Nicolaou, K. C. *Tetrahedron* **1981**, *37*, 4097.

(21) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

(22) Krapcho, A. P. *Synthesis* **1982**, 805, 893.



16

(a) R = H, R' = $CH(CO_2Me)_2$
(b) R = Me, R' = $CH(CO_2Me)_2$
(c) R = H, R' = $CH(SO_2Ph)CO_2Me$
(d) R = Me, R' = $CH(SO_2Ph)CO_2Me$
(e) R = H, R' = CH_2CO_2Me
(f) R = Me, R' = CH_2CO_2Me
(g) R = H, R' = CH_2CO_2H
(h) R = Me, R' = CH_2CO_2H

17 (a) R = H, X = SePh, Y = H
(b) R = Me, X = SePh, Y = H

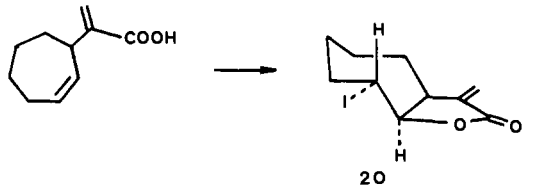
18 (a) R = H, X = PhSe, Y = H
(b) R = Me, X = PhSe, Y = H

21 (a) R = Me, X = H, Y = OH
(b) R = Me, X = H, Y = OAc

22 (a) R = Me, X = H, Y = OH
(b) R = Me, X = H, Y = OAc

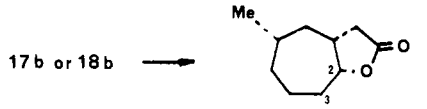
19 (2)

all substituents are equatorial. It should be pointed out that the unusual conformation **17a** translates to the chair cycloheptane



20

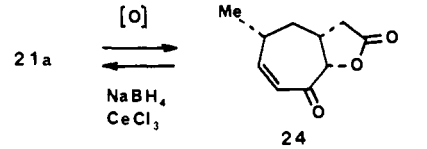
as shown for **20** by saturation of the double bond. Our data for this and the other lactones in this study indicate that the major influence on conformation of the cycloheptene ring is the lactone moiety, which prefers to occupy all-equatorial orientation, parallel with the calculated low-energy conformations of perhydroazulenes.[25] The *minor* component was also found to be a nonconjugate lactonization product and was assigned the trans lactone structure **19** from NMR spectral data. This compound adopts a pseudochair conformation with all substituents equatorial, consistent with the observed coupling constants ($J_{1,2}$ = 8.4, $J_{2,3}$ = 6.3, $J_{1,7}$ = ca. 6, $J_{1,8\beta}$ = 9.0, $J_{1,8\alpha}$ = 3.5 Hz). The middle component (19% of mixture) gave ^{1}H NMR spectrum consistent with a product of conjugate lactonization, assigned the structure **18a** with the conformation shown in which all substituents are equatorial. Further evidence for this assignment was obtained from extensive studies on the related methyl-substituted diene **16h**, phenylselenolactonization of which under identical conditions gave an approximately equimolar mixture of lactones **17b** and **18b**. During our experiments with this compound, it was found that the ratio of lactones obtained was dependent on the reaction conditions. For example, direct treatment of **16h** with PhSeBr at −20 °C, instead of commencing the reaction at −72 °C, gave an approximately 3:1 mixture in favor of the conjugate lactonization product. Use of *freshly distilled* PhSeCl at 30 °C gave the lactone **18b** as the only observable product in 80% isolated yield. A plausible explanation for these observations is that the cycloheptadiene may adopt a twisted-diene conformation, which undergoes lactonization as though it were a monoalkene, or a planar diene conformation which has considerable angle strain but is now conjugated, probably more reactive, and undergoes conjugate lactonization to give **18**. Spectroscopic studies are also suggestive of the existence of both conformations.[26] Introduction of a methyl group, as in **16h**, results in considerable transannular nonbonded repulsion between Me and the opposing C=C group, thereby favoring more the planar conformation. Presumably, at higher temperature the planar form becomes more predominant and is more reactive, leading to the possibility of controlling the ratio of lactones obtained, or else reversibility of this reaction allows some degree of thermodynamic control. The availability of both lactones **17b** and **18b** allowed us to perform experiments directed toward establishing the stereochemistry of the conjugate lactonization product **18b**. Treatment of **17b** with hydrogen peroxide (see Experimental Section) led to the allylic alcohol **22a**, by [2,3]-sigmatropic rearrangement[27] of the selenoxide derived from **17b**, and this was readily converted to the acetate **22b**. Both of these compounds showed ^{1}H NMR coupling constant data significantly different from "conjugate" seleno lactone **18b** (e.g., **22b**, $J_{1,2}$ = 7.7, $J_{4,5}$ = $J_{5,6}$ = 2.5 Hz; **18b**, $J_{1,2}$ = 6, $J_{4,5}$ = 6.3, $J_{5,6}$ = 5.5 Hz). The similarity of $J_{1,2}$ for these compounds suggests a cis lactone for **18b** (Dreiding models indicate that a trans lactone has a dihedral angle of ca. 160° connecting 1-H and 2-H, suggesting a coupling constant $J_{1,2}$ = ca. 8 Hz for such a structure: the cis lactone is more flexible, allowing fairly wide variation of values for $J_{1,2}$). This was further confirmed by reduction of the C—Se bond (Raney Ni), followed by hydrogenation of the C=C bond (H_2/PtO_2/EtOH) for *both* lactones **17b** and **18b**, which resulted in the formation of identical saturated lactones **23**. The



23

coupling constant data for this compound ($J_{1,2}$ = 6.5, $J_{2,3\alpha}$ = 10.88, $J_{2,3\beta}$ = 4.7 Hz) were entirely consistent with the structure shown.

Similar oxidation of the lactone **18b** gave the allylic alcohol **21a**, which was readily converted to acetate **21b**. These compounds showed similar coupling constant data, which differed considerably from that found for lactone **17b** (e.g., **21b**, $J_{1,2}$ = 8.9, $J_{2,3}$ = 2.2 Hz; **17b**, $J_{1,2}$ = 6.41, $J_{2,3}$ = 9.27 Hz) and which is consistent with the conformation shown, having equatorial Me and lactone groupings but axial OAc group. There appears to be an interesting parallel between the conformations preferred by lactones **17** vs. **21** and **18** vs. **22** in which the preference for a diequatorial lactone grouping is dominant (vide supra).



24

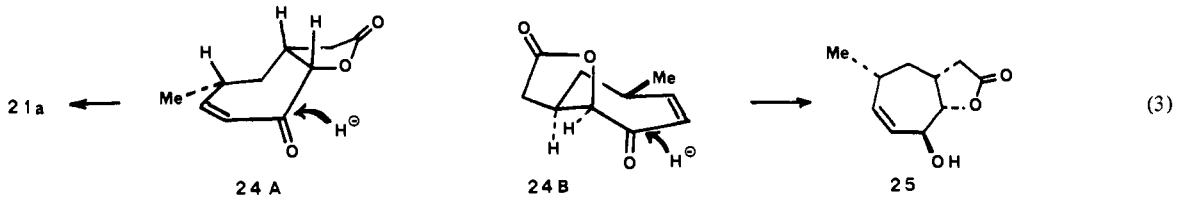
(23) For an example of conjugate phenylselenoetherification of dienes, see: Hoye, T. R.; Caruso, A. J. *J. Org. Chem.* **1981**, *46*, 1198. We have found that cyclohexadienylacetic acids and acyclic dienylacetic acids undergo conjugate phenylselenolactonization: Pearson, A. J.; Ray, T.; Richards, I. C.; Clardy, J.; Silveira, L. *Tetrahedron Lett.* **1983**, *24*, 5327.

(24) Yu, L. C.; Helquist, P. *J. Org. Chem.* **1981**, *46*, 4536.

(25) The chair form of cycloheptene itself is calculated to be *marginally* more stable than the "boat" form depicted in structures **17**, **21**, and **22**, but no information concerning the effect of substituents is available. See ref 3. For calculations on perhydroazulenes, see: House, H. O.; Gaa, P. C.; Van Derveer, D. J. *J. Org. Chem.* **1983**, *48*, 1661. House, H. O.; Gaa, P. C.; Lee, J. H. C.; Van Derveer, D. *Ibid.* **1983**, *48*, 1670.

(26) Crews, P. *J. Chem. Soc. D* **1971**, 583. Schrader, B.; Ansmann, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 364. Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1966**, *88*, 420. Hagen, K.; Traetteberg, M. *J. Chem. Scand.* **1972**, *26*, 3643.

(27) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154; **1973**, *95*, 2697. Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2570.



(3)

In addition to these arguments, the following experiments give some interesting results regarding the preferred conformations of these lactones, important for further chemical study. Oxidation of **21a** gave the unsaturated ketone derivative **24** (eq 3), which upon reduction with sodium borohydride in the presence of cerium(III) chloride gave back **21a** as the only observable product. Examination of the conformation of **24a** shown, in which all substituents are quasi-equatorial, indicates that nucleophilic attack on the enone carbonyl is favored from the β-face (peripheral attack) giving **21a** in its preferred conformation. Again the fused lactone system appears to be a dominant conformational influence in these molecules, since we should expect the enone in conformation **24B** (having axial lactone oxygen) to give mainly the hydroxy lactone **25**, epimeric with **21a**, by 1,2-reduction (peripheral attack is sterically preferred).

These experiments establish that conjugate lactonization in the cycloheptadienylacetic acid series occurs in a cis,syn manner, i.e., the lactone is cis, while the phenylseleno group is syn to the lactone moiety. This therefore provides extremely useful methodology for the stereospecific regioselective functionalization of the cycloheptadiene group, bearing in mind that high proportions of a single lactone can be obtained by propitious choice of reaction conditions. Coupled with the use of an $Fe(CO)_2L$ group to control stereochemistry during the initial attachment of substituents, the sequence of phenylselenolactonization/allylic selenoxide rearrangement promises to be a useful tool for preparation of stereodefined, highly substituted cycloheptane derivatives.

Conclusions

We have demonstrated that the reactivity of cycloheptadienyliron cationic complexes can be controlled by alteration of the ligand environment of the metal. This leads to clean reactions with a range of nucleophiles, including organometallic alkylating reagents and stabilized enolates, giving high yields of single product. The synthetic utility of these procedures is enhanced by the selective, high-yielding, demetalation of the product diene complexes to give stereochemically defined cycloheptadienylacetic acid derivatives which can be selectively functionalized by using phenylselenolactonization procedures, coupled with [2,3]-sigmatropic rearrangement of the derived allylic selenoxides. Parallel with these discoveries, we have also developed partial understanding of factors controlling electrophilic reactivity of the dienyliron complexes, and we have analyzed the conformations of substituted cycloheptadiene–$Fe(CO_2)L$ complexes. We have also gained further insight into the conformational analysis of uncomplexed cycloheptadienes and cycloheptenes that have cis-fused γ-lactone substituents. These studies should allow further developments to be made in the application of these complexes, and cycloheptane derivatives in general, to the synthesis of useful compounds such as natural products.

Experimental Section

General. Infrared spectra were recorded with a Perkin-Elmer 1420 instrument and NMR spectra with Varian EM-360 or XL-200 spectrometers. Mass spectra were determined by the Department of Pharmacology, Case Western Reserve University, and by Dr. R. P. Lattimer, the BFGoodrich Co., Brecksville, OH. HPLC separations were performed on a Gilson 802 instrument by using silica gel columns. Flash chromatography was carried out by using the method described by Still.[28] All solvents used in reactions were freshly distilled under nitrogen as follows: THF and benzene from Na/benzophenone; ether from $LiAlH_4$; dichloromethane from CaH_2; pyridine from BaO. Cuprate reagents were prepared according to standard literature methods.[29] Compounds which were characterized with IR, NMR, and mass spectral data only were ascertained to be ≥95% pure by sharp mp's, TLC, and/or HPLC and 200-MHz NMR.

Preparation of Tricarbonyl(cycloheptadiene)iron (7, L = CO). Cycloheptadiene (47 g, 0.5 mol) was stirred in di-*n*-butyl ether (300 mL) while nitrogen was bubbled through the mixture for 15 min, after which time pentacarbonyliron (147 g, 0.75 mol) was added. A reflux condenser fitted with nitrogen bubbler was attached, and the stirred mixture was heated in an oil bath at 150 °C for 44 h. The mixture was cooled and filtered through Celite (**CARE**! pyrophoric iron is produced), and the reaction flask and filter pad were washed with di-*n*-butyl ether. Removal of unreacted pentacarbonyliron and solvent under vacuum gave the known complex **7** (L = CO)[5,8b] as a golden oil, which was used in the next steps without further purification (yield 109 g, 93%).

Dicarbonyl(cycloheptadiene)(triphenylphosphine)iron (7a). A stirred solution of tricarbonyl(cycloheptadiene)iron (1.0 g, 4.27 mmol) in di-*n*-butyl ether (50 mL) was heated under reflux while triphenylphosphine (1.20 g, 4.7 mmol) in di-*n*-butyl ether (10 mL) was added dropwise. The mixture was boiled under N_2 for 24 h and worked up as above. Recrystallization of the product from ether–hexane afforded pure complex **7a** (1.88 g, 94%): mp 126–128 °C (lit.[8b] mp 128 °C); IR ν_{max} ($CHCl_3$) 1966, 1906 cm^{-1}. Anal. Found: C, 69.44; H, 5.54. $C_{27}H_{25}FePO_2$ requires: C, 69.23; H, 5.34%. This method is superior to the previous literature procedures.[5b,8b]

Dicarbonyl(cycloheptadiene)(triphenyl phosphite)iron (7b). A stirred mixture of tricarbonyl(cycloheptadiene)iron (100 g) and triphenyl phosphite (145 g, 1.1 equiv) in di-*n*-butyl ether (700 mL) was heated at reflux temperature under argon atmosphere (balloon, periodic release of CO required) for 36 h. The cooled mixture was filtered through Celite as above and solvent removed in vacuo to afford the crude product, which was purified by chromatography (silica gel, 10% EtOAc/hexane) to afford pure **7b** as pale yellow crystals: mp 89–91 °C (209 g, 95%); IR ν_{max} ($CHCl_3$) 1990, 1935 cm^{-1}. Anal. Found: C, 63.1; H, 4.7. $C_{27}H_{25}FeO_5P$ requires: C, 62.79; H, 4.84%.

Dicarbonylcycloheptadienyl(triphenylphosphine)iron (8a). Triphenylmethyl hexafluorophosphate (18 g) was dissolved in the minimum volume of dry dichloromethane, and the complex **7a** (18.0 g) was added. The mixture was swirled to dissolve the complex and set aside at room temperature for 2 h. The product was precipitated by pouring the mixture into wet ether, collected by filtration, and washed thoroughly with wet ether to afford pure **8a** (21.5 g, 91%): IR ν_{max} (CH_3CN) 2049, 2008 cm^{-1}; ^1H NMR δ (CD_3CN) 7.55 (15 H, m, PPh_3), 6.84 (1 H, t, J = 6.4 Hz, 3-H), 5.44 (2 H, m, 2-H, 4-H), 4.18 (2 H, m, 1-H, 5-H), 2.49 (2 H, m, endo-6-H, endo-7-H), 1.58 (2 H, m, exo-6-H, exo-7-H). Anal. Found: C, 52.8; H, 4.3. $C_{27}H_{24}FeO_2P_2F_6$ requires: C, 52.94; H, 3.92%.

Dicarbonylcycloheptadienyl(triphenyl phosphite)iron (8b). Treatment of complex **7b** (150 g) with triphenylmethyl hexafluorophosphate (124 g) as above gave the complex **8b** (190.0 g, 99%): IR ν_{max} (CH_3CN) 2067, 2028 cm^{-1}; ^1H NMR δ (CD_3CN) 7.49 (15 H, m, $P(OPh)_3$), 6.36 (1 H, t, J = 6.5 Hz, 3-H), 6.03 (2 H, m, 2-H, 4-H), 4.92 (2 H, m, 1-H, 5-H), 2.65 (2 H, m, endo-6-H, endo-7-H), 1.80 (2 H, m, exo-6-H, exo-7-H). Anal. Found: C, 49.4; H, 3.9. $C_{27}H_{24}FeO_5P_2F_6$ requires: C, 49.09; H, 3.87%.

Dicarbonyl[3–5-η,1-σ-(2-cyanocycloheptenyl)](triphenylphosphine)iron (9a). To a stirred solution of sodium cyanide (0.02 g, 0.4 mmol) in THF (10 mL) and water (1 mL) under nitrogen at 0 °C was added complex **8a** (0.20 g, 0.33 mmol). After 5 min at 0 °C the solution was warmed to room temperature and diluted with water (100 mL). The product was extracted with ether in the usual way, and the extracts were dried ($MgSO_4$) and evaporated to yield the crude complex. Recrystallization from ether/hexane gave pure **9a** (0.146 g, 91%): IR ν_{max} ($CHCl_3$) 2211 (w) 1987, 1930 cm^{-1}. Anal. Found: C, 68.6; H, 4.9. $C_{28}H_{24}FeNO_2P$ requires: C, 68.15; H, 4.87%.

Dicarbonyl[3–5-η,1-σ-(2-cyanocycloheptenyl)](triphenyl phosphite)iron (9b). Treatment of complex **8b** (0.225 g) with sodium cyanide (0.02 g) as above gave the crude product the NMR spectrum of which indicated

(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(29) Posner, G. H. *Org. React.* **1972**, *19*, 1.

an approximately 10:1 mixture of **9b**/**10b**. Purification by preparative TLC (25% EtOAc in hexane) afforded pure **9b**, which crystallized on storage at 0 °C: mp 93.4–94.4 °C; IR ν_{max} ($CHCl_3$) 2217 (w), 2005, 1953 cm^{-1}. Anal. Found: C, 62.4; H, 4.6. $C_{28}H_{24}FeNO_5P$ requires: C, 62.11; H, 4.44%.

Dicarbonyl(5-(phenylthio)-1,3-cycloheptadiene)(triphenyl phosphite)-iron (10c). To a stirred suspension of sodium hydride (0.013 g, from 50% dispersion in mineral oil, washed successively with dry pentane and THF) in THF (8 mL) under N_2, was added thiophenol (0.058 mL). After 10 min the flask was opened briefly with backflushing of nitrogen, while complex **8b** (0.30 g) was added. Reaction was continued for 10 min, after which time the mixture was added to 10 mL of aqueous $NaHCO_3$. Extraction with ether in the usual way followed by purification by preparative TLC (silica gel, pretreated with Et_3N; 50% EtOAc in hexane) gave the complex **10c** as a yellow-orange oil (0.264 g, 93%): IR ν_{max} (CCl_4) 1994, 1940 cm^{-1}; MS, *m/z* (%) (FD) 624 (M^+, 84), 515 (M^+ – SPh, 100), 218 (34).

Dicarbonyl[5-((4-nitrophenyl)thio)-1,3-cycloheptadiene](triphenyl phosphite)iron (10d). Treatment of complex **8b** (0.30 g) with sodium 4-nitrothiophenoxide as above gave the complex **10d**, a yellow-orange oil (0.27 g, 91%): IR ν_{max} (CCl_4) 1998, 1945 cm^{-1}; MS, *m/z* (%) (FD) 669 (M^+, 3), 515 ($M^+ - SC_6H_4 - p\text{-}NO_2$, 100), 247 (3).

Reactions of Unsubstituted Cycloheptadienyliron Complexes with Alkyllithium Reagents. Typical procedure: The iron complex (500 mg) was stirred in dry dichloromethane (10 mL) under N_2 at −78 °C while the alkyllithium reagent (1.1–1.2 equiv, commercially available solution) was added dropwise. After 15 min the excess lithium reagent was quenched by dropwise addition of methanol and the mixture was allowed to warm to room temperature. The mixture was diluted with dichloromethane (10 mL), washed with water (3 × 10 mL), dried ($MgSO_4$), and evaporated to give the crude product, which was purified by preparative TLC.

Tricarbonyl(5-methyl-1,3-cycloheptadiene)iron (2a). Reaction of tricarbonyl(cycloheptadienyl)iron tetrafluoroborate[5] with methyllithium gave **2a** as a yellow oil after chromatography on neutral alumina (26% yield): IR ν_{max} ($CHCl_3$) 2039, 1964 cm^{-1}. Anal. Found: C, 53.5; H, 5.1. $C_{11}H_{12}FeO_3$ requires: C, 53.23; H, 4.84%.

Tricarbonyl(5-*n*-butyl-1,3-cycloheptadiene)iron (2b). Reaction of tricarbonyl(cycloheptadienyl)iron tetrafluoroborate[5] with *n*-butyllithium gave **2b** as a yellow oil (13% yield). IR ν_{max} ($CHCl_3$) 2031, 1974 cm^{-1}; MS, *m/z* (%) (FD) 290 (M^+, 100).

Dicarbonyl[3–5-η,1-σ-(2-methylcycloheptenyl)](triphenylphosphine)-iron (9e). Reaction of dienyl salt **7a** with MeLi gave the complex **9e**, purified by chromatography on neutral alumina (10% EtOAc in hexane) and obtained as a yellow crystalline solid (69% yield): mp 133.5–135 °C; IR ν_{max} ($CHCl_3$) 1972, 1911 cm^{-1}; MS, *m/z* (%) 426 (M^+ – 2CO), 262 (100). Anal. Found: C, 69.6; H, 5.7. $C_{28}H_{27}FeO_2P$ requires: C, 69.72; H, 5.64%.

Dicarbonyl[3–5-η,1-σ-(2-methylcycloheptenyl)](triphenyl phosphite)-iron (9f). Reaction of **7b** with MeLi gave **9f**, purified by chromatography on neutral alumina (25% EtOAc in hexane) as a pale yellow solid: mp 85–87 °C (94% yield); IR ν_{max} ($CHCl_3$) 1986, 1925 cm^{-1}; MS, *m/z* (%) 530 (M^+, 1), 502 (19), 474 (44), 366 (100).

Dicarbonyl[3–5-η,1-σ-(2-*n*-butylcycloheptenyl)](triphenylphosphine)-iron (9g). Reaction of **7a** with *n*-BuLi gave **9g**, purified by preparative TLC (silica gel, 25% EtOAc in hexane) as a yellow solid: mp 112–113.5 °C (65% yield); IR ν_{max} ($CHCl_3$) 1973, 1912 cm^{-1}; MS, *m/z* (%) 524 (M^+, 1), 496 (5), 468 (15), 262 (100).

Dicarbonyl[3–5-η,1-σ-(2-*n*-butylcycloheptenyl)](triphenyl phosphite)-iron (9h). Reaction of **7b** with *n*-BuLi gave **9h**, obtained as a yellow oil after preparative TLC (silica gel, 25% EtOAc in hexane) (92% yield): IR ν_{max} ($CHCl_3$) 1995, 1938 cm^{-1}; MS, *m/z* (%) 544 (M^+ – CO, 33), 516 (52), 366 (100).

Dicarbonyl[3–5-η,1-σ-(2-phenylcycloheptenyl)](triphenylphosphine)iron (9i). Reaction of **7a** with phenyllithium gave **9i**, obtained as a yellow crystalline solid after purification by preparative TLC (silica gel, 25% EtOAc in hexane): mp 162.5–163.5 °C (from Et_2O/hexane; 91% yield); IR ν_{max} ($CHCl_3$) 1979, 1919 cm^{-1}; MS, *m/z* (%) 544 (M^+, 1), 516 (8), 488 (19), 262 (100).

Dicarbonyl[3–5-η,1-σ-(2-phenylcycloheptenyl)](triphenyl phosphite)-iron (9j). Reaction of **7b** with phenyllithium gave **9j** purified as above, as a pale yellow crystalline solid, mp 117–118 °C (from Et_2O/hexane; 89% yield): IR ν_{max} ($CHCl_3$) 1995, 1939 cm^{-1}; MS, *m/z* (%) 564 (M^+ – CO, 1), 536 (2), 217 (100).

Reactions of Unsubstituted Cycloheptadienyl Complexes with Grignard Reagents. General procedure: the reactions were conducted as for alkyllithium reagents but using THF as solvent, a reaction temperature of 0 °C, and reaction times of 5–10 min.

Dicarbonyl[3–5-η,1-σ-{2-(3-butenyl)cycloheptenyl}](triphenylphosphine)iron (9k). Reaction of 7a with crotylmagnesium chloride gave **9k** as a yellow crystalline solid after purification by preparative TLC as above (72% yield): mp 115.5–117 °C; IR ν_{max} ($CHCl_3$) 1974, 1913, 1636 cm^{-1}; MS, *m/z* (%) 494 (M^+ – CO, 1), 466 (5), 262 (100).

Dicarbonyl[3–5-η,1-σ-{2-(3-butenyl)cycloheptenyl}](triphenyl phosphite)iron (9l). Reaction of **7b** with crotylmagnesium chloride gave **9l** as a yellow oil after preparative TLC (69% yield): IR ν_{max} ($CHCl_3$) 1994, 1939, 1638 cm^{-1}; MS, *m/z* 542 (M^+ – CO, 1), 514 (3), 217 (100).

Dicarbonyl[3–5-η,1-σ-{2-(3-propenyl)cycloheptenyl}](triphenylphosphine)iron (9o). Reaction of **7a** with allylmagnesium chloride gave **9o** as a yellow oil after preparative TLC (67% yield): IR ν_{max} ($CHCl_3$) 1974, 1915, 1638 cm^{-1}; MS, *m/z* (%) 480 (M^+ – CO, 2), 452 (M^+ – 2CO, 22), 262 (100).

Dicarbonyl[3–5-η,1-σ-{2-(3-propenyl)cycloheptenyl}](triphenyl phosphite)iron (9p). Reaction of **7b** with allylmagnesium chloride gave **9p** as a pale yellow oil after preparative TLC (61%) yield): IR ν_{max} ($CHCl_3$) 1995, 1939, 1638 cm^{-1}; the mass spectrum of this compound was obtained using field desorption (FD), electron impact (EI), and fast atom bombardment (FAB) techniques, *m/z* (%) (FD) 556 (M^+, 100), (EI) 528 (M^+ – CO, 22), 500 (62), 217 (100), (FAB) 500 (M^+ – 2CO, 11), 366 (100).

Reactions of Unsubstituted Cycloheptadienyl Complexes with Organocuprate Reagents. General Procedure: The cuprate reagents were prepared in ether (Me_2CuLi) or THF (others) solution from the appropriate organolithium or Grignard reagent and cuprous iodide using standard procedures.[29] To the stirred cuprate reagent (twofold molar excess) at 0 °C (Me_2CuLi, Ph_2CuLi, allylcuprates) or −40 °C (*n*-Bu_2CuLi) was added the dienyl salt by brief opening of the reaction flask with backflushing of nitrogen. After completion of reaction (10–15 min) the mixture was added to excess saturated aqueous NH_4Cl and vigorously stirred in air for 30 min. Ether extraction and purification by preparative TLC as for the organolithium reactions above afforded the pure products.

Tricarbonyl(5-methyl-1,3-cycloheptadiene)iron (2a) was obtained from reaction of tricarbonylcycloheptadienyliron tetrafluoroborate with Me_2CuLi and was identical with the compound obtained from methyllithium reaction (yield 17%). **Tricarbonyl(5-*n*-butyl-1,3-cycloheptadiene)iron (2b)** was obtained from reaction of **1** with Bu_2CuLi and was identical with the product obtained from the butyllithium reaction (yield 23%).

Dicarbonyl(5-methyl-1,3-cycloheptadiene)(triphenylphosphine)iron (10e). Reaction of complex **7a** with Me_2CuLi gave, after purification by chromatography on neutral alumina (30% EtOAc in hexane), the complex **10e** as a yellow crystalline solid: mp 105–106 °C (from Et_2O/hexane) (>99% yield); IR ν_{max} ($CHCl_3$) 1968, 1907 cm^{-1}; MS, *m/z* (%) 454 (M^+ – CO, 20), 426 (59), 262 (100).

Dicarbonyl(5-methyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (10f). Reaction of **7b** with Me_2CuLi gave crystalline diene complex **10f**: mp 87.5–88.5 °C (from Et_2O/hexane) (97% yield); IR ν_{max} ($CHCl_3$) 1990, 1938 cm^{-1}; MS, *m/z* (%) 530 (M^+, 1), 502 (64), 474 (53), 366 (100).

Dicarbonyl(5-*n*-butyl-1,3-cycloheptadiene)(triphenylphosphine)iron (10g). Reaction of **7a** with Bu_2CuLi gave **10g** as a yellow oil contaminated with C-2 addition product (see Table I) (yield 89%). A pure sample of **10g** was obtained by crystallization from ether/hexane: mp 112.5–114 °C; IR ν_{max} ($CHCl_3$) 1970, 1909 cm^{-1}; MS, *m/e* (%) 496 (M^+ – CO, 7), 468 (40), 262 (100).

Dicarbonyl(5-*n*-butyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (10h). Reaction of **7b** with Bu_2CuLi gave **10h** contaminated with **9h** as a yellow oil (79% yield). A pure sample of **10h** was obtained by crystallization from ether/hexane: mp 154.5–156.5 °C; IR ν_{max} ($CHCl_3$) 1994, 1938 cm^{-1}; MS, *m/z* (%) 544 (M^+ – CO, 62) 516 (51), 366 (100).

Dicarbonyl(5-phenyl-1,3-cycloheptadiene)(triphenylphosphine)iron (10i). Reaction of **7a** with Ph_2CuLi gave **10i** as pale yellow crystals: mp 138.5–140 °C (from Et_2O/hexane), 76% yield; IR ν_{max} ($CHCl_3$) 1972, 1912 cm^{-1}; MS, *m/z* (%) 544 (M^+, 1), 516 (13), 488 (26), 262 (100).

Dicarbonyl(5-phenyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (10j). Reaction of **7b** with Ph_2CuLi gave **10j** as a yellow crystalline solid: mp 117–118 °C, 89% yield; IR ν_{max} ($CHCl_3$) 1995, 1939 cm^{-1}; MS, *m/z* (%) 564 (M^+ – CO, 2), 536 (4), 217 (100).

Dicarbonyl[5-(but-2-enyl)-1,3-cycloheptadiene](triphenylphosphine)iron (10m). Reaction of **7a** with crotylmagnesium chloride/cuprous iodide gave the product as an oily mixture of **9m** and **10m** in 74% yield (Table I) from which pure **10m** was obtained by crystallization from ether/hexane: mp 127.5–129.5 °C; IR ν_{max} ($CHCl_3$) 1968, 1908, 1636 cm^{-1}; MS, *m/z* (%) 522 (M^+, 1), 494 (M^+ – CO, 11), 466 (22), 262 (100).

Dicarbonyl[5-(but-2-enyl)-1,3-cycloheptadiene](triphenyl phosphite)-iron (10n). Reaction of **7b** with crotylmagnesium chloride/cuprous iodide gave a mixture of **9n** and **10n**, preponderant in the latter (Table I), which could not be separated (oil): yield 79%; IR ν_{max} ($CHCl_3$) 1991, 1934, 1638 cm^{-1}; MS, *m/z* (%) (FD) 570 (M^+, 100).

Dicarbonyl(5-allyl-1,3-cycloheptadiene)(triphenylphosphine)iron (10o). Reaction of **7a** with allylmagnesium chloride/cuprous iodide gave a

mixture of **10o** and **9o** (Table I), which was not separated (46% yield), IR ν_{max} ($CHCl_3$) 1968, 1910, 1638 cm^{-1}.

Dicarbonyl(5-allyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (10p). Reaction of **7b** with allylmagnesium chloride/cuprous iodide gave a mixture of **10p** and **9p** (Table I), which was not separated (54% yield), IR ν_{max} ($CHCl_3$) 1992, 1936, 1639 cm^{-1}.

Reactions of Unsubstituted Cycloheptadienyl Complexes with Stabilized Enolates. The general procedure for reaction of $NaCH(X)CO_2Me$ with these complexes was identical with that previously described[30] for the reaction of the related tricarbonylcyclohexadienyliron complexes with $NaCH(CO_2Me)_2$. *General Note*: the numbering of the carbons given in structure **10** is used for convenience of tabulation of NMR data (Table II) and does *not* conform to the *correct* names for the compounds given in this section.

Tricarbonyl[dimethyl (2-5-η-cyclohepta-2,4-dienyl)malonate]iron (2c). Reaction of **1** with $NaCH(CO_2Me)_2$ gave complex **2c** as a yellow oil, purified by preparative TLC (56% yield): IR ν_{max} ($CHCl_3$) 2017, 1966, 1741, 1721 cm^{-1}; MS, *m/z* (%) 336 (M^+ – CO, 1), 308 (17), 91 (100).

Tricarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)acetoacetate]iron (2d). Reaction of **1** with $NaCH(COMe)CO_2Me$ gave **2d** as an inseparable equimolar mixture of diastereoisomers, purified by preparative TLC (yellow oil, 67% yield): IR ν_{max} ($CHCl_3$) 2033, 1976, 1737, 1711 cm^{-1}; MS, *m/z* (%) (FD) 348 (M^+, 100).

Dicarbonyl[dimethyl (2-5-η-cyclohepta-2,4-dienyl)malonate](triphenylphosphine)iron (10q). Reaction of **7a** with $NaCH(CO_2Me)_2$ gave crystalline complex **10q** in 99% yield: mp 116.5–118.5 °C; IR ν_{max} ($CHCl_3$) 1977, 1918, 1755, 1734 cm^{-1}. Anal. Found: C, 64.4; H, 5.1. $C_{32}H_{31}FeO_6P$ requires: C, 64.21; H, 5.18%.

Dicarbonyl[dimethyl (2-5-η-cyclohepta-2,4-dienyl)malonate](triphenyl phosphite)iron (10r). Reaction of **7b** with $NaCH(CO_2Me)_2$ gave the diene complex **10r** as a yellow crystalline solid: mp 109.5–111.5 °C (99% yield); IR ν_{max} ($CHCl_3$) 1998, 1942, 1752, 1735 cm^{-1}; MS, *m/z* (%) 590 (M^+ – 2CO, 2), 217 (100). Anal. Found: C, 59.1; H, 4.9. $C_{32}H_{31}FeO_9P$ requires: C, 59.46; H, 4.83%.

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)acetoacetate](triphenylphosphine)iron (10s). Reaction of **7a** with $NaCH(COMe)CO_2Me$ gave an equimolar mixture of diastereoisomers **10s** as a yellow foam (96% yield): IR ν_{max} ($CHCl_3$) 1974, 1915, 1746, 1712 cm^{-1}; MS, *m/z* (%) 581 (M^+ – H, 2), 262 (100).

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)acetoacetate](triphenyl phosphite)iron (10t). Reaction of **7b** with $NaCH(COMe)CO_2Me$ gave the equimolar mixture of diastereoisomers **10t** as a yellow foam (98% yield): IR ν_{max} ($CHCl_3$) 1995, 1915, 1742, 1712 cm^{-1}; MS, *m/z* (%) 574 (M^+ – 2CO, 1), 217 (100).

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)(phenylsulfonyl)acetate](triphenylphosphine)iron (10u). Reaction of **7a** with $NaCH(SO_2Ph)CO_2Me$ afforded the equimolar mixture of diastereoisomers **10u** as a yellow foam (>99% yield): IR ν_{max} (CCl_4) 1980, 1925, 1747, 1438, 1330, 1140 cm^{-1}; MS, *m/z* (%) (FD) 680 (M^+, 100).

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)(phenylsulfonyl)acetate](triphenyl phosphite)iron (10v). Reaction of **7a** with $NaCH(SO_2Ph)CO_2Me$ afforded the equimolar mixture of diastereoisomers **10v** as a yellow foam (83%): IR ν_{max} (CCl_4) 1998, 1945, 1746, 1438, 1330, 1145 cm^{-1}; MS, *m/z* (%) (FD) 728 (M^+, 100).

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)cyanoacetate](triphenylphosphine)iron (10w). Reaction of **7a** with $NaCH(CN)CO_2Me$ gave the 1:1 mixture of diastereoisomers **10w** as a yellow foam (85% yield): IR ν_{max} ($CHCl_3$) 2245, 1977, 1917, 1735 cm^{-1}; MS, *m/z* (%) 509 (M^+ – 2CO, 1), 262 (100).

Dicarbonyl[methyl (2-5-η-cyclohepta-2,4-dienyl)cyanoacetate](triphenyl phosphite)iron (10x). Reaction of **7b** with $NaCH(CN)CO_2Me$ gave the 1:1 mixture of diastereoisomers **10x** as a yellow foam (81% yield). IR ν_{max} ($CHCl_3$) 2245, 2000, 1942, 1755 cm^{-1}; MS, *m/z* (%) 557 (M^+ – 2CO, 1), 217 (100).

Synthesis of Alkyl-Substituted Cycloheptadienylium–$Fe(CO)_2L$ Salts. Tricarbonyl(1-5-η-6-methylcycloheptadienylium)iron Hexafluorophosphate (5). Treatment of complex **2a** (0.631 g, 2.54 mmol) with triphenylmethyl hexafluorophosphate (1.09 g, 2.8 mmol) in dichloromethane as described above gave the complex **5** (0.80 g, 80%): IR ν_{max} (CH_3CN) 2103, 2056 cm^{-1}; ^1H NMR δ (CD_3CN, 90 MHz), 7.13 (1 H, t, *J* = 6 Hz, 3-H), 6.2 (1 H, dd, *J* = 7.5, 6 Hz, 2-H or 4-H), 5.8 (1 H, dd, *J* = 9, 6 Hz, 4-H or 2-H), 5.02–4.68 (2 H, m, 1-H, 5-H), 3.4 (1 H, m, 6-H), 2.43 (1 H, m, endo-7-H), 0.93 (3 H, d, *J* = 7 Hz, Me), 0.95 (1 H, m, obscured, exo-7-H). Anal. Found: C, 33.5; H, 3.1. $C_{11}H_{11}FeO_3PF_6$ requires: C 33.67, H, 2.81%.

Dicarbonyl(1-5-η-6-methylcycloheptadienylium)(triphenylphosphine)iron Hexafluorophosphate (11a). Treatment of complex **10e** (4.8 g) with triphenylmethyl hexafluorophosphate (4.3 g) in dichloromethane as above gave the ether-insoluble complex **11a** (6.2 g, 99%): IR ν_{max} (CH_3CN) 2042, 2002 cm^{-1}; ^1H NMR δ (CD_3CN) 7.7–7.4 (15 H, m, Ar H), 6.83 (1 H, t, *J* = 6.7 Hz, 3-H), 6.04 (1 H, dd, *J* = 8, 10.5 Hz), 5.55 (2 H, m), 5.08 (1 H, dd, *J* = 10.5, 3 Hz), 3.1 (1 H, m), 2.2 (1 H, m), 0.84 (3 H, d, *J* = 6.7 Hz), 0.69 (1 H, t, *J* = 19.3 Hz). Anal. Found: C, 53.8; H, 4.3. $C_{28}H_{27}FeO_2P_2F_6$ requires: C, 53.70; H, 4.18%.

Dicarbonyl(1-5-η-6-methylcycloheptadienylium)(triphenyl phosphite)iron Hexafluorophosphate (11b). Treatment of complex **10f** (106 g, 0.2 mol) with triphenylmethyl hexafluorophosphate (86 g, 0.22 mol) in dichloromethane as above gave the ether-insoluble complex **11b** (134 g, 99%). IR ν_{max} (CH_3CN) 2063, 2025 cm^{-1}; ^1H NMR δ (CD_3CN) 7.06 (15 H, m, $P(OPh)_3$), 6.09 (1 H, t, *J* = 6.5 Hz, 3-H), 5.36 (2 H, m, 2-H, 4-H), 4.4 (1 H, m, 1-H or 5-H), 3.74 (1 H, m, 5-H or 1-H), 3.31 (1 H, m), 2.2 (1 H, m), 0.84 (3 H, d, *J* = 6 Hz, and 1 H, m). Anal. Found: C, 49.7; H, 4.2. $C_{28}H_{26}FeO_5P_2F_6$ requires: C, 49.85; H, 3.86%.

Dicarbonyl(1-5-η-6-*n*-butylcycloheptadienylium)(triphenyl phosphite)iron Hexafluorophosphate (11c). The complex **10h** (1.71 g, 2.99 mmol) was treated with triphenylmethyl hexafluorophosphate (1.62 g, 2.99 mmol) in dichloromethane at reflux temperature under N_2 for 19 h. Precipitation with wet ether as before gave the complex **11c** as a pale yellow solid (0.97 g, 45%). IR ν_{max} (CH_3CN) 2052, 2013 cm^{-1}; ^1H NMR δ (CD_3CN) 7.53–7.23 (15 H, m, Ar H), 5.95 (1 H, t, *J* = 6 Hz, 3-H), 5.85 and 5.45 (1 H, m, each 2-H, 4-H), 4.61 and 4.40 (1 H, m, each, 1-H, 5-H), 3.1 (1 H, m, 6-H), 2.2 (1 H, m, endo-7-H), 1.2–1.0 (6 H, m), 0.83 (3 H, t, *J* = 7 Hz, and 1 H, m). Anal. Found: C, 51.8; H, 4.8. $C_{31}H_{32}FeO_5F_6$ requires: C, 51.96; H, 4.47%.

Reactions of Substituted Cycloheptadienyl–$Fe(CO)_2L$ Complexes with Nucleophiles. The general procedures were followed as described above.

Tricarbonyl(1-4-η-5,7-dimethyl-1,3-cycloheptadiene)iron (6). Reaction of **5** with Me_2CuLi (0 °C, 10 min) gave, after purification by preparative TLC, the complex **6** as a golden oil (18% yield). IR ν_{max} ($CHCl_3$) 2040, 1975 cm^{-1}. Anal. Found: C, 54.7; H, 5.3. $C_{12}H_{14}FeO_3$ requires: C, 54.96; H, 5.38%.

Dicarbonyl(1-4-η-5,7-dimethyl-1,3-cycloheptadiene)(triphenylphosphine)iron (12a). Reaction of complex **11a** with Me_2CuLi (0 °C, 20 min) gave **12a** as a yellow crystalline solid, decomposing at 140 °C (95% yield) obtained pure by crystallization from ether/hexane. Reaction of **11a** with MeLi also gave **12a** (86% yield): IR ν_{max} ($CHCl_3$) 1968, 1908 cm^{-1}; MS, *m/z* (%) 496 (M^+, 1), 468 (9), 440 (44), 262 (100).

Dicarbonyl(1-4-η-5,7-dimethyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (12b). Reaction of **11b** with Me_2CuLi (0 °C, 15 min) gave the diene complex **12b**, as a pale yellow crystalline solid, mp 80.5–82 °C (97% yield). Reaction with MeLi (CH_2Cl_2, –78 °C, 30 min) also gave **12b** (74% yield): IR ν_{max} ($CHCl_3$) 1988, 1931 cm^{-1}; MS, *m/z* (%) 516 (M^+ – CO, 7), 488 (14), 366 (100). Anal. Found: C, 63.9; H, 5.4. $C_{29}H_{29}FeO_5P$ requires: C, 63.99; H, 5.37%.

Dicarbonyl(1-4-η-5-*n*-butyl-7-methyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (12c). Reaction of **11b** with *n*-BuLi (84% yield) or with n-Bu_2CuLi (63% yield) gave **12c**. The same product was also obtained by reaction of complex **11c** with MeLi (68% yield as a mixture with **13c**) or Me_2CuLi (50% yield). The product in all cases was obtained as a yellow syrup from preparative TLC: IR ν_{max} ($CHCl_3$) 1992, 1937 cm^{-1}; MS, *m/z* (%) 558 (M^+ – CO, 10), 530 (21), 366 (100).

Dicarbonyl(1-4-η-7-methyl-5-phenyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (12d). Reaction of **11b** with PhLi (89% yield) or with Ph_2CuLi (75% yield) gave the diene complex **12d** as a golden syrup after preparative TLC: IR ν_{max} ($CHCl_3$) 1995, 1939 cm^{-1}; MS, *m/z* (%) 606 (M^+, 1), 578 (3), 550 (1), 217 (100).

Dicarbonyl[dimethyl (2-5-η-6-methyl-2,4-cycloheptadienyl)malonate](triphenylphosphine)iron (12e). (Note: numbering given in text structure is for convenience of tabulation of NMR data and is not the same as that used for naming the complex.) Reaction of complex **11a** with $NaCH(CO_2Me)_2$ gave **12e** as a yellow crystalline solid: mp 132.5–133.5 °C (Et_2O/hexane), 92% yield; IR ν_{max} ($CHCl_3$) 1976, 1917, 1756, 1744 cm^{-1}; MS, *m/z* (%) 612 (M^+, 1), 556 (4), 262 (100).

Dicarbonyl[dimethyl (2-5-η-6-methyl-2,4-cycloheptadienyl)malonate](triphenyl phosphite)iron (12f). (Note: See comment on numbering for **12e**.) Reaction of **11b** with $NaCH(CO_2Me)_2$ gave 12f as a yellow oil in 97% yield: IR ν_{max} ($CHCl_3$) 1995, 1939, 1753, 1730 cm^{-1}; MS, *m/z* (%) (FD) 660 (M^+, 100). Anal. Found: C, 60.2; H, 5.3. $C_{33}H_{33}FeO_9P$ requires: C, 60.02; H, 5.04%.

Dicarbonyl[methyl (2-5-η-6-methyl-2,4-cycloheptadienyl)acetoacetate](triphenyl phosphite)iron (12g). (Note: See comment on numbering for **12e**.) Reaction of **11b** with $NaCH(COMe)CO_2Me$ gave an equimolar mixture of diastereoisomers **12g** as a yellow foam (88% yield): IR ν_{max} ($CHCl_3$) 1994, 1938, 1740, 1707 cm^{-1}; MS, *m/z* (%) 644 (M^+, 1), 588 (2), 217 (100). Anal. Found: C, 61.3; H, 5.1. $C_{33}H_{33}FeO_8P$ requires: C, 61.51; H, 5.16%.

Dicarbonyl[methyl (2-5-η-6-methyl-2,4-cycloheptadienyl)(phenyl-

(30) See, for example: Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2069.

sulfonyl)acetate](triphenylphosphine)iron (12h). (Note: See comment on numbering for **12e**.) Reaction of **11a** with $NaCH(SO_2Ph)CO_2Me$ gave the equimolar mixture of diastereoisomers **12h** as a yellow solid: mp 80.3–84.7 °C, 83% yield; IR ν_{max} (CCl_4) 1982, 1925, 1746, 1439, 1330, 1141 cm^{-1}. Anal. Found: C, 63.7; H, 5.2. $C_{37}H_{35}FeO_6PS$ requires: C, 63.98; H, 5.04%.

Dicarbonyl[methyl (2–5-η-6-methyl-2,4-cycloheptadienyl)(phenylsulfonyl)acetate](triphenyl phosphite)iron (12i). (Note: See comment on numbering for **12e**.) Reaction of **11b** with $NaCH(SO_2Ph)CO_2Me$ gave the equimolar mixture of diastereoisomers **12i** as a yellow foam in 91% yield after purification by flash chromatography: IR ν_{max} (CCl_4) 2000, 1944, 1746, 1437, 1330, 1144 cm^{-1}; MS, *m/z* (%) (FD) 742 (M^+, 100).

Dicarbonyl[dimethyl (2–5-η-6-n-butyl-2,4-cycloheptadienyl)malonate](triphenyl phosphite)iron (12j). (Note: See comment on numbering for **12e**.) Reaction of **11c** with $NaCH(CO_2Me)_2$ gave the complex as a pale yellow oil in 91% yield after preparative TLC: IR ν_{max} ($CHCl_3$) 1990, 1940, 1731 cm^{-1}; MS, *m/z* (%) (FD) 702 (M^+, 100).

Dicarbonyl(1–4-η-5-allyl-7-methyl-1,3-cycloheptadiene)(triphenyl phosphite)iron (12k). Reaction of **11b** with allylmagnesium chloride/cuprous iodide gave the complex **12k** as a golden oil in 60% yield after preparative TLC: IR ν_{max} ($CHCl_3$) 1981, 1935, 1639 cm^{-1}; MS, *m/z* (%) 514 ($M^+ - 2CO$, 7), 217 (100). Reaction of **11b** with allylmagnesium chloride in the absence of cuprous iodide gave a 10:3 mixture of **12k** and **13k** in 71% yield.

Preparation of Dimethyl Cyclohepta-2,4-dienylmalonate (16a) and Dimethyl 6-Methylcyclohepta-2,4-dienylmalonate (16b). To a solution of the iron complex **10r** (1.29 g, 2 mmol, in case of **16a**) or **12f** (1.32 g, 2 mmol, in case of **16b**) in *N,N*-dimethylacetamide (50 mL) was added anhydrous trimethylamine *N*-oxide (5 g), and the mixture was vigorously stirred at 55 °C. The reaction was monitored by IR spectroscopy (peaks at 2000 and 1940 cm^{-1} completely disappeared after 36 h). The reaction mixture was poured into saturated brine (200 mL), cooled, and extracted with ether (3 × 100 mL). The ether solution was washed with water (3 × 100 mL), dried ($MgSO_4$), and evaporated. The residue was flash chromatographed on silica gel (25% EtOAc in hexane) to give the corresponding dienyl diester **16a** or **16b**. The products obtained were sufficiently pure for the next steps. Analytical samples were obtained by preparative HPLC.

16a: colorless oil (0.40 g, 90%); IR ν_{max} ($CHCl_3$) 2980, 2920, 2860, 1750, 1730 (s), 1630, 1500, 1480, 1470, 1460, 1450, 1430, 1410, 1390, 1350, 1260, 1230, 1180, 1110 (b), 1000, 940 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.7 (4 H, br s, vinyl), 3.7 (6 H, s, 2 CO_2Me), 3.52 (1 H, d, J = 7.5 Hz, $CH(CO_2Me)_2$), 2.5–2.2 (3 H, m), 2–1.6 (2 H, m), 1.5–1 (1 H, m); MS (EI), *m/z* (%) 224 (M^+, 8.4), 193 ($M^+ - OMe$, 9.4), 164 ($M^+ - CO_2Me - H$, 31), 133 (38), 91 ($C_7H_7^+$, 82), 77 (48); found M^+ = 224.1064, $C_{12}H_{16}O_4$ requires M^+ = 224.1044.

16b: colorless oil (0.43 g, 90%); IR ν_{max} ($CHCl_3$) 2960, 2940, 2860, 1750, 1730 (s), 1630, 1610 (m), 1600 (m), 1500 (w), 1470, 1440, 1400, 1260 (s), 1100, 1020, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.70–5.63 (4 H, m, vinyl), 3.76 (6 H, s, 2 CO_2Me), 3.51 (1 H, d, J = 7.3 Hz, $CH(CO_2Me)_2$), 1.60–1.77 (4 H, m), 1.08 (3 H, d, J = 7.2 Hz, CH_3); MS (CI), *m/z* (%) 239 ($M^+ + 1$, 100) 238 (M^+, 23.6), 197 (7.5), 178 (8), 133 (28.7), 106 (39.2), 91 (17.8); found M^+ = 238.1225, $C_{13}H_{18}O_4$ requires M^+ = 238.1205.

Preparation of Methyl (Phenylsulfonyl)(6-methylcyclohepta-2,4-dienyl)acetate (16d). This was prepared in a similar way as described above from the iron complex **12i**. The crude compound was purified by flash chromatography on silica gel eluting with 25% EtOAc in hexane giving **16d** as a pale yellow oil (90%). This product was used in the next step without further purification. An analytical sample was obtained by preparative HPLC: IR ν_{max} ($CHCl_3$) 3200, 2950, 2920, 1730, 1630 (m), 1600, 1590, 1500, 1465, 1440, 1430, 1320, 1310, 1160, 1145, 1080, 1010 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.834 (2 H, m, PhH), 7.620–7.467 (3 H, m, PhH), 5.671–5.559 (4 H, m, vinyl), 3.998 (1 H, d, J = 6.19 Hz, $CHCO_2MeSO_2Ph$), 3.546 (3 H, s, CO_2Me), 1.813–1.532 (4 H, m), 1.027 (3 H, d, J = 7.16, CH_3); MS (CI), *m/z* (%) 321 ($M^+ + 1$, 30.2), 320 (M^+, 5.9), 178 ($M^+ - PhSO_2H$, 85.5), 146 (40.2), 119 (58.4), 105 (32.1), 91 (45.5); found M^+ = 320.1063, $C_{17}H_{20}O_4S$ requires M^+ = 320.1082.

Preparation of Methyl Cyclohepta-2,4-dienylacetate (16e) and Methyl 6-Methylcyclohepta-2,4-dienylacetate (16f) from 16a and 16b, respectively. Sodium cyanide (0.98 g, 20 mmol) was dissolved in wet dimethyl sulfoxide (50 mL, containing 0.5 mL H_2O) which was previously freed from oxygen. A solution of the diester **16a** (2.24 g, 10 mmol) or **16b** (2.38 g, 10 mmol) in Me_2SO (5 mL) was added and the mixture was stirred under argon at 70 °C for 36 h. It was cooled and poured into saturated brine (200 mL) and extracted with ether (3 × 100 mL). Ether solution was washed, dried ($MgSO_4$), and evaporated. The monoester so obtained was purified by chromatography using 25% EtOAc in hexane as eluant to give a colorless oil.

16e: 1.1 g, 70%; IR ν_{max} ($CHCl_3$) 3030, 3020, 2960, 2940, 1740, 1600, 1460, 1440, 1380, 1330, 1265, 1220 (br), 1170, 1110, 1080, 1030, 1020, 920, 870, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.5 (4 H, br s, vinyl), 3.7 (3 H, s, CO_2Me), 2.4–2.2 (3 H, m), 1.7–1.5 (2 H, m), 1.3–1 (2 H, m); MS, *m/z* (%) 166 (M^+, 100), 105 (29.4), 91 (63.2); found M^+ = 166.1009, $C_{10}H_{14}O_2$ requires M^+ = 166.0994.

16f: 1.1 g, 60%; IR ν_{max} ($CHCl_3$) 3030, 2980, 2940, 1740, 1610, 1510, 1480, 1450, 1350, 1265, 1190, 1170, 1160, 1120 (br), 1080, 1050, 1030, 1010 (w), 920 (br), 895 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.5 (4 H, br s, vinyl), 3.7 (3 H, s, CO_2Me), 2.4–2.2 (3 H, m), 1.7–1.5 (2 H, m), 1.3 (1 H, m), 1.05 (3 H, d, J = 7 Hz, CH_3); MS, *m/z* (%) 180 (M^+, 61.6), 165 ($M^+ - 15$, 27.6), 149 (7.5), 121 ($165 - CO_2$, 9.8), 105 (56.6), 91 (88.3); found M^+ = 180.1166, $C_{11}H_{16}O_2$ requires M^+ = 180.11502.

Preparation of 16f from 16d. A solution of the ester **16d** (3.2 g, 10 mmol) in anhydrous methanol (100 mL) was stirred with anhydrous disodium hydrogen phosphate (5.7 g, 40 mmol) for 15 min in an ice bath. Pulverized 6% sodium–mercury amalgam (15 g) was added slowly with constant stirring at 0 °C over 1 h. The temperature was allowed to reach 23 °C, and the mixture was stirred at this temperature for 1 h. The mixture was poured into cold water and extracted with ether. The ether layer was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by chromatography as colorless oil (1.4 g, 80%). It was identical in all respects with the compound obtained by the decarbomethoxylation of **16b**.

Preparation of Cyclohepta-2,4-dienylacetic Acid (16g) and 6-Methylcyclohepta-2,4-dienylacetic Acid (16h). The ester **16e** (0.83 g, 5 mmol) or **16f** (0.90 g, 5 mmol) was dissolved in methanol (75 mL), and an aqueous solution of KOH (5 g in 30 mL H_2O) was added to it. The mixture was stirred under argon at 30 °C for 4 h. The solution was slightly acidified with 10% ice-cold HCl and extracted with ether. For preliminary purification the residue from the ether extraction was dissolved in saturated $NaHCO_3$ solution and washed with ether. The bicarbonate solution was slowly acidified and extracted with ether. The ether solution was washed with water, dried ($MgSO_4$), and evaporated. Both acids were obtained as colorless oils.

16g: 0.68 g, 90%; IR ν_{max} ($CHCl_3$) 3400–2800, 1700, 1600, 1590, 1490, 1460, 1440, 1420, 1400, 1330, 1280, 1240, 1170, 1150, 1140, 1060, 1030, 1010, 900 (s), 850 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 10.3 (1 H, br s, CO_2H), 5.68–5.60 (4 H, m, vinyl), 2.6–2.2 (5 H, m), 1.8 (2 H, m); MS, *m/z* (%) 152 (M^+, 32.2), 107 ($M^+ - CO_2H$, 29.1), 91 (100); found M^+ = 152.0860, $C_9H_{12}O_2$ requires M^+ = 152.0837.

16h: 0.75 g, 90%; IR ν_{max} ($CHCl_3$) 3400–2800, 1700, 1600, 1580, 1485, 1460, 1440, 1430, 1425, 1400, 1355, 1270, 1230, 1220, 1160, 1060, 900 (s) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 10.3 (1 H, br s, CO_2H), 5.66–5.60 (4 H, m, vinyl), 2.48–2.40 (4 H, m), 1.78 (2 H, m), 1.1 (3 H, d, J = 7.0 Hz, CH_3); MS, *m/z* (%) 166 (M^+, 56.6), 121 ($M^+ - CO_2H$, 10.6), 106 (96), 91 (100); found M^+ = 168.1019, $C_{10}H_{14}O_2$ requires M^+ = 166.1000.

Preparation of Seleno Lactones 17a, 18a, and 19. A solution of the acid **16g** (0.152 g, 1 mmol) in dry CH_2Cl_2 (20 mL) was stirred with triethylamine (0.101 g, 1 mmol) at 30 °C for 15 min, cooled to −72 °C, and treated slowly with phenylselenenyl bromide (0.260 g, 1.1 mmol) under argon. The mixture was warmed to −20 °C and stirred for further 2 h. The product was a mixture of three lactones as evident from HPLC, in a ratio of 15:5:1. Total yield 75%. All the three lactones were separated by preparative HPLC. The major one **17a** was crystallized as colorless needles from ether: mp 95 °C; IR ν_{max} ($CHCl_3$) 2920, 2830, 1770, 1650, 1580, 1470, 1440, 1380, 1350, 1320, 1300, 1170, 1100, 990, 940, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.537 and 7.256 (2 H and 3 H, m, PhH), 5.658 (2 H, br s, 4 H and 5 H), 4.684 (dd, $J_{2,3}$ = 6.46, $J_{1,2}$ = 6.18 Hz, 2-H), 4.216 (dd, $J_{2,3}$ = 6.46, $J_{3,4}$ = 3.74 Hz, 3-H), 3.12 (1 H, m, 1-H), 2.78 and 2.26 (each dd, $J_{1,8}$ = 9.3 and 2.4, respectively, $J_{8\alpha,8\beta}$ = 17.6, 8α-, 8β-H), 2.274 (3 H, br s, 6α-, 6β-, and 7α-H), 1.625 (1 H, m, 7β-H); MS, *m/z* (%) (CI) 308 ($M^+ + 1$, 93%), 307 (M^+, 29%), 151 ($M^+ - PhSe$, 100), 105 (50.7), 91 (56.2); found M^+ = 307.0777, $C_{15}H_{16}O_2Se$ requires M^+ = 307.0750. NMR double-resonance experiments: Signal at δ 4.684 collapses to d, J = 6.46 and 6.18 Hz on irradiating 1-H at δ 3.12 and 3-H at δ 4.216, respectively. Signal at δ 4.216 collapses to d, J = 6.46 and 3.74 Hz on irradiating vinyl H at δ 5.658 and 2-H at δ 4.684, respectively. Signals at δ 2.78 and 2.26 collapse to d, J = 17.6 Hz on irradiating 1-H at δ 3.12.

The next major compound was **18a**, colorless oil: IR ν_{max} ($CHCl_3$) 3000, 2945, 2915, 2860, 1770, 1470, 1440 (br), 1430, 1380, 1320–1300, 1170, 1060, 1030, 1010, 940, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.55 and 7.28 (2 H, 3 H, PhH), 5.859 (1 H, dd, $J_{3,4}$ = 12.10, $J_{4,5}$ = 4.60 Hz, 4-H), 5.592 (1 H, dd, $J_{3,4}$ = 12.10, $J_{2,3}$ = 3.1 Hz, 3-H), 5.265 (1 H, m, 2-H), 4.131 (1 H, m, 5-H), 2.783 (1 H, m, obscured, 1-H), 2.745 and 2.283 (each, 1 H, dd, $J_{8\alpha,\beta}$ = 16.5, $J_{1,8}$ = 8.7 and 5.2 Hz, 8-CH_2), 1.973 (2 H, m, 6-CH_2), 1.758 and 1.644 (each 1 H, m, 7-CH_2); MS, *m/z* (CI) 308 ($M^+ + 1$, 100), 307 (M^+, 20.1), 151 (308 − PhSeH, 90), 157 (PhSeH, 11), 105 (5.5), 91 (60); found M^+ = 307.0737, C_{15}-

$H_{16}O_2Se$ requires M^+ = 307.0750. NMR double-resonance experiments: Signal at 5.859 collapses to d, J = 12.10 and J = 4.6 Hz, irradiating 5-H at δ 4.13 and 3H at δ 5.59, respectively. Signal at δ 5.592 collapses to d, J = 12.10 and J = 3.1 Hz on irradiating 2-H at δ 5.26 and 4-H at δ 5.86, respectively.

The minor compound was **19**; IR ν_{max} ($CHCl_3$) 3000, 2920, 2910, 1775, 1660, 1610, 1530, 1510, 1480, 1430, 1400, 1230 (s), 1170, 1100 (br), 1050, 920 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.588 and 7.312 (2 H and 3 H, m, respectively, PhH), 5.687 (1 H, m, 5-H), 5.268 (1 H, d, J = 11.2 Hz, 4-H), 4.639 (1 H, dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 6.3 Hz, 2-H), 3.559 and 3.458 (each 1 H, m, 3-H and 1-H), 2.842 and 2.446 (each 1 H, dd, J_{gem} = 17.2, $J_{1,8}$ = 9 and 3.5 Hz, 8-CH_2), 2.272 (3 H, m, 6-CH_2 and one 7-H), 1.887 (1 H, m, one 7-H); MS, m/z (%) (CI) 308 (M^+ + 1, 100), 307 (M^+, 29.1), 151 (M^+ - PhSe, 79.3), 105 (71.4), 91 (70.5); found M^+ = 307.0737, $C_{15}H_{16}O_2Se$ requires M^+ = 307.075.

Seleno Lactones 17b and 18b. An approximately equimolar mixture of these two lactones was obtained when the acid **16h** (0.166 g, 1 mmol) was treated with phenylselenenyl bromide under the same condition as described above. It was found that the ratio of the products depends largely on the quality of PhSeBr or PhSeCl used and the reaction conditions. The lactone **18b** was obtained in high yield by the following procedure. A solution of the acid **16h** (0.166 g, 1 mmol) in dry CH_2Cl_2 (20 mL) was stirred with triethylamine (0.101 g, 1 mmol) at 30 °C for 15 min. It was treated with *freshly distilled* PhSeCl (0.211 g, 1.1 mmol) under argon. The mixture was stirred for further 2 h at 30 °C. The solution was concentrated under vacuum and the product was separated by flash chromatography using 25% ethyl acetate in hexane. The lactone **18b** was isolated as colorless oil (256 mg, 80% yield). Analytical samples of the lactones were obtained by preparative HPLC. The faster running compound **17b** (R_f 0.6, on TLC, silica gel, ethyl acetate:hexane = 1:1) was crystallized from ether as needles (100 mg, 31%), mp 96 °C, and the slower running compound **18b** (R_f 0.5, 50% ethylacetate in hexane, silica gel) was a colorless oil (128 mg, 40%). (Yields are those obtained from the first procedure, using PhSeBr at low temperatures.)

17b: IR ν_{max} ($CHCl_3$) 3080, 3040, 3000, 1775, 1540, 1530, 1520, 1485, 1450, 1430, 1400 (m), 1230, 1180 (sh), 1100, 1050, 920, 680, 660 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.616 (2 H, m, PhH), 7.320 (3 H, m, PhH), 5.668 (1 H, ddd, $J_{4,5}$ = 11.61, $J_{3,4}$ = 4.3, $J_{4,6}$ = 1.6 Hz, 4-H), 5.474 (1 H, ddd, $J_{4,5}$ = 11.61, $J_{5,6}$ = 3.31, $J_{5,3}$ = 1.36 Hz, 5-H), 4.59 (1 H, dd, $J_{2,3}$ = 9.27, $J_{2,1}$ = 6.41 Hz, 2-H), 4.247 (1 H, ddd, $J_{3,2}$ = 9.27, $J_{3,4}$ = 4.30, $J_{3,5}$ = 1.36 Hz, 3-H), 2.92–2.77 (1 H, m, 1-H), 2.769 (1 H, d, J_{gem} = 16.80, one 8-H), 2.54–2.36 (1 H, m, 6-H), 2.282 (1 H, dd, $J_{8\alpha,\beta}$ = 16.80, $J_{8\beta,1}$ = 5.05 Hz, one 8-H), 1.664 (2 H, dd, J_1 = 4.39 and J_6 = 6.35 Hz, 7-CH_2), 1.04 (3 H, d, J = 7.0 Hz, CH_3); MS, m/z (%) 322 (M^+ + 1, 20.9), 321 (M^+, 2), 165 (322 - PhSeH, 52.8), 164 (321 - PhSeH, 45.1), 158 (PhSeH, 27.2), 157 (34.5), 156 (15), 119 (40), 105 (68.8), 91 (64.8), 78 (100), 77 (92); found M^+ = 321.0922, $C_{16}H_{18}O_2Se$ requires M^+ = 321.0902. NMR double-resonance experiments: Signal at δ 5.668 collapses to dd, J = 11.61, 1.6 Hz, irradiating 3-H at δ 4.247. Signal at δ 5.474 collapses to dd, J = 11.61, 1.36 Hz, irradiating 6-H at δ 2.45. Signal at δ 4.247 collapses to a dd, J = 9.27, 1.36 and 4.30, 1.36 Hz on irradiating 4-H at δ 5.668 and 2-H at 4.59, respectively. Signal at δ 4.59 collapses to d, J = 9.27 and J = 6.41 Hz, irradiating 1-H at δ 2.85 and 3-H at δ 4.247, respectively. Signal at δ 2.769 collapses to a singlet on irradiating at δ 2.282. CH_3 doublet at δ 1.04 collapses on irradiating 6-H at δ 2.45.

18b: IR ν_{max} ($CHCl_3$) 3080, 3000, 2980, 2940, 1775, 1580, 1480, 1455, 1440, 1420, 1380, 1340, 1180, 1070, 1020, 1000, 950, 890, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.53 and 7.27 (2 H and 3 H, m, PhH), 5.91 (1 H, ddd, $J_{3,4}$ = 11.6, $J_{4,5}$ = 6.3, $J_{4,2}$ = 2.3 Hz, 4-H), 5.60 (1 H, ddd, $J_{3,4}$ = 11.6, $J_{3,5}$ = 1.5, $J_{3,2}$ = 2.8 Hz, 3-H), 5.31 (1 H, ddd, $J_{2,1}$ = 6.2, $J_{2,3}$ = 2.8, $J_{2,4}$ = 2.3 Hz, 2-H), 4.02 (1 H, dd, $J_{5,4}$ = 6.3, $J_{5,6}$ = 5.5 Hz, 5-H), 2.76 (1 H, m (obscured), 1-H), 2.77 and 2.19 (each 1 H, dd, $J_{8\alpha,\beta}$ = 20.7, $J_{8,1}$ = 8.8 and 8.4, 8α,8β-H), 2.19 (1 H, m (obscured), 6-H), 1.74 (1 H, ddd, $J_{7\alpha,\beta}$ = 14.06, $J_{7,1}$ = 5.86 and $J_{7,6}$ = 9.3 Hz, one 7-H), 1.57 (1 H, dd, $J_{7\alpha,\beta}$ = 14.06, $J_{7,6}$ = 4.5 Hz, one 7-H), 1.06 (3 H, d, J = 6.8 Hz, CH_3); MS (CI), m/z (%) 322 (M^+ + 1, 100), 321 (M^+, 18.6), 165 (322 - PhSeH, 94.8), 164 (M^+ - PhSeH, 76.2), 157 (PhSeH, 10.5), 119 (27.9), 105 (34.2), 91 (10.9); found M^+ = 321.0907, $C_{16}H_{18}O_2Se$ requires M^+ = 321.0902. NMR double-resonance experiments: Signal at δ 5.91 collapses to dd, J = 11.6, 6.3 Hz and J = 11.6, 2.3 Hz, irradiating 2-H at δ 5.31 and 5-H at δ 4.02, respectively. Signal at δ 5.60 collapses to dd, J = 11.6, 1.5 Hz and 11.6, 2.8 Hz, irradiating 2-H at δ 5.31 and 5-H at δ 4.02, respectively. Signal at δ 5.31 collapses to dd, J = 6.2, 2.3 Hz and J = 2.8, 2.3 Hz, irradiating 3 H at δ 5.6 and 1-H at δ 2.76, respectively. Signal at δ 4.02 collapses to d, J = 6.3 and 5.5 Hz, irradiating 6-H at δ 2.19 and 4-H at δ 5.91, respectively.

Preparation of Hydroxy Lactone 21a. A solution of the seleno lactone **18b** (0.32 g, 1 mmol) in THF (20 mL) was cooled to −20 °C. H_2O_2 (15%, v/v) (1 mL) was added, and the mixture was stirred for 2 h. Triethylamine (1 mL) was then added and the temperature of the stirred mixture was allowed to reach 23 °C. After 10 min it was extracted with chloroform, washed with water, dried ($MgSO_4$) and concentrated. The hydroxy lactone so obtained was purified by chromatography (0.11 g, 70%): IR ν_{max} ($CHCl_3$) 3600–3300, 3000, 2950, 2900, 1770, 1650 (br), 1600, 1450, 1510, 1330, 1300, 1160, 1110, 1090, 1070, 1030, 1010 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.789 (1 H, d, $J_{4,5}$ = 12.6, $J_{4,3}$ = 6.95 Hz, 4-H), 4.536 (1 H, dd, $J_{1,2}$ = 8.63, $J_{3,2}$ = 1.85 Hz, 2-H), 4.45 (1 H, dd, $J_{3,4}$ = 6.95, $J_{3,2}$ = 1.85 Hz, 3-H), 2.84 (1 H, m, 1-H), 2.56 (2 H, m), 2.04–1.77 (3 H, m), 1.07 (3 H, d, J = 7.33 Hz, CH_3); MS, m/z (%), 182 (M^+, 17.6), 164 (M^+ - H_2O, 48), 123 (100), 93 (34.7); found m/z 182.0953, $C_{10}H_{14}O_3$ requires M^+ = 182.0943. NMR double-resonance experiments: Signal at δ 5.699 collapses to d, J = 12.6 and 6.95 Hz, irradiating 3-H at δ 4.45 and 5-H at δ 5.79, respectively. Signal at δ 4.536 collapses to d, $J \approx$ 8.6 and 1.85 Hz on irradiating 3-H at 4.45 and 1-H at δ 2.84, respectively. Signal at δ 4.45 collapses to d, $J \approx$ 6.9 and 1.85 Hz, irradiating 2-H at δ 4.53 and 4-H at δ 5.69. Reported coupling constant values for $J_{1,2}$ and $J_{3,4}$ were derived from original spectrum.

Preparation of Acetoxy Lactone 21b. A mixture of acetic anhydride (0.2 mL) and a solution of hydroxy lactone **21a** (0.11 g) in pyridine (10.5 mL) was set aside at room temperature overnight. It was treated with cold water (5 mL), acidified with 10% HCl, and extracted with ether. The organic layer was washed with water, $NaHCO_3$ solution, and finally water, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography to give the acetate as colorless oil (0.1 g): IR ν_{max} ($CHCl_3$) 2930, 2910, 1770, 1735, 1520, 1440, 1410, 1360, 1300, 1220 (s), 1170, 1120, 1060, 1020, 990, 920, 890, 870 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.828 (2 H, m, vinyl), 5.354 (1 H, dd, $J_{4,3}$ = 6.5, $J_{3,2}$ = 2.1 Hz, 3-H), 4.674 (1 H, dd, $J_{3,2}$ = 2.1, $J_{1,2}$ = 8.9 Hz, 2-H), 2.928 (1 H, m, 1-H), 2.636 and 2.458 (each 1 H, dd, $J_{8\alpha,\beta}$ = 17.5, $J_{8,1}$ = 9.33 and 11.3 Hz, two 8,-H), 2.319 (1 H, m, 6-H), 2.052 (3 H, s, $OCOCH_3$), 1.877 (2 H, m), 1.09 (3 H, d, J = 7.27 Hz, CH_3); MS, m/z (%) 224 (M^+, 8.4), 182 (M - CH_2CO, 68.1), 165 (M^+ - CH_3CO_2, 100), 122 (37.8), 93 (14.8); found M^+ = 224.1059, $C_{12}H_{16}O_4$ requires M^+ = 224.1049. NMR double-resonance experiments: Signal at δ 5.354 collapses to d, J = 6.5 and J = 2.1 Hz, irradiating 2-H at δ 4.67 and 4-H at δ 5.83, respectively. Signal at δ 4.674 collapses to d, J = 2.1 and = 8.9 Hz, irradiating 1-H at δ 2.93 and 3 H at δ 5.35, respectively. Signal at δ 1.09 collapses to singlet, irradiating 6-H at δ 2.319.

Preparation of Hydroxy Lactone 22a. This was obtained from the oxidation of the seleno lactone **17b**, using a similar procedure as described in the preparation of **21a**. The rearranged product was purified by flash chromatography as colorless oil (70%); IR ν_{max} ($CHCl_3$) 3590–3280, 3010, 2920, 1770, 1610, 1590, 1450, 1300, 1120, 1070, 1000 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.94–5.70 (2 H, m, vinyl), 5.36 (1 H, d, J = 7.70 Hz), 3.87 (1 H, t, J = 6 Hz), 3.12 (1 H, m, 1-H), 2.77 (1 H, dd, J = 17.6 and 9.1 Hz, 8α-H), 2.36 (1 H, m, 6-H), 2.17 (1 H, dd, J = 17.6 and 6.35 Hz, 8β-H), 1.63 (2 H, m), 0.97 (3 H, d, J = 6.89 Hz, CH_3); MS, m/z (%), 182 (M^+, 20), 164 (55), 123 (100); found M^+ = 182.0925, $C_{10}H_{14}O_3$ requires M^+ = 182.0943.

Conversion of the Seleno Lactones 17b and 18b to the Saturated Lactone 23 by Deselenenylation Followed by Hydrogenation. Each of the lactones **17b** and **18b** (30 mg, 0.01 mmol) was separately refluxed with excess Raney Ni in THF for 1 h. The solution was filtered and the solvent was removed in vacuo. Each residue was taken up with absolute ethanol (20 mL) and hydrogenated over PtO_2 for 1 h. The reaction mixture was filtered and the filtrate evaporated, the residue being purified by flash chromatography. Each product was found to be identical as evident from their IR, ^1H NMR, and mass spectra: IR ν_{max} ($CHCl_3$) 2940, 2900, 2840, 1770, 1510, 1450, 1410, 1370, 1220, 1110, 1050, 1030, 1000, 920, 870, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 4.627 (1 H, ddd, $J_{1,2}$ = 6.5, $J_{2,3\alpha}$ = 10.88, $J_{2,3\beta}$ = 4.7 Hz, 2-H), 2.85–2.6 (2 H, m), 2.36–2.07 (2 H, m), 1.87–1.47 (8 H, m), 0.94 (3 H, d, J = 7 Hz, CH_3); MS, m/z (%) 168 (M^+, 6%), 108 (M^+ - CH_3CO_2H, 26.4), 97 (53.7); found M^+ = 168.1169, $C_{10}H_{16}O_2$ requires M^+ = 168.1150.

Preparation of Enone 24 from Hydroxy Lactone 21a. Pyridinium chlorochromate (0.1 g, 0.45 mmol) was suspended in dichloromethane (10 mL) and the hydroxylactone (0.55 mg, 0.3 mmol) was rapidly added at room temperature. The solution became briefly homogeneous before depositing a black precipitate. After 1–2 h the reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by chromatography and crystallized from $CHCl_3$–petroleum ether as colorless needles (40 mg, 70%): mp 90 °C; IR ν_{max} ($CHCl_3$) 2980, 2940, 2880, 2860, 1780, 1690, 1490, 1460, 1420, 1400, 1380, 1360, 1340, 1310, 1280, 1260, 1170, 1120, 1060, 1020, 980, 950, 900, 870, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 6.54 (1 H, d, $J_{4,5}$ = 12 Hz, 5-H), 6.09 (1 H, dd, $J_{4,5}$ = 12, $J_{4,6}$ = 3.3 Hz, 4-H), 5.179 (1 H, d, $J_{2,1}$ = 9.65 Hz, 2-H), 3.02 (1 H, m, 1-H), 2.587 (2 H, m, 8α-H, 6-H), 2.141 (2 H, m, 8β-H, 7α-H), 1.89 (1 H, m, 8β-H), 1.20 (3 H, d, J = 7.3 Hz, CH_3); MS, m/z (%) 180 (M^+, 11.2),

110 (9.9), 95 (30.4), 82 (22.9); found M^+ = 180.0764, $C_{10}H_{12}O_3$ requires M^+ = 180.0786.

Sodium Borohydride Reduction of the Enone 24 to the Hydroxy Lactone 21a. The enone **24** (36 mg, 0.2 mmol) was dissolved in methanolic $CeCl_3,6H_2O$ (0.07 g in 2.5 mL MeOH), and $NaBH_4$ (0.2 mmol) was slowly added with stirring at 0 °C. The mixture was allowed to react for 10 min and was then treated with water and extracted with ether. The ether layer was dried and evaporated. The residue was purified by chromatography and found to be identical in all respects (IR, ^1H NMR, and mass) with the hydroxy lactone **21a**.

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Registry No. 1, 12212-05-4; **2a**, 85994-17-8; **2b**, 91550-49-1; **2c**, 91550-50-4; **2d** (isomer 1), 91684-26-3; **2d** (isomer 2), 91550-51-5; **5**, 91604-69-2; **6**, 85956-43-0; **7** (L = Co), 40674-86-0; **7a**, 12213-31-9; **7b**, 67663-92-7; **8a**, 55744-14-4; **8b**, 85956-40-7; **9a**, 55938-82-4; **9b**, 91550-52-6; **9e**, 85956-45-2; **9f**, 85956-46-3; **9g**, 91550-53-7; **9h**, 91550-54-8; **9i**, 91550-55-9; **9j**, 91550-56-0; **9k**, 91550-57-1; **9l**, 91550-58-2; **9m**, 91550-59-3; **9n**, 91550-60-6; **9o**, 91550-61-7; **9p**, 91550-62-8; **10b**, 91550-63-9; **10c**, 91550-64-0; **10d**, 91550-65-1; **10e**, 85994-18-9; **10f**, 85956-47-4; **10g**, 91550-66-2; **10h**, 91550-67-3; **10i**, 91550-68-4; **10j**, 91550-69-5; **10k**, 91550-70-8; **10l**, 91550-71-9; **10m**, 91550-72-0; **10n**, 91550-73-1; **10o**, 91550-74-2; **10p**, 91550-75-3; **10q**, 85956-48-5; **10r**, 85939-52-2; **10s** (isomer 1), 91604-70-5; **10s** (isomer 2), 91604-71-6; **10t** (isomer 1), 91604-72-7; **10t** (isomer 2), 91604-73-8; **10u** (isomer 1), 91604-74-9; **10u** (isomer 2), 91604-75-0; **10v** (isomer 1), 91604-76-1; **10v** (isomer 2), 91604-77-2; **10w** (isomer 1), 91550-76-4; **10w** (isomer 2), 91604-78-3; **10x** (isomer 1), 91550-77-5; **10x** (isomer 2), 91604-79-4; **11a**, 85939-58-8; **11b**, 85939-60-2; °11°c, 91550-79-7; **12a**, 85939-61-3; **12b**, 85939-62-4; **12c**, 91550-80-0; **12d**, 91550-81-1; **12e**, 85939-63-5; **12f**, 85939-64-6; **12g** (isomer 1), 91550-82-2; **12g** (isomer 2), 91604-80-7; **12h** (isomer 1), 91604-81-8; **12h** (isomer 2), 91604-82-9; **12i** (isomer 1), 91604-83-0; **12i** (isomer 2), 91604-84-1; **12j**, 91550-83-3; **12k**, 91550-84-4; **13c**, 91550-85-5; **13k**, 91550-86-6; **16a**, 91550-40-2; **16b**, 85939-65-7; **16d**, 89860-90-2; **16e**, 91550-41-3; **16f**, 91550-42-4; **16g**, 91550-43-5; **16h**, 91550-44-6; **17g**, 91604-63-6; **17b**, 91604-64-7; **18a**, 91604-65-8; **18b**, 91604-66-9; **19**, 91604-67-0; **21a**, 91550-45-7; **21b**, 91604-68-1; **22a**, 91550-46-8; **23**, 91550-47-9; **24**, 91550-48-0; NaSPh, 930-69-8; $NaSC_6H_4$-*p*-NO_2, 13113-79-6; CC≡CCMgCl, 6088-88-6; $(CC{\equiv}CC)_2CuMgCl$, 91550-87-7; C≡CCMgCl, 2622-05-1; $(C{\equiv}CC)_2CuMgCl$, 91550-88-8; $NaCH(CO_2CH_3)_2$, 18424-76-5; $NaCH(CO_2CH_3)(COCH_3)$, 34284-28-1; $NaCH(SO_2Ph)(CO_2CH_3)$, 60729-65-9; $NaCH(CN)(CO_2CH_3)$, 24163-38-0; $Ph_3C^+PF_6^-$, 437-17-2; PhSeBr, 34837-55-3; cycloheptadiene, 4054-38-0.

Communications to the Editor

Stereospecific Synthesis of P^1,P^2-Bidentate $Co(NH_3)_4$(PPS) and P^1,P^2-Bidentate $Cr(H_2O)_4$(PPS) Enantiomers

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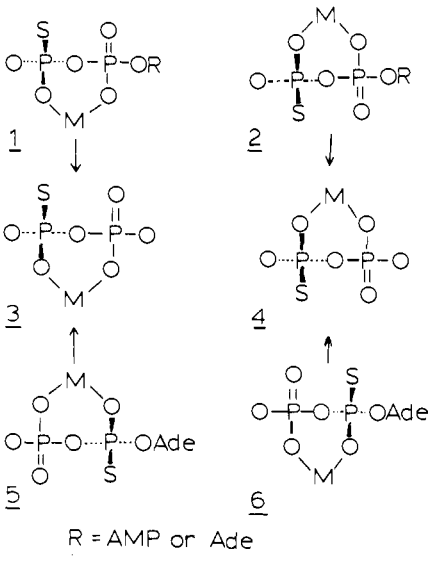
Exchange inert Cr(III) and Co(III) complexes of ATP[1] and ADP have been effectively employed as probes of enzymatic processes that involve Mg(II) complexes of ATP and ADP.[2] Current advances in this area are focussed in part on the development of more versatile enzyme active site probes having Cr(III) or Co(III) complexed to the thiophosphoryl and adjacent phosphoryl centers of the nucleotide analogues, ATPγS and ADPβS. These β,γ-bidentate M^{III}ATPγS and α,β-bidentate M^{III}ADPβS complexes each possess two chiral centers in the phosphate chain and, as a result, will receive unique application in stereochemical studies designed to elucidate the nature of enzyme activation of P–O bond cleavage.

Previous studies have demonstrated that M(III) complexes of ATPγS and ADPβS can be prepared and separated by chromatography on cycloheptaamylose columns and on reverse-phase HPLC columns.[3,4] In addition, the configurations at the chiral phosphoryl centers in these complexes can be correlated with those

Scheme I



of the corresponding bidentate M^{III}ATP and M^{III}ADP complexes through the use of CD techniques.[3,5] The final task in the elaboration of the M^{III}ATPγS and M^{III}ADPβS complexes as stereochemical probes is the assignment of the configurations at the thiophosphoryl centers. We have recently developed an unambiguous technique for accomplishing this task. Our approach, summarized in Scheme I, utilizes the P^1,P^2-bidentate M^{III}PPS enantiomers **3** and **4** as relay species to correlate the unknown configurations at the thiophosphoryl centers in β,γ-bidentate M^{III}ATPγS or α,β-bidentate M^{III}ADPβS (**1** and **2**) with the known configurations at the thiophosphoryl center of the α,β-bidentate M^{III}ADPαS diastereomers **5** and **6**.[6] Importantly,

(1) Abbreviations used: adenosine (Ade), adenosine 5′-monophosphate (AMP), adenosine 5′-triphosphate (ATP), adenosine 5′-diphosphate (ADP), adenosine 5′-(3-thiotriphosphate) (ATPγS), adenosine 5′-(2-thiodiphosphate) (ADPβS), adenosine 5′-(2-thiodiphosphate) (ADPαS), thiopyrophosphate (PPS), pyrophosphate (PP), 2-(*morpholino*)ethanesulfonate (MES).

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