Approaches to Enantioselective Syntheses using Tricarbonyl(diene)iron Complexes

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Methods for the resolution of tricarbonyl(1—5-η-cyclohexadienyl)iron salts are described involving the separation of diastereoisomeric pairs obtained by nucleophilic attack using chiral phosphines, alkoxides, and amines. Nucleophilic attack by CN^- on $[Fe(\eta^5-C_6H_7)(CO)_2L^*]BF_4$ to give $[Fe(C_6H_7CN\text{-}exo\text{-}5)(CO)_2L^*]$ [L* = (+)-neomenthyldiphenylphosphine] proceeds with significant asymmetric induction at the chiral carbon so formed.

The utility of substituted derivatives of the tricarbonyl(1—5-η-cyclohexadienyl)iron cation (A) and its precursor tricarbonyl(1—4-η-cyclohexa-1,3-diene)iron (B) in stoicheiometric organic synthesis has been amply demonstrated by the work of Birch *et al.*,[1] and the recent work of Pearson [2] has shown how such complexes may be used as synthons in the preparation of the complicated organic frameworks of several natural products. It has been recognized that the important potential for enantioselective synthesis also exists, since 1- or 2-substituted derivatives of (A) or (B) occur as enantiomeric pairs due to the lateral co-ordination of the metal moiety. Most importantly, nucleophilic attack on enantiomerically pure salts of type (A) provides access to a fully resolved asymmetric carbon at the point of nucleophilic attack due to the stereospecific addition of the nucleophile to the dienyl face *exo* to the co-ordinated metal.

(A) M = Fe(CO)3 (B)

While the 1-COOH derivative of cation (A) has been resolved by classical procedures,[3] only two generally applicable methods have been reported to date involving either (*a*) asymmetric complexation of a prochiral diene such as 2-methoxycyclohexa-1,3-diene with chiral transfer reagents based on tricarbonyl(η^4-enone)iron complexes,[4] or (*b*) a kinetic and/or thermodynamic discrimination in reactions of substituted derivatives of (A) with a deficiency of chiral nucleophile, followed by recovery of the enantiomerically enriched dienyl salt.[5] To date, the degrees of enantiomeric enrichment obtained [up to 40% in the case of method (*a*) and less than 10% in (*b*)] do not form the basis for satisfactory enantioselective syntheses. We report here on two general methods of potential use in this area.

Results and Discussion

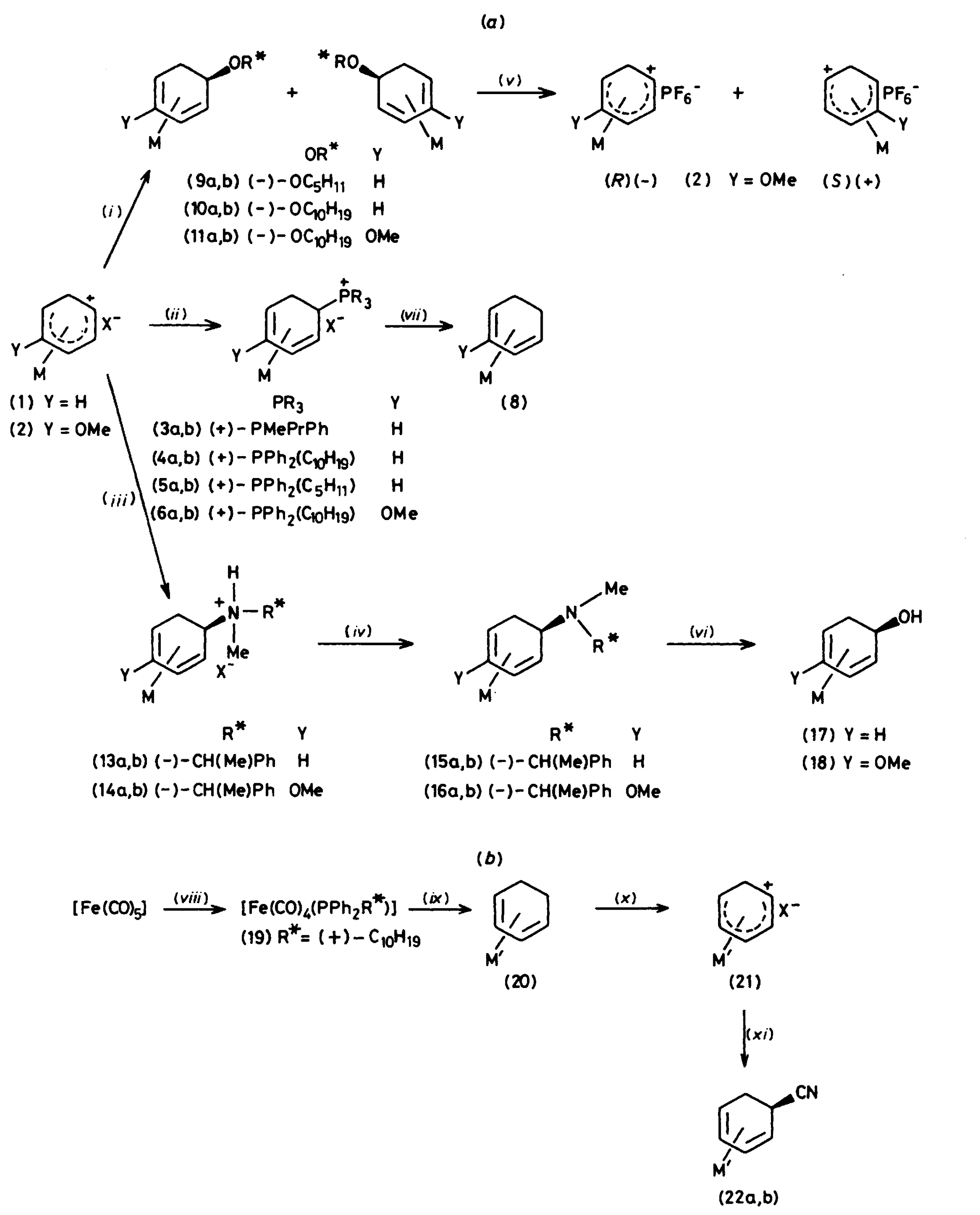
Reactions using Chiral Nucleophiles.—Nucleophilic attack on cation (A) and its substituted derivatives is known to occur in an *exo* fashion at a terminal carbon of the dienyl ligand, although in the cases of 1- or 2-substituted complexes, the attack may exhibit a regiospecificity which is dependent on the substituent, the nucleophile, and the reaction conditions used.[1] Use of chiral nucleophiles provides a route to enantiomerically pure complexes *via* the separation of diastereoisomeric pairs, followed by either elimination of the nucleophile or its transformation by substitution or other means into an achiral substituent (provided these reactions do not proceed *via* an intermediate containing a plane of symmetry). The experimental results are summarized in Scheme (*a*).

(*a*) *Chiral phosphines.* Phosphine addition to dienyl salts to give phosphonium salts is a well established reaction which has been studied mechanistically in some detail.[6] Thus, reactions of compound (1) with the phosphorus-centred (*S*)(+)-PMePrPh and the alkyl-centred (+)-$PPh_2(C_{10}H_{19})$ ($C_{10}H_{19}$ = neomenthyl) and (*S*)(+)-$PPh_2(C_5H_{11})$ [C_5H_{11} = $CH_2CH(Me)Et$] chiral phosphines provide good yields of the salts (3a,b)—(5a,b). Carbon-13 n.m.r. spectra (Table) were assigned on the basis of off-resonance experiments and a comparison with the model PMe_2Ph complex (7) [7] whose data are also given in the Table. Although complicated by phosphorus–carbon coupling, a doubling of many of the resonances may be observed (indicated by bracketed values in the Table), consistent with the presence of two diastereoisomers. Phosphorus-31 n.m.r. spectra show clearly that the complexes exist as equimolar diastereoisomeric mixtures, exhibiting two resonances of equal intensity in all cases. For simplicity, the Scheme is drawn showing arbitrary configurations for only one of the diastereoisomeric or enantiomeric pairs of all the complexes described herein, with the exception of the menthoxy-derivative (11a,b) discussed in section (*b*).

The diastereoisomeric pair (4a,b) in particular may easily be separated by fractional crystallization. Good yields of pure (4a) (70% of the theoretical maximum; >98% pure by ^{31}P n.m.r.) are obtained from early fractions, while later fractions provide smaller yields (41%) of material which is substantially enriched in isomer (4b) (*ca.* 90% by ^{31}P n.m.r.). The ^{13}C and ^{31}P n.m.r. resonances of the pure diastereoisomer (4a) are indicated in the Table. While phosphine dissociation has been observed previously in other related complexes,[8] there is no evidence that this presents here the problem of diastereoisomeric interconversion. No line broadening of the ^{31}P resonances of compound (3a,b) up to 55 °C in $CDCl_3$ is observed, while samples of (4a) kept in $CDCl_3$ solution for hours show no detectable conversion into (4b).

The resolving centre may be eliminated from (4a) by reduction using $LiAlH_4$ to give the achiral compound (8). In this context, the 2-methoxy-salt (2) also reacts with (+)-PPh_2-($C_{10}H_{19}$) exclusively at the C-5 terminus to yield (6a,b) as an equimolar diastereoisomeric mixture. A complete separation of the diastereoisomers by fractional crystallization has not yet been achieved, however. We are currently examining other transformations of (4a) which should, in principle, yield enantiomerically pure complexes. Most notable is the recently reported [7] Wittig transformation of (7) into complexes of substituted 5-methylenecyclohexa-1,3-dienes and their protonation to yield 1-substituted derivatives of (1).

(*b*) *Chiral alkoxides.* Reaction of compound (1) with simple alkoxides is known to proceed to give kinetically controlled

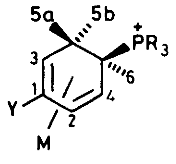


Scheme. M = $Fe(CO)_3$, M′ = $Fe(CO)_2(PPh_2R^*)$, $X^- = BF_4^-$. (*i*) (−)-menthol, $NEtPr^i_2$, room temperature (r.t.), CH_2Cl_2; (*ii*) (+)-$PPh_2(C_{10}H_{19})$, r.t., CH_2Cl_2; (*iii*) (−)-NH(Me)[CH(Me)Ph], r.t., CH_2Cl_2; (*iv*) $NEtPr^i_2$, r.t., CH_2Cl_2; (*v*) HPF_6, 0 °C, Et_2O; (*vi*) t.l.c. on silica, Et_2O eluant; (*vii*) $LiAlH_4$, 0 °C, tetrahydrofuran; (*viii*) PPh_2R^*, $CoCl_2{\cdot}2H_2O$, 110 °C, toluene; (*ix*) cyclohexa-1,3-diene, u.v. irradiation, r.t., benzene; (*x*) CPh_3BF_4, r.t., CH_2Cl_2; (*xi*) KCN, r.t., acetone–water (1 : 1)

exo attack at C-5, although under certain conditions an *exo*–*endo* equilibration may occur.[9] Thus, treatment of (1) with (*S*)(−)-$HOCH_2CH(Me)Et$ or (−)-menthol in the presence of $NEtPr^i_2$ as deprotonating agent provides good yields of complexes (9a,b) and (10a,b) respectively. Their ^{13}C and ^1H n.m.r. spectra (Table) were assigned on the basis of off-resonance and spin-decoupling experiments and by a comparison with the model 5-*exo*-methoxy-complex (12).[10] In the case of compound (10a,b) in particular, a doubling of many of the ^{13}C resonances is observed, showing (within the error of the measurement) an equimolar mixture of diastereoisomers. The mixture (10a,b) may easily be separated by preparative thin-layer chromatography (t.l.c.), and ^{13}C resonances for the separated diastereoisomers are given in the Table. The proton spectra are, however, essentially coincident, and values given in the Table refer to the diastereoisomeric mixtures.

The 2-methoxy-salt (2) undergoes reaction with (−)-

Table. Proton,[a] ^{13}C,[a,b] and ^{31}P [c] n.m.r. spectral parameters. Braces indicate resonances due to diastereoisomeric pairs; resonances marked (†) are those of the pure diastereoisomer isolated by fractional crystallization



(3)-(7)

Complex	^{13}C Assignment	
(3a,b)[d]	1, 2	84.8
M = Fe(CO)$_3$		86.2
PR$_3$ = PMePrPh	3, 4	51.8 (8.8)
Y = H		58.9 (6.8)
		59.0 (6.8)
	5	25.4 (1.9)
		26.1 (1.9)
	6	32.7 (39.1)
		33.1 (39.1)
	Pr	14.8—22.9
	Ph	129—134
	Me	3.20 (10.7)
		1.20 (10.7)

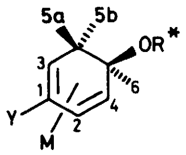
Complex	^{13}C Assignment	
(4a,b)[e]	1, 2	84.2
M = Fe(CO)$_3$		85.6 † (3.8)
PR$_3$ = PPh$_2$(C$_{10}$H$_{19}$)		85.7 (3.8)
Y = H	3, 4	50.7 † (8.8)
		51.0 (8.8)
		58.0 † (7.8)
	5	25.8 † (2.9)
		26.2 (2.9)
	C$_{10}$H$_{19}$, 6	20—43.5
	Ph	128—134

Complex	^{13}C Assignment	
(5a,b)[d]	1, 2	85.1
M = Fe(CO)$_3$		85.3
PR$_3$ = PPh$_2$(C$_5$H$_{11}$)	3, 4	51.2 (7.8)
Y = H		58.7 (7.8)
	5	26.7 (3.9)
	6	32.9 (36.2)
	C$_5$H$_{11}$	10.7—31.1
	Ph	128—134

Complex	^{13}C Assignment	
(6a,b)[f]	1, 2	66.4 (2.4)
M = Fe(CO)$_3$		[g]
PR$_3$ = PPh$_2$(C$_{10}$H$_{19}$)	3, 4	50.9 (6.1)
Y = OMe		40.8(9.7)
		40.9(9.7)
	5	27.4(4.8)
	OMe	54.7
	C$_{10}$H$_{19}$, 6	27.4 (4.8)
	Ph	18.9—43.8
		129—135

Complex	^{13}C Assignment	
(7)[h]	1, 2	84.6 (4.7)
M = Fe(CO)$_3$		86.0
PR$_3$ = PMe$_2$Ph	3, 4	51.7 (8.5)
Y = H		58.9 (8.6)
	5	25.4 (3.7)
	6	33.0 (40.3)
	Me	4.3 (12.2)
		6.2 (12.2)
	Ph	127—134

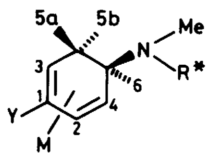
Table (*continued*)



(9) - (12)

Complex	^{13}C Assignment			^{1}H Assignment	
(9a,b)	1, 2	85.1		1, 2	5.47 (m)
M = $Fe(CO)_3$		87.2		6	3.88 (m)
R* = C_5H_{11}	3, 4	55.8		OCH_2, CH, 4	3.05 (m)
Y = H		55.9		3	2.85 (m)
		60.2		5b	2.19 (m)
	5	30.9		5a, Me, Et	0.85—1.50
	6	76.9			
	OCH_2	74.4			
	Et	26.2, 11.2			
	Me	16.6			
	CH	35.2			
(10a)	1, 2	84.9		1, 2	5.47 (m)
M = $Fe(CO)_3$		87.1		6	3.97 (m)
R* = $C_{10}H_{19}$	3, 4	55.6		4	3.02 (m)
Y = H		62.2		3	2.87 (m)
	5	31.8		$OC_{10}H_{19}$, 5a, b	0.62—2.87
	6	75.7			
	$OC_{10}H_{19}$	16.0	31.3		
		21.3	34.4 [t]		
		22.4 [t]	42.4		
		23.1	48.4		
		25.1	78.9		
(11a)	1, 2	66.2		2	5.13 (m)
M = $Fe(CO)_3$		*g*		6	3.81 (m)
R* = $C_{10}H_{19}$	3, 4	49.3		OMe	3.63 (s)
Y = OMe		50.3			3.62 (s)
	5	34.0		3, 4, 5a, b, $OC_{10}H_{19}$	0.61—3.11
	6	75.2			
	OMe	54.3 [t]			
	$OC_{10}H_{19}$	16.3	31.7		
		21.2	34.5		
		22.4 [t]	41.7		
		23.3	48.3		
		25.4	78.3		
(12)	1, 2	84.9		1, 2	5.48 (m)
M = $Fe(CO)_3$		87.3		6	3.81 (m)
R* = Me	3, 4	55.7		OMe	3.18 (s)
Y = H		56.3		4	3.06 (m)
	5	30.4		3	2.89 (m)
	6	75.9		5b	2.25 (m)
	OMe	59.3		5a	1.46 (m)
(10b)	1, 2	84.7			
		87.3			
	3, 4	56.1			
		60.9			
	5	32.8			
	6	75.1			
	$OC_{10}H_{19}$	16.3	31.7		
		21.2	34.4 [t]		
		22.4 [t]	41.6		
		23.3	48.2		
		25.4	78.1		
(11b)	1, 2	66.3			
		g			
	3, 4	49.1			
		51.6			
	5	34.5			
	6	75.8			
	OMe	54.3 [t]			
	$OC_{10}H_{19}$	16.1	31.8		
		21.3	32.7		
		22.4 [t]	42.5		
		23.2	48.4		
		25.2	79.1		

Table (*continued*)

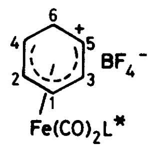


Complex	^{13}C Assignment		^{1}H Assignment	
(15a,b)	1, 2	86.1 †	1, 2	5.40 (m)
M = Fe(CO)$_3$		86.3	6, C*H*Me	3.51 (m)
R* = CH(Me)Ph		84.5	4	2.90 (m)
Y = H		84.7 †	3	2.75 (m)
	3, 4	58.9	NMe	1.97 (s)
		59.6	5b	1.84 (m)
		60.1 †	5a	1.40 (m)
	5	24.8 †	CH*Me*	1.35 (d, 6.8)
		25.2	Ph	7.24 (m)
	6	62.2 †		
		62.6		
	CH*Me*	20.4 †		
		20.9		
	NMe	32.6		
	*C*HMe	57.6		
	Ph	126—128		

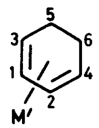
Complex	^{13}C Assignment		^{1}H Assignment	
(16a,b)	1, 2	68.3	2	5.21 (m)
M = Fe(CO)$_3$		68.1	OMe	3.62 (s)
R* = CH(Me)Ph		*g*	6, C*H*Me	3.40 (m)
Y = OMe	3, 4	48.5	3	3.16 (m)
		48.9	4	2.34 (m)
		50.7	NMe	1.94 (s)
	5	26.4		1.99 (s)
		26.5	CH*Me*	1.26 (d, 6.6)
	6	62.1		1.30 (d, 6.6)
		62.5	5a, b	1.30—1.70 (m)
	CH*Me*	20.7	Ph	7.24 (m)
		20.2		
	NMe	32.8		
	*C*HMe	58.7		
	OMe	54.3		
	Ph	127—129		

Table (*continued*)

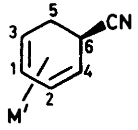
Complex	^{13}C Assignment			^{1}H Assignment	
(19)	$C_{10}H_{19}$	17.5	28.4	$C_{10}H_{19}$	0.45—3.06
$[Fe(CO)_4L^*]$		20.8	30.2 (3.9)	Ph	7.34—7.90 (m)
$L^* = PPh_2(C_{10}H_{19})$		21.4 (12.6)	31.0 (6.8)		
		23.9	39.1		
		28.3 (7.7)	41.4 (22.4)		
	Ph	128—135			
	CO	212.6 (15.7)			



Complex	^{13}C Assignment		
(21)	1	89.0	
$L^* = PPh_2(C_{10}H_{19})$	2, 3	100.8	
		101.9	
	4, 5	57.9	
		60.6	
	6	23.6	
	$C_{10}H_{19}$	17.7	28.2
		20.1	30.8
		21.0 (12.7)	31.2 (4.9)
		23.9	39.7 (22.5)
		27.9 (7.5)	40.5
	Ph	128—134	



Complex	^{13}C Assignment			^{1}H Assignment	
(20)[j]	1, 2	85.6		1, 2	4.32 (m)
$M' = Fe(CO)_2L^*$		86.5		4—6, $C_{10}H_{19}$	0.17—2.71
$L^* = PPh_2(C_{10}H_{19})$	3, 4	60.5 (2.9)		Ph	7.13—7.78 (m)
		61.0 (2.0)			
	5, 6	24.4			
		24.9			
	$C_{10}H_{19}$	17.1	28.8		
		20.4	30.3 (3.9)		
		21.3 (11.7)	31.0 (6.8)		
		24.0	38.9 (20.5)		
		28.0 (5.8)	39.7 (3.9)		
	Ph	127—135			



Complex	^{13}C Assignment		^{1}H Assignment	
(22a,b)[k]	1, 2	84.5 [l]	1	4.39 (m)
$M' = Fe(CO)_2L^*$		85.3 [l]	2	4.61 (m)
$L^* = PPh_2(C_{10}H_{19})$		87.9 [l]	$C_{10}H_{19}$, 3—6	0.23—2.83
		88.5	Ph	7.30 (m)
	3, 4	55.1 [l] (2.5)		
		55.6 (2.5)		
		56.7 (3.7)		
		57.3 [l] (3.7)		
	5	26.2		
		26.4 [l]		
	6, $C_{10}H_{19}$	17.8—39.9		
	Ph	127—135		

[a] P.p.m. from $SiMe_4$; solutions in $CDCl_3$. [b] J(P–C) in Hz in parentheses. [c] P.p.m. from 85% H_3PO_4. [d] $\delta(^{31}P)$ {31.2, 31.7} p.p.m. [e] $\delta(^{31}P)$ {32.4 †, 34.2} p.p.m. [f] $\delta(^{31}P)$ {31.7, 33.7} p.p.m. [g] Quaternary carbon not detected. [h] $\delta(^{31}P)$ 27.6 p.p.m. [i] Resonance common to the two diastereoisomers. [j] $\delta(^{31}P)$ 72.3 p.p.m. [k] $\delta(^{31}P)$ {70.5 [l], 70.1} p.p.m. [l] Resonance of major diastereoisomer.

menthol under the same conditions to yield exclusively (11a,b), the product of *exo* attack at C-5. The ^{13}C spectra again show an equimolar diastereoisomeric mixture which may be separated by t.l.c., and in this case elimination of the menthoxy-residue by protonation with HPF_6 provides pure samples of the optical isomers of (2). The absolute configurations for compound (11a,b), as shown in Scheme (*a*), can be written with confidence since enantiomerically enriched samples of (2) obtained by asymmetric complexation methods have been converted into natural products of known configuration.[11]

(*c*) *Chiral amines.* Reaction of dienyl metal salts with amines has been studied mechanistically, and proceeds through initial *exo* addition to give an ammonium salt which is then deprotonated by solvent or on addition of a second mol of amine.[12] Thus, reaction of compound (1) with 1 mol of (−)-NH(Me)-[CH(Me)Ph], followed by *in situ* additions of 1 mol of $NEtPr^i_2$ or a further mol of (−)-NH(Me)[CH(Me)Ph] as deprotonating agent, provides high yields of the neutral amine (15a,b). The intermediate ammonium salt (13a,b) may be isolated by precipitation after addition of the first mol or amine, although analytically pure samples have not been obtained. The ^{13}C and ^1H n.m.r. spectra clearly indicate an equimolar diastereoisomeric mixture from which one of the diastereoisomers (15a) may be isolated in a pure state by fractional crystallization (64% yield). Attempted chromatographic separation of (15a,b) results in hydrolysis to the *exo*-alcohol (17), identified by comparison with an authentic sample prepared by hydrolysis of (1).[10] Unfortunately, using the shift reagent tris[3-(heptafluoropropylhydroxymethylene)-D-camphorato]-europium(III),† examination of the ^1H n.m.r. spectrum of (17) formed from hydrolysis of pure diastereoisomer (15a) shows it to be an equimolar racemic mixture. This indicates clearly that the hydrolysis proceeds *via* initial electrophilic proton-induced loss of amine to generate achiral (1) as an intermediate, followed by addition of hydroxide. We are however, currently examining the possibility of *nucleophilic* substitution of the amine residue of (15a) and of the menthoxide residue of compounds (10a) and (10b).

Reaction of the methoxy-derivative (2) with (−)-NH(Me)-[CH(Me)Ph] occurs exclusively at C-5 *via* the intermediacy of the ammonium salt (14a,b) to yield (16a,b); ^{13}C spectra again indicate an equimolar mixture of diastereoisomers. Unfortunately, the compound is isolated as an oil which on attempted chromatographic separation of the diastereoisomers on silica gel or Florisil undergoes complete or partial hydrolysis to the alcohol (18).

Reactions using Metal-centred Chiral Ligands.—A variety of complexes of the type [Fe(η^4-diene)$(CO)_2$L] and [Fe(η^5-dienyl)$(CO)_2$L]$^+$ (L = phosphine, arsine, or isocyanide) have been prepared, and exhibit reactivities which in many cases parallel those of their tricarbonyl analogues. The use of chiral ligands (L*) thus presents not only the possibility of a potential method for the resolution of diastereoisomeric pairs in cases of substituted diene or dienyl complexes such as (2), but also the potential for asymmetric induction, most importantly in the reaction of [Fe(η^5-dienyl)$(CO)_2$L*]$^+$ salts with achiral nucleophiles to form a new chiral carbon centre.

Thus, $CoCl_2$-catalysed substitution of $[Fe(CO)_5]$[13] with (+)-$PPh_2(C_{10}H_{19})$ (L*) yields the $[Fe(CO)_4L^*]$ complex (19) [Scheme (*b*)] which on photochemical substitution with cyclohexa-1,3-diene yields (20); hydride abstraction using CPh_3BF_4 yields the salt (21). Significantly, nucleophilic attack on (21) proceeds with some degree of asymmetric induction. Thus, reaction with CN^- yields the 5-*exo*-cyano-complex (22a,b) which ^{13}C and ^{31}P n.m.r. studies show clearly to exist as a mixture of two diastereoisomers which is *not* equimolar but in the ratio of *ca.* 2 : 1. This therefore essentially provides a synthesis of enantiomerically enriched 5-substituted cyclohexa-1,3-dienes; we are currently examining reactions with other nucleophiles and are trying to improve the degree of asymmetric induction by judicious choice of L*.

Experimental

N.m.r. and i.r. spectra were recorded on JEOL FX-100 and Pye Unicam SP 2 000 instruments respectively. Optical rotations were measured on a Bellingham and Stanley polarimeter at a wavelength of 589 nm in all cases.

All reactions were conducted under nitrogen using purified, degassed solvents. The compounds [Fe(η^5-C_6H_7)$(CO)_3$]BF_4,[14] [Fe(η^5-C_6H_6OMe-2)$(CO)_3$]BF_4,[15] CPh_3BF_4,[16] (*S*)(+)-PMePrPh (+16.8°),[17] (+)-$PPh_2(C_{10}H_{19})$ (+94°),[18] (*S*)(+)-PPh_2-(C_5H_{11}) (+42°),[18] and (−)-NH(Me)[CH(Me)Ph] (−74°)[19] were prepared by literature methods. (−)-Menthol (−50°) and (*S*)(−)-$HOCH_2CH(Me)Et$ (−6.3°) were obtained commercially. Optical rotations given in parentheses were obtained using solvents and concentrations given in the literature and agree with published values.

(*a*) *Preparation of Complexes* (4a,b).—To a stirred suspension of complex (1) (2.5 g, 8.2 mmol) in CH_2Cl_2 (30 cm^3) was added (+)-$PPh_2(C_{10}H_{19})$ (2.9 g, 9.0 mmol). Immediate dissolution occurred to give a yellow solution which was stirred for 30 min. The yellow gum obtained on removal of solvent under reduced pressure solidified on standing in diethyl ether (100 cm^3) for 1 h at 0 °C. The pale yellow solid (5.0 g) was filtered off, washed repeatedly with diethyl ether, and dried under vacuum. Yield: 97% (Found: C, 59.0; H, 6.05. Calc. for $C_{31}H_{36}BF_4FeO_3P$: C, 59.05; H, 5.75%). I.r. (CH_2Cl_2): 2 053 and 1 993br cm^{-1}.

Complexes (3a,b), (5a,b), and (6a,b) were prepared in an identical manner. Yield of (3a,b): 63% (Found: C, 48.05; H, 4.70. Calc. for $C_{19}H_{22}BF_4FeO_3P$: C, 48.35; H, 4.70%). I.r. (CH_2Cl_2): 2 054 and 1 992br cm^{-1}. Yield of (5a,b): 86% (Found: C, 55.65; H, 4.85. Calc. for $C_{26}H_{28}BF_4FeO_3P$: C, 55.55; H, 5.05%). I.r. (CH_2Cl_2): 2 052 and 1 994br cm^{-1}. Yield of (6a,b): 98% (Found: C, 58.2; H, 6.05. Calc. for $C_{32}H_{38}BF_4FeO_4P$: C, 58.2; H, 5.80%). I.r. (CH_2Cl_2): 2 052 and 1 995br cm^{-1}.

(*b*) *Separation of Complexes* (4a,b).—The mixture of (4a,b) (9.0 g) was dissolved in CH_2Cl_2 (75 cm^3) and, after filtration, diethyl ether (30 cm^3) was added dropwise with stirring until precipitation began to occur. More CH_2Cl_2 (20 cm^3) was added to redissolve the precipitate, and the solution was cooled for 1 d at −30 °C. Filtration yielded 2.89 g of the phosphonium salt showing an 8 : 1 enrichment in one diastereoisomer. Isolation of further fractions, followed by repeated crystallization, gave a total yield of 3.17 g (70%) of the less soluble diastereoisomer (4a) shown to be pure by ^{31}P n.m.r. spectroscopy. Later fractions gave a smaller yield, 1.83 g (41%), of the more soluble diastereoisomer (4b) of *ca.* 90% purity as judged by ^{31}P n.m.r. spectroscopy.

(*c*) *Reduction of Complexes* (4a,b) *by* $LiAlH_4$.—Finely powdered (4a,b) (diastereoisomeric mixture) (1.0 g, 1.59 mmol) was suspended in dry tetrahydrofuran (40 cm^3) at 0 °C and $LiAlH_4$ (0.117 g, 3.08 mmol) was added in three portions. The reaction mixture was stirred until the i.r. spectrum indicated complete consumption of starting material (22 h). The reaction mixture was treated cautiously with 20% sodium potassium tartrate solution (50 cm^3) and extracted

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† Tris[3-(perfluorobutyryl)bornan-2-onato]europium(III).

with diethyl ether (50 cm^3). Drying over $MgSO_4$, followed by removal of solvent and chromatography of the residue on Grade II alumina using light petroleum (b.p. 40—60 °C) as eluant, gave $[Fe(\eta^4\text{-}C_6H_8)(CO)_3]$ (0.190 g, 54% yield), identified by a comparison of its i.r. and ^{1}H n.m.r. spectra with those of an authentic sample.

(*d*) *Preparation of Complexes* (10a,b).—To a stirred suspension of compound (1) (1.9 h, 6.2 mmol) and (−)-menthol (2.0 g, 12.8 mmol) in CH_2Cl_2 (40 cm^3) was added $NEtPr^i_2$ (0.960 g, 7.4 mmol). After stirring for 10 min at room temperature a clear yellow solution was formed which was stirred for an additional 30 min. Solvent was removed under reduced pressure and the residue extracted with light petroleum (b.p. 40—60 °C). The yellow oil was chromatographed on a Grade II alumina column using light petroleum (b.p. 40—60 °C)–diethyl ether (80 : 20) as eluant to give the product (10a,b) (2.2 g) as a yellow oil. An analytical sample was purified by distillation (102 °C, *ca.* 1.34 Pa). Yield: 95% (Found: C, 61.6; H, 7.10. Calc. for $C_{19}H_{26}FeO_4$: C, 60.95; H, 7.00%). I.r. (hexane): 2 044 and 1 985br cm^{-1}.

Complexes (9a,b) and (11a,b) were prepared in an identical manner. Yield of (9a,b): 98% (Found: C, 55.3; H, 5.95. Calc. for $C_{14}H_{18}FeO_4$: C, 54.9; H, 5.95%). I.r. (hexane): 2 044 and 1 988br cm^{-1}. Yield of (11a,b): 93% (Found: C, 59.35; H, 6.90. Calc. for $C_{20}H_{28}FeO_5$: C, 59.4; H, 7.00%). I.r. (hexane): 2 042 and 1 983br cm^{-1}.

(*e*) *Separation of Complexes* (10a,b) *and* (11a,b) *and Regeneration of* (2).—The diastereoisomeric pair (10a,b) was separated by chromatography on silica gel preparative plates using light petroleum (b.p. 40—60 °C)–ethyl acetate (95 : 5) as eluant. A complete separation (as judged by ^{13}C n.m.r. spectroscopy) in a total yield of 43% was achieved. Complexes listed in the Table as (10a) and (10b) were recovered from the lower and upper bands of the plates respectively. The diastereoisomers of (11a,b) were separated in a similar manner in a total yield of 75% using light petroleum (b.p. 40—60 °C)–diethyl ether (90 : 10) as eluant. The compounds listed as (11a) and (11b) in the Table were recovered from the upper and lower bands of the plates respectively.

The dienyl salt (2) was regenerated by dissolution of the separated diastereoisomers (*ca.* 360 mg) in diethyl ether (15 cm^3) at 0 °C, followed by addition of a small excess of HPF_6 (75% aqueous). The dienyl salt precipitated immediately and was filtered off, washed with diethyl ether, and reprecipitated from acetone–diethyl ether.

The two samples of complex (2) recovered exhibit equal but opposite optical rotations: (*S*)(+) isomer [generated from (11a)], α(589 nm, 20 °C, 6 g 100 cm^{-3} in MeCN, 1 dm) = +120°; (*R*)(−) isomer [generated from (11b)], $\alpha = -116°$. A rotation of +115° has been recently reported for the (*S*)(+) isomer prepared by an unpublished method.[11]

(*f*) *Preparation of Complexes* (15a,b).—To a stirred suspension of compound (1) (1.73 g, 5.66 mmol) in CH_2Cl_2 (40 cm^3) was added (−)-NH(Me)[CH(Me)Ph] (0.804 g, 5.94 mmol). After stirring for 10 min, at room temperature, a clear yellow solution was formed. A small excess of $NEtPr^i_2$ (0.842 g, 6.51 mmol) was added and the solution stirred for 30 min. After removal of solvent under reduced pressure the residue was extracted with light petroleum (b.p. 40—60 °C) (100 cm^3) to give a pale yellow solid (1.96 g) which was dried under vacuum. Yield: 98% (Found: C, 61.3; H, 5.60; N, 3.70. Calc. for $C_{18}H_{19}FeNO_3$: C, 61.2; H, 5.45; N, 3.95%). I.r. (hexane): 2 042 and 1 984br cm^{-1}.

Complexes (16a,b) are prepared in an identical fashion and isolated as a yellow oil. Yield: 98% (Found: C, 59.5; H, 5.85; N, 3.50. Calc. for $C_{19}H_{21}FeNO_4$: C, 59.55; H, 5.55; N, 3.65%). I.r. (hexane): 2 040, and 1 983br cm^{-1}.

(*g*) *Separation of Complexes* (15a,b).—A mixture of isomers (15a,b) (2.3 g) was dissolved in light petroleum (b.p. 40—60 °C) (40 cm^3) and kept at 4 °C overnight. Filtration yielded 0.470 g of pure diastereoisomer (15a), and further fractions eventually yielded a total of 0.740 g (64%) of pure (15a). Attempts to obtain pure samples of (15b) were frustrated by the increasingly poor crystallinity of the later fractions.

Attempted separation of isomers (15a,b) or (16a,b) by chromatography on silica gel plates using diethyl ether as eluant yielded only (17) and (18) respectively as the single products recovered from the single bands which developed.

(*h*) *Preparation of Complex* (19).—The compounds (+)-$PPh_2(C_{10}H_{19})$ (2.45 g, 7.55 mmol) and $CoCl_2{\cdot}2H_2O$ (0.04 g, 0.24 mmol) were added to toluene (30 cm^3) and the stirred solution brought to reflux. Pentacarbonyliron (2.96 g, 15.1 mmol) was added and the reaction mixture was refluxed until the i.r. spectrum indicated completion of reaction (*ca.* 4.5 h). The catalyst and excess of phosphine were removed by eluting the cold reaction mixture through a $CoCl_2{\cdot}6H_2O$–alumina–silica gel (5 g : 20 g : 20 g) column with benzene. Solvent and excess of $[Fe(CO)_5]$ were removed under reduced pressure, and the residue was chromatographed on a silica gel column using light petroleum (b.p. 40—60 °C)–dichloromethane (90 : 10) as eluant to give a yellow oil (2.9 g) which solidified on cooling. An analytical sample was obtained by sublimation (130 °C, *ca.* 1.34 Pa). Yield: 78% (Found: C, 63.35; H, 5.85. Calc. for $C_{26}H_{29}FeO_4P$: C, 63.4; H, 5.95%). I.r. (hexane): 2 042, 1 977, 1 947, and 1 937 cm^{-1}.

(*i*) *Preparation of Complexes* (20) *and* (21).—Cyclohexa-1,3-diene (0.650 g, 8.12 mmol) and complex (19) (2.0 g, 4.06 mmol) were dissolved in dry benzene (250 cm^3) and the resulting solution was irradiated for 44 h in a quartz reactor using a 90-W medium-pressure lamp. The progress of the reaction was monitored by i.r. spectroscopy. After removal of solvent, the resulting oil was chromatographed on Grade I alumina using light petroleum (b.p. 40—60 °C)–ethyl acetate (97.5 : 2.5) as eluant. Removal of solvent gave the product (20) as a yellow oil (1.2 g). An analytical sample was purified by sublimation to separate (20) from the small amounts of $[Fe(\eta^4\text{-}C_6H_8)(CO)_3]$ and $[Fe(CO)_3L^*_2]$ also formed (120 °C, *ca.* 1.34 Pa). Yield: 57% (Found: C, 69.95; H, 7.45. Calc. for $C_{30}H_{37}FeO_2P$: C, 69.75; H, 7.25%). I.r. (hexane): 1 978 and 1 925 cm^{-1}.

The compound CPh_3BF_4 (0.679 g, 2.06 mmol) was added to a solution of (20) (1.12 g, 2.17 mmol) in CH_2Cl_2 (20 cm^3). After stirring at room temperature for 30 min, the solution was filtered and diethyl ether was added to the filtrate to precipitate the product as a yellow solid. Cooling to 0°C, followed by filtration and washing with diethyl ether, gave compound (21) (0.750 g, yield 60%) (Found: C, 59.7; H, 6.25. Calc. for $C_{30}H_{36}BF_4FeO_2P$: C, 59.8; H, 6.05%). I.r. (CH_2Cl_2): 2 037 and 1 997 cm^{-1}.

(*j*) *Preparation of Complexes* (22a,b).—Potassium cyanide (0.345 g, 5.31 mmol) was added slowly to a solution of complex (21) (0.640 g, 1.06 mmol) in acetone–water (1 : 1, 25 cm^3). The mixture was stirred at room temperature until the i.r. spectrum indicated complete reaction (*ca.* 20 min). Water (40 cm^3) was added and the solution was extracted with diethyl ether (3 × 75 cm^3). After drying with $MgSO_4$ and removal of solvent, the residue was chromatographed on a Grade II alumina column using light petroleum (b.p. 40—60 °C)–ethyl acetate (90 : 10) as eluant. Removal of solvent gave the product (0.430 g) which was dried under vacuum to give a yellow solid. Phosphorus-31 n.m.r. analysis of the crude product before chromatography showed the same diastereoisomeric excess as that of the pure product obtained after chromatography. Yield: 75% (Found: C, 68.6; H, 7.35; N, 2.40. Calc. for $C_{31}H_{36}FeNO_2P$: C, 68.75; H, 6.70; N, 2.60%). I.r. (hexane): 1 983 and 1 932 cm^{-1}.

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