Organometallic Compounds in Organic Synthesis. Part 12.[1] Methods of Determination of the Stereochemistry of Tricarbonylcyclohexa-1,3-dieneiron Complexes

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The steric configuration (α- or β-) † of a substituent attached to an sp^3 carbon atom in tricarbonylcyclohexadieneiron complexes can be determined by ^{1}H n.m.r. spectroscopy if both epimers are available. With only one epimer present, the most useful method involves examination of the vicinal coupling constants of hydrogens attached to sp^3 carbon atoms. The β-H atoms have a vicinal coupling constant of 10—12 Hz and the corresponding α-H atoms have a value of *ca.* 8 Hz. The CH$_2$ splitting patterns are indicative of stereochemistry when flanked by two vicinal protons. In some cases simplification of the spectrum by use of a paramagnetic shift reagent is necessary for evaluation. Usually $\delta_{(\beta\text{-substituent})} > \delta_{(\alpha\text{-substituent})}$. The CO$_2$Me substituents show $\delta_{(\beta\text{-CO}_2\text{Me})} > 3.63 > \delta_{(\alpha\text{-CO}_2\text{Me})}$ and often, but not invariably, $\delta_{(\beta\text{-H})} > \delta_{(\alpha\text{-H})}$. Computer simulation confirms the expected pattern. Aromatic solvent induced shifts are not useful; ^{13}C n.m.r. have only a limited usefulness and require both isomers; mass spectrometric fragmentation is intepretable in steric terms, but is not useful for definition. ^{1}H N.m.r. spectra of the isomeric cations (45), (46), and the alkyl analogue (47) show indications of utility in connection with 6-H, but more examples are needed. The vicinal coupling of CH$_2$ seems to be at present the only reliable method for the assignment of configuration in neutral diene complexes.

THE steric configurations of substituents relative to Fe(CO)$_3$ are of fundamental importance in discussing the thermodynamic stabilities and the reactivities of tricarbonylcyclohexa-1,3-dieneiron complexes. Empirical rules for their determination which seem to hold are (*a*) cationic η^5 complexes react under kinetic control entirely or mainly on the α-face;[2] (*b*) hydride abstraction by Ph$_3$C$^+$ usually occurs at the α-face and is prevented by the presence of a substituent or adjacent α-substituent;[2d,3] (*c*) some electrophilic substitutions, *e.g.* Friedel–Crafts acetylation, mainly occur on the β-face;[4] and rearrangements catalyzed by acid occur on the β-face.[3b,5] Deductions from these rules lead to a coherent set of conclusions in accord with experimental results.

However, a direct physical means for determination of the configuration of a complex, other than X-ray analysis, would prove useful in routine applications. The possible applicability of n.m.r. and mass spectra in this connection has been examined.
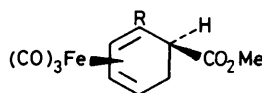
RESULTS AND DISCUSSION

^{1}H N.m.r. techniques for steric determinations in general involve chemical shifts and coupling constants, particularly with the use of different solvents and lanthanide shift reagents (LSR).[6] ^{1}H N.m.r. shifts on the dienyl segment of both neutral and cationic complexes have been extensively used to assign regiochemistry.[2d,2e,7] An analysis has been made[8] of long range H,H coupling in relation to the planarity of the diene segment. The examination for steric assignment
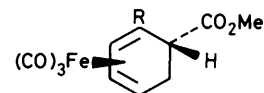
described herein is concerned with the protons attached to tetrahedral carbon atoms and to the substituent itself.
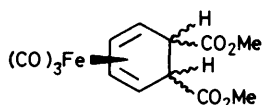
^{1}H *N.m.r. Chemical Shifts.*—The epimeric diesters (1) and (2)[9] have had their structures confirmed by X-ray analysis.[10] The chemical shift of the 6β-CO$_2$Me group in the diester (1) (δ 3.66) is slightly higher than that of the
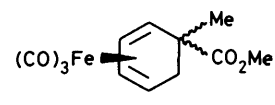

(1) R = CO$_2$Me
(3) R = H
(5) R = OMe

(2) R = CO$_2$Me
(4) R = H
(6) R = OMe

(7) β,β-(CO$_2$Me)$_2$
(8) α,α-(CO$_2$Me)$_2$
(11) α,β-(CO$_2$Me)$_2$

(9) β-CO$_2$Me, α-Me
(10) α-CO$_2$Me, β-Me

(12)
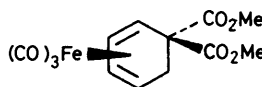
6α-CO$_2$Me group in compound (2) (δ 3.60), in agreement with the generally observed deshielding effect of Fe(CO)$_3$ on β-substituents.[3c,7,11] The monoesters (3) and (4), reported earlier as a mixture,[7,12] have now been sepa-

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† We have used for some time the letters β- and α- to define the steric relation of a group on the same or opposite face to the metal, replacing *endo-* ar *exo-*, respectively, which are misleading in relation to the approach of reagents to the complexed carbon system. The alternatives *syn-* and *anti-* are more acceptable, but the letters are purely descriptive and readily used, and have no steric connotations, except in the steroid series which are analogous with the formulae as written here.

rated.[9] Only one isomer of the pair was observed to undergo hydride abstraction and on this basis it was assigned structure (3). This assignment is in accord with the chemical shift of the β-CO_2Me group (δ 3.65) in
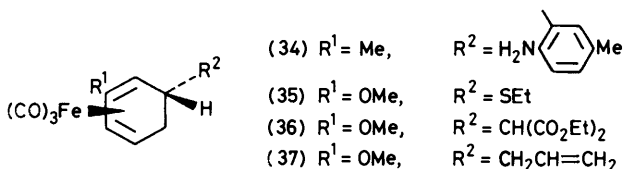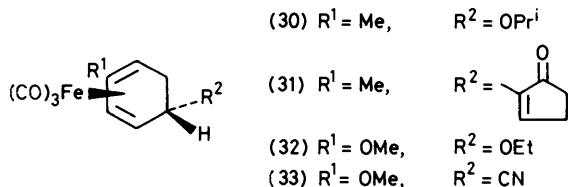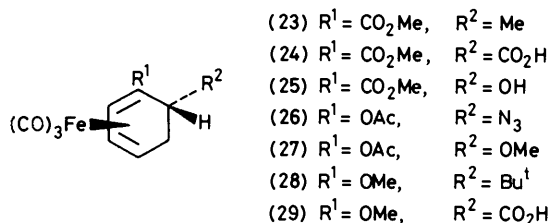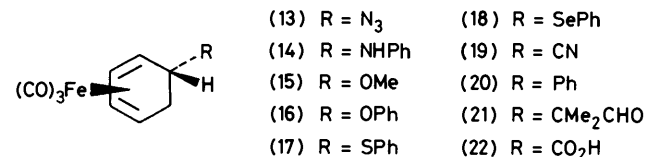
$\delta_{\beta\text{-CO}_2\text{M}}$	$\delta_{\alpha\text{-CO}_2\text{Me}}$	$\delta^{\beta\text{-CO}_2\text{Me}}_{\alpha\text{-CO}_2\text{Me}}$ [a]	$\delta_{\beta\text{-H}}$	$\delta_{\alpha\text{-H}}$	$\delta^{\beta\text{-H}}_{\alpha\text{-H}}$ [b]
(1) 3.66	(2) 3.60	0.06	(3) 3.50	(1) 2.40	1.10
(3) 3.65	(4) 3.56	0.09	(4) 2.90	(3) 2.48	0.42
(5) 3.63 [c]	(6) 3.60 [c]	0.03	(6) 3.30		
(7) 3.63	(8) 3.55	0.08	(8) 3.26	(7) 2.92	0.34
(9) 3.76	(10) 3.63	0.13			
(11) 3.70	(11) 3.63	0.08	(11) 3.40	(11) 2.97	0.43
(11) 3.73 [d]	(12) 3.63	0.10			

[a] $\delta_{\beta\text{-CO}_2\text{Me}} - \delta_{\alpha\text{-CO}_2\text{Me}}$. [b] $\delta_{\beta\text{-H}} - \delta_{\alpha\text{-H}}$. [c] See ref. 7. [d] See refs. 13 and 28.

the monoester (3) which is higher than that of the α-CO_2Me group (δ 3.56) in compound (4).

Table 1 gives the chemical shifts of a range of CO_2Me groups in compounds (1)—(12) which, on the assumption that a β-CO_2Me group resonates at lower field (δ ≤ 3.63)

(13) R = N_3	(18) R = SePh
(14) R = NHPh	(19) R = CN
(15) R = OMe	(20) R = Ph
(16) R = OPh	(21) R = CMe_2CHO
(17) R = SPh	(22) R = CO_2H

(23) R¹ = CO_2Me, R² = Me
(24) R¹ = CO_2Me, R² = CO_2H
(25) R¹ = CO_2Me, R² = OH
(26) R¹ = OAc, R² = N_3
(27) R¹ = OAc, R² = OMe
(28) R¹ = OMe, R² = Bu^t
(29) R¹ = OMe, R² = CO_2H

(30) R¹ = Me, R² = OPr^i
(31) R¹ = Me, R² = (cyclopentanone)
(32) R¹ = OMe, R² = OEt
(33) R¹ = OMe, R² = CN

(34) R¹ = Me, R² = H_2N—C_6H_4—Me
(35) R¹ = OMe, R² = SEt
(36) R¹ = OMe, R² = CH(CO_2Et)_2
(37) R¹ = OMe, R² = CH_2CH=CH_2

than an α-CO_2Me group (δ ≥ 3.63), form a self-consistent set of data, supported by consideration of the CH_2 splitting pattern data below. Assignments of configuration are consistent with other information which

includes, in some cases, the relative rates of hydrolysis.[9] A certain assignment of stereochemistry on such grounds requires both isomers, the difference between which is in the range δ 0.03—0.13.

The proton attached to the same carbon as the allylic substituent also shows (Table 1) significant effects of its α- or β-configuration; the β-H atom resonates at lower field than the corresponding α-H atom by δ 0.34—1.10. These and previous discussions indicate that available pairs can be distinguished by $\delta_{\beta\text{-CO}_2\text{Me}} > \alpha\text{-CO}_2\text{Me}$ and $\delta_{\beta\text{-H}} > \delta_{\alpha\text{-H}}$.

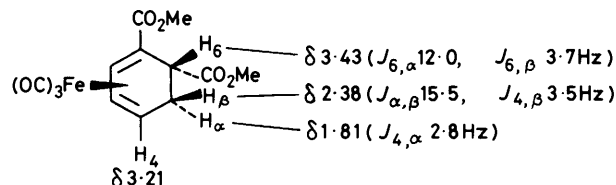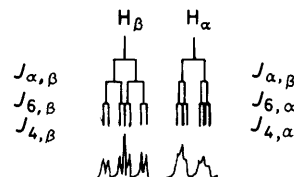*Splitting Patterns.*—A CH_2 group adjacent to the carbon to which an α- or a β-substituent is attached

FIGURE 1 Methylene splitting pattern which is characteristic of an adjacent α-substituent

displays splitting patterns characteristic of the stereochemistry. In some cases, the patterns are discernible only in the presence of a lanthanide shift reagent (LSR). In the following discussion, the methylene splitting pattern characteristic of an adjacent α-substituent is referred to as ' CH_2(α)-splitting '. Analogously, ' CH_2(β)-splitting ' implies the pattern for a β-substituent.

α-Stereochemistry. A range of α-substituted complexes [e.g. complexes (13)—(37)] show CH_2 splitting patterns similar to that of the α-CO_2Me diester (2) (Figure 1). The compounds (13)—(21), (25)—(28), and (30)—(37) were available from the addition of appropriate nucleophiles to the corresponding dienyl salts (see Experimental section for references). The assignment of the α-stereochemistry to these compounds, prepared either by sequence complexation and acid-catalyzed isomerization [compound (23)], or by base-catalyzed hydrolysis [compounds (22), (24), and (29)] results from the fact that they are unaffected by Ph_3C^+.[9]

The coupling constants and the chemical shifts responsible for the pattern were deduced by application of double resonance techniques to the spectra with reasonably large Δν/J values. The spin-decoupling also showed that the long-range couplings would be insignificant in defining this pattern, the important contribution being geminal and vicinal couplings. The coupling constants are, surprisingly, of the same order

of magnitude. Some representative examples are given in Table 2.

A computer-simulation (NMRSIM program [13]) of the $CH_2(\alpha)$-splitting was performed, based on the J and δ values indicated for the α-CO_2Me diester (2) in Figure 1. The $\Delta\delta$ $(= \delta^\beta_{\alpha\text{-H of CH}_2} - \delta_{\alpha\text{-H of CH}_2})$ was varied. Re-

Magnetically, the CH_2 protons can therefore be made significantly non-equivalent in the presence of a paramagnetic shift reagent or by appropriate ligand displacement and the simplified pattern can lead to the deduction of coupling constants. The use of LSR is experimentally superior to ligand displacement.
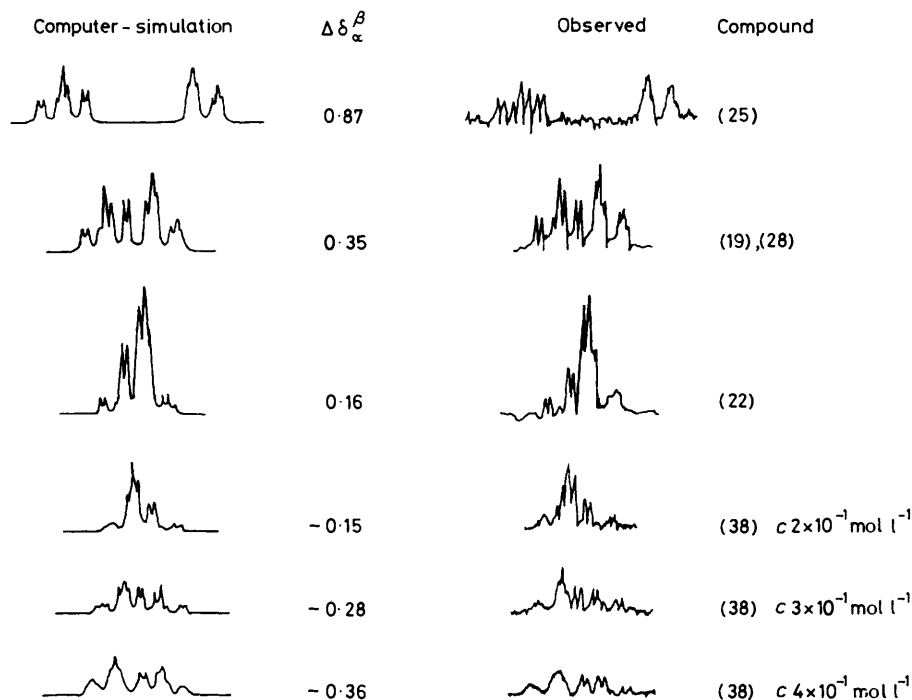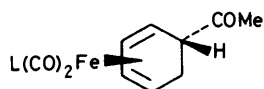
Computer-simulation	$\Delta\delta^\beta_\alpha$	Observed	Compound
	0·87		(25)
	0·35		(19),(28)
	0·16		(22)
	−0·15		(38) c 2×10^{-1} mol l^{-1}
	−0·28		(38) c 3×10^{-1} mol l^{-1}
	−0·36		(38) c 4×10^{-1} mol l^{-1}

FIGURE 2 Computer-simulated and observed CH_2 (α)-splitting patterns $\{C = [\text{Eu(fod-}d_9)_3]\}$

sults are depicted in Figure 2. Several compounds corresponded to the patterns where $\Delta\delta^\beta_\alpha = 0.35$—1.00, e.g. compounds (13)—(21), (23)—(37), and (39).

L(CO)$_2$Fe [structure: cyclohexadienyl–Fe complex with COMe and H substituents]

(38) L = CO
(39) L = PPh$_3$

An example of a more complicated pattern, possibly due to a small $\Delta\delta^\beta_\alpha$, is provided by the α-COMe complex (38) whose stereochemistry has been determined by Lewis and his co-workers.[2a] The replacement of one carbonyl group on Fe by a Ph_3P group (39)[4c] results in the typical $CH_2(\alpha)$-splitting pattern (Figure 1), which indicates that $\Delta\delta^\alpha_\beta$ may be increased appreciably by appropriate ligand displacements.

In the presence of Eu(fod-d_9)$_3$ (4×10^{-1} mol l^{-1}), compound (38) showed $CH_2(\alpha)$-splitting, but with effective reversal of the order of chemical shifts (δ) for H_β and H_α of the methylene protons. The computer simulation corresponded to $\Delta\delta^\beta_\alpha$ −0.36. The LSR, upon complexation with the α-acetyl group, produces a greater downfield shift at the adjacent α-H atom than at the corresponding β-H atom.

β-Stereochemistry. Because of difficulties in preparation, a lesser number of β-substituents was available. In the presence of Eu(fod-d_9)$_3$ (1.5×10^{-1} mol l^{-1}) the β-CO_2Me ester (1) gave the pattern shown in Figure 3,
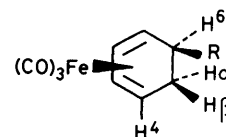
TABLE 2

Some examples to illustrate the consistency of coupling constants (Hz) in a given steric series

(CO)$_3$Fe [structure: cyclohexadienyl–Fe complex with H^6, R, Hα, Hβ, H^4 labels]

Compd.	$J_{\alpha,\beta}$	$J_{6,\beta}$	$J_{6,\alpha}$	$J_{4,\beta}$	$J_{4,\alpha}$
(2)	15.5	12.0	3.7	3.5	2.8
(16)	15.5	11.0	4.0	3.5	2.8
	(15.1)[a]		(9.1)[a]		
(18)	15.5	10.0	4.0	4.0	3.0
(23)	16.0	10.0	4.0	3.5—4.0	3.0
(25)	15.0	10.0—11.0	3.5—4.0	3.5	2.5—3.0
(30)	15.0	10.0	4.0	3.5	3.0

[a] See ref. 4a.

from which $\Delta v/J$ being significantly large, the appropriate δ and J were extracted in the usual way for computer-simulation studies.

The simulation of the $CH_2(\beta)$-splitting by variation of $\Delta\delta^\beta_\alpha$ gave patterns that resemble those which resulted

$$J_{\alpha,\beta}$$
$$J_{6,\beta}$$
$$J_{4,\beta}$$

H_β H_α

$$J_{\alpha,\beta}$$
$$J_{6,\alpha}$$
$$J_{4,\alpha}$$

CO_2Me
$(OC)_3Fe$
CO_2Me
—H6 —— $\delta\,4\cdot86\,(J_{6,\alpha}\,8\cdot0,\quad J_{6,\beta}\,6\cdot0\,Hz)$
—Hβ —— $\delta\,3\cdot62\,(J_{\alpha,\beta}\,15\cdot5,\quad J_{4,\beta}\,3\cdot3\,Hz)$
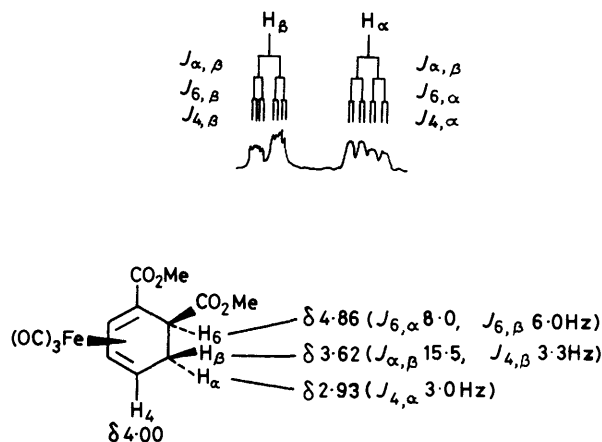—Hα —— $\delta\,2\cdot93\,(J_{4,\alpha}\,3\cdot0\,Hz)$
H_4
$\delta\,4\cdot00$

FIGURE 3 Methylene splitting pattern which is characteristic of an adjacent β-substituent {with [Eu(fod-d$_9$)$_3$] 1.5 × 10^{-1} mol l^{-1}}

from sequential addition of LSR to the β-CO_2Me diester (1) (Figure 4).

Simulation of the $CH_2(\beta)$-splitting of compounds (3), (40), and (41) required $\Delta\delta_\alpha^\beta$ 0.35. Both β-Me complexes (42) and (43) gave patterns that correspond to $\Delta\delta_\alpha^\beta$ —0.60 and —0.80, respectively. The structures (41), (42), and (43) have been confirmed either by conversion

into known compounds [e.g.[9] (41) ⟶ (3)] or by hydride abstraction [e.g.[2d] (43)]. It is likely that the β-H of the CH_2 group of compounds (42) and (43) is that which resonates at a higher field than its epimeric α-H.

Consistency in coupling constants for a given steric series, in spite of the diversity of structural types in substituents, suggests that the dihedral angles, possibly featuring Karplus relations,[14] may be approximately uniform for these complexes. A justification comes from the torsional angles extracted from the X-ray

R^1
$(CO)_3Fe$
—H
R^2
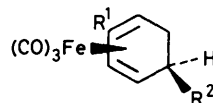
(40) R^1 = H, R^2 = CO_2H
(41) R^1 = H, R^2 = $CO_2CH_2COC_6H_4Br$–p
(42) R^1 = H, R^2 = Me
(43) R^1 = OMe, R^2 = Me

structures[10] of compounds (1), (2), (11), and (44) (Table 3).

Lanthanide Induced Shifts (LIS); Stereochemistry and Basicity.—Shift reagents have been used in classical organic chemistry[6] and, in one instance, were used to
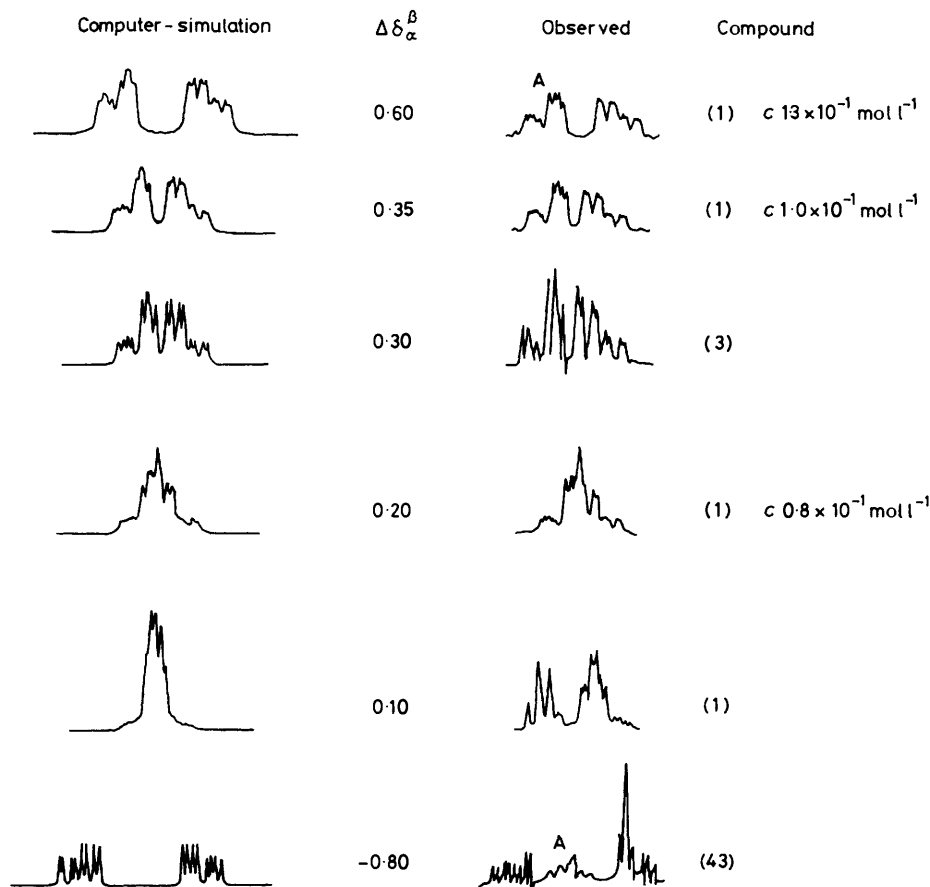
Computer-simulation	$\Delta\delta_\alpha^\beta$	Observed	Compound
	0·60	A	(1) c 13×10^{-1} mol l^{-1}
	0·35		(1) c 1·0×10^{-1} mol l^{-1}
	0·30		(3)
	0·20		(1) c 0·8 × 10^{-1} mol l^{-1}
	0·10		(1)
	—0·80	A	(43)

FIGURE 4 Computer-simulated and observed CH_2 (β)-splitting patterns. A = methine 6-H in compounds (1) and (43); c = [Eu(fod-d$_9$)$_3$]

differentiate isomeric tricarbonyldieneiron complexes in a mixture.[15]

Figure 5 shows the shifts of CO_2Me resonances on sequential addition of $Eu(fod-d_9)_3$ to $CDCl_3$ solutions of the diesters (1), (2), and (11). With increasing Eu-$(fod-d_9)_3$ concentration the α-CO_2Me signal of compound

(44)
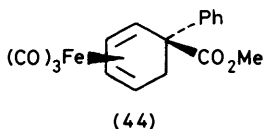
(11) increased in δ to a greater extent than the β-CO_2Me signal of the same molecule. This was anticipated since $Fe(CO)_3$ should hinder the complexing of the β-CO_2Me group.

Another indication from shift studies on compounds (1) and (2) is that the basicity of the 1-CO_2Me group compared with the 6-CO_2Me group is high, which has been already inferred from very slow alkaline hydrolysis of the 1-CO_2Me group.[9] The slope of the plot of LIS *vs.* concentration of the reagent is a measure of binding.[16] Both compounds (1) and (2) showed a significantly larger slope for 1-CO_2Me than 6-CO_2Me. The much greater selectivity that manifests between the 1- and 6β-CO_2Me groups of compound (1) compared with the α- and β-CO_2Me groups of compound (11), must be a composite of steric and basicity effects. Complexing occurs to C=O rather than OMe,[16c] so the greater polarisation of the carbonyl group of 1-CO_2Me is probably effected by electron-donation from the diene-$Fe(CO)_3$ system.

FIGURE 5 Shifts of CO_2Me resonances on sequential addition of $Eu(fod-d_9)_3$. — · — · —, β-CO_2Me; — — — —, α-CO_2Me; ——, 1-CO_2Me

The 6α-H of compound (1), the 6β-H of compound (2), and the α- and β-H of compound (11) show significant shifts, probably because of interactions through bonds rather than space.[17]

Aromatic Solvent Induced Shifts (*ASIS*).—The ASIS are useful in assignments of configurations that involve

TABLE 3

Dihedral angles from *X*-ray structures [10]

Dihedral angle (°)	Compounds			
	(1)	(2)	(9)	(44) [a]
6(β)—C(6)—C(5)—Hβ	15(1)	0(3)	3(2)	3(3)
6(β)—C(6)—C(5)—Hα	106(2)	118(3)	120(2)	107(5)
6(α)—C(6)—C(5)—Hβ	133(1)	123(2)	114(2)	112(3)
6(α)—C(6)—C(5)—Hα	12(2)	5(2)	32(2)	7(5)
R(4)—C(4)—C(5)—Hβ	57(2)	54(3)	50(2)	30(6)
R(4)—C(4)—C(5)—Hα	64(2)	69(3)	69(2)	81(6)
θ [b]	43.4	42.1	42.5	42.3

[a] For compound (44), the deviations have been calculated from the assumed errors in the location of H atoms from electron density difference maps. [b] θ = the angle between the normals to the planes through C(1), C(2), C(3), C(4), and C(4), C(5), C(6), C(1).

polar groups.[8] The complexes (1), (2), and (11) have been examined (Figure 6) in terms of equation (1).

$$\delta_{CDCl_3} - \delta_{C_6D_6} = \Delta\delta_{C_6D_6}^{CDCl_3} \qquad (1)$$

The ASIS are believed to arise from dipole interactions of benzene with the positive centres of the solute and the

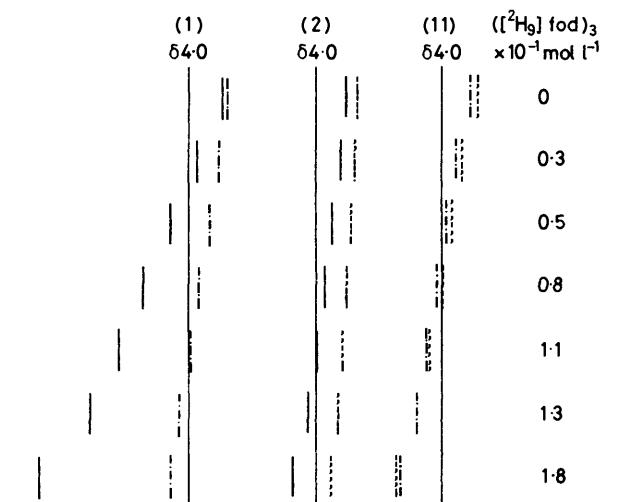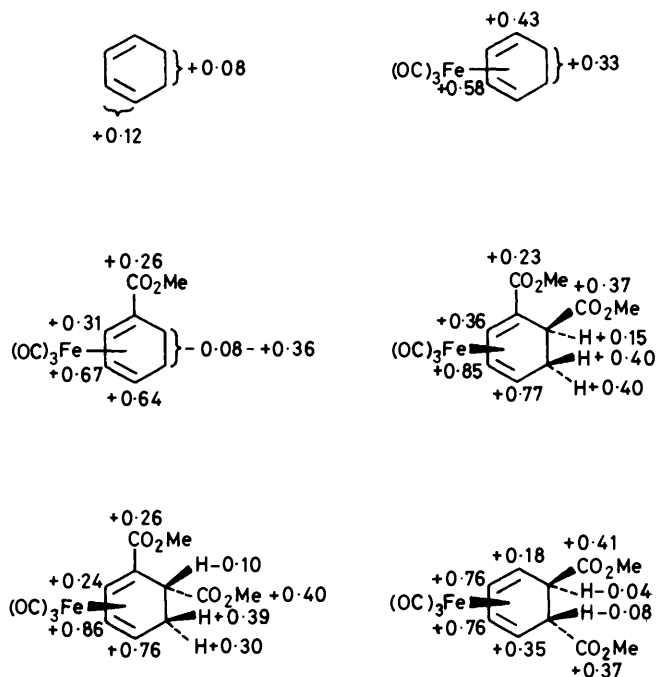FIGURE 6 Aromatic solvent induced shift (ASIS), $\Delta\delta_{C_6D_6}^{CDCl_3}$ [equation (1)] given in p.p.m.

values vary considerably with the structure.[6,18] In this series either or both $Fe(CO)_3$ and CO_2Me could be involved. In the parent tricarbonylcyclohexa-1,3-diene-iron, the $Fe(CO)_3$ produces a very large $\Delta\delta_{C_6D_6}^{CDCl_3}$ compared with the uncomplexed diene. With 1-CO_2Me, an effect in the opposite direction is observed with a reduction of $\Delta\delta_{C_6D_6}^{CDCl_3}$ for the 2-H in compounds (1) and (2). A further 6-CO_2Me group results in a negative $\Delta\delta_{C_6D_6}^{CDCl_3}$ for 6β-H (−0.10) and a positive $\Delta\delta_{C_6D_6}^{CDCl_3}$ for 6α-H (+0.15). However, the complex (11) shows $\Delta\delta_{C_6D_6}^{CDCl_3}$ of −0.08 and −0.04 for β-H and α-H, respectively. It is not at present possible to derive concrete correlations to assist in assigning stereochemistry on the basis of ASIS alone.

CO_2Me in cation (46), which was prepared by acid catalysed demethoxylation of compound (6),[7] appeared at δ 3.51 and 3.83 (triplet). From this somewhat limited data it seems that the generalization $\delta_{\beta\text{-}CO_2Me} > \delta_{\alpha\text{-}CO_2Me}$ and $\delta_{\beta\text{-}H} > \delta_{\alpha\text{-}H}$ may be valid for the cations in this series. Deuterium labelling studies have also indicated that a β-H of the methylene protons resonates at lower field.[5b]

The X-ray structure [19] of tricarbonyl-(η^5-2-methoxy-cyclohexadienylium)iron tetrafluoroborate reveals that 6β-H is approximately parallel to the dienyl system while 6α-H is almost normal to it. Inspection of the coupling constants of 6-H described above would indicate a similar structural feature for 6α-H of compound (46)

TABLE 4

^{13}C N.m.r. chemical shifts (δ, p.p.m., CCl_4) of compounds (1) and (2)

	(2) [1,6α-$(CO_2Me)_2$]	(1) [1,6β-$(CO_2Me)_2$]	$\Delta\delta_{(1)}^{(2)} = \delta_{(2)} - \delta_{(1)}$
$Fe(CO)_3$	209.77 (s)	208.422 (s)	+0.655
CO_2	172.321 (s)	172.716 (s)	−0.395
CO_2	169.989 (s)	170.378 (s)	−0.389
C-2	88.305 (d, $^1J_{CH}$ 177.7 Hz)	87.007 (d, $^1J_{CH}$ 179.7 Hz)	+1.298
C-3	85.059 (dd, $^1J_{CH}$ 171.9, $^2J_{CH}$ 7.8 Hz)	84.539 (d, $^1J_{CH}$ 170.0 Hz)	+0.520
C-1	62.982 (s)	65.839 (s)	−2.857
C-4	58.827 (d, $^1J_{CH}$ 162.1 Hz)	61.034 (d, $^1J_{CH}$ 160.0 Hz)	−2.207
2 × OMe	51.165 (q, $^1J_{CH}$ 146.5 Hz)	50.905 (q, $^1J_{CH}$ 146.5 Hz)	+0.260
C-6	40.646 (d, $^1J_{CH}$ 136.7 Hz)	37.789 (d, $^1J_{CH}$ 136.7 Hz)	+2.857
C-5	30.127 (t, $^1J_{CH}$ 130.9 Hz)	32.724 (t, $^1J_{CH}$ 128.9 Hz)	−2.597

^{13}C N.m.r. Spectra.—Crowding of carbon atoms in organic molecules, shown by ^{13}C resonance at higher fields than similar non-crowded carbon atoms, has been deduced from spectra and has been used for steric assignments in organic molecules.[6] Examination of compounds (1) and (2) using double resonance techniques permits the assignments shown in Table 4. The more
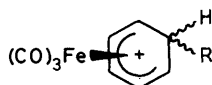
(45) R = β-CO_2Me
(46) R = α-CO_2Me
(47) R = α-Bu^t

compressed isomer (1) shows small upfield shifts (<1 p.p.m.) for $Fe(CO)_3$, both OMe groups, and C-3 compared with the isomer (2). Rather higher upfield shifts can be seen for C-2 and C-6. The remaining carbon atoms of compound (1) show downfield shifts (2—3 p.p.m.) compared with the corresponding atoms in compound (2). While attempts could be made to explain these shifts, based on exact X-ray structures, it is again obvious that the practical organic chemist, faced with a steric assignment would not be greatly helped by this data alone.

Tricarbonylcyclohexadienyliron Cations.—The ^{1}H n.m.r. spectra of the epimeric cations (45) and (46) were examined. The β-CO_2Me cation (45), which was obtained from hydride abstraction from the ester (3), displays a CO_2Me resonance at δ 3.84 and a singlet at δ 3.04 assignable to 6-H. The corresponding protons of the α-

and 6β-H of compound (45). In favourable cases, the splitting of 6-H can be correlated with the stereochemistry, a singlet being characteristic of a β-substituent and a triplet of an α-substituent. For example, the α-Bu^t cation (47),[20] formed from demethoxylation of compound (28), shows its 6β-H as a triplet at δ 2.5.

Mass spectroscopy.—Mass spectral fragmentation of organic stereoisomers can sometimes be logically related to configurations.[21]

Electron impact on diene–$Fe(CO)_3$ complexes is assumed to lead to an electron-deficient system in such a manner that the Fe atom maintains the deficiency at as low a level as possible, which leads to the stepwise loss of CO.[22] If other co-ordinating groups are attached to Fe which are more strongly electron-donating than CO, loss of the diene group from Fe (radical-ion LFe, Table 5) and a corresponding decrease in intensity of the radical-ion FeC_6H_6 is observed. Attachment of an
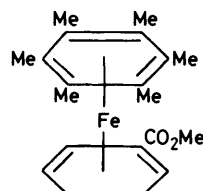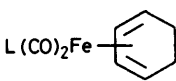

(48)

aromatic ligand to Fe as in compound (48) also results in preferential loss of the diene portion.

The efficient attachment of electron-deficient iron to the aromatic ring in the mass spectrometer seems to

result in aromatization of the complexed diene after loss of CO from the diene–Fe(CO)$_3$ complex. Loss of H or other substituent from sp^3 carbon atoms is required for such aromatization, is stereospecific and involves loss of both β-hydrogen atoms,[23] at least in the case of cyclohexadiene itself. This loss may well occur *via* intermediate transfer of H to Fe, supported by the observation of Fe(C$_5$H$_5$)H as a fragment in the analogous cyclopentadienyl complexes,[24] and C$_6$(Me)$_6$FeH in the

The most useful spectroscopic parameter for distinguishing the α- and β-stereochemistry of a substituent adjacent to CH$_2$ seems, therefore, to be the coupling constants of these H atoms. Those on the same side as the metal have a vicinal coupling constant of *ca.* 10—12 Hz, while for the α-H it is *ca.* 8 Hz. The consistency of the coupling constants leads to the CH$_2$ coupling patterns (Figures 2 and 4) irrespective of the structure of the substituent, providing the CH$_2$ is flanked by two

TABLE 5

Major mass spectral fragments of (*M*) with different L

L(CO)$_2$Fe—⟨hexadiene⟩

(*M*)

		m/z (abundance %)			
Radical-ion	CO	P(OMe)$_3$	PBu$_3$	PPh$_3$	AsPh$_3$
M	220	316	394	454	498
	(7)	(10)	(5)	(6)	(4)
M − CO	192	288	366	426	470
	(33)	(29)	(10)	(11)	(10)
M − 2CO − 2H	162	258	336	396	440
	(9)	(100)	(100)	(26)	(2)
FeC$_6$H$_6$	134	134	134	134	134
(= *M* − 2CO − 2H − L)	(100)	(18)	(3)	(2)	(7)
LFe	84	180	258	318	362
	(10)	(39)	(4)	(81)	(100)
			256 ^{a}		
			(50)		
RFe		87		133	133
		(2)		(3)	(14)
		(R = OMe)		(R = Ph)	(R = Ph)

^{a} *m/z* 256 corresponds to LFe − 2H.

arene complex (48). Migration of a substituent from the ligand to metal has also been observed,[25] attested by the presence of RFe in the spectra of dicarbonyliron complexes (Table 5), FeOMe in the spectra of diester complexes (Table 6), and C$_6$Me$_6$FeOMe in the spectrum of compound (48).

This iron-mediated loss of substituents from the organic ligand is of particular steric interest, in that it defines direct interaction of Fe with a β-substituent. An analysis of the mass-spectral fragments of five isomeric diester complexes (1), (2), (7), (8), and (12) is given in Table 6. The results do indicate that loss of OMe from the molecular ion is more prominent for β-CO$_2$Me, than for α-CO$_2$Me. Again, however, the significance of a given result is likely to be assessable only if a pair of isomers is available.

protons. Usually, also, δ-H$_{(β\text{-substituent})}$ > δ-H$_{(α\text{-substituent})}$ for example, with the esters above δ-H, β-CO$_2$Me > 3.63 > α-CO$_2$Me. However, exceptions have been noted with compounds (42) and (43). It is advantageous in general to be able to compare the two possible isomers.

EXPERIMENTAL

For general conditions see the Experimental section in Part 11.[1]

Availability of Compounds.—The complexes (1)—(4),[9] (5), (6),[7] (7), (8),[9] (9), (10),[9,26] (11),[9] (12),[9,26] (13),[27] (14),[28] (15),[29] (16) [4a,30] (17),[30,31] (18),[30] (19),[2e] (20),[20b,32] (21),[33] (22),[9] (23), (24),[9] (25),[34] (26), (27),[27b] (28),[30a] (29),[9] (30),[1] (31),[35] (32),[2d] (33),[2e] (34),[28] (35),[30] (36),[33] (37),[36] (38),[2a] (39),[4c] (40), (41),[9] (42),[33] (43),[2d] (44),[26] and (47) [20b] were obtained from the methods noted in the references. The dicarbonyliron complexes, the mass spectral fragments of

TABLE 6

Some mass spectral fragments of isomeric tricarbonyl-(η^4-dimethoxycarbonylcyclohexa-1,3-diene)iron complexes

		Relative abundance (%)				
Radical-ion	*m/z*	1,6β-(1)	1,6α-(2)	5β,6β-(7)	5α,6α-(8)	5α,6β-(11)
M	336	0.04	7.5	0.35	11.0	0.1
M − OMe	305	8.5	0.6	7.5	1.2	0.2
M − CO	308	7.5	5.0	3.3	9.0	23.0
M − 2CO	280	43.0	36.0	55.0	65.0	47.5
M − 3CO	252	37.5	39.5	100.0	100.0	100.0
M − Fe(CO)$_3$ − 2H	194	32.5	31.0	3.5	18.0	7.0
FeC$_6$H$_6$	134	100.0	100.0	70.0	81.0	77.0
FeOMe	87	12.0	9.0	33.0	13.0	16.0

which are given in Table 6, have been prepared by boiling tricarbonyl (η^4-cyclohexa-1,3-diene)iron with the appropriate phosphine or arsine.[33]

Tricarbonyl-(η^5-6β-methoxycarbonylcyclohexadienylium)-iron Hexafluorophosphate (45).—Treatment of tricarbonyl (η^4-5β-methoxycarbonylcyclohexa-1,3-diene)iron (3) [9] (100 mg, 0.36 mmol) with $Ph_3C^+ \cdot PF_6^-$ (140 mg, 0.36 mmol) in acetonitrile (2 ml) at ambient temperature for 30 min afforded, upon precipitation from diethyl ether–light petroleum (2 : 1, v/v), a yellow crystalline solid. The solid was dissolved in nitromethane, the solution was filtered, and the solid was reprecipitated by the addition of diethyl ether–light petroleum (2 : 1) and dried (93 mg, 61%). It was identified as the title salt (45); $\nu_{max.}$ (KBr) 2 120, 1 970, and 1 740 cm^{-1}; δ_H (CD$_3$CN) 7.17 (1 H, t, $J_{2.3} = J_{3.4}$ 7 Hz, 3-H), 5.91 (2 H, t, $J_{1,2} = J_{4,5}$ 7 Hz, 2- and 4-H), 4.26 (2 H, d, 1- and 5-H), 3.84 (3 H, s, Bβ-CO$_2$Me), and 3.04 (1 H, s, 6α-H).

Tricarbonyl-(η^5-6α-methoxycarbonylcyclohexadienylium)-iron Hexafluorophosphate (46).—A solution of tricarbonyl-(η^4-1-methoxy-6α-methoxycarbonylcyclohexa-1,3-diene)-iron (6) [7] (500 mg, 1.62 mmol) in nitromethane (0.3 ml) was added as drops, with occasional stirring, to ice cold concentrated H_2SO_4 (1.5 ml) which contained a few drops of formic acid.[1] After 10—15 min, an ice-cold solution (3—5 ml) of NH$_4$PF$_6$ (2—3 g) was added and the mixture was vigorously stirred. The yellow precipitate was filtered off, washed several times with water, and then with diethyl ether. The air-dried salt was dissolved in a minimum amount of nitromethane and filtered into a mixture of diethyl ether–light petroleum (2 : 1; *ca.* 25 ml). The precipitated salt (46) (295 mg, 43%) was dried under reduced pressure; $\nu_{max.}$ (KBr) 2 130, 1 980, and 1 740 cm^{-1}; δ_H (CD$_3$CN) 6.94 (1 H, t, $J_{2.3} = J_{3.4}$ 7 Hz, 3-H), 5.98 (2 H, t, $J_{1,2} = J_{4,5}$ 7 Hz, 2- and 4-H), 4.39 (2 H, t, $J_{1.6\beta} = J_{5,6\beta}$ 7 Hz, 1- and 5-H), 3.83 (1 H, t, 6β-H), and 3.51 (3 H, s, 6α CO$_2$Me).

η^6-Hexamethylbenzene-(η^4-2-methoxycarbonylcyclohexa-1,3-diene)iron (48).—A suspension of dry (C$_6$Me$_6$)$_2$Fe^{II} (PF$_6$)$_2$ (3.08 mg) and 1% Na–Hg (5 ml) in freshly distilled tetrahydrofuran (THF) (20 ml) was stirred at room temperature for 1 h.[37] The mercury was filtered off. 2-Methoxy-carbonylcyclohexa-1,3 diene (1 g) in THF (3 ml) was added and the mixture was stirred at 40 °C overnight. THF was removed under reduced pressure and the residue was taken in hexane. Removal of solid matter by filtration and concentration of the hexane solution gave a reddish solid which was placed in a sublimation apparatus (40 °C/0.1 mmHg) for 24 h to remove any hexamethylbenzene. The unsublimed residue was crystallised (hexane, −78 °C) to give air-sensitive dark red-brown crystals (*ca.* 100 mg, *ca.* 50%); $\nu_{max.}$ 2 900, 2 540, 1 700, and 1 450 cm^{-1}; δ(C$_6$D$_6$) 4.75 (1 H, d, *J* 6 Hz, 3-H), 3.44 (3 H, s, CO$_2$Me), 2.27 (1 H, m, diene 1-H), 2.05 (1 H, m, 4-H), 1.8 (18 H, s, C$_6$Me$_6$), and 1.5—1.0 (4 H, m, 5- and 6-H); *m/z* 356 (90%, *M*), 341 (10, *M* − CO$_2$Me), 249 (39, C$_6$Me$_6$FeOMe), 219 (62, C$_6$Me$_6$FeH), 218 (59, C$_6$Me$_6$Fe), 194 (11, FeC$_8$H$_{10}$O$_2$), 162 (67, C$_6$Me$_6$), 161 (47, C$_{12}$H$_{17}$), 147 (100, C$_{11}$H$_{15}$), 134 (27, FeC$_6$H$_6$), and 105 (29, C$_6$H$_5$CO) (Found: C, 67.6; H, 7.9. C$_{20}$H$_{28}$FeO$_2$ requires C, 67.4; H, 7.9%).

Lanthanide Shift Reagent (LSR) Studies on Tricarbonyl-(η^4-1,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron (1), *Tricarbonyl-(η^4-1,6α-dimethoxycarbonylcyclohexa-1,3-diene)iron* (2) *and Tricarbonyl-(η^4-5α,6β-dimethoxycarbonylcyclohexa-1,3-diene)iron* (11).—A solution (2.2M) of tris-(1,1,1,2,2,3,3-heptafluoro-d$_9$-7,7-dimethyloctane-4,6-dionate)europium(II) in deuterochloroform was added sequentially in 5 µl portions to the compound (1), (2) or (11) (35 mg, 0.13 mmol) in deuteriochloroform (0.4 ml) at ambient temperature. The [1]H n.m.r. spectrum of the solution was recorded after each addition, using a Varian HA 100 spectrometer at 100 mHz with Me$_4$Si as the standard.

Computer-simulation Studies.—The NMRSIM program [13] was used. The chemical shifts and coupling constants depicted in Figures 1 and 3 were fed into a DEC PDP11/45 computer. Simulation of the observed patterns (Figures 4 and 5, respectively) was achieved by variation of the difference in chemical shifts of β-H and α-H of methylene protons.

Aromatic Solvent-induced Shift (ASIS) Studies.—The [1]H n.m.r. of each compound (Figure 6) was recorded both in deuteriochloroform and hexadeuteriobenzene on a JOEL Minimar 100 spectrometer. Results are shown in Figure 6.

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