Conformational Analysis for the Ligands CH_2OR (R = Me, CH_2Ph, and Menthyl) and CH_2SR (R = Me, Et, CH_2Ph, and Ph) Attached to the Iron Chiral Auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ †

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A conformational analysis of iron alkyl complexes of the type $[(C_5H_5)Fe(CO)(PPh_3)CH_2XR]$ that have an oxygen or sulphur substituent attached to C(α) has been conducted in order to investigate the dependence of conformation on solvent polarity. ^1H n.m.r. analysis, including variable temperature and n.O.e. experiments, indicated that the primary factor controlling conformational preferences in these complexes is steric interaction. For the complexes that do not have a significant steric bias between alternative conformations, the preferred conformation is observed to be dependent on solvent polarity. This phenomenon is due to a dipolar interaction between the polarised C(α)–heteroatom bond and the chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ metal fragment.

Asymmetric syntheses of organic molecules have been achieved[1] based on the highly stereoselective reactions of ligands attached to the iron chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$.[1–3,‡] In order to explain the remarkable stereocontrol exhibited by the iron chiral auxiliary we have proposed a conformational analysis for cyclopentadienyl pseudo-octahedral alkyl complexes of the type $[(C_5H_5)Fe(CO)(PPh_3)CH_2R]$ (**1**).[4,5] This analysis, based on extended Hückel calculations,[4] predicted that the preferred conformation for groups R attached to C(α) will be governed primarily by steric interactions. The relative steric size of the ligands attached to the chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ is $PPh_3 \gg C_5H_5 \gg CO$. Thus the sterically most accessible site is between the small and medium sized ligands, Zone A (Figure 1). Zone C between the carbon monoxide and triphenylphosphine ligands is the sterically most demanding site due to the small 'bite' angle (90°) between these ligands, and is virtually inaccessible to all but the smallest substituents (*e.g.* hydrogen). The relatively large angle between the centroid of the cyclopentadienyl to iron and phosphorus to iron bonds makes Zone B the area of moderate accessibility. Therefore, for complex (**1**; R = alkyl, aryl) the order of stability of the three conformations was predicted to be **I** ≫ **II** ≫ **III**.[4,5] Furthermore, it was predicted that only conformation **I** would be populated when the α-substituent is alkyl regardless of its size (*e.g.*, R = Me, Bu^t, *etc.*).[4]

We have provided experimental verification for this conformational analysis[6] together with its utilisation as a rationale for some novel stereoselective reactions.[7] ^1H N.m.r. spectroscopic analysis of a range of complexes of the type (**1**) indicated from the relative magnitudes and invariance with temperature of the $^3J_{PH}$ coupling constants, between the two C(α) diastereotopic protons and the phosphorus atom, that only conformation **I** is populated in solution when R is alkyl.[6] These and other results confirmed our earlier predictions that the preferred conformations for hydrocarbon fragments attached to the chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ are determined by steric factors.[4,5] Further support for this was the observation that the $^3J_{PH}$ coupling constants for complexes (**1**; [4] = alkyl, aryl) showed no significant dependence on solvent polarity, suggesting that polar effects are not important in determining the most stable conformation for the range of complexes examined.[6]

We describe here a conformational analysis for a series of complexes $[(C_5H_5)Fe(CO)(PPh_3)CH_2OR]$ (**2**) and $[(C_5H_5)Fe(CO)(PPh_3)CH_2SR]$ (**3**) where a polar substituent is introduced on C(α) in order to examine the possible polar contributions of the iron chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$. A portion of this work has been previously communicated.[8]

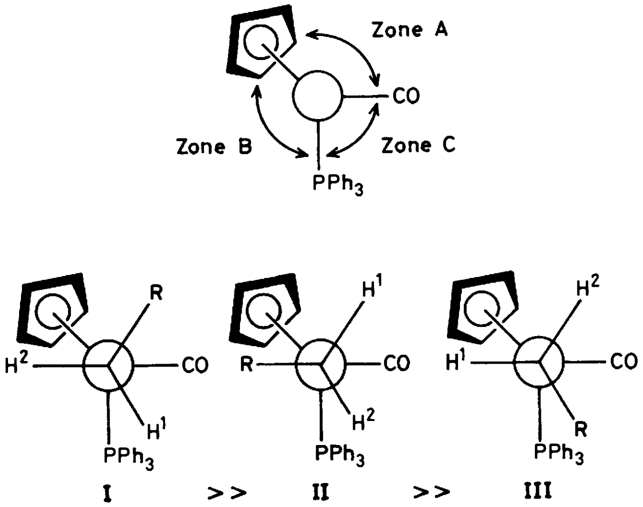

Figure 1. Sterically accessible zones about $[(C_5H_5)Fe(CO)(PPh_3)]$ and calculated stable conformations for $[(C_5H_5)Fe(CO)(PPh_3)CH_2R]$.

Results and Discussion

The major polar contribution to the overall dipole of the chiral auxiliary $[(C_5H_5)Fe(CO)(PPh_3)]$ will be due to the iron–phosphorus bond being substantially polarised

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† The descriptor η^5 for the cyclopentadienyl ligand has been omitted throughout for clarity.

‡ The iron acyl complex $[(C_5H_5)Fe(CO)(PPh_3)COCH_3]$ is available either as a racemate or in enantiomerically pure (+)-*S* and (−)-*R* forms from BP Chemicals Ltd., New Specialties Business, Belgrave House, 76 Buckingham Palace Road, London, SW1W 0SU, UK.

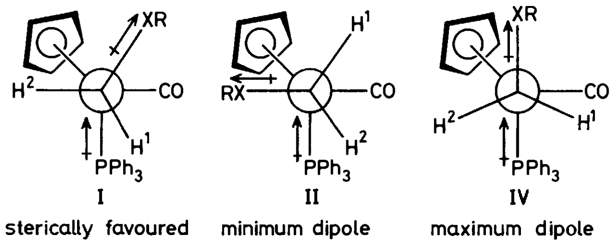


Figure 2. Stable conformations for [$(C_5H_5)Fe(CO)(PPh_3)CH_2XR$].

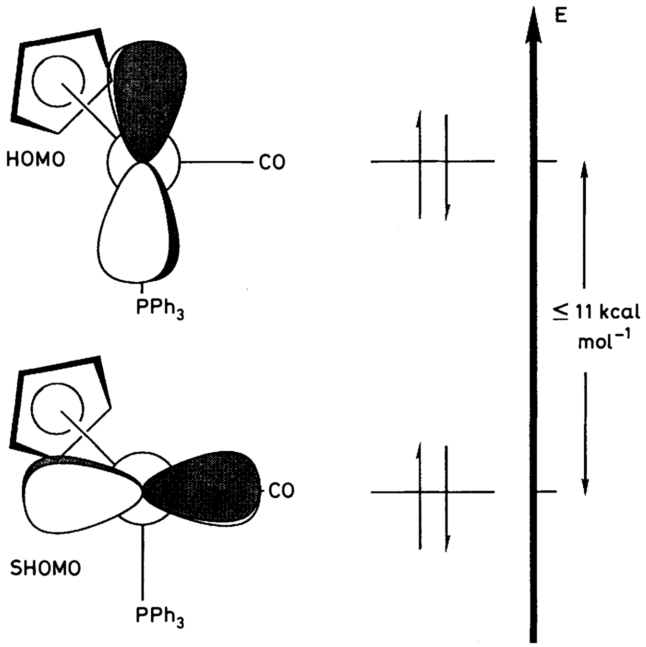
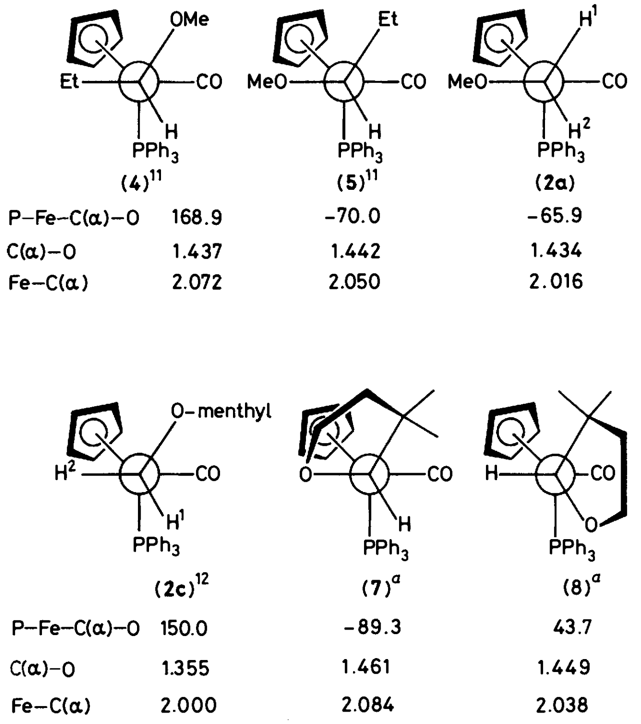


Figure 3. The HOMO and SHOMO for [$(C_5H_5)Fe(CO)(PPh_3)$].

Fe(−ve)–P(+ve), since there is essentially no back-bonding to the phosphorus. The iron to carbon monoxide bond is not expected to be significantly polarised, whereas any small polarisation that exists in the cyclopentadienyl–Fe bond is expected to partially align with the Fe–P dipole. Therefore, for complex (**2**)* or (**3**) if steric effects dominate then conformation **I** will be favoured, whereas if polar effects are important, confirmations close to **IV** will maximise the overall dipole whilst those close to **II** will minimize the overall dipole (Figure 2). Note that conformations **I** and **IV** each place the XR (X = O or S) group between the cyclopentadienyl and carbon monoxide ligands, that is in Zone A. Calculations,† which only take into account van der Waals interactions, suggest that oxygen and sulphur α- substituents are less sterically demanding than alkyl substituents and should result in conformations close to **II** and **IV** being relatively more accessible. Steric effects will always operate to exclude conformations where the C(α) substituent dips significantly below the plane defined by C(α)–Fe–CO atoms, such as into Zone C, due to the dominant steric properties of the triphenylphosphine ligand.



	(**4**)[11]	(**5**)[11]	(**2a**)
P–Fe–C(α)–O	168.9	−70.0	−65.9
C(α)–O	1.437	1.442	1.434
Fe–C(α)	2.072	2.050	2.016

	(**2c**)[12]	(**7**)[a]	(**8**)[a]
P–Fe–C(α)–O	150.0	−89.3	43.7
C(α)–O	1.355	1.461	1.449
Fe–C(α)	2.000	2.084	2.038

Figure 4. Fe–C(α) and C(α)–bond lengths Å for [$(C_5H_5)Fe(CO)(PPh_3)CH(OR)R'$] See footnote on p. 1.

We have shown that the chiral auxiliary [$(C_5H_5)Fe(CO)(PPh_3)$] does not exert any directional conformational preference due to stereoelectronic effects.[5] It can be envisioned that a stereoelectronic effect, analogous to the anomeric effect,[9] that optimises electron delocalisation through metal d_π/C(α) heteroatom σ* orbital overlap may affect conformational preferences by alignment of the LUMO on C(α) with the HOMO on the iron. However, the iron alkyl ether complexes (**2**) and (**3**) are predicted, using a simple process of electron counting,[5a] to have two energetically similar lone pairs of electrons centred at the metal that are available to participate in such an orbital interaction, which should result in no directional bias on conformation due to electronic interactions. Extended Hückel calculations support this prediction and indicate that the HOMO on the metal lies parallel to the iron–phosphorus bond which is ≤11 kcal mol^{-1} higher in energy than the second highest molecular orbital (SHOMO), which lies orthogonal to the HOMO (Figure 3).[10,‡] Examination of the C(α)–O and Fe–C(α) bond lengths for all known *alpha* alkoxy alkyl substituents attached to [$(C_5H_5)Fe(CO)(PPh_3)$] provides further evidence for this prediction (Figure 4).[7,11,12,§] Stereoelectronic effects, if important, would favour a conformation in which the *alpha* heteroatom is antiperiplanar to the phosphorus (synperiplanar being excluded on steric grounds) in order to maximise orbital overlap. In this antiperiplanar conformation the C(α)–O bond would be longer and the Fe–C(α) bond shorter than the corresponding bonds in the orthogonal conformation in which overlap is minimised. However, in the two diastereoisomers of [$(C_5H_5)Fe(CO)(PPh_3)CH(OMe)Et$] the C(α)–O bond length (1.437 Å) is shorter and the Fe–C(α) bond length (2.072 Å) longer in the *RR,SS*-diastereoisomer (**4**)

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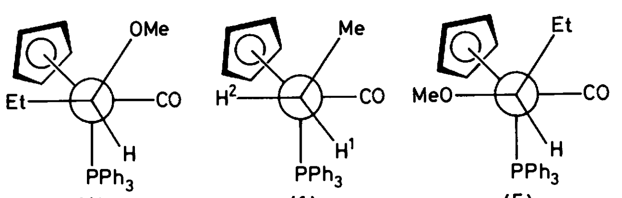
[*] Complexes (**2c**) and (**2d**) are derived from enantiomerically pure (−)-menthol (see the Experimental section).

[†] Chem-X, developed and designed by Chemical Design, Ltd., Oxford, England. Calculations were performed using the Chem-X molecular modelling program on the basis of *X*-ray crystal structure determinations using the default parameters that only take into account van der Waals interactions.

[‡] This value is taken from the EHMO calculations performed by Hoffmann and co-workers for the unsubstituted analogue [$(C_5H_5)Mo(CO)(PH_3)$]$^+$ and is the energy difference between the a″ (HOMO) and 2a′ (SHOMO) molecular orbitals for [$(C_5H_5)Fe(CO)(PPh_3)$]$^+$.[13]

[§] A. P. Ayscough and S. G. Davies, unpublished results. Complex (**8**) is the only known complex where an α-substituent other than H presides in Zone C. This is due to the strong steric requirement of the *gem*-dimethyl quaternary carbon to occupy Zone A.



(4) (1) (5)

$^3J_{PH}$ 4.3 Hz $^3J_{PH^1}$ 12.1 Hz $^3J_{PH}$ 10.0 Hz

$^3J_{PH^2}$ 2.0 Hz

Figure 5. Observed $^3J_{PH}$ coupling constants and preferred conformations for complexes (*RR,SS*)-[$(C_5H_5)Fe(CO)(PPh_3)CH(OMe)Et$] (**4**), [$(C_5H_5)Fe(CO)(PPh_3)CH_2Me$] (**1**) and (*RS,SR*)-[$(C_5H_5)Fe(CO)(PPh_3)CH(OMe)Et$] (**5**).

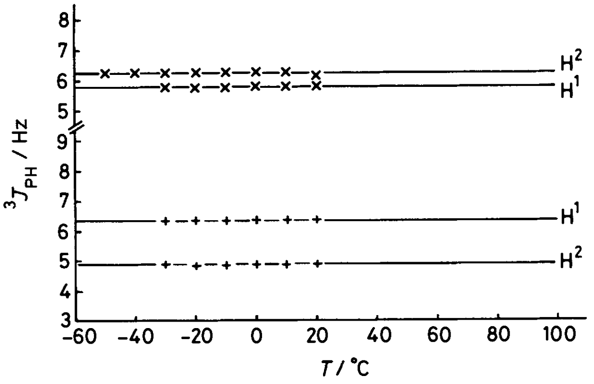


Figure 6. $^3J_{PH}$ *vs.* temperature for complexes (**2a**; R = OMe) (+), and (**2b**; R = OCH_2Ph) (×) in [$^2H_2$]dichloromethane.

with the methoxyl *anti* to the phosphorus, than the corresponding bond lengths (1.442 and 2.050 Å) in the *RS,SR* diastereoisomer (**5**)[11] leading to the conclusion that stereoelectronic effects may arise from interaction with both the HOMO and SHOMO. The conclusion being that stereoelectronic effects *do not* play a significant role in determining the preferred conformation for ligands bonded to the iron chiral auxiliary [$(C_5H_5)Fe(CO)PPh_3$].

It has been shown for complexes (**1**), where R = alkyl, which exist in a single conformation close to **I**, that in the ^1H n.m.r. spectrum H^1 is shifted upfield relative to H^2 due to the shielding effect of the proximate phenyl group.[13] The observed $^3J_{PH}$ coupling constants for the two diastereotopic protons in (**1**) (R = Me) are directly related to the Karplus equation,[14] such that H^1 having a dihedral angle close to 30° was found to have a large coupling constant (*ca.* 12–14 Hz) while H^2, dihedral angle close to 90°, possessed a small coupling constant (*ca.* 2 Hz).[6]

The Karplus relationships for $^3J_{PH}$ coupling constants have been established for a wide range of phosphorus compounds and in all cases a minimum value is observed at a dihedral angle of 90°.[15] In systems containing electronegative substituents, however, it is known that this relationship tends to be asymmetric about this point.[15] In particular, if the electronegative substituent is held *anti* to one of the coupled nuclei a reduction in the vicinal coupling constants is observed.[16,17] If complexes (**2**) and (**3**) exist in a conformation where the electronegative atom is *anti* to the phosphorus atom, *e.g.* conformation **I**, it is expected that the magnitude of the $^3J_{PH}$ coupling constant for H^1 will be reduced whereas that for H^2 will be slightly increased relative to those values observed for (**1**; R = alkyl).[16,17] In support of this is the finding that the $^3J_{PH}$ coupling constant of the methine proton of (*RR,SS*)-[$(C_5H_5)Fe(CO)(PPh_3)CH(OMe)Et$] (**4**)[16] ($^3J_{PH}$ 4.3 Hz)[18] is significantly lower than that for H^1 of [$(C_5H_5)Fe(CO)(PPh_3)CH_2CH_3$] (**1**; R = Me), ($^3J_{PH}$ 12.1 Hz, Figure 5).[6] This effect on the $^3J_{PH}$ coupling constants is directly related to the electronegativity of the *trans* α-substituent and can thus be expected to be of more importance for the oxygen containing complexes (**2**) than for the sulphur-containing complexes (**3**).[17]

The presence of an electronegative atom *cis* to the phosphine, such as in conformation **II**, should not have a significant effect on the magnitudes of the $^3J_{PH}$ coupling constants.[17] Evidence in support of this is that the value of the $^3J_{PH}$ coupling constant of the methine proton of (*RS,SR*)-[$(C_5H_5)Fe(CO)(PPh_3)$- CH(OMe)Et] (**5**) ($^3J_{PH}$ 10.0 Hz)[11] which is close to that for H^1 in complex (**1**; R = Me) ($^3J_{PH}$) 12.1 Hz, Figure 5).

A further guide to the conformational preferences for complexes (**2**) and (**3**) is differential n.O.e. n.m.r. experiments.[6,19] For example, it was found for complexes (**1**; R = alkyl), that exist solely in conformation **I**, irradiation of the *ortho*-phenyl protons of the triphenylphosphine ligand resulted in a substantial enhancement to the proximate H^1 and a small enhancement to H^2; irradiation of the cyclopentadienyl protons resulted in enhancement of H^2 and a small negative enhancement to H^1 (due to the near-linear alignment of the three-spin system defined by the cyclopentadienyl, H^1, and H^2 protons).[6,19,20] It is expected for the complexes (**2**) and (**3**), investigated here, that similar results should be obtained for conformations where the C(α) substituent occupies Zone A. A distinction between conformations **I** and **IV** in Zone A may be determined by irradiation of the *ortho*-phenyl protons which will result in enhancements to H^1 and H^2 of more similar magnitude for conformation **IV** relative to **I**. However, if conformation **II** is preferred one would expect irradiation of the *ortho*-phenyl protons to result in an enhancement of the proximate H^2 but not significantly of H^1.

As with the analysis of (**1**; R = alkyl, aryl), variable temperature n.m.r. experiments should also prove useful in determining conformational preferences in complexes (**2**) and (**3**).[6] If a single conformation is uniquely populated then no change in the $^3J_{PH}$ coupling constants to H^1 and H^2 with temperature will be observed. This will also be the case if complexes (**2**) and (**3**) adopt degenerate, equally populated conformations in which the observed $^3J_{PH}$ for H^1 and H^2 will reflect an average of those coupling constants for the individual conformations. For any two populated, non-degenerate conformations then the $^3J_{PH}$ coupling constants will be expected to vary significantly, approaching the values for the degenerate case at infinite temperature and the values of the most stable conformation at low temperatures.

Each of the complexes (**2**) and (**3**) were investigated in polar and non-polar solvents in order to determine the polar contributions of the chiral auxiliary [$(C_5H_5)Fe(CO)(PPh_3)$], a summary of the ^1H n.m.r. coupling constant data for which can be found in Table 1. The variable-temperature data are most readily illustrated in graphical form and are discussed below for each complex. A summary of differential n.O.e. n.m.r. experiments for complexes (**2**) and (**3**) is found in Table 2.

I. *Complexes* (**2**; R = Me, CH_2Ph). In the polar solvent CD_2Cl_2, the $^3J_{PH}$ coupling constants for the diastereotopic methylene protons in complexes (**2a,b**) were observed to remain invariant over the temperature range −40–40 °C (Figure 6). The differential n.O.e. n.m.r. experiments showed upon irradiation of the *ortho*-phenyl protons a near equal enhancement to 1-H (13.8%) and 2-H (15.4%) for (**2a**), but, slightly different enhancements to these protons for (**2b**) (1-H = 5.8%, 2-H = 9.2%). Irradiation to 1-H in both of these complexes showed enhancements of 2-H, the *ortho*-phenyl protons, but not of the cyclopentadienyl protons. These data indicate that complexes (**2a,b**) adopt a conformation that is sterically and electrostatically favoured where OR occupies Zone A, which is the uniquely populated conformer due to the

Table 1. Summary of coupling constants and chemical shifts at 24 °C in CD_2Cl_2 and C_6D_6.

		CD_2Cl_2				C_6D_6			
		H^1		H^2		H^1		H^2	
Complex	XR	δ	$^3J_{PH}$/Hz	δ	$^3J_{PH}$/Hz	δ	$^3J_{PH}$/Hz	δ	$^3J_{PH}$/Hz
(2a)	OMe	4.07	6.3	4.37	4.9	4.68	4.8	4.32	6.9
(2b)	OCH_2Ph	4.35	5.8	4.25	6.2	4.87	4.7	4.24	7.4
(2c)	*O*-menthyl	4.25	7.5	4.15	5.5	4.49	5.3	4.53	7.9
(2d)	*O*-menthyl	4.32	7.9	4.46	4.3	4.82	7.1	4.66	5.8
(3a)	SMe	1.74	9.9	2.08	2.9	2.35	8.9	2.01	4.3
(3b)	SEt	1.74	9.9	2.05	2.8	2.31	8.9	2.03	4.6
(3c)	SCH_2Ph	1.64	10.1	1.93	2.8	2.19	9.1	1.93	4.0
(3d)	SPh	1.85	10.3	2.41	2.5	2.47	9.6	2.40	3.4

Table 2. Summary of differential n.O.e. n.m.r. enhancements of H^1 and H^2 on irradiation of phosphine *ortho*-phenyl protons.

		CD_2Cl_2		C_6D_6	
Complex	XR	H^1(%)	H^2(%)	H^1(%)	H^2(%)
(2a)	OMe	13.8	15.4	0	7.6
(2b)	OCH_2Ph	5.8	9.2	0	7.5
(2c)	*O*-menthyl	12.0	0	0	14.0
(2d)	*O*-menthyl	4.2	11.0	5.4	11.7
(3a)	SMe	4.8	9.2	6.2	6.2
(3b)	SEt	0[a]	6.0[a]	8.9	10.0
(3c)	SCH_2Ph	0[a]	3.5[a]	11.4	10.3
(3d)	SPh	0[a]	5.4[a]	4.2	6.3

[a] N.O.e. from irradiation of cyclopentadienyl protons.

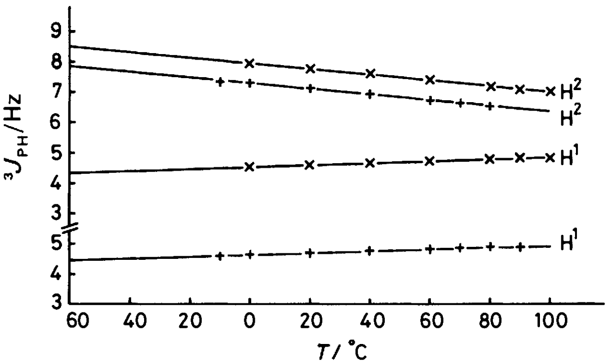


Figure 7. $^3J_{PH}$ *vs.* temperature for complexes (**2a**; R = OMe) (+), and (**2b**; R = OCH_2Ph) (×) in [$^2H_8$]toluene.

absence of variation of the $^3J_{PH}$ coupling constants for H^1 and H^2 over a wide range of temperature (Figure 6).

In contrast with the data obtained for (**2a,b**) in a polar solvent, the $^3J_{PH}$ coupling constant data in the non-polar solvent [$^2H_8$]toluene were observed to vary over a wide range of temperature (Figure 7). Differential n.O.e. n.m.r. experiments at 297 K showed that upon irradiation of the *ortho*-phenyl protons enhancements of H^2, the cyclopentadienyl protons, but *not* to H^1. These data obtained for (**2a,b**) in the non-polar solvent are consistent with the OR group occupying Zone B, *e.g.* conformation **II**.

Variation of the $^3J_{PH}$ coupling constants of the two diastereotopic protons, for complex (**2a,b**), with temperature (Figure 7) in a non-polar solvent indicates the population of more than one conformation. Extrapolation of the variable temperature data to infinite temperature (Figure 8) indicates that the $^3J_{PH}$ coupling constants tend toward those observed in CD_2Cl_2 suggesting that at infinite temperature ($T^{-1} = 0$) only a conformation where OR occupies Zone A will be populated. This situation may arise when for two conformations $\Delta H°$ is small but $\Delta S°$ is large so that at high temperature the $T\Delta S°$ term becomes dominant in controlling conformational preferences. In conformation **II** the R group is constrained to lie antiperiplanar to the C(α)–Fe bond whereas in conformation **I** many more orientations of the OR group are accessible. At higher temperatures the OR group is effectively larger due to rotation of the C(α)–O bond with the result that steric considerations, which favour conformation **I**, become dominant.

In conformation **II** the overall dipole for the complex (**2a,b**) is minimised and is thus favoured by a non-polar solvent. Increasing the solvent polarity results in smooth changes in the $^3J_{PH}$ coupling constants (Figure 9) and chemical shifts as a conformation which places the OR group in Zone A, which possesses a larger overall dipole, becomes increasingly favoured. The *X*-ray crystal structure determination for (**2a**) shows that conformation **II** is adopted in the relatively non-polar solid state environment (Figure 10). The preferred conformation of (**2a**) in the solid state, in which the methoxy group is *anti* to the carbon monoxide rather than *anti* to the phosphorus, is also consistent with the previous conclusion that the chiral iron auxiliary exerts no directional stereoelectronic effect. Final atomic positional co-ordinates can be found in Table 3 and a listing of selected bond lengths, angles, and torsional angles in Table 4.

Examination of the *X*-ray crystal structure for complex (**2a**) (Figure 10) shows that the phenyl rings of the triphenylphosphine ligand adopt a conformation where steric interactions are minimised and are arranged in a clockwise rotor configuration when the configuration at iron is *R* and anticlockwise when iron is *S*. An identical configuration is adopted in the solid state by the triphenylphosphine ligand for all other known complexes of the type [$(C_5H_5)Fe(CO)(PPh_3)R$] (R = alkyl, aryl, acyl).[5,*] Thus, the phenyl rings that stagger the C(α) ligand are tilted so as to place an *ortho*-phenyl proton in Zone B and one only partially in Zone C. This conformer of the phosphine ligand that is adopted in the solid state is postulated to predominate in solution as evidenced by the difference n.O.e. n.m.r. data for complexes (**2a,b**) in CD_2Cl_2 which showed a greater enhancement to H^2 (that occupies Zone B) than to H^1 (that occupies Zone C and lies above the proximate phenyl ring) upon irradiation of the *ortho*-phenyl protons. The barrier to rotation about the Fe-P and P–C_{ipso} bonds, however, is low since the diastereotopic *ortho*-phenyl protons are observed to rapidly exchange, on the n.m.r. timescale. This conclusion is based on the assumption that the *ortho*-phenyl protons would not be coincident if there was a high barrier to rotation about

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[*] See footnote § on p. 1144.

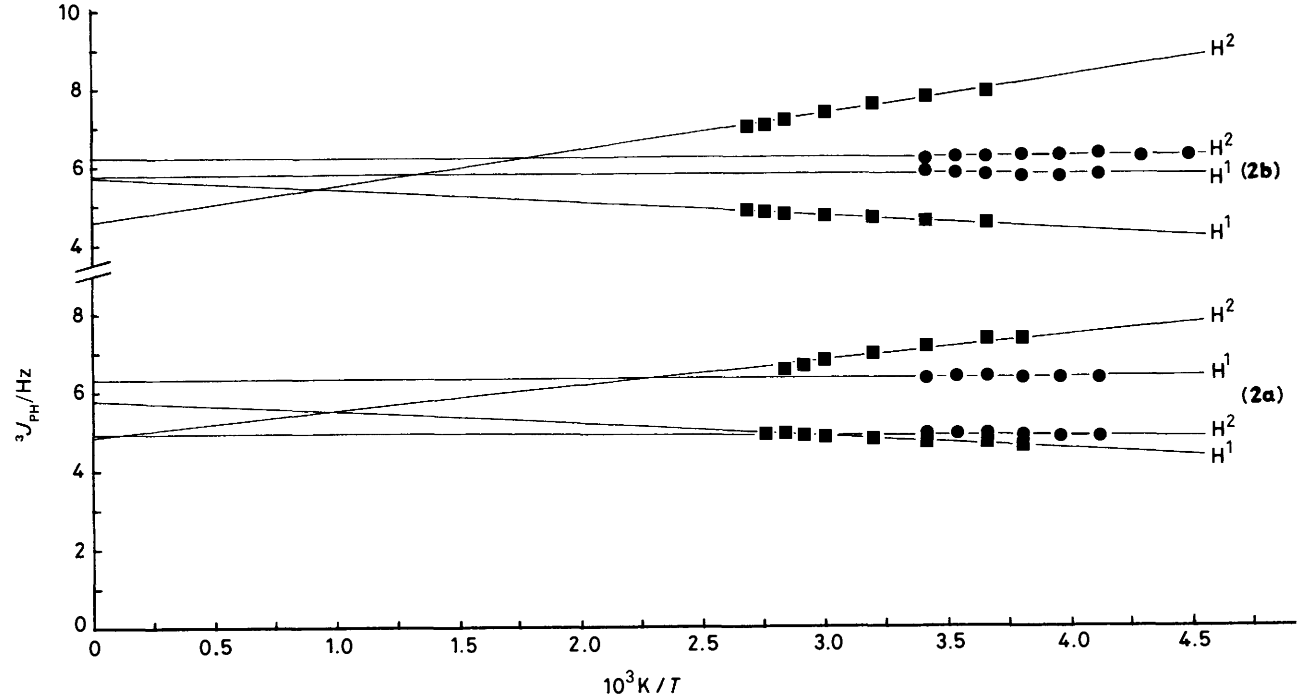

Figure 8. $^3J_{PH}$ *vs.* temperature^{-1} for complexes (**2a**; R = OMe), and (**2b**; R = OCH_2Ph): (■) = [$^2H_8$]toluene and (●) = [$^2H_2$]dichloromethane.

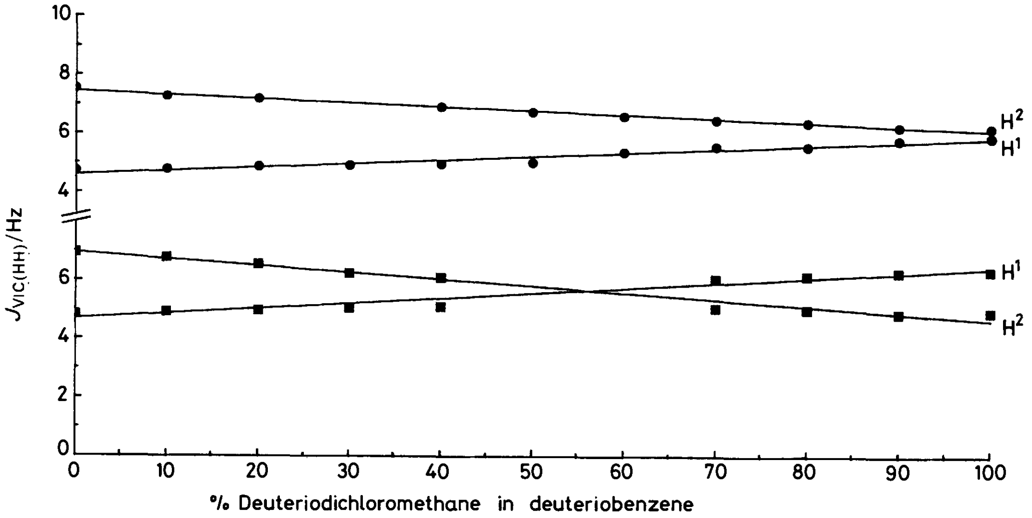

Figure 9. $^3J_{PH}$ *vs.* % CD_2Cl_2 in C_6D_6 for complexes (**2a**; R = OMe) (■), and (**2b**; R = OCH_2Ph) (●).

these bonds, which is reasonable considering the high degree of asymmetry about the iron chiral auxiliary.

II. *Complexes* (**2c,d**; R = menthyl). The results obtained from the n.m.r. experiments for the homochiral complex (−)-*R*-[$(C_5H_5)Fe(CO)(PPh_3)CH_2$Omenthyl]* (**2c**) in the polar solvent CD_2Cl_2 (Tables 1 and 2) are similar to those obtained for complexes (**2a,b**). In particular, invariance of the $^3J_{PH}$ coupling constants for H^1 and H^2 with temperature over the range −20–20 °C (Figure 11) together with a large n.O.e. enhancement to H^1 (12.0%) but not to H^2 (undetectable) upon irradiation of the *ortho*-phenyl protons is consistent with complex (**2c**), in a polar solvent, existing as a single conformer where *O*-menthyl occupies Zone A, close to the carbon monoxide ligand. In this case the greater steric bulk of the α-substituent for (**2c**) favours a conformation closer to **I** relative to (**2a,b**), which adopt a conformation closer to **IV**.

In the 300 MHz ^{1}H n.m.r. spectrum of (**2c**) at 297 K in the non-polar solvent C_6D_6 the diastereotopic protons H^1 and H^2 appear at δ 4.49 and 4.53 with $^3J_{PH}$ coupling constants of 5.3 and 7.9 Hz, respectively. Both of these coupling constants varied over the temperature range 0–60 °C in [$^2H_8$]toluene (Figure 13). Differential n.O.e. n.m.r. experiments at 297 K showed upon irradiation of the *ortho*-phenyl protons enhancements to H^2 (14.0%), and to the cyclopentadienyl protons (7.0%), but not to H^1. It was concluded from the spectroscopic data obtained for complex (**2c**) that in a non-polar environment, at ambient temperature, the *O*-menthyl group prefers to occupy Zone B

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* See footnote * on p. 1144.

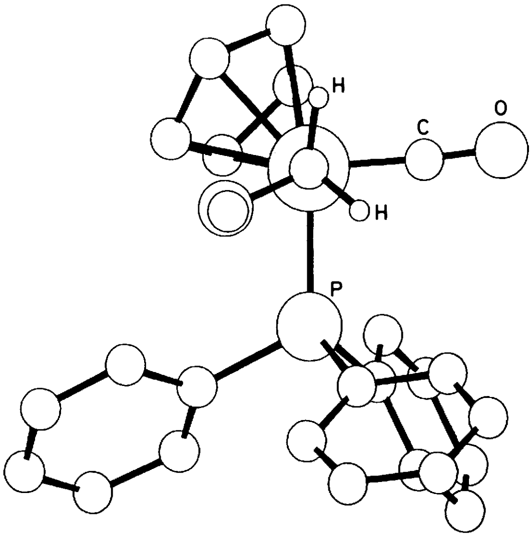

Figure 10. Molecular structure of [$(C_5H_5)Fe(CO)(PPh_3)CH_2OMe$] (**2a**). Selected protons are removed for clarity. The diagram shows the Newman projection along the *alpha* carbon-to-iron bond.

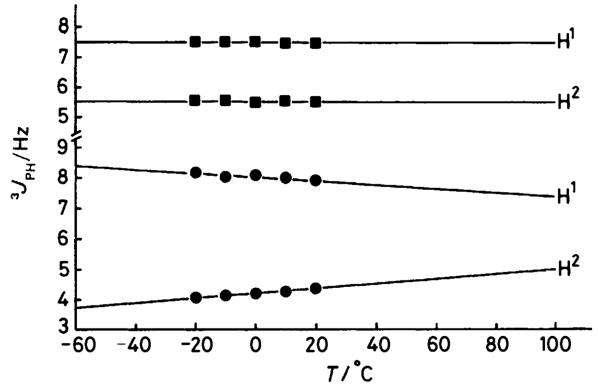

Figure 11. $^3J_{PH}$ *vs.* temperature for complexes (**2c**) (■) and (**2d**) (●) (R = *O*-menthyl) in [$^2H_2$]dichloromethane.

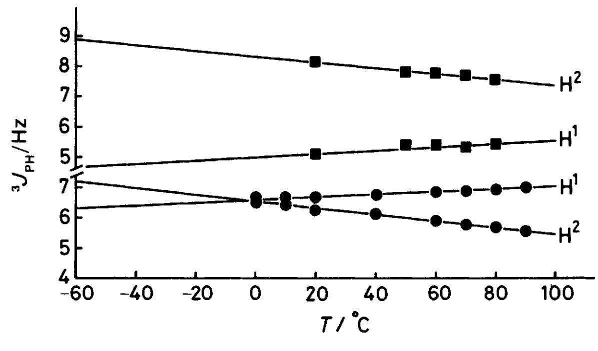

Figure 12. $^3J_{PH}$ *vs.* temperature for complexes (**2c**) (■) and (**2d**) (●) (R = *O*-menthyl) in [$^2H_8$]toluene.

Table 3. Final atomic positional co-ordinates for [$(C_5H_5)Fe(CO)(PPh_3)CH_2OCH_3$] (**2a**).

Atom	*x*	*y*	*z*
Fe(1)	0.240 01(4)	0.218 43(4)	0.342 11(2)
P(1)	0.304 56(7)	0.394 82(6)	0.260 62(3)
O(1)	0.223 5(2)	0.119 7(2)	0.174 1(1)
O(2)	0.587 7(3)	0.091 4(3)	0.404 5(1)
C(1)	0.329 9(3)	0.073 6(3)	0.246 0(2)
C(2)	0.291 6(5)	0.020 4(4)	0.106 4(2)
C(3)	0.449 3(3)	0.145 3(3)	0.378 7(2)
C(4)	0.098 8(4)	0.261 2(4)	0.463 9(2)
C(5)	0.006 8(3)	0.367 2(3)	0.403 1(2)
C(6)	−0.038 3(3)	0.291 3(3)	0.340 6(2)
C(7)	0.025 1(4)	0.137 0(4)	0.363 6(2)
C(8)	0.112 0(4)	0.116 0(4)	0.439 0(2)
C(9)	0.480 1(3)	0.330 8(2)	0.173 0(1)
C(10)	0.451 5(3)	0.353 0(3)	0.086 4(2)
C(11)	0.591 4(4)	0.301 0(4)	0.023 9(2)
C(12)	0.760 9(4)	0.227 7(3)	0.047 4(2)
C(13)	0.791 3(3)	0.203 8(3)	0.133 1(2)
C(14)	0.651 6(3)	0.253 0(3)	0.195 7(2)
C(15)	0.388 5(3)	0.518 4(2)	0.315 9(1)
C(16)	0.506 2(3)	0.584 9(3)	0.275 5(2)
C(17)	0.559 7(4)	0.682 3(3)	0.318 7(2)
C(18)	0.493 3(4)	0.717 7(3)	0.401 9(2)
C(19)	0.375 4(4)	0.654 3(4)	0.442 4(2)
C(20)	0.326 6(4)	0.551 4(3)	0.401 2(2)
C(21)	0.120 7(3)	0.533 4(3)	0.205 9(1)
C(22)	0.070 4(4)	0.686 7(3)	0.216 0(2)
C(23)	−0.072 0(4)	0.785 2(4)	0.174 6(3)
C(24)	−0.161 7(4)	0.732 4(4)	0.121 7(2)
C(25)	−0.113 0(4)	0.581 4(4)	0.110 6(2)
C(26)	0.026 2(3)	0.480 6(3)	0.153 8(2)
H(1)	0.454 5(3)	0.067 4(3)	0.226 1(2)
H(2)	0.328 6(3)	−0.027 9(3)	0.268 6(2)
H(3)	0.214 0(5)	0.056 2(4)	0.057 6(2)
H(4)	0.414 8(5)	0.018 0(4)	0.086 4(2)
H(5)	0.294 2(5)	−0.083 1(4)	0.126 8(2)
H(6)	0.147 5(4)	0.283 4(4)	0.515 7(2)
H(7)	−0.022 4(3)	0.478 7(3)	0.403 9(2)
H(8)	−0.103 9(3)	0.338 2(3)	0.289 0(2)
H(9)	0.011 0(4)	0.055 2(4)	0.331 2(2)
H(10)	0.171 4(4)	0.017 6(4)	0.469 8(2)
H(11)	0.328 8(3)	0.406 8(3)	0.068 6(2)
H(12)	0.568 8(4)	0.316 5(4)	−0.038 4(2)
H(13)	0.861 9(4)	0.192 2(3)	0.002 2(2)
H(14)	0.914 5(3)	0.150 5(3)	0.150 3(2)
H(15)	0.674 3(3)	0.232 6(3)	0.258 0(2)
H(16)	0.552 9(3)	0.562 8(3)	0.214 4(2)
H(17)	0.647 5(4)	0.727 3(3)	0.289 1(2)
H(18)	0.531 1(4)	0.789 2(3)	0.432 5(2)
H(19)	0.324 2(4)	0.681 9(4)	0.502 4(2)
H(20)	0.245 8(4)	0.501 1(3)	0.432 7(2)
H(21)	0.136 3(4)	0.727 1(3)	0.253 1(2)
H(22)	−0.109 9(4)	0.895 7(4)	0.183 3(3)
H(23)	−0.262 5(4)	0.804 7(4)	0.091 3(2)
H(24)	−0.177 3(4)	0.543 4(4)	0.071 4(2)
H(25)	0.058 1(3)	0.369 9(3)	0.147 4(2)

and increasingly favours a conformation in Zone A with increasing temperature. Similar trends were obtained and conclusions made for complexes (**2a,b**).

The data obtained for the homochiral epimer of (**2c**), (−)-*S*-[$(C_5H_5)Fe(CO)(PPh_3)CH_2O$-menthyl]* (**2d**), however, were observed to be in complete contrast with those observed for complexes (**2a–c**). Specifically, in the polar solvent CD_2Cl_2 the variation of the $^3J_{PH}$ coupling constants with temperature over the range −20–20 °C (Figure 11), suggests more than one conformation is populated in this solvent. Differential n.O.e. n.m.r. experiments showed that upon irradiation of the *ortho*-phenyl protons enhancement to H^1 (4.2%), H^2 (11.0%), and the cyclopentadienyl protons (3.0%), indicating that conformation **I** is principally populated at ambient temperature in CD_2Cl_2. Extrapolation of the variable temperature data to infinite temperature indicates that the preferred conformation at higher

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* See footnote * on p. 1144.

Table 4. Selected bond angles and bond lengths for [$(C_5H_5)Fe(CO)(PPh_3)CH_2OCH_3$] (**2a**).

Angle/°		Bond length/Å	
C(1)–Fe(1)–P(1)	90.82(7)	Fe(1)–P(1)	2.193(1)
C(3)–Fe(1)–P(1)	93.37(8)	Fe(1)–C(1)	2.016(2)
C(3)–Fe(1)–C(1)	82.7(1)	Fe(1)–C(3)	1.724(2)
O(1)–C(1)–Fe(1)	112.4(2)	Fe(1)–C(4)	2.105(2)
C(2)–O(1)–C(1)	111.9(2)	Fe(1)–C(5)	2.105(2)
		Fe(1)–C(6)	2.105(4)
		Fe(1)–C(7)	2.108(2)
		Fe(1)–C(8)	2.105(2)
		O(1)–C(1)	1.434(3)
		O(1)–C(2)	1.404(3)

Torsion angle/° O(1)–C(1)–Fe(1)–P(1) = −65.92.

temperatures can best be described as a conformation in Zone A, that closely resembles **IV** (Figure 13). This assignment is based on the fact that as the temperature is increased the values of chemical shifts and coupling constants for each of the diastereotopic protons move towards one another, which is most easily reconciled as an increasing tendency to adopt conformation close to **IV** thus maximising the dipole.

The spectroscopic data obtained for (**2d**) in a non-polar medium were also observed to differ from those obtained for complexes (**2a**–**c**). For example, at low temperature the $^3J_{PH}$ coupling constants for (**2d**) in [$^2H_8$]toluene are nearly equal, suggesting an equilibrium between conformations **I** and **II** averaged to a conformation resembling **IV**. As the temperature is increased, however, these values become dissimilar, anomolous to (**2c**) where the values of the $^3J_{PH}$ coupling constants were observed to come together with increasing temperature (Figure 12). Extrapolation to infinite temperature shows that the $^3J_{PH}$ coupling constants tend towards those values obtained for (**2d**) at low temperature in CD_2Cl_2, which was determined to prefer a conformation close to **I** (Figure 13). Thus, in a non-polar environment at low temperature complex (**2d**) is in equilibrium between conformations **I** and **II**, which with increasing temperature tends to prefer a conformation where the *O*-menthyl group occupies Zone A, close to **I**. This is consistent with the $T\Delta S°$ term dominating conformational preferences at higher temperatures.

Examination of molecular models for complexes (**2c**,**d**) suggests that the *O*-menthyl group can be accommodated between the cyclopentadienyl and triphenylphosphine ligands, *i.e.* in Zone B in the former but not the latter complex due to service steric interactions. This is in agreement with the spectroscopic data obtained that indicated that in a non-polar solvent (**2c**) prefers to occupy Zone B whereas (**2d**) does not achieve such a conformation.

The conformational preferences for the epimeric complexes (**2c**,**d**) provide an explanation for the difference in the relative solubility of (**2c**,**d**). These materials are typically prepared as a mixture and are separated by crystallisation from heptane to give crystalline (**2d**). This is in accord with the model described above which predicts compound (**2d**) is the more polar diastereoisomer, since it cannot easily achieve conformation **II** which would minimise its overall dipole, and is thus less soluble in the non-polar solvent than (**2c**), which can achieve conformation **II** and hence a lower overall dipole. Flood and co-workers have conducted an *X*-ray crystal structure analysis of complex (**2d**) which shows that conformation **I** is adopted in the solid state, where steric interactions associated with the bulky

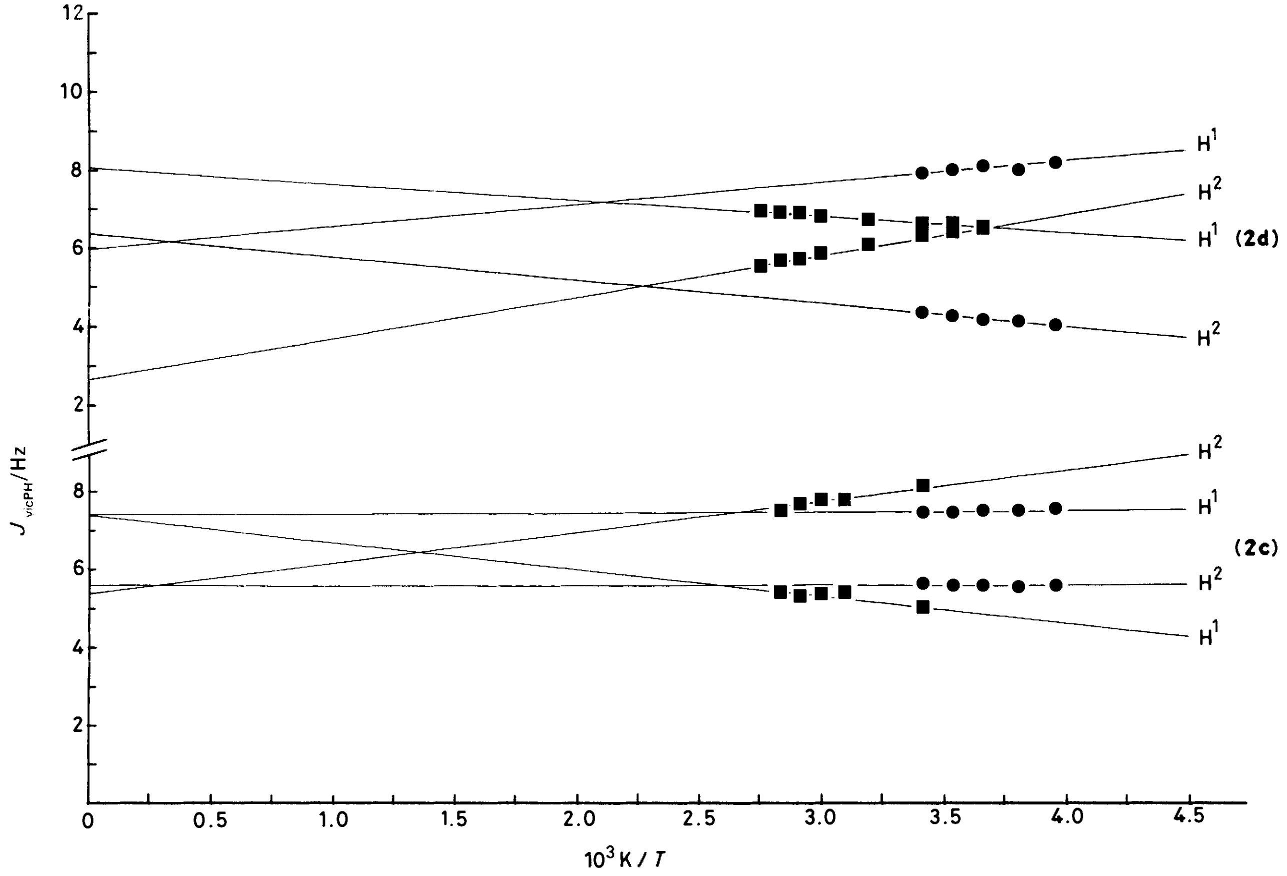

Figure 13. $^3J_{PH}$ *vs.* T^{-1} for complexes (**2c**) and (**2d**) (R = *O*-menthyl): ■, [$^2H_8$]toluene; ●, [$^2H_2$]dichloromethane.

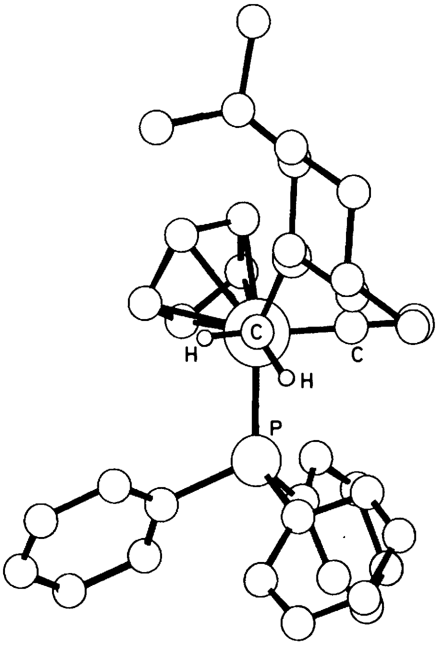

Figure 14. For ease in structural comparison, the diagram shows the enantiomer of (*S*)-[$(C_5H_5)Fe(CO)(PPh_3)CH_2O$(menthyl)] (**2d**), which was derived by inverting its *X*-ray crystal structure as determined by Flood and co-workers.[12] The diagram shows the Newman projection along the *alpha* carbon-to-iron bond. Selected protons are removed for clarity. Selected bond length/Å, angle, and torsional angle/° are Fe–C(α) = 2.001, Fe–C(α)–O = 109.38, and P–Fe–C(α)–O = 155.03, respectively.

menthyl group are minimised (Figure 14).[12] All our attempts to prepare suitable crystals of (**2c**) for *X*-ray analysis were unsuccessful.

IV. *Complexes* (**3**). The sulphide complexes (**3**) are considered as a group since the $^3J_{PH}$ coupling constants (Table 3), differential n.O.e. n.m.r. experiments (Table 4), and variable temperature n.m.r. experiments (Figures 15 and 16) obtained for each of these complexes showed similar trends. In comparison with the ether complexes (**2a**–**d**) one would expect that the larger, less electronegative sulphur atom of the sulphides will result in steric effects being more important than dipolar effects in determining the preferred conformation.

Examination of the data for the sulphide complexes (**3**) in the polar solvent CD_2Cl_2 indicates that a conformation that places the SR group in Zone A tending towards **I** is preferred; H^1 is upfield from H^2, and possesses the larger $^3J_{PH}$ coupling constant (Table 1). The slight change in the $^3J_{PH}$ coupling constants with temperature (Figure 15) is consistent with conformation **IV** becoming increasingly populated at higher temperatures. Note that as the size of the alkyl group bonded to the sulphur atom increases, there is observed an increase in the $^3J_{PH}$ for H^1 with a corresponding decrease in the $^3J_{PH}$ for H^2. As the alkyl groups become larger there exists a conformational preference, on average, for complexes (**3**) to adopt a conformation closer to **I**, which is sterically more accessible than **IV**.

The data obtained in a non-polar medium for the sulphide complexes (**3**) suggests an equilibrium between conformations **I** and **II** which lies towards conformation **I**; H^1 possesses a larger $^3J_{PH}$ coupling constant than H^2, but H^2 is upfield of H^1 (Table 1), similar n.O.e. enhancements are seen to both H^1 and H^2 upon irradiation the *ortho*-phenyl protons, and no observable

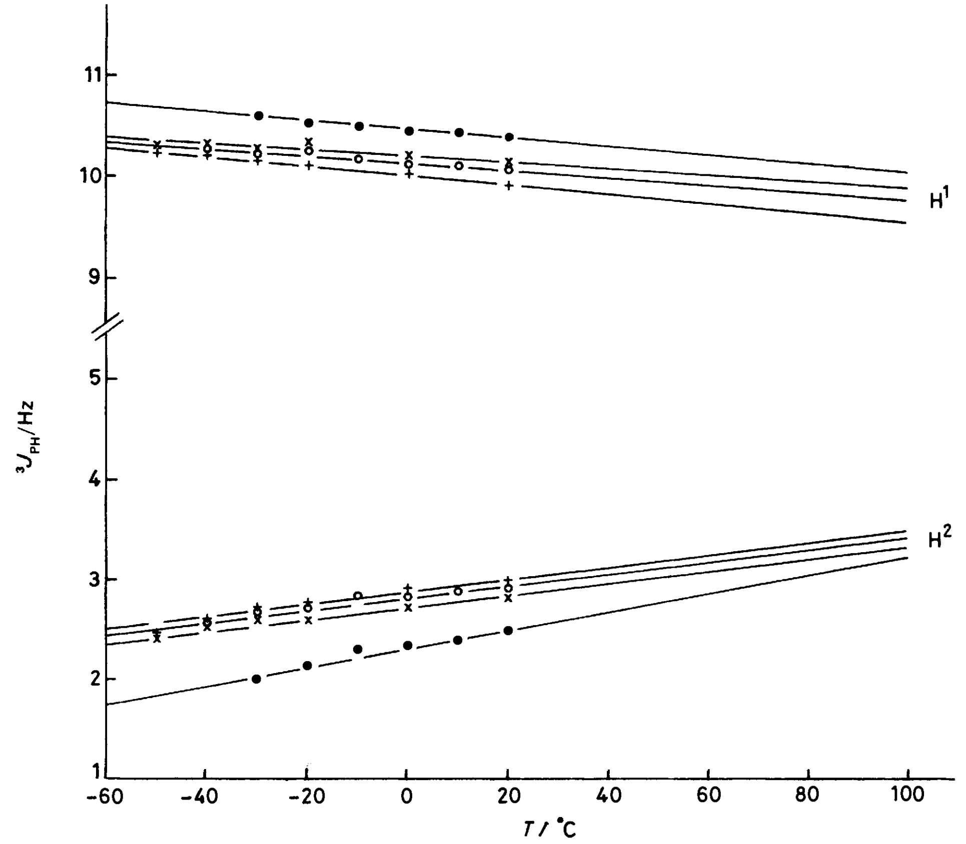

Figure 15. $^3J_{PH}$ *vs.* temperature for complexes (**3a**; R = SMe) (+), (**3b**; R = SEt) (○), (**3c**; R = SCH_2Ph) (×), and (**3d**; R = SPh) (●) in [$^2H_2$]dichloromethane.

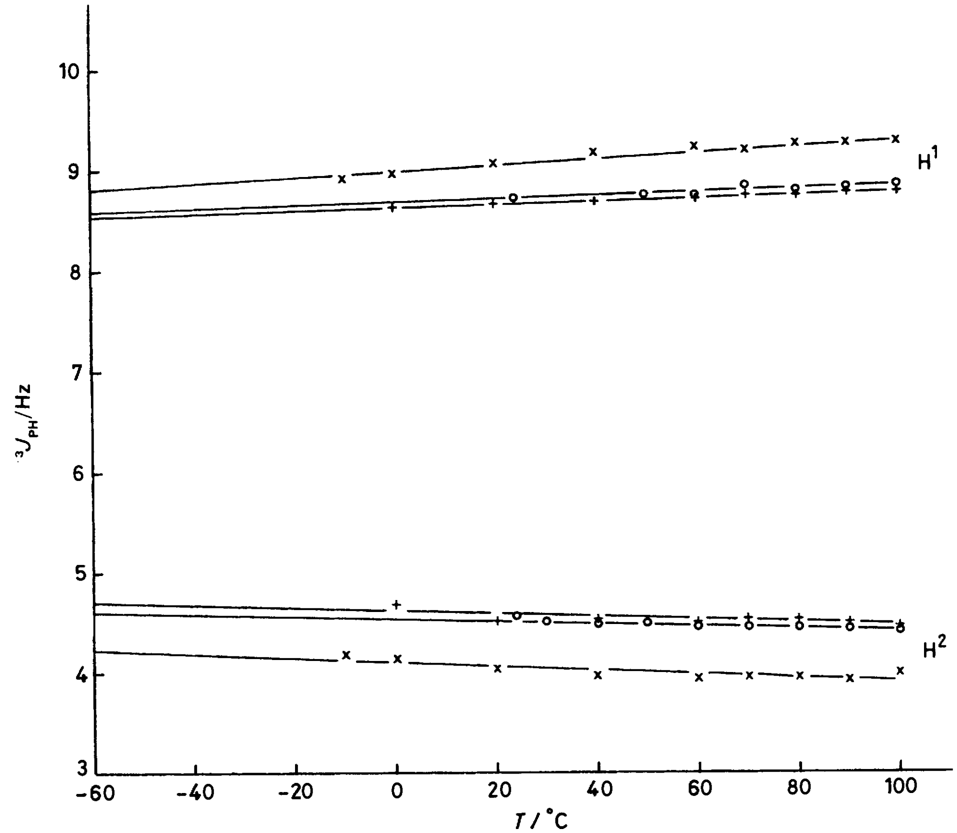

Figure 16. $^3J_{PH}$ *vs.* temperature for complexes (**3a**; R = SMe) (+), (**3b**; R = SEt) (○), and (**3c**; R = SCH_2Ph) (×) in [$^2H_8$]toluene.

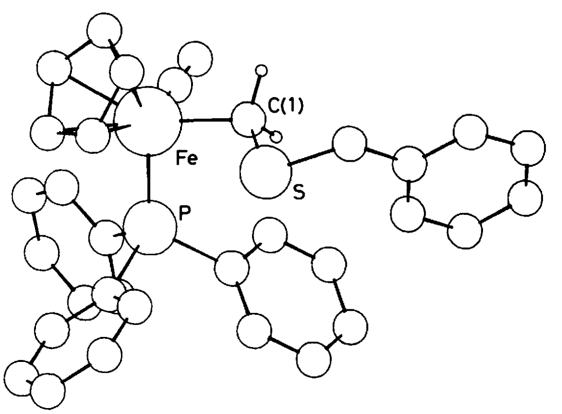

Figure 17. Molecular structure of [$(C_5H_5)Fe(CO)(PPh_3)CH_2SCH_2Ph$] (**3c**). Selected protons are removed for clarity.

enhancement to H^1 by irradiation of the cyclopentadienyl protons (Table 2). In further support of an equilibrium between conformations **I** and **II** is the observed variance in the $^3J_{PH}$ coupling constants over a range of temperature (Figure 16). The variable temperature data for complex (**3d**; R = SPh) was found to be unreliable due to virtual coupling of the two diastereotopic protons but, considering the remarkable similarity in the spectroscopic data in this series of compounds, are expected to possess a similar trend to those of complexes (**3a–c**).

The *X*-ray crystal structure determination of (**3c**; R = CH_2Ph) shows that the thioalkyl group is situated between the cyclopentadienyl and triphenylphosphine ligands in the relatively non-polar solid-state environment (Figure 17). Final atomic positional co-ordinates can be found in Table 5 and a listing of selected bond lengths, angles, and torsional angles in Table 6.

Extrapolation of the variable temperature n.m.r. data obtained in both the polar and the non-polar solvent to infinite temperature reveals (Figure 18) that the same values for the $^3J_{PH}$ coupling constants for the two diastereotopic protons at $T^{-1} = 0$ are obtained in each of the solvent systems, suggesting similar conformational preferences at high temperature in either solvent. This is consistent with a dominant $T\Delta S°$ term resulting in a decrease in the population of conformation **II** as the temperature is raised in the non-polar solvent, with an equal population of conformations **I** and **IV** in either solvent at high temperature.

Conclusions

The preferred conformation for the alkyl ligands CH_2OR and CH_2SR attached to the chiral auxiliary [$(C_5H_5)Fe(CO)(PPh_3)$] is primarily dictated by steric interactions between the alkyl ligand and the proximate ligands. For the complexes studied here, an electrostatic interaction between the polarised iron–phosphorus and C(α)–heteroatom bonds has been shown to be important in dictating conformational preferences in solvents of different polarity where there is no compelling steric bias between accessible conformations. This behaviour is similar to the conformational preferences of *trans*-2-chloro-5-methylcyclohexanone which change as a direct result of the polar strength of its environment.[21] To our knowledge, this is the first example of this effect being observed for an organometallic complex.

Table 5. Final atomic positional co-ordinates for [$(C_5H_5)Fe(CO)(PPh_3)CH_2SCH_2Ph$] (**3c**)

Atom	*x*	*y*	*z*
Fe(1)	7 960.9(4)	1 789.9(5)	5 187.2(3)
S(1)	8 735.1(8)	4 453(1)	5 037.9(7)
P(1)	7 856.5(8)	2 343.8(9)	6 318.5(6)
C(1)	7 677(3)	3 457(4)	4 694(2)
C(2)	8 419(3)	5 682(4)	4 351(3)
C(3)	7 566(3)	3 457(4)	4 369(2)
C(4)	7 207(3)	7 302(4)	3 763(2)
C(5)	6 438(4)	8 118(4)	3 741(3)
C(6)	6 015(3)	8 157(4)	4 338(3)
C(7)	6 360(3)	7 383(4)	4 949(3)
C(8)	7 125(3)	6 576(4)	4 962(2)
C(9)	6 662(3)	1 577(4)	4 823(2)
C(10)	8 374(4)	696(5)	4 388(3)
C(11)	8 385(3)	13(4)	5 042(3)
C(12)	9 099(3)	514(4)	5 678(3)
C(13)	9 544(3)	1 507(4)	5 424(3)
C(14)	9 105(4)	1 601(4)	4 631(3)
C(15)	7 107(3)	1 333(4)	6 739(2)
C(16)	6 752(3)	1 702(4)	7 349(2)
C(17)	6 176(3)	932(5)	7 652(3)
C(18)	5 944(4)	− 187(5)	7 366(3)
C(19)	6 297(4)	− 566(4)	6 775(3)
C(20)	6 874(3)	191(4)	6 457(3)
C(21)	7 209(3)	3 754(3)	6 416(2)
C(22)	7 664(3)	4 659(4)	6 920(2)
C(23)	7 093(4)	5 644(4)	6 998(3)
C(24)	6 083(4)	5 737(4)	6 585(3)
C(25)	5 625(3)	4 849(4)	6 080(3)
C(26)	6 193(3)	3 866(4)	5 996(2)
C(27)	9 080(3)	2 447(3)	7 086(2)
C(28)	9 313(3)	1 718(4)	7 730(2)
C(29)	10 261(3)	1 804(4)	8 276(2)
C(30)	10 973(3)	2 611(4)	8 193(3)
C(31)	10 751(3)	3 336(4)	7 554(2)
C(32)	9 815(3)	3 251(4)	6 998(2)
O(1)	5 792	1 457	4 547
H(1)	7 068(3)	3 808(4)	4 815(2)
H(2)	7 526(3)	3 372(4)	4 125(2)
H(3)	9 052(3)	6 177(4)	4 442(3)
H(4)	8 243(3)	5 326(4)	3 825(3)
H(5)	7 517(3)	7 276(4)	3 330(2)
H(6)	6 195(4)	8 676(4)	3 296(3)
H(7)	5 455(3)	8 739(4)	4 324(3)
H(8)	6 060(3)	7 413(4)	5 388(3)
H(9)	7 369(3)	6 010(4)	5 403(2)
H(10)	7 921(4)	562(5)	3 853(3)
H(11)	7 957(3)	− 709(4)	5 048(3)
H(12)	9 267(3)	218(4)	6 219(3)
H(13)	10 074(3)	2 049(4)	5 754(3)
H(14)	9 285(4)	2 206(4)	4 289(3)
H(15)	6 916(3)	2 523(4)	7 564(2)
H(16)	5 921(3)	1 201(5)	8 086(3)
H(17)	5 520(4)	− 728(5)	7 585(3)
H(18)	6 134(4)	− 1 393(4)	6 569(3)
H(19)	7 128(3)	− 88(4)	6 024(3)
H(20)	8 403(3)	4 600(4)	7 219(2)
H(21)	7 418(4)	6 293(4)	7 366(3)
H(22)	5 674(4)	6 450(4)	6 646(3)
H(23)	4 866(3)	4 912(4)	5 780(3)
H(24)	5 866(3)	3 227(4)	5 622(2)
H(25)	8 795(3)	1 130(4)	7 796(2)
H(26)	10 429(3)	1 279(4)	8 740(2)
H(27)	11 654(3)	2 671(4)	8 591(3)
H(28)	11 271(3)	3 924(4)	7 492(2)
H(29)	9 660(3)	3 773(4)	6 533(2)

Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum-line and Schlenk-tube techniques.[22] Tetrahydrofuran (THF) was dried over sodium–benzophenone and distilled. Dichloromethane was distilled from calcium hydride. I.r. spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 297 instrument. ^1H N.m.r. spectra were recorded on a Bruker WH 300 spectrometer at 300.13 MHz and referenced to residual protio-solvent, with chemical shifts being reported in δ from $(CH_3)_4Si$. Proton differential n.O.e. n.m.r. experiments were conducted at ambient temperature (*ca.* 297 K) (with presaturation greater than 5 × longest T_1 on a Bruker WH 300 spectrometer at 300.13 MHz for complexes (**3**) and on a Bruker AM 500 spectrometer at 500.13 MHz for complexes (**2**) using either CD_2Cl_2 or C_6D_6 as the solvent and internal standard. ^{13}C N.m.r. spectra were recorded on a Bruker AM 250 spectrometer at 62.90 MHz using either $CDCl_3$ or benzene C_6D_6 as the solvent and internal standard and are reported in δ from $(CH_3)_4Si$. ^{31}P N.m.r. spectra were recorded on a Bruker AM 250 spectrometer at 101.26 MHz and are reported in δ from an external reference of trimethylphosphate in D_2O. Mass spectra were recorded on a V.G. micromass ZAB 2F instrument using an FD technique. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by the Dyson Perrins Laboratory Analytical Service (Oxford, UK).

General Procedure for Preparation of (**2**; R = Me, CH_2Ph, menthyl) *and* (**3**; R = Me, Et, CH_2Ph, Ph).—To a stirred solution of $[(C_5H_5)Fe(CO)_2]^-Na^+$ (prepared from 6.00 g, 17.0 mmol cyclopentadienyldicarbonyliron dimer by a standard procedure)[23] in THF at 0 °C was added, over a period of 15 min, a solution of the chloromethyl ether or the chloromethyl sulphide RCH_2Cl {R = OMe, OCH_2Ph, O[(−)-menthyl)], SMe, SEt, SCH_2Ph, SPh} * (35 mmol) in THF (5 cm³). After the reaction had been stirred overnight at ambient temperature the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and filtered through Celite and the solvent removed. Chromatography of the oil on alumina (Grade V) eluting with light petroleum (b.p. 40–60 °C) gave [$(C_5H_5)Fe(CO)_2CH_2R$)] as an amber oil This material was taken directly to the desired complex by being dissolved with triphenylphosphine (8.0 g, 31 mmol) in either benzene (100 cm³) or 1:1 pentane–benzene (100 cm³) and irradiated in a quartz immersion apparatus using a Hanovia 125 W medium-pressure mercury arc lamp. The reaction was monitored by i.r. spectroscopy (disappearance of carbonyl stretches at *ca.* 2 020 and *ca.* 1 970 cm⁻¹ relative to the emergence of carbonyl stretch at *ca.* 1 900 cm⁻¹) and irradiation was stopped after 12–16 h. The solvent was removed and the residue [for complexes (**2**) was treated with methyl iodide (2 cm³) for 30 min], extracted with light petroleum (b.p. 40–60 °C) and filtered rapidly through alumina (Grade V). The filtrate was concentrated until crystallisation occurred. Recrystallisation from either dichloromethane–light petroleum (b.p. 40–60 °C) or dichloromethane–heptane gave complexes (**2**) and (**3**) as a red crystalline solids in 20–80% overall yield from cyclopentadienyldicarbonyliron dimer. Diastereoisomeric complexes (**2c**,**d**) were separated by repeated fractional crystallisation.[12] Crystallisation from heptane gave complex (**2d**), the supernatant provided complex (**2c**) upon crystallisation from pentane.

Carbonyl(cyclopentadienyl)methoxymethyl[triphenylphosphine)iron (**2a**).[12]—Red crystalline solid (37%). ν(C≡O) 1 900 cm⁻¹; $\delta_H(CD_2Cl_2$; 297 K) 7.59–7.46 (15 H, m, Ph), 4.37 (1 H, dd,

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* These materials were prepared using a modified procedure described: H. Bohme and H. Fisher, *Justus Liebigs Ann. Chem.*, 1949, **563**, 54.

Table 6. Selected bond angles and bond lengths for [(C_5H_5)Fe(CO)(PPh_3)CH_2SCH_2Ph] (**3c**).

Angle/°		Bond length/Å	
C(1)–Fe(1)–P(1)	95.5(1)	Fe(1)–P(1)	2.196(1)
C(9)–Fe(1)–P(1)	93.2(1)	Fe(1)–C(1)	2.060(4)
C(9)–Fe(1)–C(1)	85.2(1)	Fe(1)–C(9)	1.720(4)
S(1)–C(1)–Fe(1)	112.6(2)	Fe(1)–C(10)	2.103(4)
C(2)–O(1)–C(1)	103.2(2)	Fe(1)–C(11)	2.114(4)
		Fe(1)–C(12)	2.109(4)
		Fe(1)–C(13)	2.104(4)
		Fe(1)–C(14)	2.110(4)
		S(1)–C(1)	1.790(4)
		S(1)–C(2)	1.824(4)

Torsion angle/° S(1)–C(1)–Fe(1)–P(1) = −72.75.

$^3J_{PH}$ 4.9, $^2J_{HH}$ 4.6 Hz, $FeCH^2$), 4.35 (5 H, d, $^3J_{PH}$ 1.2 Hz, C_5H_5), 4.07 (1 H, dd, $^3J_{PH}$ 6.3, $^2J_{HH}$ 4.6 Hz, $FeCH^1$), and 2.93 (3 H, s, CH_3); δ_H(C_6D_6; 297 K) 7.67–7.58 (6 H, m, PhH_{ortho}), 7.09–6.98 (9 H, m, Ph-H_{meta} and -H_{para}), 4.68 (1 H, dd, $^3J_{PH}$ 4.8, $^2J_{HH}$ 4.5 Hz, $FeCH^1$), 4.35 (5 H, d, $^3J_{PH}$ 1.0 Hz, C_5H_5), 4.32 (1 H, dd, $^3J_{PH}$ 6.9, $^2J_{HH}$ 4.4 Hz, $FeCH^2$), and 3.11 (3 H, s, CH_3); δ_C($CDCl_3$) 220.08 (d, ^2J 31.0 Hz, C≡O), 136.46 (d, ^1J 40.5 Hz, PhC_{ipso}), 133.36 (d, ^2J 9.8 Hz, PhC_{ortho}), 129.32 (s, PhC_{para}), 127.87 (d, ^3J 9.4 Hz, PhC_{meta}), 84.97 (s, C_5H_5), 68.89 (d, ^2J 20.6 Hz, CH_2), and 61.23 (s, OCH_3); δ_P($CDCl_3$) 81.2; *m/z* 456 (M^+) (Found: C, 68.20; H, 5.34; P, 6.93. Calc. for $C_{26}H_{25}FeO_2P$: C, 68.44; H, 5.52; P, 6.79%).

Crystallographic Data and Data-collection Parameters for (**2a**).—X-*Ray Crystal-structure Analysis of* (C_5H_5)Fe(CO)(PPh_3)CH_2OMe. Cell parameters and reflections were

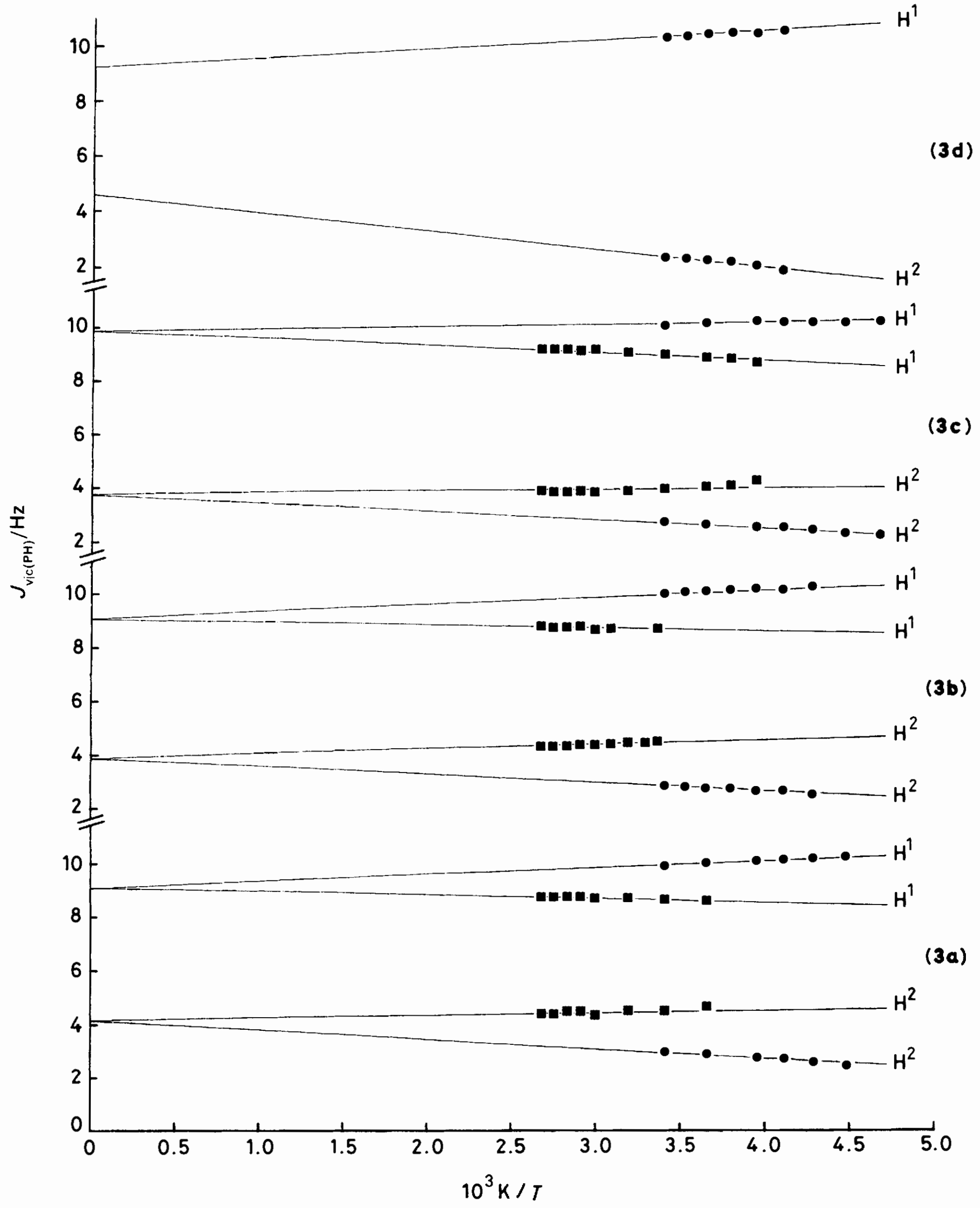

Figure 18. $^3J_{PH}$ *vs.* T^{-1} for complexes (**3a**; R = SMe), (**3b**; R = SEt), (**3c**; R = SCH_2Ph), and (**3d**; R = SPh): ■, [$^2H_8$]toluene; ●, [$^2H_2$]-dichloromethane.

measured using graphite monochromated Mo-K_α radiation on an Enraf Nonius CAD4-F diffractometer operating in the $\omega/2\theta$ mode. The scan range (ω) was calculated from [0.95 + 0.35 tanθ] and the scan speed was varied from 1.1 to 6.7° min^{-1} depending upon intensity. Reflections were measured in the range $0 < \theta < 25$. Three standard reflections were measured regularly to scale the intensity data and correct for any crystal decay. The data was corrected for Lorentz, polarisation, and absorption effects[24] and equivalent reflections were merged to give 3 887 unique reflections of which 3 226 were considered to be observed [$I > 3\sigma(I)$] and used in subsequent structure analysis. The structure was solved using direct methods, using the Patterson method, and electron density Fourier analysis. Final full-matrix least-squares refinement included parameters for atomic positions, anisotropic temperature factors (for non-hydrogen atoms), an overall scale factor, and an extinction parameter.[26,*] All non-hydrogen atoms were located by difference Fourier analyses and hydrogen atoms were placed in calculated positions and allowed to 'ride' on their respective atoms. Weights for each reflection were calculated from a Chebyschev series of the form $W = [385.8t_1(X) - 534.8t_2(X) + 159.8t_3(X)]$where$X = F_o/F_{max.}$[27]Final-difference Fourier analysis showed no significant electron density. All calculations were performed using the CRYSTALS package on the Chemical Crystallography Laboratory VAX 11/750 computer.

Crystal data. $C_{26}H_{25}FeO_2P$, $M = 456.3$, triclinic, $a = 8.038(2)$, $b = 9.462(2)$, $c = 15.632(2)$, $\alpha = 85.550$, $\beta = 84.000$, $\gamma = 69.690°$, $U = 1\,109.7$ Å^3, $Z = 2$, $D_{calc} = 1.37$ g cm^{-3}, μ(Mo-K_α) = 7.903 cm^{-1}, space group $P\bar{1}$, relative transmission factors 1.00—1.19, crystal dimensions 0.50 × 0.98 × 0.18 mm, number of reflections [$I > 3\sigma(I)$] 3 226, $R = 0.034$, $R_w = 0.043$.

Benzyloxymethyl(carbonyl)cyclopentadienyl(triphenylphosphine)iron (**2b**).—Red crystalline solid (54%). $\nu_{max.}$(C≡O) 1 905 cm^{-1}; δ_H(CD$_2$Cl$_2$; 297 K) 7.45–7.21 (20 H, m, Ph), 4.40 (5 H, d, $^3J_{PH}$ 1.0 Hz, C$_5$H$_5$), 4.35 (1 H, dd, $^3J_{PH}$ 6.2, $^2J_{HH}$ 4.5 Hz, FeCH^2), 4.25 (1 H, dd, $^3J_{PH}$ 5.8, $^2J_{HH}$ 4.5 Hz, FeCH), 4.16 (1 H, d, $^2J_{HH}$ 11.6 Hz, OC*H*HPh), and 3.87 (1 H, d, $^2J_{HH}$ 11.6 Hz, OCH*H*Ph); δ_H(C$_6$D$_6$; 297 K) 7.68–7.58 (6 H, m, PPh$_3$H$_{ortho}$), 7.38–7.15 (5 H, m, OCH$_2$C$_6$H$_5$), 7.07–7.02 (9 H, m, PPh$_3$ H$_{meta}$ and H$_{para}$), 4.87 (1 H, dd, $^3J_{PH}$ 4.7, $^2J_{HH}$ 4.5 Hz, FeCH^1), 4.35 (5 H, d, $^3J_{PH}$ 1.1 Hz, C$_5$H$_5$), 4.28 (1 H, d, $^2J_{HH}$ 11.2 Hz, OC*H*HPh), 4.24 (1 H, dd, $^3J_{PH}$ 7.4, $^2J_{HH}$ 4.5 Hz, FeCH), and 4.02 (1 H, d, $^2J_{HH}$ 11.5 Hz, OCH*H*Ph); δ_C(CDCl$_3$) 221.86 (d, $^2J_{PC}$ 30.5 Hz, C≡O), 140.21 (s, OCH$_2$PhC$_{ipso}$), 136.47 (d, $^1J_{PC}$ 40.1 Hz, PPh$_3$C$_{ipso}$), 133.48 (d, $^2J_{PC}$ 9.5 Hz, PPh$_3$C$_{ortho}$), 129.29 (s, PPh$_3$C$_{para}$), 127.95 (s, OCH$_2$Ph C$_{ortho}$ or C$_{meta}$), 127.81 (d, $^3J_{PC}$ 9.7 Hz, PPh$_3$ C$_{meta}$), 127.61 (s, OCH$_2$Ph C$_{meta}$ or C$_{ortho}$), 126.71 (s, OCH$_2$Ph C$_{para}$), 85.06 (s, C$_5$H$_5$), 76.10 (s, OCH$_2$Ph), and 66.52 (d, $^2J_{PC}$ 20.8 Hz, FeCH$_2$); δ_P(CDCl$_3$) 81.1; *m/z* 532 (M^+) (Found: C, 72.25; H, 5.53; P, 5.93. Calc. for C$_{32}$H$_{30}$FeOP: C, 72.19; H, 5.49; P, 5.82%).

(−)-(R)-*Carbonyl(cyclopentadienyl)menthyloxymethyl(triphenylphosphine)iron* (**2c**).[12]—Red crystalline solid; a 3:1 mixture of (**2c**,**d**) as determined by ^{1}H n.m.r. $[\alpha]_{578}{}^{28}$ −177.2° (benzene, c 0.1) [lit.,[12] $[\alpha]_{578}{}^{25}$ −407° (benzene, c 0.1]. $\nu_{max.}$(C≡O) 1 900 cm^{-1}; δ_H(CD$_2$Cl$_2$; 297 K) 7.52–7.28 (15 H, m, PH), 4.37 (5 H, d, $^3J_{PH}$ 1.1 Hz, C$_5$H$_5$), 4.25 (1 H, dd, $^3J_{PH}$ 7.5, $^2J_{HH}$ 3.6 Hz, FeCH), 4.15 (1 H, dd, $^3J_{PH}$ 5.5, $^2J_{HH}$ 3.6 Hz, FeCH^2), 2.68 (1 H, dt, $^3J_{HH}$ 10.4, 4.0 Hz, OCH), 2.36 [1 H, dseptets, $^3J_{HH}$ 7.0, 2.5 Hz, C*H*(CH$_3$)$_2$], 1.62–0.62 (7 H, m, cyclohexyl H), 0.94 (3 H, d, $^3J_{HH}$ 7.1 Hz, CH$_3$), 0.77 (3 H, d, $^3J_{HH}$ 6.9 Hz, CH$_3$), 0.71 (3 H, d, $^3J_{HH}$ 6.5 Hz, CH$_3$), and −0.08 (1 H, dt, $^{2,3}J_{HH}$ 12.0, 11.1 Hz, cyclohexyl H); δ_H(C$_6$D$_6$; 297 K) 7.70–7.57 (6 H, m, PhH$_{ortho}$), 7.12 (9 H, m, Ph H$_{meta}$ and H$_{para}$), 4.53 (1 H, dd, $^3J_{PH}$ 7.9 $^2J_{HH}$ 3.5 Hz, FeCH^2), 4.49 (1 H, dd, $^3J_{PH}$ 5.3, $^2J_{HH}$ 3.6 Hz, FeCH^1), 2.85 [1 H, dt, $^3J_{HH}$ 10.4, 2.5 Hz, C*H*(CH$_3$)$_2$], 1.75–0.80 (7 H, m, cyclohexyl H), 1.08 (3 H, d, $^3J_{HH}$ 7.1 Hz, CH$_3$), 0.95 (3 H, d, $^3J_{HH}$ 7.2 Hz, CH$_3$), 0.82 (3 H, d, $^3J_{HH}$ 6.5 Hz, CH$_3$), and 0.08 (1 H, dt, $^{2,3}J_{HH}$ 12.0, 11.2 Hz, cyclohexyl H); δ_C(CDCl$_3$) 221.72 (d, $^2J_{PC}$ 30.7 Hz, C≡O), 136.64 (d, $^1J_{PC}$ 40.6 Hz, PhC$_{ipso}$), 133.60 (d, $^2J_{PC}$ 9.8 Hz, PhC$_{ortho}$), 129.20 (s, PhC$_{para}$), 127.77 (d, $^3J_{PC}$ 9.1 Hz, PhC$_{meta}$), 85.11 (s, C$_5$H$_5$), 81.60 (s, menthyl C-1), 61.29 (d, $^2J_{PC}$ 21.8 Hz, FeCH$_2$), 49.30 (s), 38.86 (s), 34.86 (s), 31.31 (s), 25.38 (s), 23.18 (s), 22.45 (s), 21.45 (s), and 16.10 (s); δ_P(CDCl$_3$) 81.74; *m/z* 580 (M^+) (Found: C, 72.27; H, 7.42; P, 5.32. Calc. for C$_{35}$H$_{41}$FeO$_2$P: C, 72.41; H, 7.12; P, 5.34%).

(+)-(S)-*Carbonyl(cyclopentadienyl)menthyloxymethyl(triphenylphosphine)iron* (**2d**).[12]—Orange crystalline solid, diastereoisomerically pure by ^{1}H n.m.r. $[\alpha]_{578}{}^{24}$ +199.3 (benzene, *c* 0.1); [lit.[12] $[\alpha]_{578}{}^{25}$ +209 (benzene, *c* 0.1)]. IR ν(C≡O) 1 900 cm^{-1}; δ_H(500 MHz; CD$_2$Cl$_2$, 297 K) 7.45—7.32 (15 H, m, Ph), 4.46 (1 H, dd, $^3J_{PH}$ 4.3 $^2J_{HH}$ 3.6 Hz, FeCH^2), 4.37 (5 H, d, $^3J_{PH}$ 1.1 Hz, C$_5$H$_5$), 4.32 (1 H, dd, $^3J_{PH}$ 7.9, $^2J_{HH}$ 3.5 Hz, FeCH^1), 2.64 (1 H, dt, $^3J_{HH}$ 10.4, $^3J_{HH}$ 4.2 Hz, OCH), 1.99–1.95 (2 H, m, C*H*(CH$_3$)$_2$ and cyclohexyl H), 1.59–0.61 (7 H, m, cyclohexyl H), 0.86 (3 H, d, $^3J_{HH}$ 6.6 Hz, CH$_3$), and 0.82 (3 H, d, $^3J_{HH}$ 7.1 Hz, CH$_3$), 0.56 (3 H, d, $^3J_{HH}$ 6.9 Hz, CH$_3$); δ_H(C$_6$D$_6$; 297 K) 7.63–7.55 (6 H, m, Ph H$_{ortho}$), 7.10–6.98 (9 H, m, Ph H$_{meta}$ and H$_{para}$), 4.82 (1 H, dd, $^3J_{PH}$ 7.1, $^2J_{HH}$ 3.5 Hz, FeCH^1), 4.66 (1 H, dd, $^3J_{PH}$ 5.8 Hz, $^2J_{HH}$ 3.5 Hz, FeCH^2), 4.39 (5 H, d, $^3J_{PH}$ 1.1 Hz, C$_5$H$_5$), 2.84 (1 H, dt, $^3J_{HH}$ 10.4, 4.1 Hz, OCH), 2.33–2.18 [2 H, m, C*H*(CH$_3$)$_2$ and cyclohexyl H], 1.62–1.73 (7 H, m, cyclohexylH), 0.98 (3 H, d, $^3J_{HH}$ 7.1 Hz, CH$_3$), 0.92 (3 H, d, $^3J_{HH}$ 6.6 Hz, CH$_3$), and 0.73 (3 H, d, $^3J_{HH}$ 6.9 Hz, CH$_3$); δ_C(CDCl$_3$) 222.29 (d, $^2J_{PC}$ 31.5 Hz, C≡O), 136.76 (d, $^1J_{PC}$ 40.9 Hz, Ph C$_{ipso}$), 133.43 (d, $^2J_{PC}$ 10.1 Hz, Ph C$_{ortho}$), 129.29 (s, PhC$_{para}$), 127.91 (d, $^3J_{PC}$ 8.8 Hz, Ph C$_{meta}$), 85.28 (s, C$_5$H$_5$), 82.17 (s, menthyl C-1), 63.56 (d, $^2J_{PC}$ 20.1 Hz, FeCH$_2$), 48.90 (s), 40.87 (s), 34.77 (s), 31.67 (s), 25.10 (s), 23.17 (s), 22.51 (s), 21.38 (s), and 16.04 (s); δ_P(CDCl$_3$) 81.27; *m/z* 580 (M^+) (Found: C, 72.28; H, 7.34. Calc. for C$_{35}$H$_{41}$FeO$_2$P: C, 72.41; H, 7.12%).

Carbonyl(cyclopentadienyl)methylthiomethyl(triphenylphosphine)iron (**3a**).—Red crystalline solid (82%). $\nu_{max.}$(C≡O) 2 900, 1 910 cm^{-1}; δ_H(CD$_2$Cl$_2$; 297 K) 7.45–7.30 (15 H, m, Ph), 4.40 (5 H, d, $^3J_{PH}$ 1.2 Hz, C$_5$H$_5$), 2.08 (1 H, dd, $^3J_{PH}$ 2.9, $^2J_{HH}$ 6.2 Hz, FeCH), 1.8 (3 H, s, SMe), and 1.74 (1 H, dd, $^3J_{PH}$ 9.9, $^2J_{HH}$ 6.2 Hz, FeCH); δ_H(C$_6$D$_6$; 297 K) 7.62 (6 H, m, PhH$_{ortho}$), 7.0 (9 H, m, Ph H$_{meta}$ and H$_{para}$), 4.33 (5 H, d, $^3J_{PH}$ 1.2 Hz, C$_5$H$_5$), 2.35 (1 H, dd, $^3J_{PH}$ 8.9, $^2J_{HH}$ 6.2 Hz, FeCH^1), 2.01 (1 H, dd, $^3J_{PH}$ 4.3, $^2J_{HH}$ 6.2 Hz, FeCH^2), 1.99 (3 H, s, SMe); δ_C(C$_6$D$_6$) 222.1 (d, $^2J_{PC}$ 32.7 Hz, C≡O), and 136.9 (d, $^1J_{PC}$ 39.9 Hz, PPh$_3$C$_{ipso}$), 133.8 (d, $^2J_{PC}$ 9.1 Hz, PPh$_3$C$_{ortho}$), 129.6 (s, PPh$_3$C$_{para}$), 128.1 (d, $^3J_{PC}$ 10.0 Hz, PPh$_3$C$_{meta}$), 84.9 (s, C$_5$H$_5$), 25.1 (s, SMe), and 11.5 (d, $^2J_{PC}$ 19.5 Hz, FeCH$_2$); δ_P(C$_6$D$_6$); 80.36; *m/z* 472 (M^+) (Found: C, 66.31; H, 5.63. Calc. for C$_{26}$H$_{25}$FeOPS: C, 66.11; H, 5.33%).

Carbonyl(cyclopentadienyl)ethylthiomethyl(triphenylphosphine)iron (**3b**).—Red crystalline solid (68%). $\nu_{max.}$(C≡O) 1 910 cm^{-1}; δ_H(CD$_2$Cl$_2$; 297 K) 7.50–7.30 (15 H, m, Ph), 4.39 (5 H, d, $^3J_{PH}$ 1.0 Hz, C$_5$H$_5$), 2.17 (2 H, q, $^3J_{HH}$ 7.3 Hz, SCH$_2$), 2.05 (1 H, dd, $^3J_{PH}$ 2.8 Hz, $^2J_{HH}$ 6.0 Hz, FeCH^2), 1.74 (1 H, dd, $^3J_{PH}$ 9.9, $^2J_{HH}$ 6.0 Hz, FeCH^1), and 0.98 (3 H, t, $^3J_{HH}$ 7.3 Hz, CH$_3$); δ_H(C$_6$D$_6$; 297 K) 7.65 (6 H, m, PhH$_{ortho}$), 7.05 (9 H, m, PhH$_{meta}$ and H$_{para}$), 4.35 (5 H, d, $^3J_{PH}$ 1.1 Hz, C$_5$H$_5$), 2.35 (2 H, q, $^3J_{HH}$ 7.3 Hz), 2.31 (1 H, dd, $^3J_{PH}$ 8.9 $^2J_{HH}$ 5.7 Hz, FeCH^1), 2.03 (1 H, dd, $^3J_{PH}$ 4.6, $^2J_{HH}$ 5.7 Hz, FeCH^2), and 1.12 (3 H, t, $^3J_{HH}$ 7.3 Hz,

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[*] *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Full lists of bond lengths and angles and of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

CH_3); $\delta_C(C_6D_6)$ 222.1 (d, $^2J_{PC}$ 31.6 Hz, C≡O), 136.92 (d, $^1J_{PC}$ 39.6 Hz, PPh_3C_{ipso}), 133.71 (d, $^2J_{PC}$ 9.7 Hz, PPh_3C_{ortho}), 129.61 (s, PPh_3C_{para}), 128.12 (d, $^3J_{PC}$ 9.2 Hz, PPh_3C_{meta}), 84.97 (s, C_5H_5), 34.59 (s, SCH_2), 14.55 (s, CH_3), and 6.85 (d, $^2J_{PC}$ 18.2 Hz, $FeCH_2$); $\delta_P(C_6D_6)$ 80.48; *m/z* 486 (M^+) (Found: C, 66.52; H, 5.64; P, 6.13. Calc. for $C_{27}H_{27}FeOPS$: C, 66.07; H, 5.59; P, 6.37%).

Benzylthiomethyl(carbonyl)cyclopentadienyl(triphenylphosphine)iron (**3c**).—Red crystalline solid (28%). $\nu_{max.}$(C≡O) 1 925 cm^{-1}; $\delta_H(CD_2Cl_2$; 297 K) 7.52–7.36 (15 H, m, Ph), 7.23–7.06 (5 H, m, $CH_2C_6H_5$), 4.35 (5 H, d, $^3J_{PH}$ 0.9 Hz, C_5H_5), 3.35 (2 H, s, SCH_2), 1.93 (1 H, dd, $^3J_{PH}$ 2.8, $^2J_{HH}$ 6.1 Hz, $FeCH^2$), 1.64 (1 H, dd, $^3J_{PH}$ 10.1, $^2J_{HH}$ 6.1 Hz, $FeCH^1$); $\delta_H(C_6D_6$; 297 K) 7.54 (6 H, m, PhH_{ortho}), 7.18 (5 H, m, $SCH_2C_6H_5$), 7.01 (9 H, m, Ph H_{meta} and H_{para}), 4.26 (5 H, d, $^3J_{PH}$ 1.1 Hz, C_5H_5), 3.50 (1 H, d, $^2J_{HH}$ 12.9 Hz, SC*H*HPh), 3.45 (1 H, d, $^2J_{HH}$ 12.9 Hz, SCH*H*Ph), 2.19 (1 H, dd, $^3J_{PH}$ 9.1, $^2J_{HH}$ 6.3 Hz, $FeCH^1$), and 1.93 (1 H, dd, $^3J_{PH}$ 4.0, $^2J_{HH}$ 5.8 Hz, $FeCH^2$); $\delta_C(C_6D_6)$ 222.0 (d, $^2J_{PC}$ 32.8 Hz, C≡O), 140.68 (s, CH_2Ph C_{ipso}), 136.78 (d, $^1J_{PC}$ 40.6 Hz, PPh_3C_{ipso}), 133.60 (d, $^2J_{PC}$ 9.8 Hz, PPh_3C_{ortho}), 129.61 (s, PPh_3C_{para}), 129.2 (s, CH_2PhC_{meta}), 128.25 (s, Ch_2PhC_{ortho}), 128.12 (d, $^3J_{PC}$ 9.9 Hz, PPh_3C_{meta}), 126.09 (s, CH_2PhC_{para}), 84.84 (s, C_5H_5), 46.05 (s, SCH_2), 7.22 (d, $^2J_{PC}$ 19.5 Hz, $FeCH_2$); $\delta_P(C_6D_6)$ 79.83; *m/z* 548 (M^+) (Found: C, 70.07; H, 5.32. Calc. for $C_{32}H_{29}FeOPS$: C, 70.08; H, 5.33%).

Crystallographic Data and Data-collection Parameters for (**3c**).—*X-Ray Crystal Structure Analysis of* $(C_5H_5)Fe(CO)(PPh_3)CH_2SCH_2Ph$. Data collected as for compound (**2a**) with the following exceptions: The scan range (ω) was calculated from [1.35 + 0.35 tanθ] and the scan speed was varied from 1.4 to 82° min^{-1} depending on intensity. Equivalent reflections were merged to give 3 521 unique reflections of which 2 480 were considered to be observed [$I > 3\sigma(I)$]. The structure was solved using the SHELXS-86 program.[25] Weights for each reflection were calculated from a Chebyschev series of the form $W = [3.95t_1(X) - 1.44t_2(X) + 2.50t_3(X)]$.

Crystal Data. $C_{32}H_{29}FeOPS$, M = 548.4612, monoclinic, a = 13.677(2), b = 111.212(2), c = 18.207(1) Å, β = 107.11°, U = 2668.5 Å^3, Z = 4, D_{calc} = 1.37 g cm^{-3}, μ(Mo-K_α = 7.2074 cm^{-3}, space group $P2_{1/c}$, relative transmission factors 1.00–1.08, crystal dimensions 0.18 × 0.90 mm, number of reflections [$I > 3\sigma(I)$] 2 480, R = 0.033, R_W = 0.034.

Carbonyl(cyclopentadienyl)phenylthiomethyl(triphenylphosphine)iron (**3d**).—Red crystalline solid (75%). $\nu_{max.}$(C≡O) 2 890 and 1 910 cm^{-1}; $\delta_H(CD_2Cl_2$; 297 K) 7.48–7.34 (15 H, m, Ph), 7.16 (2 H, t, $^3J_{HH}$ 7.5 Hz, SC_6H_5 H_{meta}), 7.01 (2 H, d, $^3J_{HH}$ 8.4 Hz, $SPhH_{ortho}$), 6.91 (1 H, t, $^3J_{HH}$ 7.5 Hz, $SPhH_{para}$), 4.45 (5 H, d, $^3J_{PH}$ 1.1 Hz, C_5H_5), 2.41 (1 H, dd, $^3J_{PH}$ 2.5, $^2J_{HH}$ 5.9 Hz, $FeCH^2$), and 1.85 (1 H, dd, $^3J_{PH}$ 10.3, $^2J_{HH}$ 5.9 Hz, $FeCH^1$); $\delta_H(C_6D_6$; 297 K) 7.65 (6 H, m, PhH_{ortho}), 7.44 (2 H, d, $^3J_{HH}$ 7.5 Hz, SPh H_{ortho}), 7.16 (2 H, t, $^3J_{HH}$ 7.5 Hz, SPh H_{meta}), 7.08 (9 H, m, Ph H_{meta} and H_{para}), 6.97 (1 H, t, $^3J_{HH}$ 7.3 Hz, SPh H_{para}), 4.40 (5 H, d, $^3J_{PH}$ 1.1 Hz, C_5H_5), 2.47 (1 H, dd, $^3J_{PH}$ 3.4 Hz, $^2J_{HH}$ 5.95 Hz, $FeCH^1$), and 2.40 (1 H, dd, $^3J_{PH}$ 9.6, $^2J_{HH}$ 5.95 Hz, $FeCH^2$); $\delta_C(C_6D_6)$ 221.9 (d, $^2J_{PC}$ 32.1 Hz, C≡O), 148.05 (s, $SPhC_{ipso}$), 136.5 (d, $^1J_{PC}$ 41.3 Hz, PPh_3C_{ipso}), 133.55 (d, $^2J_{PC}$ 9.5 Hz, PPh_3 C_{ortho}), 129.77 (s, PPh_3 C_{para}), 128.31 (d, $^3J_{PC}$ 8.8 Hz, PPh_3C_{meta}), 125.78 (s, $SPhC_{meta}$), 123.41 (s, $SPhC_{para}$), 85.05 (d, $^2J_{PC}$ 22.9 Hz, C_5H_5), 5.10 (d, $^2J_{PC}$ 18.9 Hz, $FeCH_2$); $\delta_P(C_6D_6)$ 79.57; *m/z* 534 (M^+) (Found: C, 69.71; H, 5.08; P, 5.70. Calc. for $C_{31}H_{27}FeOPS$: C, 69.67; H, 5.09; P. 5.79%).

Variable-temperature and Polarity N.M.R. Experiments.—Variable-temperature spectra were recorded at higher temperatures in [$^2H_8$]toluene, whilst at lower temperatures [$^2H_2$]dichloromethane was the solvent of choice. The temperature control was accurate to ±1 °C.

Variable-solvent spectra were recorded at ambient temperature (*ca.* 297 K) and the solvent solutions were prepared by measuring, with a 250 mm^3 syringe, the appropriate percentage of [$^2H_6$]benzene and [$^2H_2$]dichloromethane such that the total volume of solution was 750 mm^3. These solutions were subsequently degassed by the freeze–thaw method and were accurate to ±2.0%.

^{1}H N.m.r. experiments were conducted on a Bruker WH 300 spectrometer at 300.13 MHz. Typically, a sweep width of 3 500 Hz was used and the FID recorded and processed in 16 K blocks of computer memory. Thus, the values obtained for the coupling constants are accurate to ±0.2 Hz.

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References

1 (*a*) R. P. Beckett and S. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1988, 160; (*b*) G. Bashiardes and S. G. Davies, *Tetrahedron Lett.*, 1987, 5563; (*c*) R. J. Capon, J. K. MacLeod, S. J. Coote, S. G. Davies, L. Gravatt, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *Tetrahedron*, 1988, **44**, 1637; (*d*) S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and J. C. Walker, *Tetrahedron*, 1986, **42**, 5123.

2 Reviews: (*a*) S. G. Davies, I. M. Dordor-Hedgecock, R. J. C. Easton, S. C. Preston, K. H. Sutton, and J. C. Walker, *Bull. Chim. Soc. Fr.*, 1987, 608; (*b*) S. G Davies, G. Bashiardes, R. P. Beckett, S. J. Coote, I. M. Dordor-Hedgecock, C. L. Goodfellow, G. L. Gravatt, J. P. McNally, and M. Whittaker, *Philos. Trans. R. Soc. London*, 1988, in press.

3 L. S. Liebeskind, M. E. Welker, and R. W. Fengl, *J. Am. Chem. Soc.*, 1986, **108**, 6328 and references cited therein.

4 (*a*) J. I. Seeman and S. G. Davies, *J. Am. Chem. Soc.*, 1985, **107**, 6522; (*b*) J. I. Seeman and S. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1984, 1019; J. I. Seeman and S. G. Davies, *Tetrahedron Lett.*, 1984, 1845; (*d*) *J. Chem. Soc., Dalton Trans.*, 1985, 2691; (*e*) S. G. Davies, J. I. Seeman, and I. H. Williams, *Tetrahedron Lett.*, 1986, **27**, 619; (*f*) S. L. Brown, I. M. Dordor-Hedgecock, S. G. Davies, D. F. Foster, J. I. Seeman, and P. Warner, *Tetrahedron Lett.*, 1986, **27**, 623.

5 Reviews: (*a*) B. K. Blackburn, S. G. Davies, K. H. Sutton, and M. Whittaker, *Chem. Soc. Rev.*, 1988, 147; (*b*) B. K. Blackburn, S. G. Davies, and M. Whittaker in 'Stereochemistry of Organometallic and Inorganic Compounds,' ed., I. Bernal, vol. 3, Elsevier, Amsterdam, 1988.

6 (*a*) S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *J. Organomet. Chem.*, 1987, **320**, C19; (*b*) S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *Chem. Ind. (London)*, 1987, 338; (*c*) S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, and M. Whittaker, *J. Am. Chem. Soc.*, 1987, **109**, 5711.

7 (*a*) A. P. Ayscough and S. G. Davies, *J. Chem. Soc., Chem. Commun.*, 1986, 1648; (*b*) S. G. Davies and M. Wills, *J. Organomet. Chem.*, 1987, **328**, C29; (*c*) S. G. Davies and M. Wills, *J. Chem. Soc., Chem. Commun.*, 1987, 1647.

8 B. K. Blackburn, S. G. Davies, and M. Whittaker, *J. Chem. Soc., Chem. Commun.*, 1987, 1344.

9 A. J. Kirby, 'Anomeric Effect and Related Stereoelectronic Effects at Oxygen,' Springer Verlag, Berlin, 1983.

10 (*a*) B. E. R. Schilling, R. Hoffmann, and Lichtenberger, D. L. *J. Am. Chem. Soc.*, 1979, **101**, 585; (*b*) B. E. R. Schilling, R. Hoffmann, and J. W. Faller, *ibid.*, 1979, **101**, 592.

11 G. J. Baird, S. G. Davies, and T. R. Maberly, *Organometallics*, 1984, **3**, 1764.

12 C.-K. Chou, D. L. Miles, R. Bau, and T. C. Flood, *J. Am. Chem. Soc.*, 1978, **100**, 7271.

13 J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, 1957, **79**, 846.

14 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2869.

15 D. G. Gorenstein, 'Phosphorus-31 NMR, Principles and Applications,' Academic Press, Orlando, 1984.

16 J. Booth, *Tetrahedron Lett.*, 1965, 411.

17 C. A. G. Haasnoot, F. A. A. M. De Leeuw, and C. Altona, *Tetrahedron*, 1980, **36**, 2783.

18 T. R. Maberly, D.Phil. Thesis, Oxford University, 1986.

19 (*a*) J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect,' Academic Press, New York, 1971; (*b*) A. E. Derome, 'Modern NMR Techniques for Chemistry Research,' Pergamon Press, Oxford, 1987.

20 M. C. Baird and B. K. Hunter, *Organometallics*, 1985, **4**, 1481.

21 C. Djerassi, L. E. Geller, and E. J. Eisenbraun, *J. Org. Chem.*, 1960, **25**, 1.

22 (*a*) D. F. Shriver and M. A. Drezdzon, 'The Manipulation of Air-sensitive Compounds,' Wiley–Interscience, New York, 1986; (*b*) J. P. McNally, V. S. Leong, and N. J. Cooper in 'Experimental Organometallic Chemistry,' eds. A. L. Wayda and M. Y. Darensbourg, ACS, Washington DC, 1987, ch. 2.

23 J. J. Eisch and R. B. King, 'Organometallic Synthesis,' Academic Press, New York, 1965, vol. 1: (*a*) p. 114, (*b*) p. 151.

24 A. C. T. North, D. C. Philips, and F. S. Matthews, *Acta Crystallogr., Sect A*, 1968, **24**, 351.

25 G. M. Sheldrick in 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, 1985.

26 A. C. Larson, 'Crystallographic Computing,' ed. F. R. Ahmed, Munttsguard, 1970, p. 170.

27 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.

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