[1] FERROCENOPHANES. SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF [1] FERROCENOPHANES WITH GROUP IV AND V ELEMENTS AS BRIDGE ATOMS

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Summary

The [1] ferrocenophanes, 1,1'-ferrocenediyldiphenylsilane, bis(1,1'-ferrocenediyl)silane, 1,1'-ferrocenediyldiphenylgermane and 1,1'-ferrocenediylphenylphosphine have been prepared by the reaction of 1,1'-dilithioferrocenebis(N,N,N',N'-tetramethylethylenediamine) with dichlorodiphenylsilane, tetrachlorosilane, dichlorodiphenylgermane and P,P-dichlorophenylphosphine, respectively. Similar reactions with dichlorodimethyltin or dichlorodiphenyltin yielded only polymeric products. The Group IV [1]ferrocenophanes are red, air-stable, crystalline solids; the phosphorus compound is red-purple and is moderately air-sensitive. The spectroscopic properties of the compounds, which are consistent with ring-tilted structures, are reported and discussed.

Introduction

Although there are many known examples of [m]ferrocenophanes ($m \geq 2$), the first examples of [1]ferrocenophanes have been reported only recently [1—3]. We now report the details of the preparation and spectroscopic properties of some [1]ferrocenophanes with Group IV and V elements as bridge atoms.

Results and discussion

Reaction of the N,N,N',N'-tetramethylethylenediamine (TMED) adduct of 1,1'-dilithioferrocene with $(C_6H_5)_2SiCl_2$, $SiCl_4$, $(C_6H_5)_2GeCl_2$ and $C_6H_5PCl_2$

yielded the [1]ferrocenophanes I, II, III and IV, respectively.
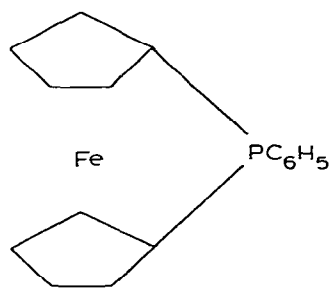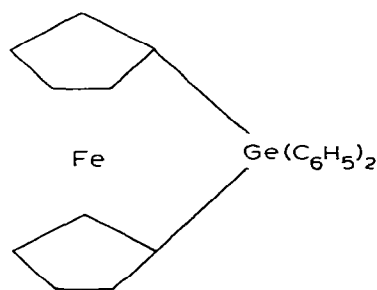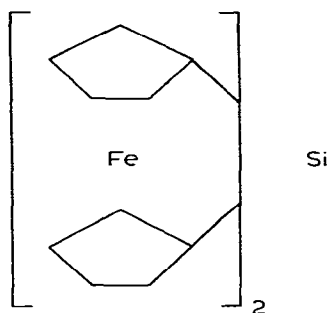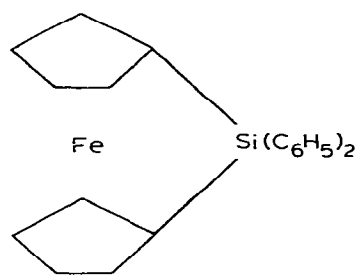
Compounds I, II and III are red, air-stable, crystalline solids; IV is a red-purple crystalline solid and is moderately air-sensitive. All the compounds are stable under an inert atmosphere in hydrocarbon solvents, but slowly decompose in solvents such as chloroform or ethanol. In all the preparations a considerable amount of polymeric material was also formed, as is to be expected with the free rotation of the cyclopentadienyl rings in the dilithio-intermediate. Indeed, in attempts to prepare a [1]ferrocenophane with Sn as the bridge atom, using $(CH_3)_2SnCl_2$ or $(C_6H_5)_2SnCl_2$, only polymeric material was obtained. The polymeric product from the $(CH_3)_2SnCl_2$ reaction was formulated as $C_{10}H_9Fe$-$[C_{10}H_8FeSnMe_2]_xH$, $x \approx 13$, on the basis of analytical results, ^1H NMR spectrum and molar mass measurements. No attempt was made to characterise polymeric products from other reactions. Analytical data, reaction yields, colours and melting temperatures for the [1]ferrocenophanes are listed in Table 1. The [1]ferrocenophanes show molecular ions in their mass spectra with isotope patterns in good agreement with theory.

In ferrocene the cyclopentadienyl rings are planar and parallel with an inter-ring separation [4] of 332 pm. Thus in [1]ferrocenophanes distortions from the ferrocene structure must occur with the cyclopentadienyl rings being inclined towards each other and towards the bridging atom. The structures of I, II and

TABLE 1

REACTION YIELDS, PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR [1]FERROCENO-
PHANES

Com-pound	Yield (%)	m.p. (°C)	Colour	Analytical results (%) [a]			
				C	H	Fe	P
I	32	196—197 [b]	Red	72.1(72.1)	5.9(5.0)		
II	17	>300 dec. [b]	Red	60.5(60.6)	4.3(4.1)		
III	19	>250 dec. [b]	Red	64.2(64.3)	4.4(4.4)		
IV	51	104—147 dec.	Red-purple	65.5(65.8)	4.6(4.5)	19.4(19.1)	10.3(10.6)

[a] Calculated figures in brackets. [b] Sealed under vacuum.

III have been determined [5] and show that in addition to ring tilting there
is considerable bond angle distortion at the substituted C(1) atoms of the cyclo-
pentadienyl rings, see Fig. 1 and Table 2. The spectroscopic properties of the
[1]ferrocenophanes reflect these structural distortions.

Details of the ^{1}H NMR spectra of the [1]ferrocenophanes and of some
related non-bridged compounds for comparison purposes are shown in Table 3.
The spectra of I, II and III all contain, as expected, a pair of unsymmetrical
triplets corresponding to the H(2,5) and H(3,4) protons on the cyclopentadienyl
rings (Fig. 2). The observed coupling is ≈1.6 Hz in all three cases, which is
similar to that found for other substituted ferrocenes. The principal difference
is that the separation between the triplets is usually larger for the [1]ferro-
cenophane than for non-bridged analogues. In the case of [2]ferrocenophanes
bridged by carbon atoms it has been suggested [6] that this spectral feature is
caused by ring tilting, the pairs of protons H(2,5) and H(3,4) being no longer
equidistant from the iron atom, with the H(2,5) protons undergoing greater
shielding from the iron atom and so giving rise to the upfield signal in the spec-
trum. This assignment was later confirmed by a study [7] of multibridged
ferrocenes, but the explanation in terms of Fe—C(Cp) distances has been ques-
tioned [8]. It was further suggested, again in terms of Fe—C(Cp) distances, that
the separation of the triplets is directly related to the angle of tilt of the rings.
In the case of [1]ferrocenophanes this suggestion is unlikely to apply with any
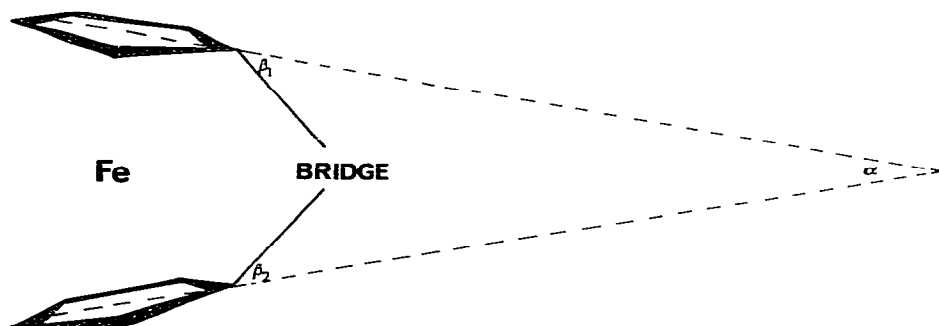consistency since the ring-tilt distortion observed is the sum of two types of

Fig. 1. Distortions in [1]ferrocenophanes.

TABLE 2

SOME STRUCTURAL PARAMETERS FOR [1]FERROCENOPHANES ^{a}

Compound	α (°)	$\bar{\beta}$ (°)
I	19.2	40
III	16.6	38
IV	26.7	32.5

^{a} For explanation of symbols see Fig. 1. $\bar{\beta} = (\beta_1 + \beta_2)/2$.

distortion; (a) ring tilt using the Fe atom as a fulcrum, and (b) ring tilt about the centroids of the cyclopentadienyl rings, and it is only type b, which was found to be almost constant in compounds I, III and IV, which will change Fe—C(Cp) distances. Furthermore, the C(1) bond angle distortion may also affect the magnitude of the separation.

In the absence of further data the assignment of the C_5H_4 signals in the ^1H NMR spectra of I, II and III remains unresolved. In the spectrum of IV, however, the triplet at $\delta = 4.18$ ppm is probably due to the H(3,4) protons and the signals at $\delta = 4.29$ and 4.53 ppm, are presumably due to the H(2) and H(5)

Fig. 2.
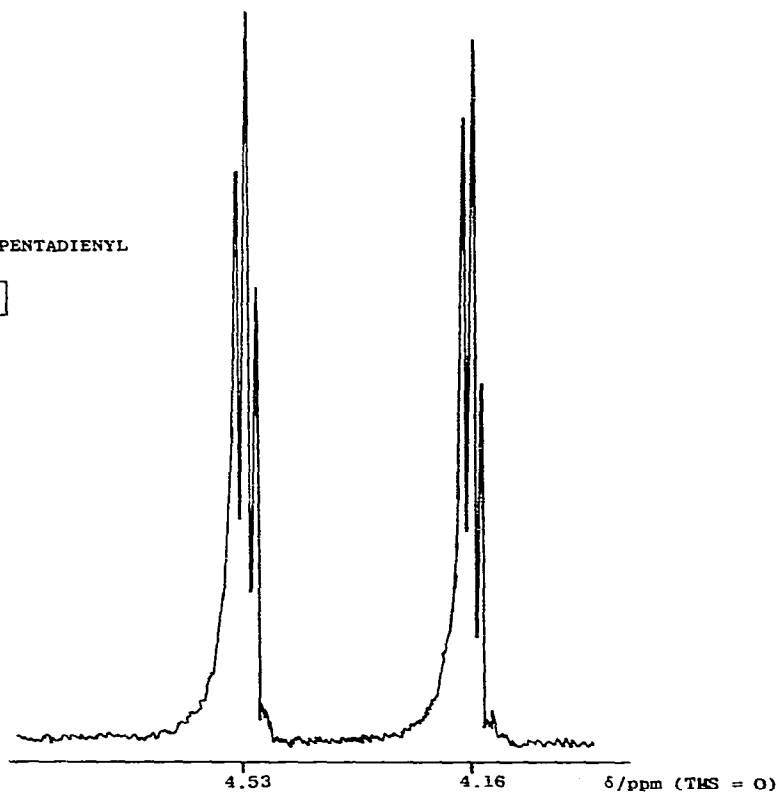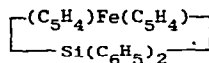
^1H NMR SPECTRUM OF THE CYCLOPENTADIENYL

GROUP IN $\quad$ [—(C$_5$H$_4$)Fe(C$_5$H$_4$)— / —Si(C$_6$H$_5$)$_2$—]

4.53　　　　4.16　　　δ/ppm (TMS = 0)

TABLE 3

1H NMR DATA FOR SILICON, GERMANIUM AND PHOSPHORUS SUBSTITUTED FERROCENES [a]

Compound	Chemical shift [b] (multiplicity, relative intensity) [c]			
	C_5H_5	C_5H_4	C_6H_5 (meta and para)	C_6H_5 (ortho)
$[(C_5H_5)Fe(C_5H_4)]_2Si(C_6H_5)_2$	3.86(s, 5)	4.28(t, 2), 4.39(t, 2)	7.25–7.50(m, 3)	7.50–7.75(m, 2)
$[C_5H_4Si(C_6H_5)_3]_2Fe$		3.98(s, 4)	7.05–7.65(m, 16)	
$(C_5H_4)Fe(C_5H_4)$ —— $Si(C_6H_5)_2$		4.16(t, 2), 4.53(t, 2) [4.01(t, 1), 4.41(t, 1)] [d]	7.30–7.60(m, 3)	7.90–8.10(m, 2)
$[(C_5H_4)Fe(C_5H_4)]_2$ —— Si		4.50(t, 1), 4.65(t, 1) [4.47(s)] [d]		
$[(C_5H_5)Fe(C_5H_4)]_2Ge(C_6H_5)_2$	3.84(s, 5)	4.22(t, 2), 4.34(t, 2)	7.25–7.45(m, 3)	7.45–7.70(m, 2)
$(C_5H_4)Fe(C_5H_4)$ —— $Ge(C_6H_5)_2$		4.24(t, 2), 4.48(t, 2)	7.35–7.65(m, 3)	7.75–8.05(m, 2)
$[(C_5H_5)Fe(C_5H_4)]_2PC_6H_5$ [d]	3.88–4.15(s/m)	and 4.15–4.32(m, 18)	7.00–7.30(m, 3)	7.55–7.85(m, 2)
$[C_5H_4P(C_6H_5)_2]_2Fe$ [d]		4.01(t, 1), 4.11(t, 1)	6.85–7.20(m, 3)	7.20–7.55(m, 2)
$(C_5H_4)Fe(C_5H_4)$ —— PC_6H_5 [d]		4.18(t, 4), 4.29(m, 2), 4.53(m, 2)	7.05–7.40(m, 3)	7.50–7.80(m, 2)
$\left[(C_5H_4)Fe(C_5H_4)\underset{PC_6H_5}{}\right]_2PtCl_2$		4.14(m, 4), 4.33(m, 4), 4.57(m, 2)	7.2–7.7(m, 3)	7.7–8.2(m, 2)

[a] In CDCl₃ solution unless otherwise stated. [b] δ, ppm (TMS = 0 ppm). [c] s, singlet; d, doublet; t, unsymmetrical triplet; m, multiplet; s/m, singlet overlapping multiplet. [d] C_6D_6 solution.

protons one of which (δ = 4.53 ppm) is preferentially deshielded by the neighbouring phenyl group.

Because of the asymmetry of IV it should, in principle, be possible to observe inversion at the phosphorus atom. ^{1}H NMR spectra in C_6D_6 were recorded at temperatures up to 70°C, but there was no evidence for inversion.

IV will act as a conventional ligand towards transition metals, reacting with (COD)PtCl$_2$ to form cis-bis(1,1'-ferrocenediylphenylphosphine)dichloroplatinum(II), which crystallises from benzene as dark red needles with molecules of solvent in the crystals. In the ^{31}P NMR spectrum of IV, the signal at δ = 11.2 ppm ($\delta(H_3PO_4)$ = 0 ppm) was observed to shift downfield to δ = 17.8 ppm, $^1J(^{195}Pt—^{31}P)$ = 3643 Hz, in the spectrum of the platinum complex. The magnitude of the coupling confirms a cis geometry for the metal complex. The shift of 6.6 ppm downfield was rather smaller than was expected [9].

It is in the ^{13}C NMR spectra of the [1]ferrocenophanes that the most noticeable effect of the molecular distortion is observed. Data for the [1]ferrocenophanes and for some related non-bridged compounds are given in Table 4. The most striking feature is the high field value of the C(1) signal in the spectra of the [1]ferrocenophanes which occurs 35—60 ppm upfield from the resonance position for a C(1) atom of non-bridged analogues. This upfield shift is undoubtedly allied to the structural distortions at the C(1) atoms, but it does not seem possible to quantitatively relate the magnitude of the shift to any single structural parameter, and thus use the shift for structural diagnostic purposes. In IV the C(1) atoms are strongly coupled to the phosphorus atom, $J(^{31}P—^{13}C)$ = 55 Hz; this compares with values of 7 Hz and 10 Hz in the non-bridged compounds $(C_{10}H_9Fe)_2PC_6H_5$ and $[C_5H_4P(C_6H_5)_2]_2Fe$.

The results of some selective ^{1}H decoupling experiments are shown in Table 5. The data show that for the silicon and germanium bridged [1]ferrocenophanes the upfield C_5H_4 signal in each ^{13}C NMR spectrum is associated with the upfield C_5H_4 triplet in the corresponding ^{1}H NMR spectrum, whereas the opposite is the case in the spectra of the non-bridged analogues.

The electronic spectrum of ferrocene has two main absorptions, viz 325 and 440 nm. For ferrocenophanes with tilted rings it has been found [10] that it is the 440 nm band which is the most affected by the ring tilt. This is also true for [1]ferrocenophanes; the 440 nm band undergoes a bathochromic shift and also increases in intensity (see Table 6 and Fig. 3). It can be seen from the data in Table 6 that, by itself, substitution of the rings has little effect on the 440 nm band, the predominant causes of the bathochromic shift are therefore the structural distortions. Again it is not possible to relate the magnitude of the shift just to the ring tilt, e.g. any one of these shifts is larger than that observed for any other ferrocenophane and yet the ring tilting observed for I and III is less than is observed in some [2]ferrocenophanes. The C(1) bond angle distortion must again be an important factor.

In the Mössbauer spectra the [1]ferrocenophanes also show some interesting results. By comparison with ferrocene and the non-bridged ferrocene derivatives studied, the [1]ferrocenophanes show a fall in quadrupole splitting from values $\approx$2.3—2.4 to $\approx$1.95—2.0 mm s^{-1}. The effect of bridging on the isomer shift is very much less marked and hardly significant. These results are in contrast with those quoted by Hillman and Nagy for other bridged ferrocene

TABLE 4

13C NMR DATA FOR SILICON, GERMANIUM AND PHOSPHORUS SUBSTITUTED FERROCENES [a]

Compound	Chemical shift [b]							
	$C_{10}H_9Fe$ or $C_{10}H_8Fe$			C_6H_5				
	C(1)	C_5H_5	C(2,3,4,5)	C(1)	C(2,6)	C(3,5)	C(4)	
$[(C_5H_5)Fe(C_5H_4)]_2Si(C_6H_5)_2$	66.4	68.7	71.1, 74.8	137.6	135.4	127.4	129.1	
$[C_5H_4Si(C_6H_5)_3]_2Fe$	66.4	—	72.8, 75.4	135.5	135.9	127.7	129.4	
$(C_5H_4)Fe(C_5H_4)$—$Si(C_6H_5)_2$	31.0	—	76.7, 77.8	134.4	134.3	128.3	130.3	
$[(C_5H_4)Fe(C_5H_4)]_2$—Si	30.6	—	75.1, 77.9					
$[(C_5H_5)Fe(C_5H_4)]_2Ge(C_6H_5)_2$	69.6	68.5	70.4, 73.6	139.1	134.7	127.9	128.7	
$(C_5H_4)Fe(C_5H_4)$—$Ge(C_6H_5)_2$	28.5	—	76.7, 76.9	135.9	134.0	128.6	129.8	
$[(C_5H_5)Fe(C_5H_4)]_2PC_6H_5$ [c,d]	78.8(7)	69.4	70.1(3), 70.8(3) 72.3(12), 73.0(16)	[e]	134.3(21)	—	—	
$[C_5H_4P(C_6H_5)_2]_2Fe$ [c,d]	77.6(10)	—	72.6(4), 74.2(15)	139.8(12)	133.8(21)	—	—	
$(C_5H_4)Fe(C_5H_4)$—PC_6H_5 [c,d]	18.7(55)	—	77.2(34), 77.5(29) 77.6(7), 77.7(21)	137.9(12)	130.7(14)	—	—	

[a] In CDCl$_3$ solution unless otherwise stated. [b] ppm downfield from TMS. [c] C$_6$D$_6$ solution. The C meta and C para signals were obscured. [d] The figures in brackets are coupling constants, $J(^{31}P-^{13}C)$ (Hz). [e] Not observed.

TABLE 5

^{13}C NMR SIGNALS AND ASSOCIATED ^{1}H NMR SIGNALS IN SOME FERROCENE DERIVATIVES

Compound	^{13}C Resonance [^{1}H Resonance] (ppm)	
$\left[(C_5H_5)Fe(C_5H_4)\right]_2 Si(C_6H_5)_2$	71.1 [4.39],	74.8 [4.28]
$\begin{array}{l} (C_5H_4)Fe(C_5H_4) \\ Si(C_6H_5)_2 \end{array}$	76.7 [4,16],	77.8 [4.53]
$\begin{array}{l} \left[(C_5H_4)Fe(C_5H_4)\right]_2 \\ Si \end{array}$	75.1 [4.50],	77.9 [4.65]
$\left[(C_5H_5)Fe(C_5H_4)\right]_2 Ge(C_6H_5)_2$	70.4 [4.22],	73.6 [3.84]
$\begin{array}{l} (C_5H_4)Fe(C_5H_4) \\ Ge(C_6H_5)_2 \end{array}$	76.7 [4,24],	76.9 [4.48]
$\left[C_5H_4 P(C_6H_5)_2\right]_2 Fe$	72.6 [4.11],	74.2 [4.01]
$\begin{array}{l} (C_5H_4)Fe(C_5H_4) \\ PC_6H_5 \end{array}$	77.2 [4.53], 77.5 [4.18], 77.6 [4.29], 77.7 [4.18]	

Fig. 3.

UV-VISIBLE SPECTRA OF FERROCENE AND SOME

[1] FERROCENOPHANES

$- - - -$ $(C_5H_5)_2 Fe$
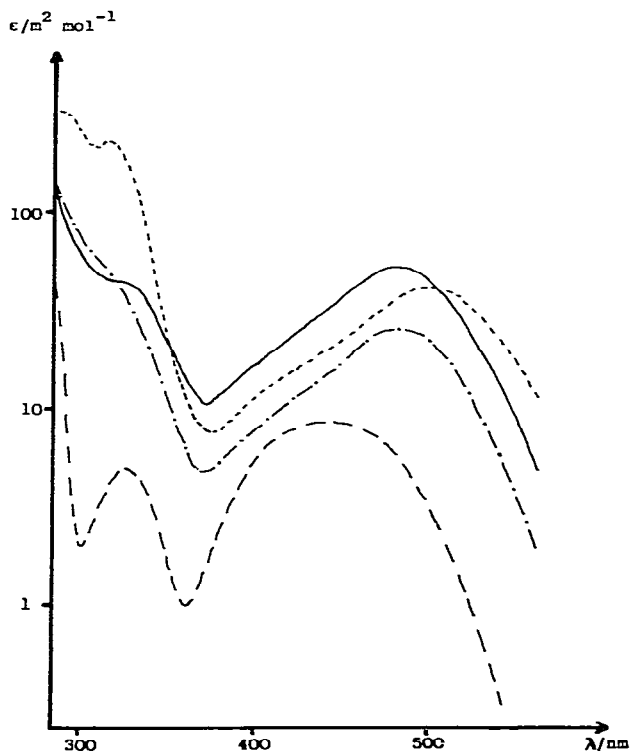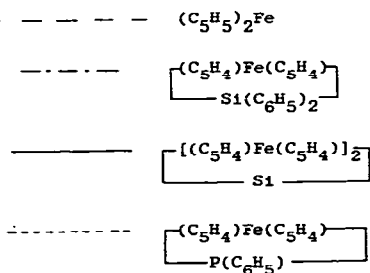
$-\cdot-\cdot-$ $\begin{array}{l}(C_5H_4)Fe(C_5H_4)\\ Si(C_6H_5)_2\end{array}$

$\underline{\hspace{2cm}}$ $\begin{array}{l}[(C_5H_4)Fe(C_5H_4)]_2\\ Si\end{array}$

$- - - - - -$ $\begin{array}{l}(C_5H_4)Fe(C_5H_4)\\ P(C_6H_5)\end{array}$

TABLE 6

ELECTRONIC SPECTRAL DATA FOR SILICON, GERMANIUM AND PHOSPHORUS SUBSTITUTED FERROCENES [a]

	λ_{max} (nm)	ϵ (m^2 mol^{-1})
$(C_5H_5)_2Fe$	440	9.0
$[(C_5H_5)Fe(C_5H_4)]_2PC_6H_5$	442	29.5 [b]
$[C_5H_4P(C_6H_5)_2]_2Fe$	442	20.7
┌─ $(C_5H_4)Fe(C_5H_4)$ ─┐ └──── PC_6H_5 ────┘	501	43.0
$[(C_5H_5)Fe(C_5H_4)]_2Si(C_6H_5)_2$	452	24.3 [b]
$[C_5H_4Si(C_6H_5)_3]_2Fe$	447	16.7
┌─ $(C_5H_4)Fe(C_5H_4)$ ─┐ └──── $Si(C_6H_5)_2$ ────┘	483	27.0
┌─ $[(C_5H_4)Fe(C_5H_4)]_2$ ─┐ └──── Si ────┘	483	54.0 [b]
$[(C_5H_5)Fe(C_5H_4)]_2Ge(C_6H_5)_2$	451	23.5 [b]
┌─ $(C_5H_4)Fe(C_5H_4)$ ─┐ └──── $Ge(C_6H_5)_2$ ────┘	486	23.0

[a] In cyclohexane solution. [b] N.B. These compounds contain two ferrocene units per molecule and therefore for comparison purposes ϵ should be halved.

derivatives, some containing several bridges [11]. These authors found a linear relationship between the changes in quadrupole splitting and isomer shift (relative to ferrocene) and the mean iron—ring distance. They suggested that this distance is the significant factor rather than the angle of tilt of the rings. In the form of ring tilt observed in the present work, changes in iron—ring distance are relatively small (from 166 pm in ferrocene to 163—165 pm in I, III and IV) and yet the change in quadrupole splitting reported here is much larger than would be expected from the linear relationship observed by Hillman and Nagy for such a small change in the iron—ring distance.

An alternative possibility is that the distortion at the C(1) carbon atoms leads to changes in the metal—ring bonding. Such changes might cause withdrawal of electrons from the iron d_{xy} orbital and a reduction of the quadrupole splitting. The fall in quadrupole splitting when ferrocene is oxidised to the ferrocinium ion is interpreted in this way [12]. Now that the molecular

TABLE 7

MOSSBAUER PARAMETERS FOR [1]FERROCENOPHANES AND RELATED NON-BRIDGED COMPOUNDS

Compound	T (K)	ΔE_q (mm s⁻¹)	δ (mm s⁻¹) [a]
$(C_5H_5)_2Fe$	77	2.42	0.53
	~295	2.37	0.44
$[(C_5H_5)Fe(C_5H_4)]_2Si(C_6H_5)_2$	77	2.29	0.53
$[C_5H_4Si(C_6H_5)_3]_2Fe$	77	2.32	0.55
$(C_5H_4)Fe(C_5H_4)$ / $Si(C_6H_5)_2$	77	1.97	0.51
$[(C_5H_4)Fe(C_5H_4)]_2$ / Si	77	2.01	0.51
$[(C_5H_5)Fe(C_5H_4)]_2PC_6H_5$	~295	2.35	0.44
$[C_5H_4P(C_6H_5)_2]_2Fe$	77	2.37	0.53
	~295	2.31	0.43
$(C_5H_4)Fe(C_5H_4)$ / PC_6H_5	77	1.97	0.52
	~295	1.96	0.43
$[(C_5H_5)Fe(C_5H_4)]_2Ge(C_6H_5)_2$	77	2.30	0.52
	~295	2.29	0.44
$(C_5H_4)Fe(C_5H_4)$ / $Ge(C_6H_5)_2$	77	2.02	0.51
	~295	2.01	0.43

[a] Relative to iron metal.

structures of I, III and IV are known [5], it would be useful to perform some molecular orbital calculations on these molecules to try to rationalise these values.

In conclusion, it can be seen that the [1]ferrocenophanes are unusual and interesting compounds whose spectroscopic properties do not fit the patterns established for other ring-tilted ferrocenophanes. Further work is in progress to extend the range of [1]ferrocenophanes, to investigate their solution chemistry and to prepare this type of compound with other metallocene systems.

Experimental

¹H NMR spectra were recorded at 100 MHz using a JEOL MH 100 spectrometer. ¹³C and ³¹P NMR spectra were recorded at 25 MHz and 40.5 MHz respectively using a JEOL PS/PFT100 spectrometer. Electronic spectra were recorded on a Pye-Unicam SP1800 spectrophotometer. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU 6 instrument. ⁵⁷Fe Mössbauer spectra

were recorded on a conventional constant-acceleration Mössbauer spectrometer [13], using a 25 mCi ^{57}Co(Pd) source supplied by the Radiochemical Centre, Amersham, England, using iron metal as a standard. Analyses were obtained from the Exeter University departmental service or from Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use and all reactions were carried out under nitrogen. N,N,N',N'-tetramethylethylenediamine (TMED) was fractionally distilled and the fraction boiling between 121.5—122.5°C was used.

1,1'-dilithioferrocene-bis(N,N,N',N'-tetramethylethylenediamine) was prepared according to a published procedure [14] with the modification that a much longer reaction time ($\approx$18 hours) was found to give improved yields. Non-bridged ferrocene derivatives were prepared by literature methods [15,16].

Preparation of 1,1'-ferrocenediyldiphenylsilane (I)

TMED (15.05 cm^3; 100 mmol) and n-butyllithium (100 mmol) were added to a stirred solution of ferrocene (7.44 g; 40 mmol) in n-hexane (400 cm^3). After 18 hours the stirred mixture was cooled to —78°C and a solution of dichlorodiphenylsilane (6.2 cm^3; 30 mmol) in n-hexane (100 cm^3) was added. The mixture was left to warm to room temperature then heated under reflux for 1 hour. The cooled mixture was stirred for 30 minutes with water (5 cm^3), then filtered through a glass sinter (porosity 2). The red filtrate was washed several times with water, dried over MgSO$_4$, filtered and the volume of solution reduced to approximately 10 cm^3 under reduced pressure. The precipitated product was filtered off, washed with cold n-hexane and dried in vacuo. The yield was 3.02 g. A further crop of pure product was obtained from the filtrate by chromatographing it on neutral alumina (1% H$_2$O) using benzene as eluent. Total yield of pure product was 3.49 g (32%). Molar mass (osmometrically in benzene) 372; calculated 366.

Preparation of bis-(1,1'-ferrocenediyl)silane (II)

A sample of 1,1'-dilithioferrocene-bis(N,N,N',N'-tetramethylethylenediamine), prepared as above from ferrocene (1.86 g; 10 mmol) was washed with n-hexane (25 cm^3) and then suspended in n-hexane (50 cm^3). The suspension was cooled to —78°C and tetrachlorosilane (4.0 mmol) as a 0.65 M solution in n-hexane was added with stirring. The mixture was allowed to warm to room temperature then heated under reflux for 1½ hours. The cooled mixture was stirred for 30 minutes with 0.1 M potassium hydroxide solution (75 cm^3) and then filtered to give a red solid which was washed with water and n-hexane and dried at 50°C in vacuo. Soxhlet extraction of the red solid with n-hexane, evaporation to dryness and recrystallisation from benzene gave 264 mg (17%) of the pure product. Molar mass (osmometrically in benzene) 403, calculated 396.

Preparation of 1,1'-ferrocenediyldiphenylgermane (III)

The preparation was carried out as described for the preparation of I, using the following amounts of reactants; TMED (3.76 cm^3; 22.3 mmol), n-butyllithium (22.4 mmol), ferrocene (1.68 g; 9.0 mmol) and dichlorodiphenylgermane (1.82 g; 6.1 mmol). The total yield of III was 485 mg (19%).

Preparation of 1,1'-ferrocenediylphenylphosphine (IV)

A sample of 1,1'-dilithioferrocene-bis(N,N,N',N'-tetramethylethylene-diamine) prepared as above from ferrocene (1.86 g; 10 mmol) was washed with n-hexane and then suspended in n-hexane (50 cm^3). The stirred suspension was cooled to $-78°$C and a solution of P,P-dichlorophenylphosphine (1.2 g; 6.6 mmol) in n-hexane (60 cm^3) was added. The mixture was allowed to warm to room temperature and then stirred for a further 20 hours. Water (50 cm^3) was added and the mixture stirred for 30 minutes before being filtered. The burgundy coloured filtrate was washed several times with water, dried over MgSO$_4$, filtered and the volume reduced to about 40 cm^3 when dark red-purple crystals began to form. The solution was left to crystallise overnight at $-18°$C. The product obtained in this way contained a small amount of a powdery brown material as an impurity, which was easily removed by washing the product in n-hexane. Alternatively the phosphine could be purified by chromatography on Grade II alumina under a nitrogen atmosphere, using benzene as solvent. The yield of IV, as a moderately air-sensitive solid, was 994 mg (51%).

Preparation of cis-dichlorobis(1,1'-ferrocenediylphenylphosphine)platinum(II)

A solution of IV (200 mg; 0.69 mmol) in benzene (50 cm^3) was added to a stirred solution of dichloro(cis,cis,1,5-cyclooctadiene)platinum(II) (100 mg; 0.27 mmol) in benzene (100 cm^3). The mixture was left to stand at $5°$C for 18 hours during which time the product crystallized as small dark-red needles. The solid was filtered off and dried in vacuo, the yield was 185 mg (79%). (Found: C, 46.3; H, 3.5; Cl, 7.6; P, 6.7. $C_{32}H_{26}Cl_2FeP_2Pt \cdot 0.3$-$C_6H_6$ calcd.: C, 46.5; H, 3.2; Cl, 8.1; P, 7.1%). The compound decomposes above $160°$C without melting.

Preparation of poly(1,1'-ferrocenediyldimethyltin)

A sample of 1,1'-dilithioferrocene-bis(N,N,N',N'-tetramethylethylene-diamine) was prepared as above from ferrocene (1.03 g; 5.5 mmol) and was suspended in tetrahydrofuran (40 cm^3). The stirred suspension was cooled to $-78°$C and a solution of dichlorodimethyltin (0.79 g; 3.6 mmol) in tetra-hydrofuran (30 cm^3) was added. The mixture was allowed to warm to room temperature and then stirred for further 26 hours, after which the volume of the solution was reduced to 15 cm^3 and toluene (60 cm^3) was added. The mixture was filtered, the volume of the solution reduced to 15 cm^3 and n-hexane (80 cm^3) was added. This caused an orange viscous oil to precipitate, which was washed with n-hexane and dried ($60°$C; 0.4 mmHg). The yield of crude product was 651 mg (35%). A sample for analysis was purified by column chromato-graphy to given an orange resinous material (Found: C, 44.1; H, 4.3; Molar mass (osmometrically in chloroform) approximately 4600; ^{1}H NMR, CH$_3$, δ = 0.44 ppm (s, 3); C$_5$H$_4$, δ = 4.07 (t, 2) and 4.29 ppm (t, 2); C$_5$H$_5$, δ = 4.13 ppm (s, 0.4)). These results are consistent with the formulation $C_{10}H_9Fe(C_{10}H_8FeSn$-$(CH_3)_2)_xH$, $x \approx 13$; for $x = 13$ calcd.: C, 44.2; H, 4.3% Molar Mass = 4508.

A similar reaction with $(C_6H_5)_2SnCl_2$ also gave a polymeric product which was not completely characterised.

Acknowledgments

References

1 A.G. Osborne and R.H. Whiteley, J. Organometal. Chem., 101 (1975) C27.
2 H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, Helv. Chim. Acta, 59 (1976) 2402.
3 A.G. Osborne, R.H. Whiteley and R.E. Hollands, IXth International Conference on Organometallic Chemistry, Dijon, Sept. 3—7, 1979, P14T.
4 J.D. Dunitz, L.E. Orgel and A. Rich, Acta Cryst., 9 (1956) 373.
5 H. Stoeckli-Evans, A.G. Osborne and R.H. Whiteley, J. Organometal. Chem., in press.
6 K.L. Rinehart, A.K. Frerichs, P.A. Kittle, L.F. Westmann, C.H. Gustafson, R.L. Pruett, and J.E. McMahon, J. Amer. Chem. Soc., 82 (1960) 4111.
7 K.L. Rinehart, D.E. Bublitz and C.H. Gustafson, J. Amer. Chem. Soc., 85 (1963) 970.
8 T.H. Barr and W.E. Watts, Tetrahedron, 24 (1968) 6111.
9 B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, Inorg. Nuclear Chem. Letters, 7 (1971) 881.
10 T.H. Barr and W.E. Watts, J. Organometal Chem., 15 (1968) 177.
11 M. Hillman and A.G. Nagy, IXth International Conference on Organometallic Chemistry, Dijon, Sept. 3—7, 1979, P11F.
12 R.L. Collins, J. Chem. Phys., 42 (1965) 1072.
13 P.E. Clark, A.W. Nichol and J.S. Carlow, J. Scientific Instruments, 44 (1967) 1001.
14 M.D. Rausch and D.J. Ciappenelli, J. Organometal. Chem., 10 (1967) 127.
15 H. Rosenberg, U.S. Patent, 3426053 (1969).
16 J.C. Kotz and C.L. Nivert, J. Organometal. Chem., 52 (1973) 387.