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RING-TILTED FERROCENOPHANES. THE CRYSTAL AND MOLECULAR STRUCTURES OF (1,1′-FERROCENEDIYL)DIPHENYLGERMANE AND (1,1′-FERROCENEDIYL)PHENYLPHOSPHINE

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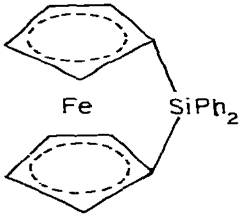
Summary

The structures of (1,1′-ferrocenediyl)diphenylgermane (B) and (1,1′-ferrocenediyl)phenylphosphine (C) have been determined from a three-dimensional X-ray analysis using diffractometer data. Crystals of compound B are orthorhombic, space group, *Pnma*, with $Z = 4$ in a unit cell of dimensions a 14.867(9), b 12.522(7) and c 9.373(6) Å. Full matrix least-squares refinement has given a final R-factor of 0.069 for 956 reflections for which $I > 3\sigma(I)$. The structure is isomorphous with (1,1′-ferrocenediyl)diphenylsilane [3]. The molecule has crystallographic m symmetry, with atoms Fe and Ge lying in the mirror plane, which bisects the two phenyl groups. The planar cyclopentadienyl rings are bridged by a single Ge atom and are inclined at an angle of 16.6° to one another. The bridge angle, C(1)—Ge—C(1′) is 93.6° and the shortest inter-ring distance, C(1)—C(1′), is 2.86 Å. The exocyclic C(1)—Ge bond makes an angle of 38° with the plane of the cyclopentadienyl ring.

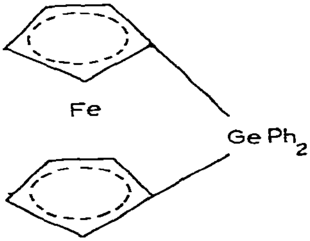
Crystals of compound C are orthorhombic, space group *Pbca*, with $Z = 8$ in a unit cell of dimensions a 27.130(10), b 12.701(8) and c 7.380(5) Å. Full matrix least-squares refinement converged at $R = 0.059$ for 996 reflections for which $I > 3\sigma(I)$. The molecule has only an approximate mirror plane, close to which lie atoms Fe, P, C(6) and C(9). The planar cyclopentadienyl rings are bridged by a single P atom and are inclined at an angle of 26.7° to one another. The bridge angle C(1)—P—C(1′) is 90.6° and the shortest inter-ring distance, C(1)—C(1′), is 2.62 Å. The exocyclic C(1)—P and C(1′)—P bonds make angles of 32° and 33° to their respective cyclopentadienyl rings.

Introduction

Derivatives of ferrocene in which the cyclopentadienyl rings are linked by one bridging group are known as [*m*]ferrocenophanes, where *m* denotes the number of atoms in the bridge. The inter-ring separation in ferrocene is 3.32 Å [1] and thus bridges which are shorter than this would be expected to cause molecular distortion by tilting of the planar cyclopentadienyl rings. For compounds containing bridges of less than four atoms this has been found to be the case, the largest dihedral angle (23.7°) between the cyclopentadienyl rings being found in a [2]ferrocenophane [2]. The molecular structure has been determined [3] for one [1]ferrocenophane, (1,1'-ferrocenediyl)diphenylsilane, (A), and the observed ring tilt (19.2°) was rather less than might have been expected. Herein we discuss the results of calculations concerning the geometry of [1]ferrocenophane structures based on the known structures of [2]- and [3]ferrocenophanes, and we report on the crystal and molecular structures of two [1]ferrocenophanes, viz (1,1'-ferrocenediyl)diphenylgermane (B) and (1,1'-ferrocenediyl)phenylphosphine (C). Crystals of bis(1,1'-ferrocenediyl)silane [4] were found to be disordered and not suitable for diffraction studies [5].



(A)



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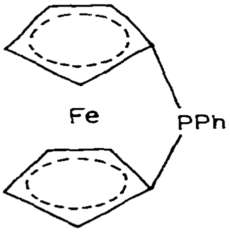


(C)

Experimental

X-ray data for (1,1'-ferrocenediyl)diphenylgermane, (B)

Preliminary Weissenberg and precession photographs showed the orange-red crystals to be orthorhombic, space group $Pna2_1$ or *Pnma* (the latter confirmed by structure analysis). $a = 14.867(9)$, $b = 12.522(7)$, $c = 9.373(6)$ Å, $V = 1745$ Å^3, $d_X = 1.56$ g cm^{-3}, $Z = 4$, ($C_{22}H_{18}FeGe$, $M = 410.5$), $d_c = 1.562$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 2.50$ mm^{-1}. Intensity data were collected for layers *hk*0—*hk*8 and

$h0l$—$h2l$ for the 2θ range 5—55° on a Stoe STADI-2 two circle diffractometer (graphite monochromated Mo-K_α radiation). The ω scan technique was used and the optimum scan width was computed for each reflection [6]. This gave 2214 data of which 956 unique reflections with $I > 3\ \sigma\ (I)$ were used in subsequent calculations and to which Lorentz and polarisation corrections only were applied.

The structure was solved by Patterson and Fourier methods using SHELX-76 [7], which was used for all calculations. Weighted full-matrix least-squares refinement (including isotropic H atoms, $U_{iso} = 0.04$), converged at $R = 0.069$. ($R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$); $R_w = 0.069$ {$R_w = \Sigma(||F_0| - |F_c||/w^{1/2})/\Sigma(|F_0|w^{1/2})$, $w = 2.39/[\sigma^2(F_0) + 0.0017\ F_0^2]$}. Final atomic parameters are listed in Table 1. Bond distances and angles are given in Tables 2 and 3 respectively. The atomic numbering scheme is outlined in Fig. 1.

X-ray data for (1,1'-ferrocenediyl)phenylphosphine, (C)

Preliminary Weissenberg and precession photographs showed the purple rod-like crystals to be orthorhombic, space group *Pbca*. $a = 27.130(10)$, $b = 12.701(8)$, $c = 7.380(5)$ Å, $V = 2543$ Å^3, $d_X = 1.52$ g cm^{-3}, $Z = 8$, ($C_{16}H_{13}FeP$, $M = 291.8$), $d_c = 1.529$ g cm^{-3}, μ(Mo-K_α) = 1.21 mm^{-1}. Intensity data were collected for layers $h0l$—$h10l$ for the 2θ range 5—55° on a Stoe STADI-2 two circle diffractometer (graphite monochromated Mo-K_α radiation). This gave 2190 data of which 996 unique reflections with $I > 3\ \sigma\ (I)$ were used in subsequent calculations and to which Lorentz and polarisation corrections only were applied. The structure was solved by Patterson and Fourier methods.

Weighted full-matrix least-squares refinement (isotropic H atoms, $U_{iso} = 0.04$), converged at $R = 0.059$, $R_w = 0.048$ ($w = 3.016/[\sigma^2(F_0) + 0.00\ F_0^2]$). Final atomic parameters are listed in Table 4. Bond distances and angles are given in Tables 5 and 6 respectively. The atomic numbering scheme is outlined in Fig. 2.

TABLE 1

POSITIONAL PARAMETERS (X10^4) WITH STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)DIPHENYLGERMANE

Atom	x	y	z
Fe	2530 (1)	2500	4380 (2)
C(1)	3406 (7)	1359 (8)	3828 (12)
C(2)	3149 (9)	1246 (10)	5310 (14)
C(3)	2225 (9)	1099 (12)	5369 (18)
C(4)	1874 (9)	1098 (11)	3957 (16)
C(5)	2604 (8)	1225 (10)	3023 (16)
Ge	4237 (1)	2500	3267 (2)
C(6)	4426 (10)	2500	1189 (16)
C(7)	4467 (9)	1539 (11)	457 (14)
C(8)	4657 (9)	1546 (12)	—970 (15)
C(9)	4761 (11)	2500	—1729 (23)
C(10)	5358 (10)	2500	4363 (15)
C(11)	5753 (8)	1544 (9)	4772 (12)
C(12)	6537 (8)	1553 (11)	5564 (16)
C(13)	6957 (11)	2500	5964 (18)

TABLE 2

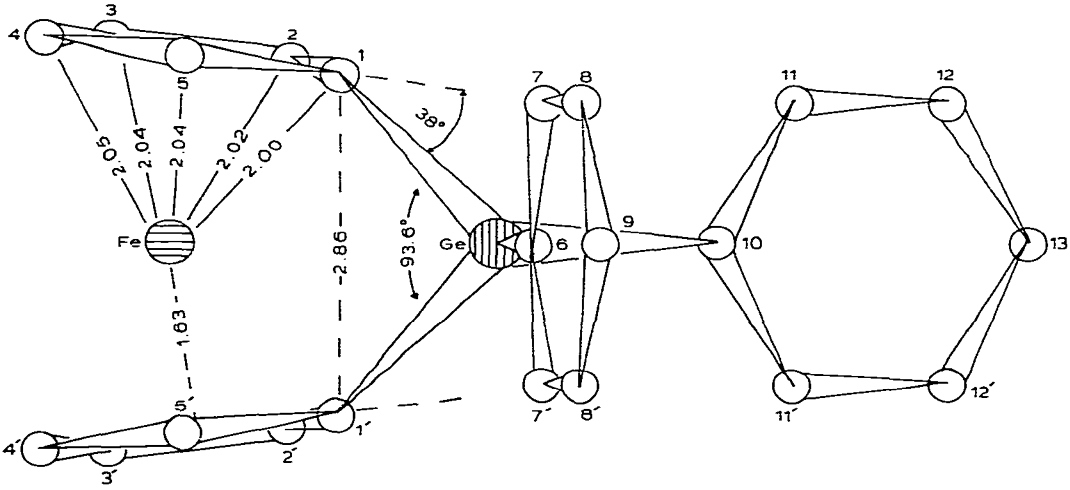
BOND DISTANCES (Å) AND STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)DIPHENYLGERMANE

Fe . . . Ge	2.744 (3)	Ge—C(1)	1.960 (10)
C(1) . . . C(1')	2.858 (14)	Ge—C(6)	1.968 (15)
Fe—C(1)	2.001 (11)	Ge—C(10)	1.958 (15)
Fe—C(2)	2.018 (13)	C(6)—C(7)	1.387 (14)
Fe—C(3)	2.035 (14)	C(7)—C(8)	1.367 (17)
Fe—C(4)	2.048 (14)	C(8)—C(9)	1.399 (16)
Fe—C(5)	2.043 (14)	C(10)—C(11)	1.388 (13)
C(1)—C(2)	1.449 (16)	C(11)—C(12)	1.382 (16)
C(2)—C(3)	1.387 (18)	C(12)—C(13)	1.391 (16)
C(3)—C(4)	1.422 (21)		
C(4)—C(5)	1.404 (18)		
C(1)—C(5)	1.421 (16)		

TABLE 3

BOND ANGLES (°) WITH STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)DIPHENYLGERMANE

C(1)—Ge—C(6)	110.8 (4)	C(7)—C(6)—C(7')	120.4 (15)
C(1)—Ge—C(1')	93.6 (4)	C(6)—C(7)—C(8)	119.2 (14)
C(1)—Ge—C(10)	113.3 (4)	C(7)—C(8)—C(9)	121.8 (15)
C(6)—Ge—C(10)	113.5 (6)	C(8)—C(9)—C(8')	117.3 (11)
Ge—C(1)—C(2)	119.7 (8)	C(11)—C(10)—C(11')	119.3 (14)
Ge—C(1)—C(5)	118.2 (9)	C(10)—C(11)—C(12)	119.9 (11)
Ge—C(6)—C(7)	119.7 (8)	C(11)—C(12)—C(13)	122.0 (12)
Ge—C(10)—C(11)	120.3 (7)	C(12)—C(13)—C(12')	116.9 (15)
C(5)—C(1)—C(2)	106.0 (10)		
C(1)—C(2)—C(3)	108.2 (12)		
C(2)—C(3)—C(4)	109.1 (13)		
C(3)—C(4)—C(5)	107.2 (12)		
C(4)—C(5)—C(1)	109.3 (12)		



Atoms Fe, Ge, C(6), C(9), C(10) and C(13) lie in the crystallographic mirror plane

Fig. 1. Molecular structure of (1,1'-ferrocenediyl)diphenylgermane.

TABLE 4

POSITIONAL PARAMETERS (X10^4) WITH STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)PHENYLPHOSPHINE

Atom	*x*	*y*	*z*
Fe	752 (0)	5032 (1)	2857 (2)
C(1)	1232 (3)	4573 (6)	1006 (13)
C(2)	1347 (3)	4105 (7)	2727 (13)
C(3)	951 (5)	3469 (8)	3302 (13)
C(4)	581 (4)	3544 (8)	1950 (17)
C(5)	745 (4)	4182 (8)	542 (13)
C(1')	991 (3)	6452 (7)	2168 (13)
C(2')	1077 (3)	6270 (7)	4082 (12)
C(3')	619 (4)	6086 (8)	4910 (14)
C(4')	239 (4)	6153 (8)	3629 (16)
C(5')	464 (4)	6396 (8)	1952 (16)
P	1383 (1)	5925 (2)	329 (3)
C(6)	1999 (3)	6124 (7)	1261 (10)
C(7)	2363 (4)	5377 (7)	1092 (11)
C(8)	2846 (4)	5593 (8)	1667 (11)
C(9)	2957 (3)	6546 (8)	2402 (12)
C(8')	2604 (4)	7296 (7)	2574 (13)
C(7')	2124 (3)	7070 (7)	2026 (12)

Thermal parameters, hydrogen atom positions and tables of observed and calculated structure factors for both compounds are available from H.St.-E.

Results and discussion

Strain in [*m*]ferrocenophanes is observed in (a) ring tilting, (b) bond angle distortion at the bridging atom(s) and (c) deviation of the exocyclic bonds from the planes of the cyclopentadienyl rings (Fig. 3). The molecular structures

TABLE 5

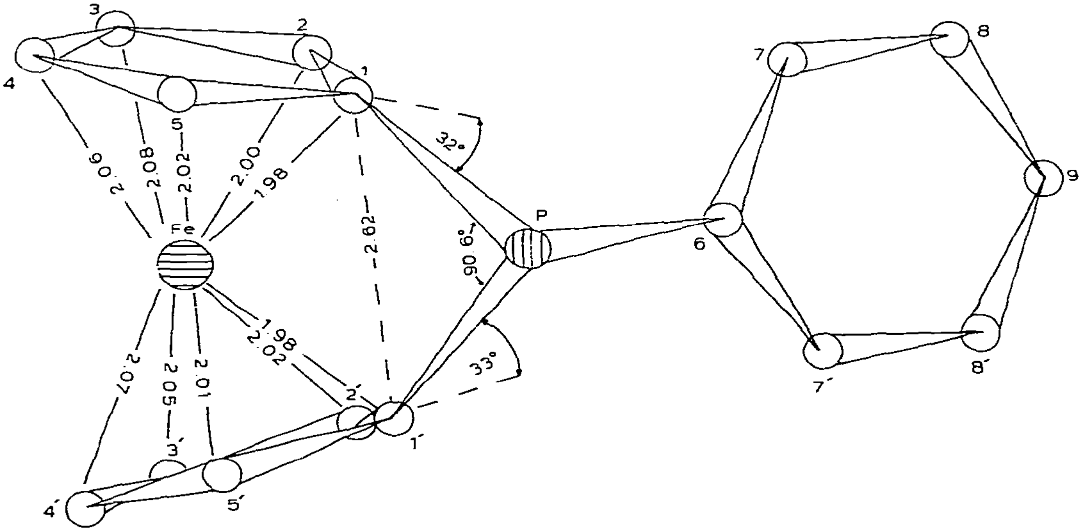
BOND DISTANCES (Å) AND STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)PHENYLPHOSPHINE

Fe . . . P	2.774 (3)	C(1')—C(2')	1.451 (13)
C(1) . . . C(1')	2.619 (12)	C(2')—C(3')	1.404 (14)
Fe—C(1)	1.975 (9)	C(3')—C(4')	1.400 (15)
Fe—C(2)	2.000 (9)	C(4')—C(5')	1.414 (16)
Fe—C(3)	2.084 (10)	C(5')—C(1')	1.440 (14)
Fe—C(4)	2.058 (11)	P—C(1)	1.836 (9)
Fe—C(5)	2.021 (10)	P—C(1')	1.849 (10)
Fe—C(1')	1.983 (9)	P—C(6)	1.825 (9)
Fe—C(2')	2.017 (9)	C(6)—C(7)	1.374 (13)
Fe—C(3')	2.054 (10)	C(7)—C(8)	1.404 (14)
Fe—C(4')	2.070 (10)	C(8)—C(9)	1.360 (13)
Fe—C(5')	2.014 (10)	C(9)—C(8')	1.357 (13)
C(1)—C(2)	1.437 (13)	C(8')—C(7')	1.391 (13)
C(2)—C(3)	1.408 (15)	C(7')—C(6)	1.371 (12)
C(3)—C(4)	1.420 (17)		
C(4)—C(5)	1.391 (15)		
C(5)—C(1)	1.452 (14)		

TABLE 6

BOND ANGLES (°) WITH STANDARD DEVIATIONS FOR (1,1'-FERROCENEDIYL)PHENYLPHOSPHINE

C(1)—P—C(1')	90.6(3)
C(1)—P—C(6)	103.4(4)
C(1')—P—C(6)	101.6(4)
P—C(1)—C(2)	125.4(7)
P—C(1)—C(5)	117.4(7)
P—C(1')—C(2')	124.4(7)
P—C(1')—C(5')	118.2(7)
P—C(6)—C(7)	121.9(7)
P—C(6)—C(7')	120.2(7)
C(1)—C(2)—C(3)	109.8(8)
C(2)—C(3)—C(4)	106.8(9)
C(3)—C(4)—C(5)	109.7(10)
C(4)—C(5)—C(1)	108.3(9)
C(5)—C(1)—C(2)	105.3(8)
C(1')—C(2')—C(3')	108.0(8)
C(2')—C(3')—C(4')	110.3(9)
C(3')—C(4')—C(5')	106.7(9)
C(4')—C(5')—C(1')	110.0(9)
C(5')—C(1')—C(2')	105.0(8)
C(6)—C(7)—C(8)	120.5(8)
C(7)—C(8)—C(9)	120.0(9)
C(8)—C(9)—C(8')	120.4(9)
C(9)—C(8')—C(7')	119.2(8)
C(8')—C(7')—C(6)	122.1(8)
C(7')—C(6)—C(7)	117.7(8)



Atoms Fe, P, C(6) and C(9) lie close to an approximate mirror plane.

Fig. 2. Molecular structure of (1,1'-ferrocenediyl)phenylphosphine.

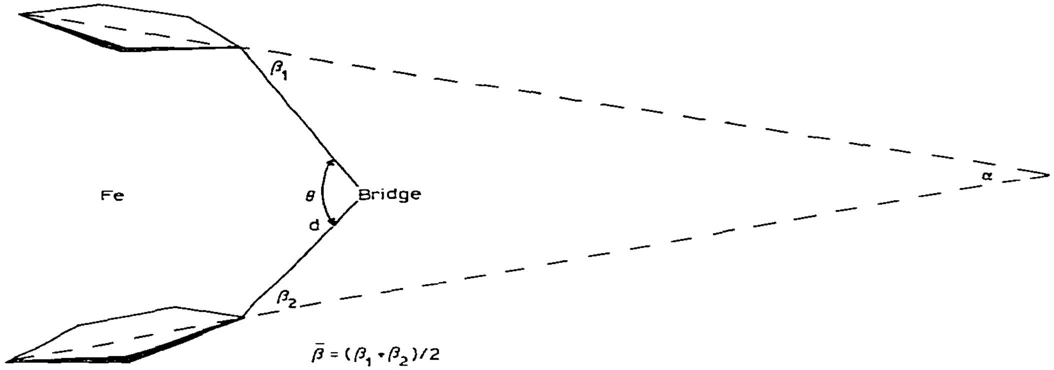


Fig. 3. Distortions in ring-tilted ferrocenophanes.

of ten [2]- and [3]ferrocenophanes have been published [2,8—16] and from these data the following observations can be made; (a) in all the compounds the cyclopentadienyl rings retain their regular pentagonal symmetry and planarity, (b) there is a linear relationship between α and $\bar{\beta}$; $\bar{\beta}(^\circ) = 0.53\ \alpha(^\circ) - 0.10$, correlation coefficient = 0.93 (Fig. 4), (c) the mean C—C bond length in the cyclopentadienyl rings is approximately constant (average value = 1.429 Å, standard deviation = 0.014 Å) and is not related to α, (d) the mean Fe—C(1,1′) distance, Z, decreases with increasing α; $Z(\text{Å}) = 2.053 - 0.0034\ \alpha(^\circ)$, correlation coefficient = —0.97, (e) the mean Fe—C(3,4,3′,4′) distance, Y, increases slightly with increasing α; $\text{Y}(\text{Å}) = 2.057 + 0.00097\ \alpha(^\circ)$, correlation coefficient = 0.62, and (f) the mean Fe—C_5 ring (centroid) distance is almost constant at about 1.64 Å. These observations appear not to be valid for multibridged ferrocenes [17].

On the basis of these observations and assuming an eclipsed (C_{2v}) symmetry for the ferrocene part of the molecule, possible structural parameters for [1]-ferrocenophanes could be calculated [18]. It was found that for any one given C(1)—bridging atom bond length, (d), a set of possible structures was obtained and, for this value of d, a given ring tilt, (α), defined a unique structure. The solid lines in Fig. 4 show the calculated values of α and $\bar{\beta}$ for phosphorus (d = 1.83 Å) [19], silicon (d = 1.87 Å) [20—22] and germanium (d = 1.96 Å) [23] as bridging atoms. As expected, [1]ferrocenophane structures were predicted to be much more distorted than any [2]ferrocenophane, with the distortion increasing as d decreased. Furthermore, if [1]ferrocenophanes followed the structural trends of [2]- and [3]ferrocenophanes, large ring tilts of between 36 and 39° would be expected for compounds A, B and C.

Here we discuss the molecular structures of molecules B and C and draw comparisons with the structure of A and with [2]- and [3]ferrocenophane structures.

Deviations of various atoms from different least-square planes in molecules B and C are given in Tables 7 and 8 respectively. Fig. 1 is a perspective view of molecule B and illustrates some interesting intramolecular distances and angles. Molecule B is isomorphous with the silicon analogue [3], A. Crystallographic requirements impose C_s symmetry for both A and B. The mirror plane of B, in which lie atoms Fe and Ge, bisects each phenyl ring. The mole-

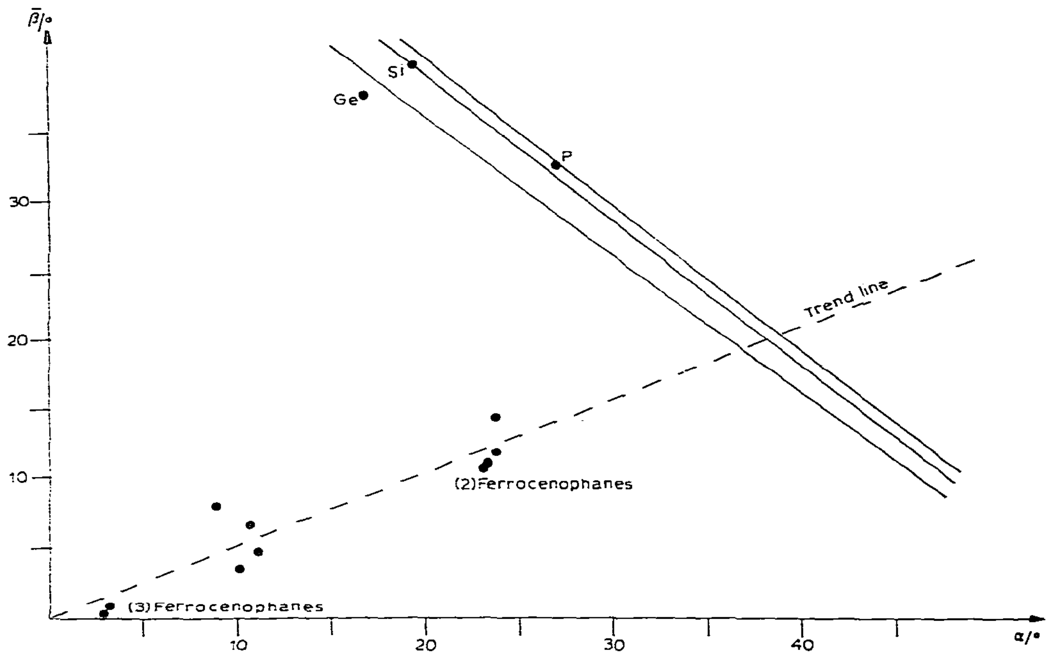


Fig. 4. Calculated (-) and observed (·) α and $\bar{\beta}$ values for ring-tilted ferrocenophanes.

cule has pseudo C_{2v} symmetry with an approximate 2-fold axis, on which lie atoms Fe and Ge; and a second approximate mirror plane containing atoms Fe, Ge, C(1) and C(1′). The deviation from pure C_{2v} symmetry is indicated by the deviation of atoms from this psuedo mirror plane (Table 7).

Fig. 2 is a perspective view of molecule C, which has only an approximate mirror plane, close to which lie atoms Fe, P, C(6) and C(9), see Table 8. In Table 9 some important structural parameters of molecules A, B and C are summarised.

TABLE 7

LEAST-SQUARES PLANES WITH DEVIATIONS (±0.01 Å) FOR (1,1′-FERROCENEDIYL)DIPHENYLGERMANE

Plane C(1), C(2), C(3), C(4), C(5)
$0.137x - 0.990y - 0.044z + 1.128 = 0$
Deviations C(1), −0.02; C(2), 0.01; C(3), 0.00; C(4), −0.01; C(5), 0.02;

Plane Fe, Ge, C(1), C(1′)
$-0.380x + 0.000y - 0.925z + 5.235 = 0$
Deviations Fe, 0.01; Ge, 0.01; C(1), −0.01; C(1′), −0.01; C(2), −1.15; C(3), −0.68; C(4), 0.75; C(5), 1.14; C(6), 1.70; C(7), 2.31; C(8), 3.44; C(9), 4.04; C(10), −1.58; C(11), −2.15; C(12), −3.28; C(13), −3.87;

Plane C(6), C(7), C(8), C(9), C(8′), C(7′)
$-0.982x + 0.000y - 0.188z + 6.630 = 0$
Deviations C(6), −0.04; C(7), 0.03; C(8), 0.00; C(9), −0.02; C(8′), 0.00; C(7′), 0.03;

Plane C(10), C(11), C(12), C(13), C(12′), C(11′)
$0.535x + 0.000y - 0.845z - 0.798 = 0$
Deviations C(10), 0.01; C(11), 0.00; C(12), −0.01; C(13), 0.01; C(12′), −0.01; C(11′), 0.00.

TABLE 8

LEAST-SQUARES PLANES WITH DEVIATIONS (±0.01 Å) FOR (1,1′-FERROCENEDIYL)PHENYLPHOSPHINE

Plane C(1), C(2), C(3), C(4), C(5)
$0.404x - 0.789y - 0.464z + 3.570 = 0$
Deviations C(1), −0.01; C(2), 0.00; C(3), 0.01; C(4), −0.01; C(5), 0.01:

Plane C(1′), C(2′), C(3′), C(4′), C(5′)
$0.085x - 0.979y - 0.188z + 8.101 = 0$
Deviations C(1′), 0.01; C(2′), −0.01; C(3′), 0.00; C(4′), 0.01; C(5′), −0.01:

Plane C(6), C(7), C(8), C(9), C(8′), C(7′)
$0.219x + 0.353y - 0.910z - 3.079 = 0$
Deviations C(6), 0.01; C(7), 0.00; C(8), 0.00; C(9), 0.00; C(8′), 0.01; C(7′), −0.01:

Plane Fe, P, C(6), C(9)
$0.276x - 0.914y - 0.298z + 5.905 = 0$
Deviations Fe, 0.00; P, −0.01; C(6), 0.02; C(9), −0.01; C(1), 1.30; C(2), 1.55; C(3), 1.86; C(4), 1.80; C(5), 1.49; C(1′), −1.32; C(2′), −1.46; C(3′), −1.77; C(4′), −1.86; C(5′), −1.60; C(7), 1.19; C(8), 1.18; C(8′), −1.18; C(7′), −1.16.

The cyclopentadienyl (Cp) rings are planar and eclipsed in both B and C, and the geometry of the rings is normal in both molecules. The cyclopentadienyl rings are inclined at an angle of 16.6° in B and 26.7° in C. The value of 26.7° for C is the largest inclination of the rings yet reported for an [*m*]ferrocenophane. The geometry of the ferrocene moiety in molecule B is normal and similar to that reported [3] for molecule A. Although the Fe—Cp (centroid) distances are approximately the same in all three molecules, see Table 9, there is a variation in the Cp(centroid)—Fe—Cp(centroid)angle viz 160° in C, 170° in B, and 167° in A.

The ring tilt, α, in these compounds can be considered as the sum of two types of distortion; α_1-ring tilt about the Fe atom as a fulcrum, and α_2-ring tilt about the Cp centroids. Only the latter distortion will cause differences in the Fe—C(Cp) bond lengths, and it is of interest that although α varies considerably amongst A, B and C, α_2 is approximately constant in all three compounds viz 6° in A, 7° in B and C. The most significant difference between the molecules is in the inter-ring distance (C(1)—C(1′), Table 9). The shortest inter-ring distance observed previously was 2.73 Å in a [2]ferrocenophane [2] where the Cp rings were inclined at an angle of 23.7°.

The interatomic distance Fe to Ge in B is 2.74 Å compared with 2.68 Å for the Fe—Si distance in A and 2.77 Å for the Fe—P distance in C. There is clearly

TABLE 9

SELECTED STRUCTURAL DATA FOR [1]FERROCENOPHANES [a]

Compound	α (°)	$\bar{\beta}$ (°)	θ (°)	C(1)—C(1′) (Å)	Fe—Cp (centroid) (Å)
A	19.2	40	99.1	2.86	1.65
B	16.6	38	93.6	2.86	1.63
C	26.7	32.5	90.6	2.62	1.63

[a] See fig. 3 for explanation of symbols.

no bonding between these atoms as the interatomic distances are appreciably longer than the bond lengths calculated from metallic covalent radii [24] (Fe—Ge = 2.47; Fe—Si = 2.37; Fe—P = 2.37 Å).

The C(1)—Ge—C(1′) bridging angle, θ (Fig. 3), in molecule B is 93.6°, giving the Ge atom a distorted tetrahedral environment (Table 3). The Ge—C bond lengths, whose average is 1.96 Å, are normal for Ge—C(sp^2) bonds [23]. The phenyl groups are planar (Table 7) and their bond lengths and angles are normal. The exocyclic C(6)—Ge bond makes an angle of 7° with the plane of the phenyl group, whilst bond C(10)—Ge makes an angle of 4° with the corresponding phenyl group.

In molecule C, θ is 90.6°, hence the P atom has a very distorted tetrahedral environment (Table 6). The P—C bond lengths, average value 1.84 Å, are normal for P—C(sp^2) bonds [19]. The phenyl group is planar (Table 8) and its bond lengths and angles are normal. The exocyclic bond C(6)—P makes an angle of 6° to the plane of the phenyl ring.

In conclusion it can be seen that although the structures of all three compounds are close to calculated possible structures (Fig. 4) they do not follow the trend established for [2]- and [3]ferrocenophanes. The [1]ferrocenophanes have a relatively low value of α compared with $\bar{\beta}$, whereas the trend would indicate α values of between 36 and 39°, and $\bar{\beta}$ values of between 19 and 21°. This can be rationalised by considering two factors. Firstly, such large ring tilts would cause short C(1)—C(1′) distances, in the range 2.33—2.39 Å, compared with 3.32 Å in ferrocene and the normal separation distance, 3.40 Å, of parallel aromatic rings in unstrained compounds [25].

Secondly, large ring tilts would result in θ values very much smaller than would be the case in unstrained compounds e.g. 79° ($\alpha = 39°$) in C compared with 103° in PPh_3 [19] and 75° ($\alpha = 36°$) in B compared with 109.5° in $GePh_4$ [23]. Thus large ring tilts, and hence reduced values of θ and C(1)—C(1′) distance, are not easily accommodated by such molecules and consequently large distortions occur at C(1) and C(1′), i.e. large $\bar{\beta}$ values are observed.

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