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The preparation and structure of 1,4,5,6,7,7-hexachloro-2-*endo*-ferrocenylhydroxymethyl-3-*endo*-hydroxymethyl-5-norbornene

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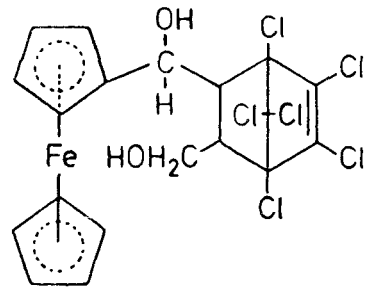
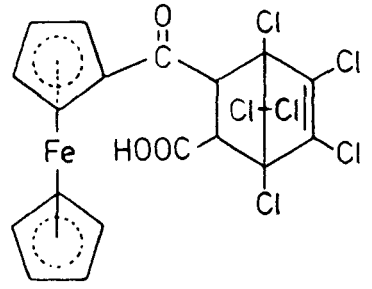
The crystal structure of a novel ferrocene derivative with potential flame-retardant/smoke-suppressant activity, 1,4,5,6,7,7-hexachloro-2-*endo*-ferrocenylhydroxymethyl-3-*endo*-hydroxymethyl-5-norbornene, has been determined. Some of the carbon—carbon bonds within the chlorendic residue are unusually long, and there is no interaction between the hydroxyl groups and the iron atom. There is evidence of intramolecular hydrogen bonding between the two hydroxyl groups.

Keywords: Structure, ferrocenyl, flame retardant, smoke-suppressant, polyvinyl chloride, x-ray structure



I



II

INTRODUCTION

Continuing our work on the synthesis of novel ferrocene[1,2] and ferrocenium[3,4] derivatives with potential flame-retardant and smoke-suppressant activity for polymer mouldings such as poly(vinyl chloride) (PVC), we report the synthesis and structure of a novel compound (**I**). In earlier work we reported the synthesis, infrared and 1H NMR spectra of the monocarboxylic acid (**II**) and its methyl ester formed from ferrocene and chlorendic anhydride, two readily available and moderately inexpensive starting materials.[1]

oxides in particular, have been known as effective flame-retardant (FR) and smoke-suppressants (SS) agents for several decades. Ferrocene has been extensively studied and used for its FR/SS activity,[5,6] but its use is limited in practice by its volatility, since ferrocene can be lost during normal processing operations of thermoplastic materials such as extrusion. Provided that the activity of ferrocene occurs predominantly via a condensed-phase rather than a gas-phase process, less volatile derivatives would be expected to exhibit improved FR/SS properties. Indeed we have found that ferrocene 1,1′-dicarboxylic acid and the corresponding zinc salt are effective FR/SS additives for PVC.[2] The precise mechanism of action of these compounds is still under dispute, for whilst it is accepted that ferrocene may well behave like other effective transition metal compounds in promoting char formation by cross-linking during thermal degradation, other workers have maintained that the catalytic oxidation of carbonaceous char to oxides of carbon is the major mechanism for the suppression of smoke.[7,8] It should be pointed out

that nearly all the fundamental mechanistic studies have been carried out on rigid PVC, which is inherently flame-retardant (LOI, Limiting Oxygen Index = 45–49) by virtue of its high chlorine content. This is because the hydrogen chloride (HCl) produced during degradation is an efficient free-radical scavenger in the gas phase, whereas flexible PVC, containing large amounts of phthalate esters as plasticizers, is much more flammable (LOI = 25–30). The flame retardance of flexible PVC can be greatly improved by the addition of antimony trioxide (Sb_2O_3), but smoke production is increased. In contrast, ferrocene itself, whilst it is a less effective flame retardant than antimony trioxide, does exhibit both FR and SS activity. The aims of the present work include producing a ferrocene derivative that has significantly greater FR/SS activity than ferrocene itself, and it was felt that the high chlorine content and low volatility of the chlorendic acid derivatives could give rise to improved performance.

EXPERIMENTAL

The syntheses of $(C_5H_5)Fe(C_5H_4CORCOOH)$ (**II**) and the methyl ester $(C_5H_5)Fe(C_5H_4CORCOOMe)$, where R is derived from chlorendic anhydride (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic anhydride), have been described.[1] A solution of the methyl ester of **II** (1.0 g) in sodium-dried ether (100 cm^3) was added slowly to a suspension of lithium aluminium hydride (1.0 g) in the same solvent, cooled to 0°C and stirred under a flow of dry nitrogen gas. The resulting yellow solution was decomposed by adding dry ethanol and the product (structure, Fig. 1) was extracted into dry ether. Rotary evaporation of the dried ether solution afforded a yellow solid (0.7 g; yield 74%) which gave yellow crystals (m.p. 156–158°C) on recrystallization from 40/60 petroleum ether. Elemental analysis (Found: C, 42.2; H, 2.9; Calcd: C, 41.9, H, 2.9%), 1H NMR and infrared spectra confirmed the main structural features. A single crystal for X-ray analysis was prepared by slow recrystallization from chloroform.

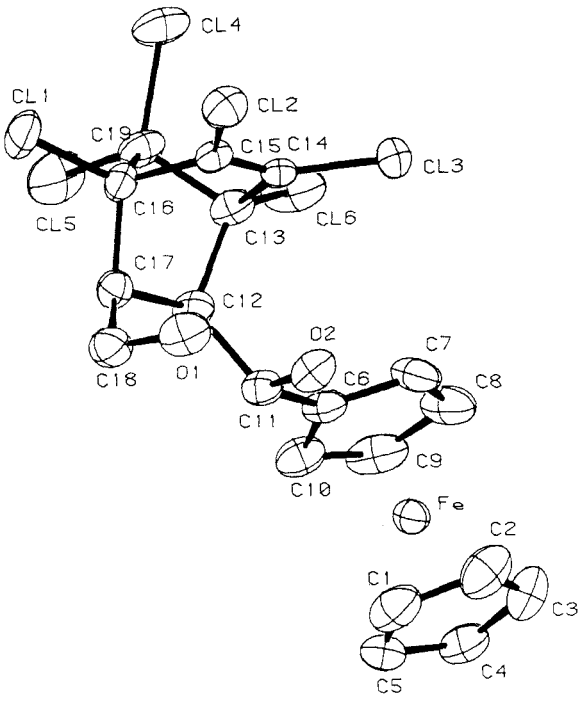


Figure 1 Structure of **I**.

Table 1a Fractional atomic coordinates with ESD[a] in parentheses and B_{eq} thermal parameters ($Å^2$)
The B_{eq} values are calculated according to the equation $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij}a_i a_j$.

Atom	*x*	*y*	*z*	$B(Å^2)$
Fe	0.34370(4)	0.03630(6)	0.13816(2)	2.30(1)
Cl(1)	0.09586(9)	0.2970(2)	−0.22327(4)	4.01(2)
Cl(2)	−0.02978(8)	0.5155(1)	−0.12699(4)	3.15(2)
Cl(3)	0.13550(9)	0.6124(1)	0.00008(4)	3.49(2)
Cl(4)	0.25884(9)	0.6394(2)	−0.16315(4)	4.16(2)
Cl(5)	0.36180(9)	0.2935(2)	−0.16795(5)	5.13(3)
Cl(6)	0.37345(9)	0.4984(2)	−0.02734(5)	4.51(2)
O(1)	0.0021(2)	0.0863(4)	−0.0781(1)	3.50(6)
O(2)	0.1367(2)	0.1656(4)	0.0188(1)	2.99(5)
C(1)	0.3847(3)	−0.1306(6)	0.2111(2)	3.64(9)
C(2)	0.3150(4)	0.0074(7)	0.2261(2)	4.2(1)
C(3)	0.2218(4)	−0.0086(7)	0.1874(2)	4.4(1)
C(4)	0.2319(4)	−0.1566(6)	0.1475(2)	4.3(1)
C(5)	0.3326(4)	−0.2313(5)	0.1626(2)	3.91(9)
C(6)	0.3213(3)	0.1417(5)	0.0522(2)	2.62(7)
C(7)	0.3233(3)	0.2852(5)	0.0958(2)	3.62(9)
C(8)	0.4211(4)	0.2776(5)	0.1322(2)	4.14(9)
C(9)	0.4794(3)	0.1330(6)	0.1114(2)	4.13(9)
C(10)	0.4182(3)	0.0466(6)	0.0624(2)	3.31(9)
C(11)	0.2335(3)	0.1013(5)	0.0030(2)	2.52(7)
C(12)	0.2556(3)	0.1781(5)	−0.0588(2)	2.48(7)
C(13)	0.2640(3)	0.3919(5)	−0.0665(2)	2.59(7)
C(14)	0.1594(3)	0.4803(4)	−0.0595(1)	2.25(7)
C(15)	0.0941(3)	0.4378(4)	−0.1076(1)	2.06(7)
C(16)	0.1522(3)	0.3142(5)	−0.1478(1)	2.34(7)
C(17)	0.1764(3)	0.1250(5)	−0.1166(2)	2.51(7)
C(18)	0.0801(4)	0.0049(5)	−0.1093(2)	3.26(9)
C(19)	0.2596(3)	0.4084(5)	−0.1367(2)	3.01(8)

[a]Estimated standard deviation

X-ray structure determination

Crystal data: $C_{19}H_{16}Cl_6FeO_2$, MW = 544.90, monoclinic, a = 12.875(2), b = 7.261(1), c = 22.266(3) Å, β = 96.73(3)°, V = 2067(1) Å^3, Z = 4, space group $P2_1/n$, $F(000)$ = 1116, ρ_{calc} = 1.751 g cm^{-3}, $\mu(MoK_\alpha)$ = 15.1 cm^{-1}, λ = 0.71069 Å.

Unit cell parameters were determined from a least-squares analysis using 25 accurately centred reflections (13° ≤ θ ≤ 15°) measured on an Enraf Nonius CAD4 diffractometer from a crystal of dimensions 0.5 mm × 0.3 mm × 0.15 mm; 3700 reflections with (sin θ)/λ ≤ 0.57, range of hkl: $h(0 \rightarrow 14)$, $k(0 \rightarrow 8)$, $l(-25 \rightarrow 25)$, were collected on the diffractometer using graphite-monochromated MoK_α radiation. The data were corrected for Lorentz polarization and for absorption (ψ-scans to determine an empirical transmission surface). A standard reflection monitored during the course of data collection indicated no decay of the crystal. After elimination of systematic absences and symmetry-equivalent reflections, a total of 2812 reflections remained of which 2473 (88%) were considered observed [$I \geq 3\sigma(I)$].

The structure was solved using the SHELXS[9] suite of programs using the direct Patterson interpretation option. Full-matrix least-squares refinement was carried out with anisotropic temperature factors for all non-hydrogen atoms. The positions of the hydrogen atoms were calculated from geometric criteria and were included as fixed contributions in the least squares. During the final stages of refinement, a weighting scheme was applied resulting in final values of R = 0.036, R_w = 0.055. All calculations excluding the structure solution were carried out with a DEC PDP 11/73 computer using the SDP Plus System.[10] Final positional and thermal parameters for non-hydrogen

Table 1b Anisotropic thermal parameters with ESD in parentheses

The temperature factor expression for the non-hydrogen atoms is $\exp(-2\pi^2\{U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}ha^*kb^* + 2U_{13}ha^*lc^* + 2U_{23}kb^*lc^*\})$.

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Fe	0.0312(3)	0.0250(2)	0.0295(2)	−0.0012(2)	−0.0038(2)	0.0000(2)
Cl(1)	0.0687(7)	0.0601(6)	0.0224(4)	0.0094(6)	0.0008(4)	−0.0022(4)
Cl(2)	0.0324(6)	0.0456(5)	0.0417(4)	0.0066(4)	0.0036(4)	0.0055(4)
Cl(3)	0.0709(7)	0.0314(4)	0.0309(4)	−0.0054(5)	0.0077(4)	−0.0060(4)
Cl(4)	0.0548(7)	0.0508(5)	0.0549(5)	−0.0062(5)	0.0163(5)	0.0246(4)
Cl(5)	0.0496(7)	0.0817(7)	0.0707(6)	0.0187(6)	0.0362(5)	0.0168(6)
Cl(6)	0.0403(6)	0.0593(5)	0.0669(6)	−0.0255(5)	−0.0144(5)	0.0190(5)
O(1)	0.033(2)	0.049(1)	0.050(1)	−0.010(1)	0.001(1)	0.007(1)
O(2)	0.030(1)	0.048(1)	0.035(1)	−0.006(1)	0.001(1)	0.006(1)
C(1)	0.047(3)	0.050(2)	0.040(2)	0.001(2)	−0.002(2)	0.013(2)
C(2)	0.058(3)	0.070(3)	0.031(2)	−0.001(2)	0.004(2)	−0.004(2)
C(3)	0.040(3)	0.081(3)	0.047(2)	0.005(2)	0.012(2)	0.009(2)
C(4)	0.058(3)	0.061(2)	0.041(2)	−0.025(2)	−0.005(2)	0.010(2)
C(5)	0.074(3)	0.028(2)	0.047(2)	−0.004(2)	0.011(2)	0.006(2)
C(6)	0.032(2)	0.030(2)	0.035(2)	−0.005(2)	−0.006(2)	0.009(1)
C(7)	0.056(3)	0.024(2)	0.053(2)	−0.003(2)	−0.017(2)	0.006(2)
C(8)	0.059(3)	0.035(2)	0.056(2)	−0.015(2)	−0.024(2)	0.008(2)
C(9)	0.035(2)	0.056(2)	0.061(2)	−0.015(2)	−0.012(2)	0.026(2)
C(10)	0.034(2)	0.049(2)	0.043(2)	−0.002(2)	0.006(2)	0.012(2)
C(11)	0.030(2)	0.032(2)	0.033(2)	−0.001(2)	−0.003(1)	0.004(1)
C(12)	0.027(2)	0.033(2)	0.033(2)	0.001(2)	−0.003(1)	0.005(1)
C(13)	0.026(2)	0.037(2)	0.034(2)	−0.009(2)	−0.001(1)	0.007(2)
C(14)	0.039(2)	0.021(1)	0.026(1)	−0.006(1)	0.009(1)	0.004(1)
C(15)	0.024(2)	0.028(1)	0.027(1)	0.000(1)	0.005(1)	0.005(1)
C(16)	0.033(2)	0.034(2)	0.022(1)	0.001(2)	0.004(1)	−0.001(1)
C(17)	0.034(2)	0.032(2)	0.029(2)	0.001(2)	0.001(1)	−0.001(1)
C(18)	0.050(3)	0.033(2)	0.040(2)	−0.009(2)	−0.000(2)	0.000(2)
C(19)	0.033(2)	0.045(2)	0.039(2)	0.007(2)	0.016(1)	0.015(2)

Table 2 Bond lengths and bond angles with ESD in parentheses

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Cl(1)	C(16)	1.755(3)	C(6)	C(7)	1.422(5)	C(16)	C(17)	1.554(5)
Cl(2)	C(15)	1.699(4)	C(6)	C(10)	1.421(6)	C(16)	C(19)	1.536(6)
Cl(3)	C(14)	1.695(3)	C(6)	C(11)	1.509(5)	C(17)	C(18)	1.540(6)
Cl(4)	C(19)	1.777(4)	C(7)	C(8)	1.417(6)	Fe	C(1)	2.045(4)
Cl(5)	C(19)	1.768(4)	C(8)	C(9)	1.401(7)	Fe	C(2)	2.046(4)
Cl(6)	C(13)	1.749(4)	C(9)	C(10)	1.415(6)	Fe	C(3)	2.044(5)
O(1)	C(18)	1.415(5)	C(11)	C(12)	1.541(5)	Fe	C(4)	2.036(4)
O(2)	C(11)	1.413(5)	C(12)	C(13)	1.567(5)	Fe	C(5)	2.027(4)
C(1)	C(2)	1.411(6)	C(12)	C(17)	1.593(5)	Fe	C(6)	2.050(3)
C(1)	C(5)	1.407(6)	C(13)	C(14)	1.516(6)	Fe	C(7)	2.041(4)
C(2)	C(3)	1.398(7)	C(13)	C(19)	1.562(5)	Fe	C(8)	2.028(4)
C(3)	C(4)	1.411(7)	C(14)	C(15)	1.318(5)	Fe	C(9)	2.036(4)
C(4)	C(5)	1.409(7)	C(15)	C(16)	1.523(5)	Fe	C(10)	2.038(4)

Atom 1	Atom 2	Atom 3	Angle (deg)	Atom 1	Atom 2	Atom 3	Angle (deg)	Atom 1	Atom 2	Atom 3	Angle (deg)
C(2)	C(1)	C(5)	107.0(4)	C(11)	C(12)	C(17)	117.7(3)	Cl(1)	C(16)	C(19)	116.6(2)
C(1)	C(2)	C(3)	108.6(4)	C(13)	C(12)	C(17)	101.3(3)	C(15)	C(16)	C(17)	110.1(3)
C(2)	C(3)	C(4)	108.4(4)	Cl(6)	C(13)	C(12)	116.4(3)	C(15)	C(16)	C(19)	98.0(3)
C(3)	C(4)	C(5)	107.0(4)	Cl(6)	C(13)	C(14)	115.8(3)	C(17)	C(16)	C(19)	101.1(3)
C(1)	C(5)	C(4)	109.0(4)	Cl(6)	C(13)	C(19)	113.5(3)	C(12)	C(17)	C(16)	102.9(3)
C(7)	C(6)	C(10)	107.6(3)	C(12)	C(13)	C(14)	109.6(3)	C(12)	C(17)	C(18)	120.0(3)
C(7)	C(6)	C(11)	126.2(4)	C(12)	C(13)	C(19)	101.0(3)	C(16)	C(17)	C(18)	115.1(3)
C(10)	C(6)	C(11)	126.2(4)	C(14)	C(13)	C(19)	98.2(3)	O(1)	C(18)	C(17)	116.2(3)
C(6)	C(7)	C(8)	107.8(4)	Cl(3)	C(14)	C(13)	124.4(3)	Cl(4)	C(19)	Cl(5)	106.9(2)
C(7)	C(8)	C(9)	108.3(4)	Cl(3)	C(14)	C(15)	127.7(3)	Cl(4)	C(19)	C(13)	113.7(3)
C(8)	C(9)	C(10)	108.4(4)	C(13)	C(14)	C(15)	107.9(3)	Cl(4)	C(19)	C(16)	113.4(3)
C(6)	C(10)	C(9)	107.9(4)	Cl(2)	C(15)	C(14)	128.2(3)	Cl(5)	C(19)	C(13)	114.6(3)
O(2)	C(11)	C(6)	111.2(3)	Cl(2)	C(15)	C(16)	123.9(3)	Cl(5)	C(19)	C(16)	115.1(3)
O(2)	C(11)	C(12)	111.4(3)	C(14)	C(15)	C(16)	107.7(3)	C(13)	C(19)	C(16)	93.0(3)
C(6)	C(11)	C(12)	112.1(3)	Cl(1)	C(16)	C(15)	115.4(3)				
C(11)	C(12)	C(13)	118.6(3)	Cl(1)	C(16)	C(17)	113.8(2)				

atoms are given in Tables 1a and 1b respectively and bond distances and angles involving these atoms are given in Table 2.

DISCUSSION

The structure is shown in Fig. 1. The bond lengths and angles are all within the expected range for the iron-cyclopentadienyl fragment. However, in the chlorendic residue, there are significant variations from expected values in some of the carbon–carbon bond lengths, notably C(12)–C(13), 1.567 Å; C(12)–C(17), 1.593 Å; and C(13)–C(19), 1.562 Å. A search through the Cambridge crystallographic database[11] located 18 compounds containing this chlorendic residue either alone or bonded to other fragments. A summary of equivalent bond lengths for the 18 compounds is shown in Table 3.

Table 3 Equivalent bond lengths

Bond length equivalent	Maximum (Å)	Minimum (Å)	Average (Å)
C(12)–C(13)	1.625	1.544	1.570
C(12)–C(17)	1.623	1.519	1.565
C(13)–C(19)	1.604	1.482	1.555

The results of this analysis show that, in this type of moiety, longer than expected carbon–carbon bond lengths can be found, especially where the environment of the chlorendic residue most closely resembles that in the title compound.

The explanation of this lengthening appears to lie in the severe strain which the ring undergoes. The

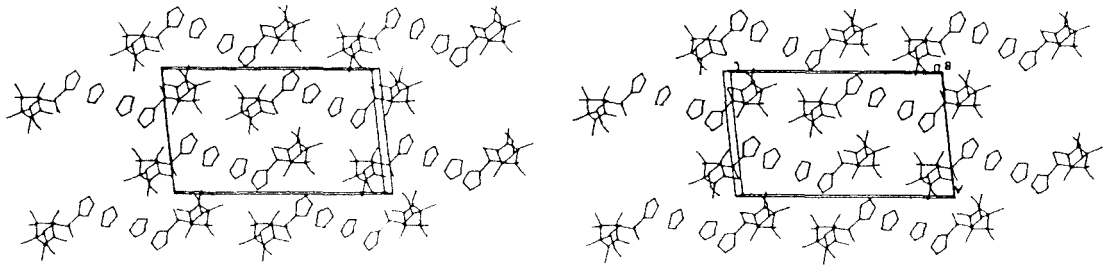


Figure 2 Stereoscopic view of unit cell packing.

C(13)–C(19)–C(16) bridging angle is only 93.0°, substantially less than that expected at an sp^3-hybridized carbon atom. The average geometries found from the database search were 95.3° (maximum), 88.4° (minimum) and 92.4° (average). Since the hybridization at C(14) and C(15) is sp^2, the planarity of the C(13)–C(14)–C(15)–C(16) fragment is maintained. The remainder of the cyclic system, C(12)–C(13)–C(19)–C(16)–C(17), deforms to relieve the strain with a consequential lengthening of the bond lengths.

The carbon–chlorine bond lengths show the expected variation dependent upon the hybridization state of the parent carbon atom: sp^3 (av.C–Cl, 1.762 Å); sp^2 (av.C–Cl, 1.697 Å).

There are no intramolecular hydrogen bonds of the type Cl···H–O even though rotation of O(1) about the C(17)–C(18) bond might have suggested the possibility of a Cl(1)–O(1) interaction. However, there is a preferred hydrogen-bond interaction between O(1) and O(2) at 2.67 Å. Neither O(1) nor O(2) interacts with the iron atom; O(2) makes the closest approach at 3.66 Å. Intramolecular hydrogen bonding appears to be the preferred configuration in this molecule. In view of the known Lewis base properties of the iron atom in other ferrocene systems[12] it is rather surprising that intramolecular hydrogen bonding of the iron atom with the alcohol groups does not appear to occur.

A stereoscopic view of the unit cell packing is shown in Fig. 2. The only significant intermolecular interaction is between O(1) and O(2), 2.97 Å, suggesting another hydrogen bond. There are no other intermolecular contacts less than 3.3 Å.

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APPENDIX

Supplementary Data for 1,4,5,6,7,7-hexachloro-2-*endo*-ferrocenylhydroxymethyl-3-*endo*-hydroxymethyl-5-norbornene

(1) Calculated hydrogen atom positions and associated C—H bond lengths;
(2) Torsion angles;
(3) Observed and calculated structure factors.

These are lodged with the Cambridge Crystallographic Database, UK, (Cambridge Crystallographic Data Centre).