SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF [TETRA-μ₃-IODOTETRAKIS{1′-(DIPHENYLPHOSPHINO)FERROCENE-CARBOXYLIC ACID-*P*}TETRACOPPER(I)]–ACETIC ACID (1 : 2)

Petr STEPNICKA[1], Robert GYEPES[2] and Jaroslav PODLAHA[3]

Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic;
e-mail: [1] stepnic@mail.natur.cuni.cz, [2] gyepes@mail.natur.cuni.cz, [3] podlaha@mail.natur.cuni.cz
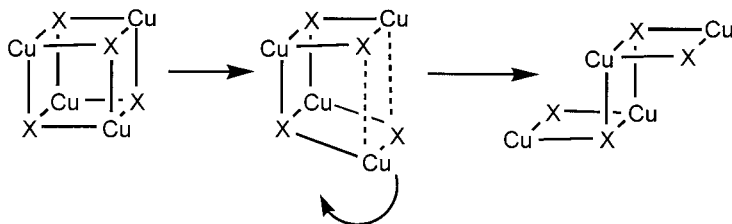
The title compound was prepared by the reaction of 1′-(diphenylphosphino)ferrocenecarboxylic acid with copper(I) iodide in acetic acid. It has the tetrameric structure of the heterocubane type and all four monomeric units are crystallographically independent. The central Cu_4I_4 core is severely distorted from the O_h symmetry as a consequence of disparate radii of the atoms; however, this does not lead to transformation of the core into a stepped arrangement, the feature otherwise common for similar tetrameric structures. The ligand behaves as a monodentate phosphine and completes the approximately tetrahedral coordination polyhedron around copper(I). The carboxyl groups remain undissociated and uncoordinated but participate in intermolecular hydrogen bonding. Two carboxyl groups link the molecules of the tetramer into a zig-zag chain; the remaining two are bonded to molecules of solvating acetic acid which act as spacers between the chains. As expected, the geometry of the flexible ligand is remarkably influenced by the hydrogen bonding, the main conformation changes taking place at the P–C bonds and in the mutual arrangement of the cyclopentadienyl rings.
Key words: Sandwich complexes; Heterocubanes; Copper(I) complexes; X-Ray structure.

Due to its position at the borderline between transition and main-group metal ions, copper(I) exhibits a large diversity of structural types in its compounds. Oligomeric structures are frequently encountered, among which the tetramers $Cu_4X_4L_4$ (X = halide, L = Lewis base) are archetypical. For a number of the members of this class whose crystal structures are known*, two basic types can be distinguished. They differ in the Cu–X connectivity and are usually referred to as the stepped (or chair) and the cubane structure; intermediate cases are also known in which two opposite bonds of one cubane face are more or less elongated (Scheme 1).
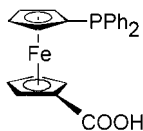
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* The list of CODENs for 64 structures retrieved from the Cambridge Structural Database (1997 release) is available from the authors upon request.

There has been no lack of explanations to account for adopting the particular structure for a given compound, the following being the most important: the van der Waals radius of the halide[1], the cone angle and denticity of the Lewis base[2] and its σ-donor *vs* π-acceptor character, supported by extended Hückel electron distribution calculations for model compounds[3]. However, these factors can counterbalance effectively in certain cases and more subtle effects may then control the structural type, giving rise to unexpected situations. A flagrant example is the series $Cu_4Br_4(PR_3)_4$ in which the sterically less demanding triethylphosphine derivative has the cubane structure[4], the triphenylphosphine complex[5] is stepped but, surprisingly, the most crowded tri-*tert*-butylphosphine analogue is again[6] a cubane. Clearly, the state of affairs is far from being well understood and further experimental material is needed.

SCHEME 1

We have recently synthesized a new organometallic phosphine ligand, 1′-(diphenylphosphino)ferrocenecarboxylic acid[7] (Hdpf). This molecule possesses both soft and hard donor atoms and also the ferrocene/ferricinium redox system, thus providing novel features which may be expected to influence the structure and/or reactivity of its complexes. The investigation of its Pd(II), Pt(II) and Hg(II) derivatives[8] demonstrated that, under conditions prohibiting the dissociation of the carboxyl group, the ligand behaves

simply as a monodentate phosphine; however, the solid-state structures exhibit supramolecular features invoked by hydrogen bonding through the carboxyl group. For the Cu_4X_4 clusters, the hydrogen bonding may even provide enough energy for controlling the geometry of the central cluster since, on the basis of the arguments mentioned above, neither the energetic difference nor the barrier of the conversion of the two structural types seem to be unrealistically high. The investigation of one such cluster containing this novel phosphine ligand is the object of this report.

EXPERIMENTAL

General Comments

Liquid secondary ion mass spectrometry (LSIMS) data were obtained on a VG ZabSpec spectrometer (CRMPO Centre, University of Rennes, France) operating in the positive ion mode with CsI as the primary ion source and 3-nitrobenzyl alcohol as the matrix. Poly(ethylene glycol) was used as the mass-scale calibrant for high resolution (HR LSIMS) measurements. IR spectra were recorded on an FT IR ATI Mattson Genesis instrument in the range of 400–4 000 cm^{-1}. ^{1}H (200.06 MHz) and ^{31}P{^{1}H} NMR (80.98 MHz) spectra in hexadeuteriodimethyl sulfoxide solutions were measured at room temperature on a Varian Unity 200 spectrometer.

Synthesis and Characterization

In an argon atmosphere, a suspension of 316.5 mg (764 µmol) Hdpf and 287.5 mg (1.51 mmol) CuI in glacial acetic acid (20 cm^3) was refluxed for 5 h. The resulting mixture was filtered while hot to remove unreacted CuI. The clear filtrate was left to stand for several days at room temperature, the precipitate formed was filtered off, washed with glacial acetic acid (3 × 2 cm^3), diethyl ether (3 × 2 cm^3) and dried on air. Yield: 329.3 mg of an orange microcrystalline solid (68%). For $C_{24}H_{21}CuFeIO_3P$ ([(Hdpf)CuI]·0.5 $C_2H_4O_2$, 634.7) calculated: 45.42% C, 3.34% H, 19.99% I; found: 45.43% C, 3.36% H, 19.94% I. IR spectrum (Nujol; $\tilde{\nu}$, cm^{-1}): 1 695 s, 1 682 s (C=O), 1 294 s, 1 166 s, 1 098 s, 1 028 s, 948 br w, 915 w, 835 m, 743 s, 695 s, 536 m, 517 m, 499 m, 466 br composite. ^{1}H NMR (internal standard TMS): δ 1.92 s, 1.5 H (0.5 C**H**$_3$CO$_2$H); 4.33 bs, 2 H, 4.47 bs, 2 H, 4.57 bs, 4 H (2 × C$_5$**H**$_4$); 7.37–7.61 m, 10 H (P(C$_6$**H**$_5$)$_2$); 12.14 bs, 1.5 H (CO$_2$**H**). ^{31}P{^{1}H} NMR (external reference 85% aqueous H$_3$PO$_4$): δ –13.3 bs. HR LSIMS, m/z: found 2 418.5346, for [C$_{92}$H$_{77}$Cu$_4$Fe$_4$I$_4$O$_8$P$_4$]$^+$, $i.e.$ [Cu$_4$(Hdpf)$_4$I + H]$^+$, calculated 2 418.5344. LSIMS (the most abundant ion of the isotopic cluster given here), m/z (relative abundance): 2 419 (0.2) [Cu$_4$(Hdpf)$_4$I$_4$ + H]$^+$, 2 291 (0.5) [Cu$_4$(Hdpf)$_4$I$_3$]$^+$, 1 877 (0.9) [Cu$_4$(Hdpf)$_3$I$_3$]$^+$, 1 749 (0.4) [Cu$_4$(Hdpf)$_3$I$_2$]$^+$, 1 687 (0.2) [Cu$_3$(Hdpf)$_3$I$_2$]$^+$, 1 273 (1) [Cu$_3$(Hdpf)$_2$I$_2$]$^+$, 1 081 (8) [Cu$_2$(Hdpf)$_2$I]$^+$, 891 (24) [Cu(Hdpf)$_2$]$^+$, 781(12) [Cu(Hdpf)$_2$ – C$_6$H$_5$O$_2$ – H]$^+$, $i.e.$ a formal loss of carboxylated cyclopentadiene from m/z 891, 667 (12) [Cu$_2$(Hdpf)I]$^+$, 477 (98) [Cu(Hdpf)]$^+$, 414 (100) [Hdpf]$^+$.

Crystal Structure Determination

Thin, plate-like single crystals of the complex were prepared as follows. In an argon atmosphere, the mixture of 20.4 mg (49.2 µmol) Hdpf, 23.5 mg (12.3 µmol) CuI and glacial acetic acid (5 cm^3) was refluxed for 5 h, filtered while hot, and the clear filtrate was cooled slowly to room temperature. The crystals formed were filtered off and dried in air. Their IR spectrum was identical with that of the polycrystalline sample prepared as described above. The selected specimen was mounted on a glass fiber by epoxy cement. Reflections were collected at 296(1) K on an Enraf–Nonius CAD 4-MACH III diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) and θ–2θ scan, and analytically corrected for absorption (AGNOSTIC, ref.[9]; T_{min}, T_{max} values are given in Table I). The cell parameters were determined by least-squares fitting of 25 centered diffraction with 14.5 ≤ θ ≤ 15.0°. The structure was solved by direct methods (SIR92, ref.[10]) followed by consecutive Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXL93, ref.[11]). All non-hydrogen atoms were refined anisotropically. The aromatic (ferrocenyl, phenyl) and methyl (solvating acetic acid) hydrogens were fixed in geometrically calculated positions with C–H lengths of 0.93 Å and 0.96 Å, respectively, and the thermal parameters were taken in the form U_{iso}(H) = 1.2 U_{eq}(C). The carboxylic hydrogens were omitted in the refinement. Selected bond lengths and angles are given in Table II, a

list of important torsion angles and dihedral angles of least-squares planes in Table III. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The title complex is an orange solid insoluble in poorly coordinating solvents such as diethyl ether, petroleum ether, toluene, but soluble in donor solvents such as dimethyl sulfoxide or hot acetic acid. In spite of some decomposition of the solution in hexa-

TABLE I
Crystallographic parameters, data collection and refinement of the cubane

Formula unit	$C_{96}H_{84}Cu_4Fe_4I_4O_{12}P_4$
M	2 536.61 g mol^{-1}
Crystal system; space group	monoclinic; $P2_1/c$ (No. 14)
a	16.061(2) Å
b; β	24.435(5) Å; 101.08(1)°
c	24.719(5) Å
V; Z	9 520(3) Å^3; 4
D_c	1.77 g cm^{-3}
D_m	1.76 g cm^{-3} (flotation in aqueous $ZnBr_2$)
$F(000)$	4 976
Crystal size	$0.06 \times 0.8 \times 1.0$ mm^3
Crystal description	orange plate
μ; T_{min}, T_{max}	2.891 mm^{-1}; 0.132, 0.850
Range of 2θ	2.4–48.0°
Range of hkl	0→18; 0→27; –28→27
Diffractions collected; $R(\sigma)^a$	15 595; 3.7%
Diffractions unique	14 703
Diffractions observed: $F_o \geq 4\sigma(F_o)$	10 756
Standard diffractions	3 monitored every 1 h
Variation in standards	3.6%
Weighting scheme: w_1, $w_2{}^b$	0.0690, 31.6211
Number of parameters	1 117
$R_{all}(F)$, $R_{obs}(F)^a$	7.4%, 3.9%
$wR_{all}(F^2)$, $wR_{obs}(F^2)^a$	19.3%, 10.8%
$GOF_{all}{}^a$	1.05
$(\Delta/\sigma)_{max}$	–0.001
$\Delta\rho$	0.88, –0.90 e Å^{-3}

^{a} $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2]^{1/2}$,
   $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$, $R(\sigma) = \Sigma\sigma(F_o^2)/\Sigma F_o^2$.
^{b} Weighting scheme used: $w = [\sigma^2(F_o^2) + w_1 P^2 + w_2 P]^{-1}$; $P = [\max(F_o^2) + 2F_c^2]/3$.

Selected bonding interatomic distances (Å) and angles (°) for the cubane

Bond	Distances	Bond	Angles
		Average values[a]	
Fe–C(Cp)	2.04(1), $n = 40$		
C–C(Cp)	1.42(2), $n = 40$	C–C–C(Cp)	108(1), $n = 40$
C–C(Ph)	1.38(2), $n = 48$	C–C–C(Ph)	120(1), $n = 48$
		Core geometry	
I1–Cu1	2.659(1)	Cu1–I1–Cu2	70.60(3)
I1–Cu2	2.690(1)	Cu1–I1–Cu3	64.63(3)
I1–Cu3	2.701(1)	Cu2–I1–Cu3	69.86(3)
I2–Cu1	2.756(1)	Cu1–I2–Cu2	68.44(3)
I2–Cu2	2.740(1)	Cu1–I2–Cu4	70.03(3)
I2–Cu4	2.617(1)	Cu2–I2–Cu4	70.37(3)
I3–Cu2	2.658(1)	Cu2–I3–Cu3	70.17(3)
I3–Cu3	2.711(1)	Cu2–I3–Cu4	70.42(4)
I3–Cu4	2.698(1)	Cu3–I3–Cu4	72.78(3)
I4–Cu1	2.678(1)	Cu1–I4–Cu3	64.82(3)
I4–Cu3	2.669(1)	Cu1–I4–Cu4	69.59(3)
I4–Cu4	2.728(1)	Cu3–I4–Cu4	72.96(3)
Cu1–P1	2.255(2)	I1–Cu1–I2	105.82(4)
Cu2–P2	2.250(2)	I1–Cu1–I4	114.05(4)
Cu3–P3	2.246(2)	I2–Cu1–I4	105.17(4)
Cu4–P4	2.240(2)	I2–Cu1–I3	106.77(4)
P1–C101	1.787(8)	P1–Cu1–Cu3	145.61(7)
P1–C118	1.825(9)	P1–Cu1–I1	112.23(6)
P1–C112	1.834(7)	P1–Cu1–I2	107.60(6)
P2–C201	1.809(8)	P1–Cu1–I4	111.34(7)
P2–C212	1.824(8)	I1–Cu2–I2	105.42(4)
P2–C218	1.833(8)	I1–Cu2–I3	107.59(4)
P3–C301	1.807(8)	I2–Cu2–I3	106.49(4)
P3–C318	1.816(8)	P2–Cu2–I1	109.86(6)
P3–C312	1.834(8)	P2–Cu2–I2	109.30(6)
P4–C401	1.800(8)	P2–Cu2–I3	117.48(6)
P4–C412	1.818(7)	I1–Cu3–I3	105.76(4)
P4–C418	1.837(8)	I1–Cu3–I4	112.96(4)
		I3–Cu3–I4	102.79(4)
C101–P1–C112	101.9(3)	I3–Cu3–Cu1	104.17(4)
C101–P1–C118	109.3(4)	I3–Cu3–Cu1	143.15(7)
C112–P1–C118	102.1(3)	P3–Cu3–I1	106.31(6)

TABLE II
(*Continued*)

Bond	Distances	Bond	Angles
		Core geometry	
C201–P2–C212	105.4(3)	P3–Cu3–I3	112.30(6)
C201–P2–C218	102.0(3)	P3–Cu3–I4	116.34(6)
C212–P2–C218	101.5(3)	I2–Cu4–I3	108.94(4)
C301–P3–C312	105.4(4)	I2–Cu4–I4	107.71(4)
C301–P3–C318	103.3(3)	I3–Cu4–I4	101.59(4)
C312–P3–C318	101.6(4)	P4–Cu4–I2	121.19(7)
C401–P4–C412	103.3(3)	P4–Cu4–I3	111.56(7)
C401–P4–C418	105.5(4)	P4–Cu4–I4	103.84(6)
C412–P4–C418	100.9(3)		
		Carboxylic groups	
O101–C111	1.30(1)	O101–C111–O102	122.1(9)
O102–C111	1.22(1)	O101–C111–C106	115.5(8)
C106–C111	1.48(1)	O102–C111–C106	122.3(8)
O201–C211	1.27(1)	O201–C211–O202	123.6(8)
O202–C211	1.24(1)	O201–C211–C206	116.7(8)
C206–C211	1.49(1)	O202–C211–C206	119.6(8)
O301–C311	1.30(1)	O301–C311–O302	122.6(9)
O302–C311	1.22(1)	O301–C311–C306	115.2(8)
C306–C311	1.47(1)	O302–C311–C306	122.2(8)
O401–C411	1.27(1)	O401–C411–O402	124(1)
O402–C411	1.25(1)	O401–C411–C406	117(1)
C406–C411	1.48(1)	O402–C411–C406	119.0(9)
O10–C11	1.26(1)	O10–C11–O11	122(1)
O11–C11	1.24(1)	O10–C11–C10	118(1)
C10–C11	1.49(1)	O11–C11–C10	120(1)
O20–C21	1.25(2)	O20–C21–O21	124(1)
O21–C21	1.23(2)	O20–C21–C20	119(2)
C20–C21	1.52(2)	O21–C21–C20	117(2)

[a] Arithmetic mean of *n* entries.

deuteriodimethyl sulfoxide as indicated by slow darkening, the solution could be used for the determination of the amount of solvating acetic acid by ^{1}H NMR. Generally, the ^{1}H NMR spectra exhibit all signals expected for four equivalent Cu(Hdpf-P)I fragments and two molecules of acetic acid. Only one signal is observed in the ^{31}P{^{1}H} NMR spectrum which is broadened by direct bonding to the quadrupole copper nucleus ([63]Cu and [65]Cu with spin quantum numbers of 3/2). Heterocubanes of the $Cu_4X_4P_4$ type (X = halide) are generally prone to dissociation in donor solvents and attempts to recrystallize them often fail due to preferential separation of compounds with different stoichiometry resulting from scission of the core. For instance, recrystallization[4] of $[(PPh_3)CuI]_4$ produces $[(PPh_3)_3Cu_2I_2]$ while the crystallization of its AsPh$_3$ analogue from acetonitrile[12] leads to another dinuclear complex of the composition $[(AsPh_3)(CH_3CN)CuI]_2$. Any solution data (*e.g.* electrochemical) ascribed to the whole $Cu_4X_4P_4$ core should be therefore taken with caution and such measurements are not attempted here. Similarly, it cannot be distinguished whether the positively charged fragment ions observed in LSIMS are the result of the Cs^{+} bombardment or result already by dissociation on the dissolution in the matrix. The dissociation in the matrix used, if any, is however incomplete as demonstrated by the presence of the Cu$_n$ clusters (n = 1–4) in the spectrum. Due to the loss of solvating acetic acid on dissolution in 3-nitrobenzyl alcohol, there are no peaks in the LSIMS spectra assignable to the solvated heterocubane and its fragments.

The solid-state molecular structure of $Cu_4I_4(Hdpf)_4$ is of the heterocubane type (Figs 1 and 2) and, in contrast to the majority of other heterocubane structures, possesses no

TABLE III
Selected torsional angles and dihedral angles of important least-squares planes (°) (e.s.d's in parentheses) for the cubane

Torsional angles					
I1–Cu1–I4–Cu3	15.02(4)		Cu4–I2–Cu2–I3		−15.02(4)
I1–Cu1–I2–Cu2	−23.85(3)		Cu4–I4–Cu1–I2		−20.29(3)
I1–Cu3–I3–Cu2	19.66(3)		Cu4–I4–Cu3–I3		23.84(3)
Dihedral angles of planes[a]					
Cp1, Cp1′	4.4(6)	Cp1, Ph1 73.4(3)	Cp1, Ph1′ 32.7(5)	Cp1, COO1	16(1)
Cp2, Cp2′	3.2(6)	Cp2, Ph2 61.3(3)	Cp2, Ph2′ 75.9(3)	Cp2, COO2	4(1)
Cp3, Cp3′	2.6(7)	Cp3, Ph3 57.3(3)	Cp3, Ph3′ 71.8(3)	Cp3, COO3	10(1)
Cp4, Cp4′	1.2(6)	Cp4, Ph4 73.9)3)	Cp4, Ph4′ 58.4(3)	Cp4, COO4	5(1)

[a] Least-squares planes are defined as follows: Cpn: Cn01, Cn02, Cn03, Cn04, Cn05 (P-substituted cyclopentadienyl ring); Cpn': Cn06, Cn07, Cn08, Cn09, Cn10 (carboxylated cyclopentadienyl ring); Phn: Cn12, Cn13, Cn14, Cn15, Cn16, Cn17 (P-bonded phenyl ring); Phn': Cn18, Cn19, Cn20, Cn21, Cn22, Cn23 (P-bonded phenyl ring); COOn: Cn11, On01, On02 (carboxyl group); where n = 1–4.

crystallographically imposed symmetry. Even though, the Cu_4I_4 core is only slightly distorted when considered as two interpenetrating tetrahedra of fairly different size built up of four copper and four iodine atoms, respectively. The local symmetry of the core is not far from T_d but, of course, suffers from serious distortion when naively looked upon as an idealized O_h cube. This is the common situation for $Cu_4X_4P_4$ with $X = I$ and the reason for the distortion is undoubtedly steric, being caused mostly by the large size of iodide. The support for this comes from the comparison with bromide and, in pariular, chloride heterocubanes where the interpenetrating tetrahedra are almost of the same size and the cube is therefore nearly or even perfectly (by symmetry) regular in shape. In terms of the interatomic distances, angles and least-squares planes, the structure of the present complex can be rationalized in a number of ways. Somewhat unconventionally but conveniently, it may be described as being composed of four
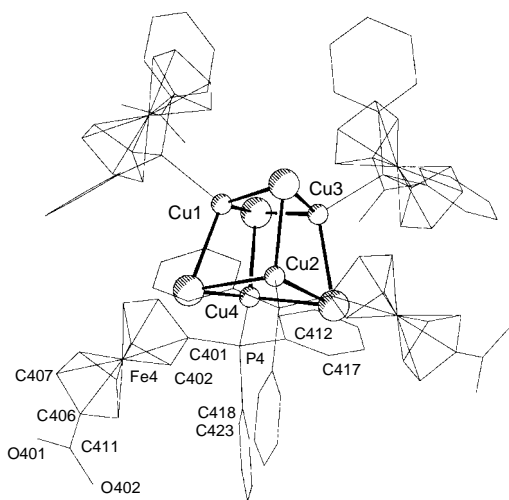

FIG. 1

Perspective drawing of the molecule. For clarity, the ligand molecules are drawn only schematically, hydrogen atoms and solvating acetic acid are omitted. Labelling scheme is given for one ligand only; for other ligands, change the first digit of the label
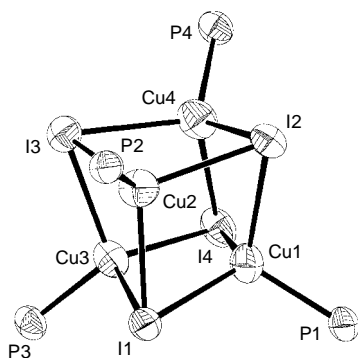

FIG. 2

Detailed geometry of the heterocubane core. The thermal motion ellipsoids are scaled to the 50% probability level

more or less distorted tetrahedra of various size but with a common centre of gravity. The smallest Cu_4 tetrahedron with the non-bonding Cu–Cu distances 2.865–3.209 Å and the Cu–Cu–Cu angles 54.1–65.1° interpenetrates with a larger I_4 tetrahedron (4.204–4.477 Å, 57.1–62.5°), giving rise to the cubane core. The mean I⋯I distance closely approaches the van der Waals contact of these two atoms[13] (4.3 Å), thus confirming the steric origin of the core distortion. Moving to the periphery, there is a third P_4 tetrahedron (6.529–6.882 Å, 57.7–62.1°) and even a fourth Fe_4 moiety (9.349–11.388 Å, 51.5–72.5°), the large distortion of which can be easily understood as the result of free rotation about the P–cyclopentadienyl (Cp) bonds, as well as of hydrogen bonding through the carboxyl groups located on the remote cyclopentadienyl rings. All faces of the central heterocubane core are remarkably non-planar, their edges are of different length and the least-squares rhombohedral planes of the faces are mutually non-orthogonal. The "butterfly"-type distortion of the faces covers the range of 17.2–47.7° for the dihedral angles about the plane diagonals, the I1–Cu1–I4–Cu3 face being the most distorted one. Despite these deformations, the bond angles at copper atoms remain approximately tetrahedral (with maximal spread of 101.6–121.2° at Cu4).

The structure of the phosphine ligand is similar to that known from its other complexes[8,14]. Calculation of the cone angle for eleven symmetry-independent ligands from these solid-state structures provided the limiting value of 166° (taking 1.2 Å for the van der Waals radius of hydrogen[13]) which classifies Hdpf as significantly more sterically demanding than triphenylphosphine. However, the cone angle can become as small as 117° in the crowded environment of *cis*-PtCl$_2$(Hdpf)$_2$. Hence, the ligand is sterically very flexible, in accordance with its conformational mobility either at the P–cyclopentadienyl bond or in the relative arrangement of the substituents on ferrocenyl. In the present structure the cone angle for the four crystallographically independent ligands is 153–157°. The cyclopentadienyl rings of the ligands are essentially coplanar (the corresponding dihedral angles of their mean planes are 1.2–4.4°) but further conformational details differ significantly from ligand to ligand (Fig. 3). A significant difference is in the relative arrangement of the cyclopentadienyl rings. This is nearly eclipsed for the
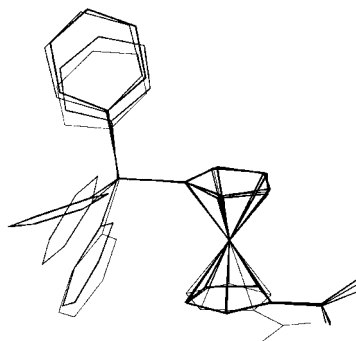

F$_{IG}$. 3

Superposition of the four independent Hdpf molecules drawn with line thickness decreasing from molecule 1 to molecule 4. The overlap is defined by phosphorus atoms in a common origin, C101 as the *x*-axis and the centroid of the C106–C110 pentagon as the *xy*-plane

ligand involving Fe2 [all five torsion angles defined as (carbon of ring 1–centroid of the Cp-ring 1–centroid of the Cp-ring 2–eclipsed carbon of the Cp-ring 2) are less than 4°] but becomes half-way between staggered and eclipsed for the other ligands (12–17°; the value for the exactly staggered conformation is 36°).

The present structure is the first case of the $Cu_4X_4P_4$ archetype whose crystal structure is not purely molecular. Instead, the individual molecules are linked by double hydrogen bonds typical for dimers of carboxylic acids. Although the carboxylic hydrogen atoms were not located, the hydrogen bonding follows from the mutual orientation of the carboxyl groups involved. There are two types of hydrogen bonds. The carboxyl group of the ligand coordinated to Cu1 is linked to its counterpart at Cu3 ($1 + x$, $1/2 - y$, $1/2 + z$) with the O···O distances of 2.590 and 2.634 Å; this links the molecules into zig-zag chains running along the crystallographic c-direction (Fig. 4). The remaining ligands at Cu2 and Cu4 are hydrogen-bonded at O···O 2.616–2.647 Å to the molecules of solvating acetic acid which, together with the phenyl groups, act as spacers between the chains. This system of hydrogen bonding is the combination of the two types previously found separately in different complexes of Hdpf (ref.[8]). The direction in which the molecules are linked intramolecularly roughly corresponds to the largest compression of the cubane core. The hydrogen bonding, together with the essentially free rotation of the cyclopentadienyl rings, influences further details of the ligand conformation. The relative arrangement of the diphenylphosphino and carboxyl substituents (in terms of the torsion angle phosphorus–centroids of cyclopentadienyls–carboxylic carbon) is *synclinal* in one ligand (that with Fe4, $\tau = -118°$) but *anticlinal* in the other three ($\tau = 150$–$155°$). Moreover, the carboxyl groups are also oriented relatively to the parent cyclopentadienyls in a different way: while the carboxyl groups which are hydrogen-bonded to acetic acid are nearly coplanar with the parent cyclopentadienyl rings (4.2 and 5.1° in the dihedral angle), the other two which link the heterocubane moieties are
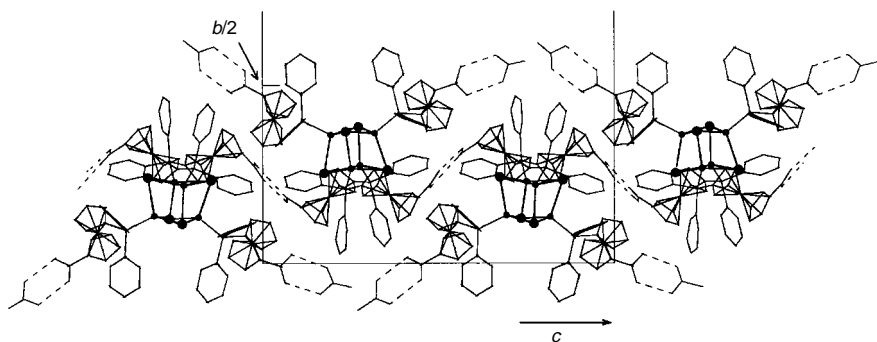

FIG. 4
Crystal packing viewed along the crystallographic a-axis. For clarity, only one chain of complex molecules is drawn

tilted from the cyclopentadienyl planes by 12.4 and 15.7°; this, together with the distortion of the core, probably reflects certain strain within the zig-zag chain of the molecules. Further significant differences are in the orientation of the phenyl groups which display no intra- or intermolecular π–π interactions but are, as expected, arranged such as to avoid short intermolecular contacts.

REFERENCES

1. Churchill M. R., DeBoer B. G., Donovan D. J.: *Inorg. Chem.* **1975**, *14*, 617.
2. Dyason J. C., Healy P. C., Engelhardt L. M., Pakawatchai C., Patrick V. A., Raston C. L., White A. H.: *J. Chem. Soc., Dalton Trans*. **1985**, 831; Attar S., Bowmaker G. A., Alcock N. W., Frye J. S., Bearden W. H., Nelson J. H.: *Inorg. Chem.* **1991**, *30*, 4743.
3. Hakanson M., Jagner S., Clot E., Eisenstein O.: *Inorg. Chem.* **1992**, *31*, 5389.
4. Churchill M. R., DeBoer B. G., Mendak S. J.: *Inorg. Chem.* **1975**, *14*, 2041.
5. Churchill M. R., Kalra K. L.: *Inorg. Chem.* **1974**, *13*, 1427.
6. Goel R. G., Beauchamp A. L.: *Inorg. Chem.* **1983**, *22*, 395.
7. Podlaha J., Stepnicka P., Ludvik J., Cisarova I. : *Organometallics* **1996**, *15*, 543.
8. Stepnicka P., Podlaha J., Gyepes R., Polasek M.: *J. Organomet. Chem.*, in press.
9. Templeton D. H., Templeton L. K.: *AGNOSTIC, Program for Absorption Correction*. University of California, Berkeley 1978.
10. Altomare A., Burla M. C., Camalli M., Cascarano G., Giacovazzo C., Guagliardi A., Polidori G.: *J. Appl. Crystalogr.* **1994**, *27*, 435.
11. Sheldrick G. M.: *SHELXL93, Program for Crystal Structure Refinement from Diffraction Data*. University of Gottingen, Gottingen 1993.
12. Dyason J. C., Engelhardt L. M., Pakawatchai C., Healey P. C., White A. H.: *Aust. J. Chem.* **1985**, *38*, 1243.
13. Pauling L.: *The Nature of Chemical Bond*, p. 260. Cornell University Press, Ithaca 1960.
14. Stepnicka P., Gyepes R., Lavastre O., Dixneuf P. H.: *Organometallics* **1997**, *16*, 5089.