Journal of Organometallic Chemistry, 291 (1985) 53–60
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METAL COMPLEXES OF CYCLOPHANES

VIII *. THE CRYSTAL AND MOLECULAR STRUCTURES OF 5,13-DIMETHYL[2.2]METACYCLOPHANE AND [3–8-η-5,13-DIMETHYL[2.2]METACYCLOPHANE(η^5-CYCLOPENTADIENYL)IRON]-HEXAFLUOROPHOSPHATE

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(Received February 15th, 1985)

Summary

The crystal structures of 5,13-dimethyl[2.2]metacyclophane and [3–8-η-5,13-dimethyl[2.2]metacyclophane(η^5-cyclopentadienyl)iron]hexafluorophosphate have been determined in order to examine the effect of metal π-bonding to the geometry of the metacyclophane molecule.

Introduction

Transition metal complexes of cyclophanes constitute a new and exciting area of organometallic chemistry [2]. There have been many publications dealing with the synthesis and the spectroscopic characterization of such complexes, but surprisingly few crystallographic studies. Such studies are of interest, because they can provide useful information about the changes in the cyclophane skeleton due to metal π-bonding [3]. We regard flexible cyclophanes as suitable model compounds for this purpose, since the structural perturbations deriving from complexation with metal atoms are more significant here than in the rigid cyclophanes [4].

5,13-Dimethyl[2.2]metacyclophane (**1**) is a markedly distorted molecule and we were interested in finding out what further distortion and skeletal changes would

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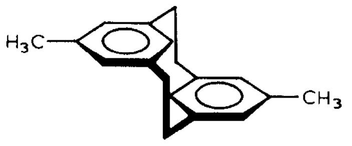
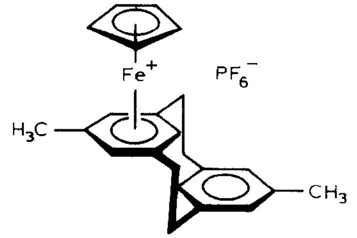
0022-328X/85/$03.30

arise upon complexing one of the aromatic rings of this molecule with a (η^5-cyclopentadienyl)iron$^+$ moiety. With this in mind we have carried out an X-ray structural analysis of **1** and its organometallic derivative **2**, which was recently synthesized and characterized by Koray [5].



(**1**)



(**2**)

Structure determination and refinement of 1 and 2

A white crystal of **1**, 0.15 mm in diameter, was selected for a measurement on a Syntex P3 four-circle diffractometer. The unit cell constants were derived by least-squares analysis of the 2θ-values of 25 reflections ($6° < 2\theta < 25°$). For intensity measurement graphite monochromatized Mo-K_α radiation was used (θ–2θ scan; $3° < 2\theta < 55°$). Lorentz and polarization and an empirical absorption correction (ψ-scan, 6 reflections) were applied. 429 independent reflections ($I > 2.5\sigma(I)$) were used for calculations. Since **1** has $Z = 1$ the molecules have to be centrosymmetric. The structure was solved by direct methods, refinement was carried out by least-squares methods (Program SHELXTL) [6]. Scattering factors were taken from the International Tables for X-ray Crystallography [7]. A difference Fourier map allowed the location of all hydrogen atoms. Isotropic refinement of all atoms lead to a conventional R value of 0.180, only the methyl H atoms showing high thermal motion. After anisotropic refinement of all carbon atoms R converged to 0.044. The

TABLE 1

CRYSTAL DATA OF 1 AND 2

1	**2**
$C_{18}H_{20}$	$C_{23}H_{25}Fe^+\ PF_6^-$
Triclinic, Space group $P\bar{1}$	Monoclinic, Space group $P2_1/c$
M 236.36	M 502.26
a 5.222(2) Å	a 12.817(4) Å
b 8.125(2) Å	b 9.674(4) Å
c 8.388(3) Å	c 18.176(6) Å
α 95.40(2)°	
β 107.79(2)°	β 95.5(3)°
γ 94.34(2)°	
V 335.31 Å^3	V 2244.04 Å^3
$Z = 1$	$Z = 4$
D_c 1.17 g cm^{-3}	D_c 1.49 g cm^{-3}
$F(000) = 128$	$F(000) = 1032$
μ 0.61 cm^{-1}	μ 7.96 cm^{-1}

weighted R value ($R_w = \Sigma|F_c - F_0|\sqrt{\text{wght}}|\Sigma F_0\sqrt{\text{wght}}$; wght $= 1/\sigma^2(F)$) was 0.037.

A hexagonal orange crystal of compound **2** (0.25 × 0.25 × 0.1 mm) was used for determination of unit cell constants and intensity measurement. The structure was solved by Patterson- and Fourier synthesis using 1101 independent reflections ($I > 2.5\sigma(I)$). Isotropic refinement of all atoms gave $R = 0.10$. Hydrogen atoms were located by the program H-FIX [6]. Anisotropic refinement of all atoms except

(Continued on p. 58)

TABLE 2

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($\times 10^3$) OF **1** AND **2**

Atom	x	y	z	U [a]
C(1)	685(8)	730(5)	2348(5)	42(2)
C(2)	3072(11)	1743(6)	3179(7)	48(2)
C(3)	3962(9)	3092(5)	2495(6)	45(2)
C(4)	2453(10)	3342(6)	884(7)	48(2)
C(5)	17(9)	2362(5)	−0(6)	44(2)
C(6)	−931(10)	1154(6)	831(6)	42(2)
C(7)	125(9)	−960(6)	2849(7)	51(2)
C(8)	−1254(9)	2311(6)	−1895(7)	51(2)
C(9)	6610(13)	4140(8)	3407(10)	66(3)
Fe	1964(2)	806(2)	1610(1)	43(1)
P	2156(4)	5284(6)	3704(3)	73(2)
C(1)	1702(12)	6343(14)	6382(8)	39(6)
C(2)	1219(12)	5903(16)	7030(7)	52(7)
C(3)	1777(15)	5255(17)	7602(9)	53(8)
C(4)	2835(12)	4970(15)	7557(10)	61(8)
C(5)	3374(13)	5351(16)	6942(9)	41(7)
C(6)	2769(11)	5910(15)	6345(9)	54(6)
C(7)	1187(13)	7328(15)	5803(8)	54(7)
C(8)	4559(12)	5372(15)	6919(9)	55(7)
C(9)	1203(14)	4754(18)	8252(8)	71(8)
C(11)	4514(11)	7790(14)	6426(8)	43(6)
C(12)	4887(12)	7779(15)	5734(8)	54(7)
C(13)	4311(13)	8313(16)	5115(10)	66(8)
C(14)	3292(12)	8761(14)	5204(8)	56(7)
C(15)	2868(12)	8780(13)	5874(9)	53(7)
C(16)	3529(11)	8388(13)	6489(8)	47(6)
C(17)	4984(11)	6865(15)	7031(8)	60(7)
C(18)	1684(13)	8810(17)	5921(9)	67(8)
C(19)	4709(16)	8295(21)	4347(10)	88(10)
C(20)	2473(14)	2256(18)	6392(11)	74(9)
C(21)	2139(20)	2954(21)	5735(12)	81(11)
C(22)	1081(20)	3223(20)	5763(13)	80(10)
C(23)	810(16)	2796(18)	6438(12)	80(10)
C(24)	1664(14)	2148(15)	6837(8)	70(8)
F(1)	1332(8)	5341(10)	2996(6)	102(4)
F(2)	3046(10)	5589(13)	3240(7)	148(5)
F(3)	2336(10)	3669(13)	3629(7)	145(5)
F(4)	1230(10)	4979(13)	4195(7)	141(5)
F(5)	1933(10)	6863(13)	3827(6)	127(4)
F(6)	2959(8)	5249(11)	4423(6)	113(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) OF **1**

C(1)–C(2)	1.386(6)	C(1)–C(6)	1.386(6)
C(1)–C(7)	1.507(7)	C(2)–C(3)	1.397(8)
C(3)–C(4)	1.383(7)	C(3)–C(9)	1.508(7)
C(4)–C(5)	1.400(6)	C(5)–C(6)	1.400(7)
C(5)–C(8)	1.519(7)	C(7)–C(8a)	1.554(8)
C(8)–C(7a)	1.554(8)		
C(2)–C(1)–C(6)	117.8(4)	C(2)–C(1)–C(7)	121.6(4)
C(6)–C(1)–C(7)	119.4(4)	C(1)–C(2)–C(3)	122.5(4)
C(2)–C(3)–C(4)	117.6(4)	C(2)–C(3)–C(9)	121.3(5)
C(4)–C(3)–C(9)	120.9(5)	C(3)–C(4)–C(5)	121.9(5)
C(4)–C(5)–C(6)	117.7(4)	C(4)–C(5)–C(8)	121.9(5)
C(6)–C(5)–C(8)	119.0(4)	C(1)–C(6)–C(5)	121.4(4)
C(1)–C(7)–C(8a)	110.7(5)	C(5)–C(8)–C(7a)	110.6(4)

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) OF **2**

Fe–C(1)	2.14(1)	Fe–C(2)	2.09(2)
Fe–C(3)	2.11(2)	Fe–C(4)	2.10(2)
Fe–C(5)	2.16(2)	Fe–C(6)	2.04(2)
Fe–C(20)	2.04(2)	Fe–C(21)	2.02(2)
Fe–C(22)	2.05(2)	Fe–C(23)	2.01(2)
Fe–C(24)	2.07(2)	C(1)–C(2)	1.45(2)
C(1)–C(6)	1.44(2)	C(1)–C(7)	1.52(2)
C(3)–C(9)	1.53(2)	C(2)–C(3)	1.36(2)
C(4)–C(5)	1.42(3)	C(3)–C(4)	1.39(3)
C(5)–C(6)	1.38(2)	C(5)–C(8)	1.52(2)
C(7)–C(18)	1.58(2)	C(8)–C(17)	1.55(2)
C(11)–C(12)	1.34(2)	C(11)–C(16)	1.40(2)
C(11)–C(17)	1.50(2)	C(12)–C(13)	1.38(2)
C(13)–C(14)	1.40(2)	C(13)–C(19)	1.53(3)
C(14)–C(15)	1.38(2)	C(15)–C(16)	1.39(2)
C(15)–C(18)	1.53(2)	C(20)–C(21)	1.40(3)
C(20)–C(24)	1.38(3)		
C(21)–C(22)	1.39(4)		
C(22)–C(23)	1.37(3)		
C(23)–C(24)	1.40(3)		
C(2)–C(1)–C(6)	116(1)	C(2)–C(1)–C(7)	124(1)
C(6)–C(1)–C(7)	120(1)	C(2)–C(3)–C(4)	119(2)
C(1)–C(2)–C(3)	122(2)	C(4)–C(3)–C(9)	122(2)
C(2)–C(3)–C(9)	119(2)	C(3)–C(4)–C(5)	123(2)
C(4)–C(5)–C(6)	116(2)	C(4)–C(5)–C(8)	126(1)
C(6)–C(5)–C(8)	117(1)	C(1)–C(7)–C(18)	109(1)
C(1)–C(6)–C(5)	123(2)	C(12)–C(11)–C(16)	118(1)
C(5)–C(8)–C(17)	110(1)	C(16)–C(11)–C(17)	119(1)
C(12)–C(11)–C(17)	121(1)	C(12)–C(13)–C(14)	117(2)
C(11)–C(12)–C(13)	122(1)	C(14)–C(13)–C(19)	120(2)
C(12)–C(13)–C(19)	123(2)	C(14)–C(15)–C(16)	116(1)
C(13)–C(14)–C(15)	124(1)	C(16)–C(15)–C(18)	120(1)
C(14)–C(15)–C(18)	122(1)	C(8)–C(17)–C(11)	110(1)
C(14)–C(16)–C(15)	122(1)	C(21)–C(20)–C(24)	111(2)
C(7)–C(18)–C(15)	111(1)	C(21)–C(22)–C(23)	108(2)
C(20)–C(21)–C(22)	106(2)	C(20–C(24)–C(23)	105(2)
C(22)–C(23)–C(24)	110(2)		

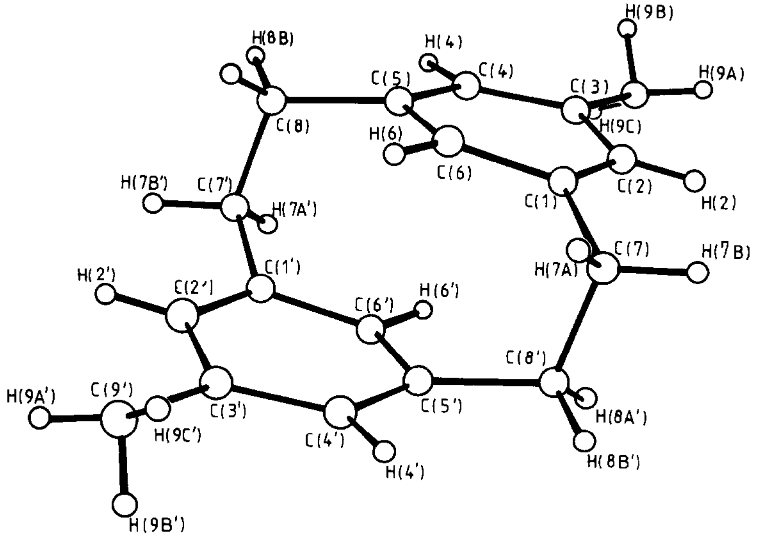
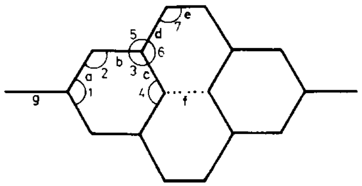


Fig. 1. Structure of **1** with atom numbering.

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (°) OF 5,13-DIMETHYL[2.2]METACYCLOPHANE (**1**) AND [3–8-η-5,13-DIMETHYL[2.2]METACYCLOPHANE-(η^5-CYCLOPENTADIENYL)IRON][PF$_6$] (**2**) (* average)



	1	**2**		
		Complexed ring		Uncomplexed ring
a	1.390(7)*	1.38(2)*		1.39(2)*
b	1.393(6)*	1.43(2)*		1.38(2)*
c	1.393(7)*	1.41(2)*		1.40(2)*
d	1.513(7)*	1.52(2)*		1.51(2)*
e	1.554(8)*		1.56(2)*	
f	2.649(7)		2.59(2)	
g	1.509(7)	1.52(2)		1.53(3)
1	117.6(4)	119(2)		117(2)
2	122.2(5)*	112(2)*		123(1)*
3	117.8(4)*	116(2)*		117(1)*
4	121.4(4)	123(2)		122(1)
5	121.8(5)*	125(1)*		121(1)*
6	119.2(4)*	119(1)*		119(1)*
7	110.7(4)*	110(1)*		111(1)*

hydrogen and fluorine gave a final R index of 0.075 and $R_w = 0.069$.

Crystal data for **1** and **2** are listed in Table 1. Table 2 shows the final atomic positions and thermal parameters of the compounds. Bond distances and bond angles are listed in Table 3 and 4 respectively.

Discussion

As shown in Fig. 1, the molecules of **1** possess a transoid, stepped configuration with the methyl groups are positioned away from each other. Some selected bond distance and angles of **1** and **2** are presented schematically in Table 5.

Figure 2 shows the deviations of atoms from the least-squares planes.

The C atoms C(1), C(2), C(4) and C(5) form the least-squares plane A, the largest deviation being 0.003 Å. Both C(3) and C(6) deviate from this basal plane away from the center of symmetry, and so the benzene ring (C(1)–C(6)) adopts an asymmetrically distorted boat form. The deviation of C(6) is almost three times that of C(3). H(6) deviates from the plane towards the inner part of the molecule by 7.8°. The average intra-ring bond distance is 1.392 Å. There is good agreement between the bond distances of chemically equivalent but crystallographically independent parts of the molecule and between the bond angles in chemically equivalent parts.

The general structural parameters of the molecule are almost identical with those reported for [2.2]metacyclophane (**3**) [8]. A significant difference between the molecules **1** and **3** derives from the presence of methyl groups in **1**. The electron-releasing substituent CH_3 causes a decrease of the angle C(2)–C(3)–C(4), from 120.3° in **3** to 117.6° in **1**. Such an effect has also been observed for another methyl substituted metacyclophane [9].

Another significant feature of the molecule is the decrease of the angles C(4)–C(5)–C(6) and C(2)–C(1)–C(6) to 117.7° and 117.8° respectively. This can be rationalized in terms of a change in the hybrid state of C(1) and C(5) due to the strains induced by the bridging. Figure 3 presents a view of **2**.

The accuracy of the structure analysis is limited by the small number of observed reflections and by the marked thermal motion of the PF_6^- ion.

The geometry of the uncomplexed ring in **2** is almost the same as that observed in **1**, while the complexed ring shows significant perturbation attributable to metal π-bonding.

As can be seen from Fig. 4, C(3) deviates from plane A′ (C(1), C(2), C(4) and C(5)) only by 1.0°, whereas the deviation of C(6) from this plane is about 11°. C(3) is bent away and C(6) is bent towards the iron atoms, so that in contrast to that in **1**,

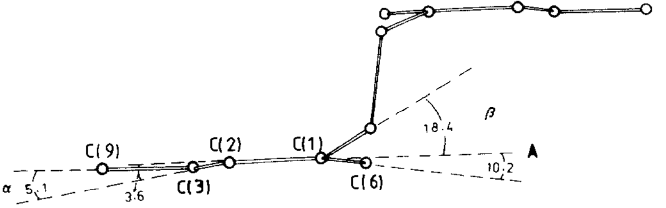


Fig. 2. Molecular projection of **1** along the vector passing through the midpoint of the C(7)–C(8′) bond and the centre of symmetry showing the atomic deviation (°) from the least-squares plane A.

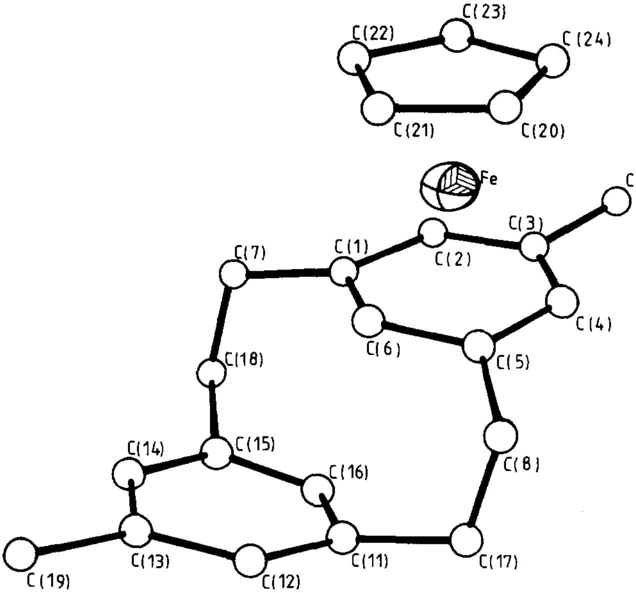


Fig. 3. Structure of **2** with atom numbering.

the conformation of the benzene ring is best described as a "half-chair" conformation. Due to the steric repulsion, C(6) and C(16) (non-bonding distance: 2.59(2) Å) deviate from the "planes" of the corresponding aromatic rings (C(6): 11°; C(16): 8.5°. It is also quite significant, that the complexation causes a decrease of the angles α' and β' (Figs. 2 and 4) compared to α and β. C(9) is bent towards, C(7) and C(8) are bent away from the iron atom. The Fe atom lies 1.59(2) Å from plane A' and 1.66(3) Å from the plane of the cyclopentadienyl ring.

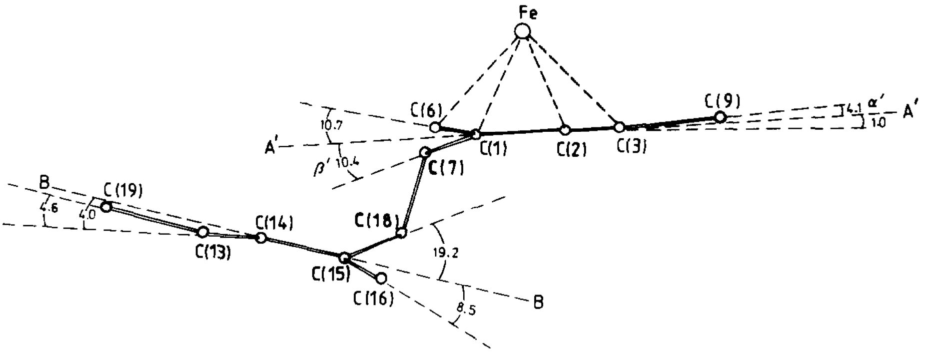


Fig. 4. Molecular projection of **2** along the vector passing through the midpoints of the C(8)–C(17) and the C(7)–C(18) bond showing the atomic deviation (°) from the least-squares planes A' and B respectively.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie; the authors are also grateful to N. Riegler, who supplied 5,13-dimethyl[2.2]metacyclophane. A.R.K. expresses his appreciation of the award of a postdoctoral fellowship by the Max-Planck-Gesellschaft.

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