Geometry-dependent Carbon-13 Chemical Shifts in (η⁶-[2.2]Cyclophane)-(η⁵-cyclopentadienyl)iron(II) Hexafluorophosphates

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The complexation shifts for the complexed-ring carbons in the title compounds are dependent on both degree and direction of the ring deformation and correlate with the interatomic distances between the Fe and the complexed-ring carbons.

As is well known, complexations of arenes with transition metals cause large upfield shifts for the aryl carbons. Many attempts have been made to explain the origin of the complexation shift in terms of a variety of causes associated with the π-bonding,[1,2] but they are all hampered by the approximations involved in any theoretical approach. It should be noted that no special regard was paid to geometrical factors, such as changes in molecular geometry on complexation.[3] One of the geometrical changes in π-complexed arenes is a small boat-type deformation of the arene ring.[4] Such ring deformation would be an important factor in determining complexation shifts for the ring carbons. In this connection, quite recently, we found the correlation between the complexation shift and the interatomic Cr–C distance in tricarbonyl(π-[2.2]cyclophane)chromium complexes.[5]

The present paper deals with the mixed-sandwich system of (η⁶-[2.2]cyclophane)(η⁵-cyclopentadienyl)iron(II) hexafluorophosphates.

Results and Discussion

Scheme 1 gives the ¹³C chemical shifts for the cyclophane complexes (1)—(8) examined. In Scheme 2 are given the results for the mono- and bi-cyclic arene complexes (9)—(12) used as references. In Schemes 1 and 2, values in parentheses are the shift differences from the uncomplexed hydrocarbons, i.e., the complexation shifts: $\Delta\delta = -[\delta(\text{complex}) - \delta(\text{hydrocarbon})]$. The chemical shifts (δ from internal SiMe₄, recorded in [²H₆]acetone unless otherwise noted) were assigned by off-resonance continuous-wave decoupling, intensity considerations, comparison with analogous compounds, and, particularly for the hydrocarbons, by reference to their literature assignment in [²H]chloroform.[6] [²H₆]Acetone had a downfield effect of ca. 0.8 p.p.m. compared with [²H]chloroform.

Basic Geometry.—The molecular structures of some of the uncomplexed cyclophanes in the solid state are known. In [2.2]paracyclophane,[7] the two stacked benzene rings are bent by 12.6° from their normal planar structure into boat forms. A lesser boat-type deformation is known for the benzene ring of [8]paracyclophane with a bending angle of 9.1°.[8] In [2.2]metacyclophane,[9] the stepwise-stacked benzene rings are bent into unsymmetrical boats, where C(5) is displaced out of the mean plane by 4.1° away from the other ring and C(8) is displaced by 9.5° in the same direction and in close proximity to C(16) of the other ring. In [2.2]metaparacyclophane,[10] the para-ring is more strongly bent than in [2.2]paracyclophane, the bending angle being 14°. The meta-ring is bent into an inclined chair, where C(8) is 0.09 Å above and C(5) is 0.07 Å below the mean plane.

Only few reports have appeared recently on the crystal structures of [Feⁱⁱ(η⁶-arene)(η⁵-C₅H₅)]⁺ salts,[11] such as [Feⁱⁱ(η⁶-C₆Et₆)(η⁵-C₅H₅)][PF₆][11a] and complex (1), but with

a BF₄⁻ counter anion.[11b] In the former, the average of the interatomic distances between the Fe and the complexed-ring carbons is 2.11 Å, which lies between the 2.22 Å to C(3) and the 2.08 Å to C(4) in the latter. The same order of metal–carbon distances is known in the Cr(CO)₃ complexes of [2.2]paracyclophane and benzene.[5]

Complexation Shifts.—In mono- and bi-cyclic complexes (9)—(12), the Δδ values for the tertiary carbons lie in a narrow range, 38.7—41.0 p.p.m., and those for the quaternary ones are similarly 32.3—34.8 p.p.m. The smaller shift of the latter group is probably ascribed to a lower electron density on the carbon resulting from the electronic effects of the attached alkyl substituent.[2] In cyclophane complexes (1)—(8), interestingly, Δδ values for the tertiary and the quaternary carbons are scattered in wide ranges: ca. 39—51 and ca. 18—38 p.p.m., respectively. The scattering may be related to the interatomic Fe–C distance, as will be described below.

Table 1 summarizes the complexation-shift data for several cyclophane complexes together with the ring-deformation data for their parent hydrocarbons. In the table, ΔΔδ is the difference in Δδ for the cyclophane complex from the indicated reference complex, i.e., the complexation-shift difference: ΔΔδ = Δδ(cyclophane complex) − Δδ(reference complex). In the complexed rings of the [2.2]paracyclophane complexes (1) and (2), the tertiary carbons all show a positive ΔΔδ value of ca. 9 p.p.m., whereas a negative value of ca. −11 p.p.m. is found for the quaternary carbons which are bent away from the Fe atom. Smaller ΔΔδ values are found in the less-bent monocyclic complex (8). In the [2.2]metacyclophane complex (3), the tertiary C(5) and C(8) atoms which are bent toward the Fe atom to different degrees show positive ΔΔδ values of ca. 3 and 10 p.p.m. and the quaternary C(3) atom, −5.1 p.p.m. Similar results are found in the 5,13-dimethyl[2.2]metacyclophane complexes (4) and (5). Furthermore, in the [2.2]metaparacyclophane complexes (6) and (7), the para-ring carbons show results similar to those for (1) and (2). In the meta-ring of (7), having a slight chair-type deformation, only C(8) which is bent toward the Fe shows a large positive value of 7.8 p.p.m. The observed upfield and downfield trends of ΔΔδ depending on the ring deformation are in complete agreement with those in the corresponding tricarbonyl(η⁶-cyclophane)chromium system.[5]

It is apparent that the magnitude of Δδ is dependent on both degree and direction of the ring deformation and correlates with the interatomic Fe–C distance. It thus appears that Δδ is directly related to the orbital interaction between the Fe and the complexed-ring carbon atoms, such as back bonding of the metal to the ligand.[12] The interaction would be dependent on both interatomic Fe–C distance (*d*) and orientation of the $2p_z$ orbital of the carbon with respect to the Fe atom. On this basis, a smaller Δδ is expected when *d* is larger and the $2p_z$-orbital axis is oriented away from the Fe. This is the case for C(3) and C(6) of (1) and (2), C(11) and C(14) of (6) and (7), and C(9) and C(12)

(1) **(2)** **(3)**

(4)

(5) **(6)** **(7)** **(8)**
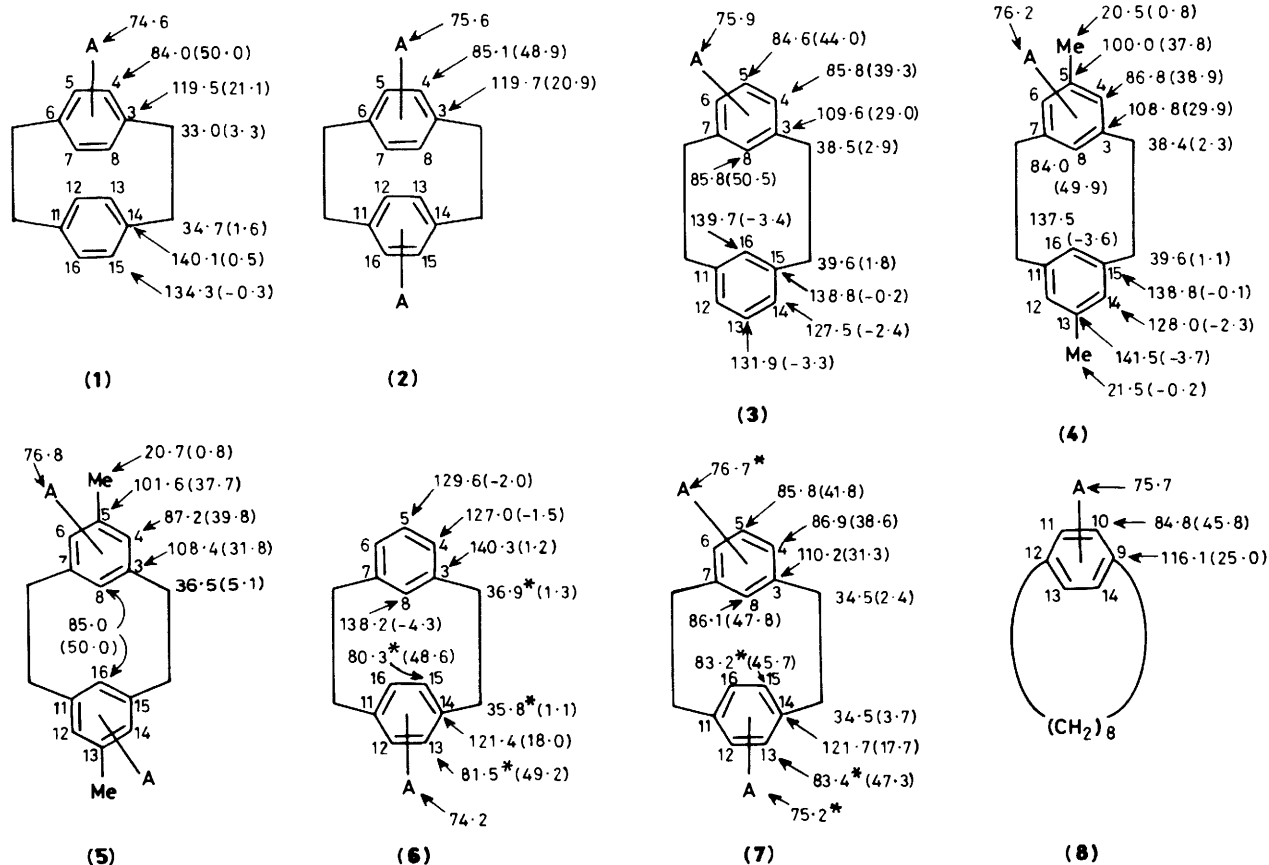
Scheme 1. Carbon-13 chemical shifts (in [^{2}H$_6$]acetone, relative to internal SiMe$_4$) for the (cyclophane)(cyclopentadienyl)iron(II) hexafluorophosphates (1)—(8) [A = Fe(η-C$_5$H$_5$)$^+$]. Δδ Values are given in parentheses. Shifts for the free hydrocarbons of (3) and (4) ([^{2}H]chloroform) are from ref. 6. Data for (5) ([^{2}H$_3$]acetonitrile) are from ref. 21. Assignments with an asterisk may be reversed

(9) **(10)** **(11)**

(12)
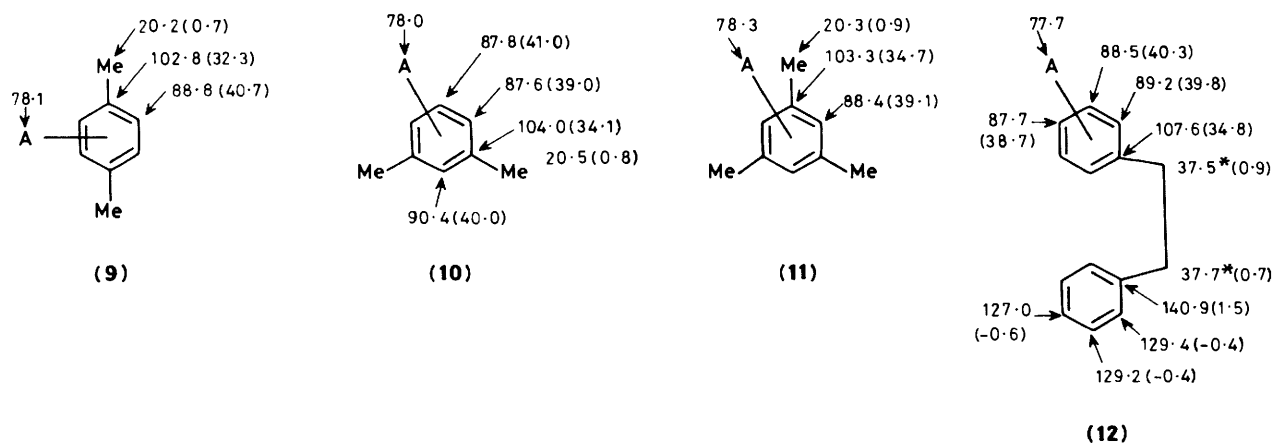
Scheme 2. Carbon-13 chemical shifts (in [^{2}H$_6$]acetone, relative to internal SiMe$_4$) for the (arene)(cyclopentadienyl)iron(II) hexafluorophosphates (9)—(12) [A = Fe(η-C$_5$H$_5$)$^+$]. Δδ Values are given in parentheses. Assignments with an asterisk may be reversed

of (8). The reverse conditions predict a larger Δδ, as has been observed for C(5) and C(8) of (3)—(5).

In this connection it should be noted that the magnetic anisotropy and field effects of the Fe(C$_5$H$_5$)$^+$PF$_6^-$ moiety are less important factors in determining Δδ because the methylene carbons attached to the complexed ring, which are strongly bent away from the Fe atom,[7–10] show positive ΔΔδ values of ca. 2 p.p.m. from complexes (9)—(12); large negative values would otherwise be observed. In addition, changes in transannular

electronic interaction, such as π–π repulsion[13] and charge transfer,[14] on complexation, if any, are also not so significant as to influence Δδ, because C(5) of the [2.2]metacyclophane complexes (3)—(5), which is far away from the other ring, and the [8]paracyclophane complex (8) also show large Δδ values. Further evidence is given by the fact that the uncomplexed-ring carbons of the mono-complexes of [2.2]cyclophanes show small shifts comparable to those of open-chain complex (12).

Table 1. Geometrical parameters and complexation shift data

Complex	Complexed ring carbons	$\theta^a/°$	$\Delta\delta^b$/p.p.m.	$\Delta\Delta\delta^c$/p.p.m.
(1)	C^3, C^6	−12.6	21.1	−11.2^d
	C^4, C^5, C^7, C^8	0	50.0	9.3^d
(2)	C^3, C^6	−12.6	20.9	−11.4^d
	C^4, C^5, C^7, C^8	0	48.9	8.2^d
(3)	C^3, C^7	0	29.0	−5.1^e
	C^4, C^6	0	39.3	0.3^e
	C^5	4.1	44.0	3.0^e
	C^8	9.5	50.5	10.5^e
(6)	C^{11}, C^{14}	−14	18.0	−14.3^d
	C^{12}, C^{13}	0	49.2	8.5^d
	C^{15}, C^{16}	0	48.6	7.9^d
(7)	C^3, C^7	0	31.3	−2.8^e
	C^4, C^6	0	38.6	−0.4^e
	C^5	(−0.07 Å)	41.8	0.8^e
	C^8	(0.09 Å)	47.8	7.8^e
	C^{11}, C^{14}	−14	17.7	−14.6^e
	C^{12}, C^{13}	0	47.3	6.6^d
	C^{15}, C^{16}	0	45.7	5.0^d
(8)	C^9, C^{12}	−9.1	25.0	−7.3^d
	$C^{10}, C^{11}, C^{13}, C^{14}$	0	45.8	5.1^d

^{a} Angle of the indicated carbon bent out of the mean plane of the benzene ring; a minus sign denotes the bending away from Fe. Values in parentheses are the distance of the carbon to the mean plane. $\theta = 0$ means the mean plane made with the indicated carbons. ^{b} Complexation shift. ^{c} Difference in $\Delta\delta$ from the indicated reference complex. ^{d} From (9). ^{e} From (10).

Table 2. One-bond $^{13}C-^1H$ coupling constants, ^1J(CH), for some complexes and their free ligands

Complex		Complexed ligand^a	Free ligand^b	Δ^1J/Hz	$\Delta\delta$/p.p.m.
		^1J(CH)/Hz		
(1)	C^4-H	177	156	21	50.0
	$C^{12}-H$	160	156	4	−0.3
	C_5H_5	182			
(3)	C^4-H	176	157	19	39.3
	C^5-H	179	159	20	44.0
	C^8-H	176	158	18	50.5
	$C^{12}-H$	160	157	3	−2.4
	$C^{13}-H$	160	159	1	−3.3
	$C^{16}-H$	157	158	−1	−3.4
	C_5H_5	182			
(8)	$C^{10}-H$	178	156	22	45.8
	C_5H_5	182			
[Fe(η-C$_6$H$_6$)(η-C$_5$H$_5$)][PF$_6$]	C$_6$H$_6$	176^c	159.2^d	17	40.3^c
	C$_5$H$_5$	177^c			
(11)	C$_6$H$_3$(Me)$_3$	174^c	159.8^d	14	39.1
	C$_5$H$_5$	182^c			

^{a} Measured in (CD$_3$)$_2$CO. ^{b} Measured in CDCl$_3$. ^{c} Data in CD$_3$NO$_2$ taken from ref. 2. ^{d} Data for neat liquids taken from ref. 15.

One-bond $^{13}C-^1H$ *Coupling Constants.*—Transition-metal complexations of arenes generally increase one-bond C–H coupling constants in the arenes[2,15] and the origin of the complexation effect has been ascribed to several causes.[15–18]

In complexes (1) and (3), the magnitude of the complexation effect (Δ^1J) is much larger in the complexed ring than in the uncomplexed one, as Table 2 shows. In all complexes, the correlation between Δ^1J and $\Delta\delta$ is fairly good, but the Δ^1J values for C(4)–H of (1) and for C(8)–H of (3) are small for the large $\Delta\delta$ values. It seems likely that the factors which influence $\Delta\delta$ have some direct influence on Δ^1J.[5]

Cyclopentadienyl Resonances.—The cyclopentadienyl-ring carbons give a singlet signal in all cases indicating rapid rotation of the ring.[2] The chemical shifts for the cyclophane complexes (1)—(8) lie in an upfield range of 74.2—76.8 p.p.m. compared

with 77.7—78.3 p.p.m. for the reference compounds (9)—(12). On the other hand, the one-bond C–H coupling constants for the cyclopentadienyl rings of the cyclophane complexes (1), (3), and (8) are 182 Hz compared to the 182 and 176 Hz for complex (11) and (η^6-benzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate respectively. It would be premature to judge from the few data whether δ correlates with ^1J(CH).

Experimental

Samples (1),[19] (2),[19] (3),[20] (4),[21] (5),[21] (9),[2] (10),[2] and (11)[2] were prepared by literature methods and the other, new materials were similarly prepared.

(η^5-*Cyclopentadienyl*)(11—16-η-[2.2]*metaparacyclophane*)*iron*(II) *Hexafluorophosphate*, (6).—M.p. 198 °C (de-

comp.) (from ethanol); $\delta[(CD_3)_2CO$, 100 MHz], 2.16—3.35 (8 H, m), 4.91 (5 H, s, C_5H_5), 5.03—5.05 (2 H, m, H^{15} and H^{16}), 5.76—5.79 (1 H, m, H^8), 6.28—6.30 (2 H, m, H^{12} and H^{13}), and 6.75—7.39 (3 H, m, H^4, H^5, and H^6) (Found: C, 53.05; H, 4.40. $C_{21}H_{21}F_6FeP$ requires C, 53.2; H, 4.45%).

μ-(3—8-η:11—16-η'-[2.2]*Metaparacyclophane*)-*bis*-[(η^5-*cyclo-pentadienyl*)*iron*(II)] *Bis*(*hexafluorophosphate*), (**7**).—M.p. 210 °C (decomp.) (from acetone–ethanol); $\delta[(CD_3)_2CO$, 100 MHz], 2.46—3.56 (8 H, m), 4.72 (1 H, m, H^8), 4.91 (5 H, s, C_5H_5), 5.00 (5 H, s, C_5H_5), 5.31—5.33 (2 H, m, H^{15} and H^{16}), 5.93—6.45 (3 H, m, H^4, H^5, and H^6), and 6.54—6.57 (2 H, m, H^{12} and H^{13}) (Found: C, 42.1; H, 3.45. $C_{26}H_{26}F_{12}Fe_2P_2$ requires C, 42.2; H, 3.55%).

(η^5-*Cyclopentadienyl*)(η^6-[8]*paracyclophane*)*iron*(II) *Hexafluorophosphate*, (**8**).—M.p. 195 °C (decomp.) (from ethanol); $\delta[(CD_3)_2CO$, 100 MHz], 0.20—0.34 (4 H, m), 0.78—1.01 (4 H, m), 1.55—1.78 (4 H, m), 2.57—2.85 (4 H, m), 5.10 (5 H, s, C_5H_5), and 6.46 (4 H, s, C_6H_4) (Found: C, 50.25; H, 5.50. $C_{19}H_{25}F_6FeP$ requires C, 50.25; H, 5.55%).

(η^5-*Cyclopentadienyl*)(η^6-1,2-*diphenylethane*)*iron*(II) *Hexafluorophosphate*, (**12**).—M.p. 125—127 °C (from ethanol); $\delta[(CD_3)_2CO$, 100 MHz], 2.86—3.30 (4 H, m), 5.17 (5 H, s, C_5H_5), 6.23—6.52 (5 H, m, complexed C_6H_5), and 7.05—7.36 (5 H, m, free C_6H_5) (Found: C, 51.0, H, 4.25. $C_{19}H_{19}F_6FeP$ requires C, 50.9, H, 4.25%).

The ^{13}C spectra were recorded on a JEOL JNM-FX-100 spectrometer (25 MHz) at ambient temperature, as described previously,[6] for *ca.* 5% (w/v) or less solutions in [$^2H_6$]acetone unless otherwise stated. Tetramethylsilane was used as an internal reference. The coupling constants were measured with gated decoupling.

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