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A COMMENTARY ON THE EFFECT OF METAL π-COMPLEXATION ON THE STRUCTURES AND PROPERTIES OF VARIOUS PENTAFULVENES

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Summary

The structures and properties of pentafulvenes π-complexed with 12-electron L_nM residues, particularly L_nM = $(OC)_3Cr$ and $CpFe^+$, are discussed and compared with those of the uncomplexed pentafulvenes.

Introduction

Interest in the ground-state electronic properties of pentafulvene (Ia) and its 6-substituted derivatives, e.g. (Ib—Id), lies primarily in assessment of the extent of polarisation of the exocyclic double bond of the cross-conjugated triene system (IA); the corresponding dipolar form (IB) derives stabilisation through acquisition by the five-membered ring of Hückel 6 π-electron aromatic character [1]. * For pentafulvene (Ia) itself, it has been estimated [2] from NMR spectroscopic studies that the dipolar form contributes about 10% to the overall electronic character. The predominant trienic character of this hydrocarbon [3] and simple 6-alkylated derivatives, e.g. Ic [4], is evidenced by the bond-length alternation of the ring geometry, which is similar to that of cyclopenta-1,3-diene [5], and by the exocyclic bond length which is typical of a full double bond (Table 1).

Attachment to C(6) of pentafulvene of a group which can effectively delocalise positive charge (e.g. a +R group) causes an enhancement of the polarisation of the exocyclic double bond. For example, the structures (Table 1) of the 6-(dimethylamino) derivatives IIa [6] and IIb [7] are more iminium-like (IIC) than amino-trienic (IIA) or amino-carbocationic (IIB); i.e. bond-length alternation in the ring is less exaggerated, the exocyclic bond is lengthened, and the

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* A related situation obtains with heptafulvenes (i.e. 7-alkylidenecyclohepta-1,3,5-trienes) where polarisation of the exocyclic double bond in the opposite sense leads to a dipolar structure which incorporates an aromatic 6 π-electron tropylium ring.

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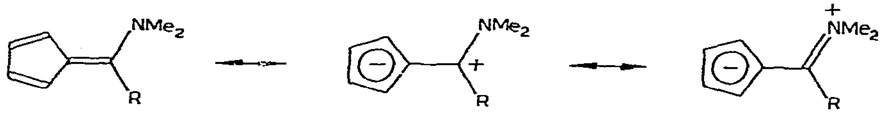
(IA) (IB)

a ; $R^1 = R^2 = H$
b ; $R^1 = CMe_3$, $R^2 = H$
c ; $R^1 = R^2 = Me$
d ; $R^1 = R^2 = Ph$



(IIA) (IIB) (IIC)

a ; R = H
b ; R = NMe_2
c ; R = Me

C(6)—N distances (1.331 Å for IIa; 1.348 and 1.361 Å for IIb) show substantial double-bond character. In consequence, the dipole moments of IIa and IIb (4.48 [8] and 5.4 D [9], respectively) are much larger than those for Ia and Ic (0.42 [3] and 1.44 D [10], respectively), and the C(5)$\overset{\cdots}{-}$C(6) and C(6)$\overset{\cdots}{-}$N rotational barriers (92.5 and 56.5 kJ mol^{-1}, respectively [11]) for IIa deviate markedly from values usually associated with C=C and C—N bonds [6,12]. The dipole moment of Id [1,10] is similar in magnitude to that of Ic, suggesting that the 6-phenyl groups are unable, because of steric repulsion, to attain coplanarity with the pentafulvene system and that resonance stabilisation of the dipolar form (IBd) is consequently attenuated.

It is clear from the foregoing that the electronic character (and hence chemical reactivity) of pentafulvenes is sensitive to the presence and nature of substituent group(s) at the exocyclic carbon atom. In this paper, the effect of π-complexation of the ring in pentafulvenes with a transition metal will be discussed.

Discussion

A wide variety of π-complexes of transition metals with pentafulvenes is known [13], and various metal—ligand bonding modes have been found. For

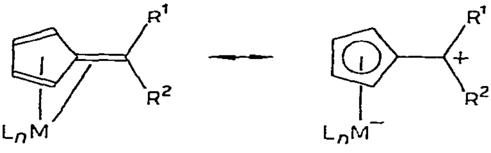
TABLE 1

BOND LENGTHS (Å) FOR PENTAFULVENES AND THEIR π-COMPLEXES [a]

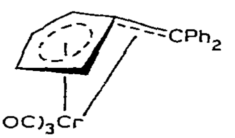
Compound	C(1)—C(2)	C(2)—C(3)	C(3)—C(4)	C(4)—C(5)	C(5)—C(1)	C(5)—C(6)	Ref.
Ia	1.355	1.476	1.355	1.470	1.470	1.349	3 [b]
Ic	1.346	1.435	1.346	1.439	1.439	1.343	4a [c]
	1.340	1.462	1.340	1.476	1.476	1.347	4b [d]
IIa	1.353	1.414	1.362	1.427	1.438	1.387	6 [c]
IIb	1.367	1.416	1.383	1.432	1.430	1.407	7 [c]
IV	1.452	1.422	1.445	1.494	1.467	1.446	20 [c]
V BF_4^-	1.413	1.425	1.402	1.445	1.438	1.416	21 [c]
VI	1.370	1.386	1.392	1.416	1.432	1.404	25 [c]
VII PF_6^-	1.409	1.366	1.379	1.451	1.512	1.410	26 [c]

[a] See structure IA for atom-numbering system. [b] Microwave spectroscopy (vapour). [c] X-ray diffraction (crystal). [d] Electron diffraction (vapour).

example, complexes of Id have been prepared in which the ligand is attached to the metal by coordination of the exocyclic double bond, e.g. (Id)Rh(CO)$_2$Cl [14] *, the ring diene system, e.g. (Id)Re(CO)$_3$ [16], and as a 6 π-electron donor, e.g. (Id)Cr(CO)$_3$ [17] **. Complexes of the last type are particularly interesting because bonding of a metal atom to the six alkenic carbon atoms of a pentafulvene is structurally difficult unless the triene system is bent from its usual [1] coplanar geometry (cf. IIIA). However, 6π-electron donation can be achieved, in principle, without structural problem by attachment of the metal to the ligand in its dipolar form (IB) such that only the ring carbon atoms are metal-bonded, and the ring bears a carbocationic substituent (cf. IIIB).



(IIIA) (IIIB)



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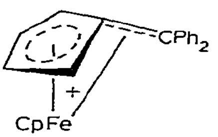

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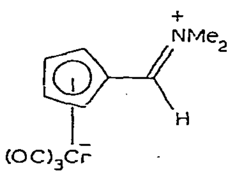

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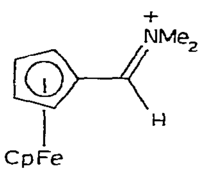

(VII)

Crystal structures

The best known types of complex in which a pentafulvene serves as a 6 π-electron donor are those in which there is attached an (OC)$_3$M (M = Cr, Mo, or W) [13,18], a CpM$^+$ (M = Fe, Ru, or Os) [18,19], or an (L)$_3$Mn$^+$ (L = CO, phosphine, or phosphite ligand) [18,19] residue. The crystal structures of IV [20] and V BF$_4^-$ [21] show that, for both, the exocyclic bond C(5)—C(6) is displaced from the ring plane [by 31° for IV and 21° for V] towards the metal atom such that C(6) is brought within weak bonding distance [2.548 Å for IV and 2.715 Å for V] ***. The metal—ring carbon and ring carbon—ring carbon distances are typical of those for (η^5-cyclopentadienyl)metal complexes [24], and there is no indication of systematic bond-length alternation within the ring (Table 1). Such folding of the pentafulvene ligand of these complexes reduces the concentration of positive charge at the exocyclic carbon atom C(6) relative to the situation which would obtain for a planar ligand (cf. IIIB), thereby affording stabilisation. It is noteworthy that the two phenyl rings in each

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* To our knowledge [15], the structure of this complex has not been definitely established.

** Complexes have also been prepared in which a μ-pentafulvene ligand bridges two metal atoms, and others in which each of the ring double bonds is π-complexed with a different metal atom [13].

*** Similar ligand-folding deformation has been found in the crystal structures of salts of the diferrocenylmethyl cation (III; R^1 = Fc, R^2 = H; L$_n$M = CpFe$^+$) [22] and the 1-ferrocenyl-2,3-diphenylcyclopropenyl cation (III; R^{1}R^2 = PhC=CPh; L$_n$M = CpFe$^+$) [23].

of these complexes adopt a propellor-like conformation such that $p\pi$—$p\pi$ conjugative interaction with C(6) is minimal.

For complexes in which the substituent(s) R^1, R^2 attached to the exocyclic carbon atom in IIIB can effectively stabilise a carbocationic centre, the driving force for ligand folding is reduced, Thus, the exocyclic bond in the 6-(dimethylamino) complex VI is displaced by 10° only from the ring plane in the crystal structure [25], and deformation from planarity of the pentafulvene system of the related complex VII PF_6^- is minimal [26]. In these complexes, the ring substituent corresponds to a planar cationic iminium group $CH{=}\overset{+}{N}Me_2$ [C(6)—N distances, ca. 1.30 Å] and the separation of C(6) from the metal atom (ca. 3.0 Å) rules out significant bonding interaction; i.e. structurally, these complexes can be regarded as ring-substituted derivatives of $[CpCr(CO)_3]^-$ and Cp_2Fe, respectively (Table 1).

MO bonding treatments

MO calculations of the bonding of pentafulvenes to transition metals have been reported [27,28]. Five of the six π-MOs of pentafulvene have energies and symmetry properties similar to those of cyclopentadienyl [29]. The remaining π-MO (LUMO of uncomplexed hydrocarbon), which is only weakly antibonding ($E_\pi = \alpha - 0.25\beta$), has an appropriate symmetry and energy to mix with the filled metal d_{z^2} orbital which is nonbonding for 18-electron complexes such as Cp_2Fe [30]. The resulting metal → ligand charge transfer * weakens the exocyclic C(5)—C(6) bond of the pentafulvene and thereby facilitates out-of-plane bending towards the metal atom (cf. crystal structures) which deformation, in turn, allows an improvement of the metal d_{xy}—ligand π-HOMO overlap (ligand → metal charge transfer) [27].

Calculations [28] for $[(Ia)FeCp]^+$ ($\equiv Fc\overset{+}{C}H_2$) give an energy-minimum structure in which the exocyclic bond is displaced by 40° (regarded as perhaps an overestimate) from the ring plane. The corresponding charge distribution places 0.5+ on the iron atom with the remainder shared uniformly by the ten carbon atoms of the rings and the exocyclic carbon atom. These calculations also show that, whereas all electrons are paired in the ground state of the ligand-folded structure of $[(Ia)FeCp]^+$, a structure incorporating a planar pentafulvene ligand would have a triplet ground electronic state. Evidence has been obtained [31] to suggest that such singlet and triplet structures of ferrocenylalkylium ions (IIIA; $L_nM = CpFe^+$) may be separated by a relatively small energy barrier. It may also be significant that a particular cation for which ligand folding is structurally difficult spontaneously dimerises to give a bis-ferricenium dication [32].

Rotational barriers

A consequence of the enhancement of polarisation of the exocyclic double bond of pentafulvenes, brought about by metal complexation of the ring, is a substantial lowering of the energy barrier to rotation about this bond. Thus, whereas this barrier is sufficiently high for 6-alkyl- or 6-aryl-substituted penta-

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* It is this metal—ligand orbital interaction which is responsible, in the main, for the exceptional ability of the ferrocenyl group to stabilise a ring-attached carbocationic centre, a property whose source has engendered much debate and controversy [19].

fulvenes to prevent rotation, even at elevated temperatures, rotational barriers in the range 70—90 kJ mol^{-1} have been measured [33] for 6-methyl- and 6,6-dialkyl-pentafulvenes π-complexed with a CpFe$^+$ residue.

Similarly, π-complexation of the 6-aminopentafulvene (IIa) with an (OC)$_3$M residue leads to a reduction in the C(5)—C(6) rotational barrier and an increase in the C(6)—N rotational barrier [11,34], with the magnitude of this effect increasing through the series M = W < Mo < Cr. It follows that the contribution of the iminium form (IICa) to the electronic character of the pentafulvene is increased by metal complexation of the ring. These rotational barrier heights for the pentafulvenes (II) [11] and their (OC)$_3$M complexes [34] are quite sensitive to solvent effects; i.e. the dipolar iminium character becomes more pronounced with increase in solvent polarity.

^{13}*C NMR spectroscopic correlations*

It is instructive to compare the ^{13}C chemical shifts for the pentafulvenes with those for their metal π-complexes (Table 2), particularly in view of the marked dependence of ^{13}C shielding upon electron density [37]. For each pentafulvene, complexation with either an (OC)$_3$Cr or a CpFe$^+$ residue causes a substantial shielding of the resonances of the ring carbons C(1—5), as is usually the case with metal-olefin π-complexes. However, the effect of metal complexation upon the ^{13}C(6) chemical shift varies widely with the identity of the pentafulvene and the attached residue. For example, whereas C(6) in pentafulvene (Ia) itself is strongly shielded as a result of π-attachment of a CpFe$^+$ residue, an opposite effect is found for 6,6-diphenylpentafulvene (Id) and the 6-(dimethylamino)pentafulvenes (IIa, c), where complexation with CpFe$^+$ causes substantial deshielding of C(6). On the other hand, whereas π-complexa-

TABLE 2

^{13}C CHEMICAL SHIFTS (δ) FOR PENTAFULVENES AND THEIR π-COMPLEXES [a]

Compound	Solvent	C(1,4)	C(2,3)	C(5)	C(6)	Ref.
Ia	CDCl$_3$	124.9	134.3	152.6	123.4	2
Ib	CDCl$_3$	119.6	128.5	141.8	153.9	2
		128.3	133.8			
Ic [b]	CDCl$_3$	120.5, 130.6		142.6	149.6	38
Id	CH$_2$Cl$_2$	124.4	128.9	144.0	152.0	35
IIa	CDCl$_3$	114.0	119.4	116.6	149.1	2
		124.4	125.1			
IIc [b]	CDCl$_3$	106.8, 108.9		107.5	148.5	39
		110.5, 111.5				
[(Ia)FeCp]$^+$	CF$_3$CO$_2$H	85.5	95.6	111.8	88.6	40
[(Ib)FeCp]$^+$	CF$_3$CO$_2$H	81.1	95.1	101.6	145.0	40
		82.6	95.3			
[(Ic)FeCp]$^+$	CF$_3$CO$_2$H	78.7	94.7	101.2	158.6	40
[(Id)FeCp]$^+$	CF$_3$CO$_2$H	80.2	94.4	94.4	170.1	35
[(IIa)FeCp]$^+$	(CD$_3$)$_2$CO	75.0	78.5	69.4	171.7	36
[(IIc)FeCp]$^+$	(CD$_3$)$_2$CO	75.8	74.4	72.5	185.2	38
[(Id)Cr(CO)$_3$]	CH$_2$Cl$_2$	89.4	93.9	107.5	126.2	35
[(IIa)Cr(CO)$_3$]	Me$_2$CO	89.9	89.9	88.8	155.0	35

[a] As for Table 1. [b] C(1—4) resonances not assigned.

TABLE 3

^{13}C CHEMICAL-SHIFT DIFFERENCES FOR EXOCYCLIC BOND CARBONS [a]

Pentafulvene	π-Attached residue	δ(C(6))—δ(C(5))
Ia	none	—29.2
	CpFe$^+$	—23.2
Ib	none	12.1
	CpFe$^+$	43.4
Ic	none	7.0
	CpFe$^+$	57.4
Id	none	8.0
	$(OC)_3Cr$	18.7
	CpFe$^+$	75.7
IIa	none	32.5
	$(OC)_3Cr$	66.2
	CpFe$^+$	102.3
IIc	none	41.0
	CpFe$^+$	112.7

[a] Calculated from data in Table 2.

tion of Id with $(OC)_3Cr$ causes shielding of C(6), the effect upon the C(6) shift for IIa is small.

However, caution is necessary in the interpretation of these results because different solvents were used in recording the spectra of the pentafulvenes and of their metal complexes. This problem is circumvented if comparison is made (Table 3) between the C(5)/C(6) chemical-shift separations for a given pentafulvene and its π-complexes, where it can be assumed that differential solvent effects are of minor importance only.

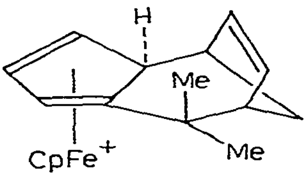
For each of the 6-substituted pentafulvenes, C(6) is more deshielded than C(5), and the magnitude of the chemical-shift separation parallels the dipolar character of the molecule; i.e. the 6-amino derivatives (IIa, IIc) show much larger separations than those for the 6-alkyl and 6-aryl derivatives (Ib—Id). For each of these pentafulvenes, π-attachment of a metal causes an increase in the C(5)/C(6) chemical-shift separation, with the effect of CpFe$^+$ complexation much greater than that resulting from attachment of an $(OC)_3Cr$ residue. Two factors appear to be cooperatively responsible for this effect, viz. shielding of C(5) as a result of the strong metal-bonding interaction (see earlier), and deshielding of C(6) consequent upon ligand polarisation which places a partial positive charge on this atom (cf. IIIB). If other effects are of relatively minor importance, these data then suggest that attachment of a CpFe$^+$ residue to a given pentafulvene causes a much more pronounced polarisation of the π-electron system of the ligand than that resulting from complexation with $(OC)_3Cr$.

Finally, the chemical-shift patterns for pentafulvene Ia itself and its CpFe$^+$ complex are anomalous in that, for both, C(6) is more shielded than C(5). This reversal of the usual situation is understandable because this hydrocarbon is the least polarised of the series, and its C(6) chemical shift is not affected by substituent increments, while for its CpFe$^+$ complex, ligand folding is more pronounced, C(6)Fe bonding is stronger, and positive-charge concentration at C(6) is lower than for related complexes of the 6-substituted pentafulvenes.

Chemical reactivity

Pentafulvenes readily undergo reactions which lead to the formation of substituted cyclopentadienyl anions; examples include addition to C(6) of strong nucleophiles (e.g. H^- from $LiAlH_4$, R^- from RLi) giving alkylcyclopentadienyl anions, base abstraction of an allylic proton from a 6-alkyl group giving alk-1-enylcyclopentadienyl anions, and reductive dimerisation on treatment with metallic Na to give bis(cyclopentadienyl)ethane dianions [1]. This pattern of behaviour is not changed by metal complexation; e.g. 1-ferrocenylalkyl cations such as $[(Ic)FeCp]^+$ likewise undergo nucleophilic addition, deprotonation, and reductive dimerisation reactions to give substituted ferrocenes [19]. It seems likely that complexes of the type III [L_nM = $(OC)_3Cr$, etc.] would behave similarly [1,13], the first-formed anionic products reacting further, e.g. to give ring-substituted derivatives of $[CpM(CO)_3]_2$.

Another characteristic property of pentafulvenes is the readiness with which they undergo Diels-Alder reactions, most commonly as the diene component but in a few examples as the dienophile (e.g. self-condensation reactions). Not surprisingly, reactions of this type do not occur with metal-complexed pentafulvenes. However, it has been shown [41] that cations such as $[(Ic)FeCp]^+$ undergo stereospecific cycloaddition of cyclopentadiene to give a product of the type IX. This must arise by deprotonation of the first-formed cyclo-adduct VIII, the product of a [$6\pi + 4\pi$] cycloaddition. Examples of pentafulvenes serving as 6π-electron cycloaddends are rare [42].



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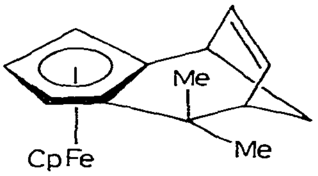

(IX)

Conclusions

The known types of metal complexes in which a pentafulvene serves as a 6π-electron ligand are relatively few. Besides those discussed earlier, two examples of a bis(pentafulvene)metal complex have been reported, viz. $[(Ic)_2Fe]^{2+}$ [43] and $[(Id)_2M]^+$ (M = Co, Rh, and Ir) [44], but little is known of their chemistry. However, from the known properties of the complexes III [L_nM = $(OC)_3Cr$ and $CpFe^+$], some general conclusions can be drawn.

(a) Attachment to a pentafulvene of a 12-electron L_nM residue causes a folding of the ligand at C(5) such that the metal atom is strongly bonded to the ring carbon atoms but, at best, only weakly bonded to the exocyclic carbon atom.

(b) The extent of ligand-folding is dependent upon the electronic properties of the substituent(s), if any, attached to C(6); i.e. the better the capacity of such substituents to stabilise a carbocationic centre, the smaller the displacement of the exocyclic bond from the ring plane, and the weaker the metal—C(6) bonding interaction which, in the limit, may be negligible.

(c) The barrier to rotation around the C(5)—C(6) bond of a pentafulvene is lowered by π-complexation of the ring with a 12-electron L_nM residue.

(d) For a given pentafulvene, complexation of the ring with a $CpFe^+$ residue causes a greater π-electron polarisation of the exocyclic double bond of the ligand than that consequent upon complexation with an $(OC)_3Cr$ residue.

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