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Transition Metal Complexes of Cyclopentadienylides and Pentafulvenes

V.I.Zdanovich, A.Zh.Seitembetova, and V.N.Setkina

The π-complexes of cyclopentadienylides and pentafulvenes with six-electron coordination are examined. The question of the influence of the π-coordination with the transition metal atom on the properties of the cyclopentadienyl ring carrying a full or partial negative charge are discussed.
The bibliography includes 70 references.

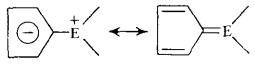
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I. INTRODUCTION

Complexes with cyclopentadienyl ligands are particularly widely represented among the π-complexes of transition metals. Typical examples of such compounds are ferrocene and cymantrene. The chemistry of these π-complexes has already developed extensively but some of their features have not been adequately explained. In particular, one of the cardinal problems remains obscure, namely how the properties and reactivity of the cyclopentadienyl anion change on π-coordination to the transition metal atom. The study of the properties of coordinated and non-coordinated cyclopentadienyl anions under comparable conditions involves considerable experimental difficulties. Fairly stable dipolar compounds, namely dicyclopentadienylides, in which the negative charge is distributed over the cyclopentadienyl ring linked to a heteroatom carrying a positive charge, as well as pentafulvenes, which are related to cyclopentadienylides, are therefore of great interest.

The structures of compounds of both types can be represented by two extreme forms: the ylide form (A) and the ylene form (B), whose contributions to the molecular structure depend significantly on the nature of the onium-forming atom E and the nature of the substitutents at this atom:



(A) (B)

In cyclopentadienylides the onium-forming atoms are usually those of Group V—VII elements. The contribution of structure (A) in such systems is fairly large. For example, the contribution of the ylide structure in triphenylphosphonium cyclopentadienylide $C_5H_4PPh_3$ exceeds 80%.[1] In pentafulvenes the atom E is carbon and the ylene structure (B) makes the greatest contribution. However, when powerful electron-donating groups with O, N, and S heteroatoms are attached to the exocyclic bond of the pentaulvenes, as, for example, in $C_5H_4CHN(CH_3)_2$, then pentafulvenes of this kind have large dipole moments and are characterised by a considerable contribution of the dipolar structure (A).

It has been found that cyclopentadienylides and pentafulvenes are capable of being coordinated to transition metal atoms, forming π-complexes. Thus it has been observed in 1959 [2] that the cyclopentadienyl fragment of triphenylphosphonium cyclopentadienylide is capable of being coordinated to Group VIB metal carbonyls as a six-electron ligand, forming π-cyclopentadienylide complexes.

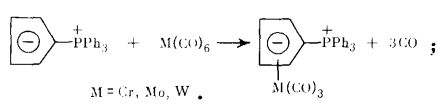
During the past 20 years, a wide variety of transition metal complexes have been synthesised, in which cyclopentadienylides and pentafulvenes play the role of π-ligands. However, hitherto there have been no surveys of cyclopentadienylide π-complexes in the literature (a review of fulvene complexes was published in 1970).[3] Presumably, examination of the literature data on transition metal π-complexes of cyclopentadienylides will make it possible to elucidate the nature of the influence of the π-coordination to the transition metal atom on the properties of the cyclopentadienyl ring carrying a full or partial negative charge. This review deals in detail only with the π-complexes of pentafulvenes in which they are coordinated to a transition metal atom as six-electron ligands. Such π-complexes of pentafulvenes are in many respects similar to the π-complexes of cyclopentadienylides and it is therefore of interest to compare the physical and chemical properties of complexes of the two types.

II. TRANSITION METAL COMPLEXES OF CYCLOPENTADIENYLIDES

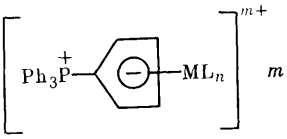
Group IV, VI, VII, and VIII transition metal π-complexes of phosphorus, sulphur, nitrogen, and arsenic cyclopentadienylides are known at present. All the complexes described in the literature are presented on page 660.

1. Synthesis

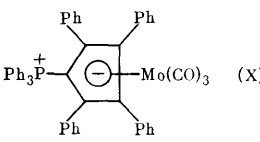
The complexes of cyclopentadienylides with metal carbonyls were first obtained by the reaction of triphenylphosphonium cyclopentadienylide with chromium, molybdenum, and tungsten hexacarbonyls in diglyme[2]:



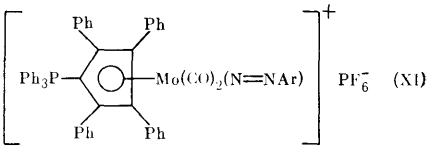
M = Cr, Mo, W.



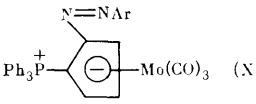
$m X^-$ (I)-(IX)



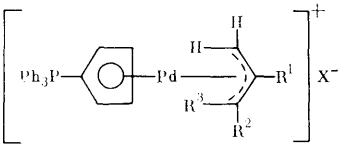
(X);



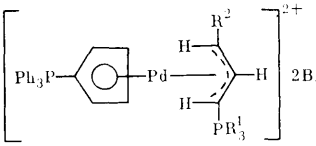
(XI)



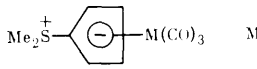
(XII);



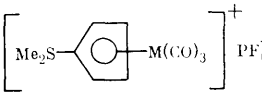
$R^1, R^2, R^3 = H$ or Me, $X = BF_4$ or CF_3SO_3 (XIII)-(XVIII);



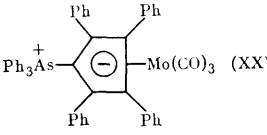
$R^1 = Et$ or Ph; $R^2 = H$ or Me (XIX)-(XXI);



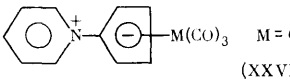
M = Cr, Mo, W (XXII)-(XXIV);



M = Mn, Re (XXV)-(XXVI)



(XXVII);



M = Cr, Mo (XXVIII)-(XXIX)

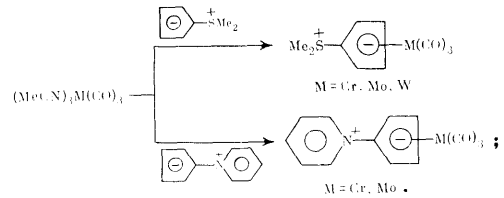
No.	ML_n		X^-
(I)	$Cr(CO)_3$	0	—
(II)	$Mo(CO)_3$	0	—
(III)	$W(CO)_3$	0	—
(IV)	$Mo(CO)_2(N{=}NAr)$	1	PF_6^-
(V)	$W(CO)_2(N{=}NAr)$	1	PF_6^-
(VI)	$Mo(CO)(PPh_3)(N{=}NAr)$	1	PF_6^-
(VII)	$Mn(CO)_3$	1	PF_6^-
(VIII)	$Re(CO)_3$	1	PF_6^-
(IX)	$Co(CO)_2$	1	$Co(CO)_4^-$

$(Ph_3PC_5H_4)_2WCl_6$ (XXX); $(Ph_3PC_5H_4)MoCl_3(CH_2$ (XXXI);
$[(Ph_3PC_5H_4)HgX_2]_2$ (X = Cl, Br, I) (XXXII) — (XXXIV);
$(Ph_3PC_5H_4)_2TiCl_4$ (XXXV); $(Ph_3PC_5H_4)TiCl_3$ (XXXVI);
$(Ph_3PC_5H_4)ZrCl_4$ (XXXVII); $(Ph_3PC_5H_4]HfCl_4$ (XXXVIII).

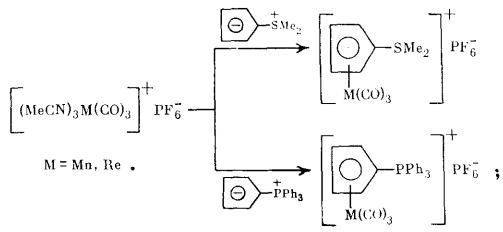
The yield of the complexes was up to 60%. Their compositions and structures were established by elemental analysis, infrared spectroscopy, and ^1H NMR. Subsequently a method of synthesis of cyclopentadienylide complexes from acetonitrile derivatives of Group VIB metal carbonyls was proposed[4]. Tetraphenyl-substituted triphenylphosphonium and triphenylarsonium cyclopentadienylidemolybdenum tricarbonyls have been obtained in high yields via the acetonitrile complex of molybdenum[5]. The attempt to obtain the molybdenum complex with stibonium cyclopentadienylide was unsucessful[5].

Complexes of dimethylsulphonium cyclopentadienylide with Group VIB metal carbonyls were obtained in 1974, also via the acetonitrile derivatives of the metals in diglyme[6,7] (yield up to 50%).

Complexes of pyridinium cyclopentadienylide with chromium and molybdenum carbonyls have been synthesised by an analogous method[8]. The tungsten analogue has not so far been obtained:

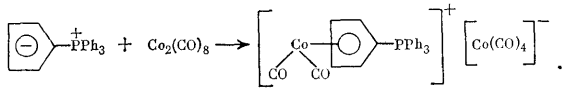


It has been found that, on treatment with charged acetonitrile complexes of manganese and rhenium, cyclopentadienylides form π-complexes with Group VII metal carbonyls[9,10].

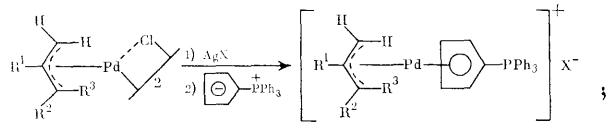


The reaction was carried out in tetrahydrofuran at room temperature in the case of the manganese complexes and with refluxing in the case of the rhenium complexes, the yields being 20–50%.

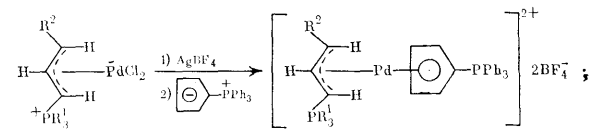
A report concerning the reaction of triphenylphosphonium cyclopentadienylide with cobalt carbonyl was published in 1978 [11]:



A series of palladium complexes containing triphenylphosphonium cyclopentadienylide as the π-ligand have been synthesised by the reaction of halogen-containing palladium compounds with cyclopentadienylide in the presence of silver salts[12]:



$X^- = BF_4^-$ или $CF_3SO_3^-$; $R^1 = R^2 = R^3 = H$; $R^1 = Me$, $R^2 = R^3 = H$; $R^1 = R^3 = H$, $R^2 = Me$



$R^1 = Ph$, $R^2 = H$, Me; $R^1 = Et$, $R^2 = H$.

Reports of the synthesis of triphenylphosphonium cyclopentadienylide complexes with transition metal salts have appeared in the literature in recent years[13,14]. This ylide reacts with tungsten hexachloride in dry benzene[13]:

$$2Ph_3PC_5H_4 + WCl_6 \rightarrow (Ph_3PC_5H_4)_2WCl_6 .$$

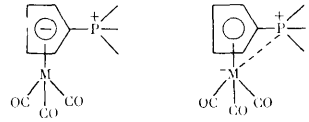
On the basis of ^1H and ^{13}C NMR spectra, the authors attribute a sandwich structure to the complex.

In an analogous reaction $MoCl_5$ gives rise to the complex $(Ph_3PC_5H_4)MoCl_3(OH)_2$, whose structure and authors do not discuss[14]. Complexes with mercury halides, namely $[Ph_3PC_5H_4HgX_2]_2$ (X = Cl, Br, or I), which are stable in air in the solid state, have also been obtained[14]; the complex with X = I has been comprehensively investigated.

Complexes of triphenylphosphonium cyclopentadienylide with titanium, zirconium, and hafnium salts have also been described: $(Ph_3PC_5H_4)_2TiCl_4$, $(Ph_3PC_5H_4)TiCl_3$, $(Ph_3PC_5H_4).ZrCl_4$, and $(Ph_3PC_5H_4)HfCl_4$.[15] The study of these complexes, which are very sensitive to atmospheric oxygen, involves considerable experimental difficulties; their structures have not so far been finally established. The authors[15], proposed the metallocene structure for $(Ph_3PC_5H_4)_2.TiCl_4$.

2. Structure

There have been two points of view concerning the structure of the π-complexes of phosphorus cyclopentadienylides with Group VIB metal carbonyls. On the one hand, such complexes have been treated as analogues of arenemetal tricarbonyls, assuming that the charges are neutralised in the ligand itself [structure (C)].[2] On the other hand, Cashman and Lalor[16] assumed that triphenylphosphonium cyclopentadienylide complexes are similar to cyclopentadienylmetal tricarbonyl anions $[C_5H_5M(CO)]_3^-$ (M = Cr, Mo, or W) and are stablised by the interaction of one of the filled non-bonding metal orbitals with the vacant *d* orbital of the phosphorus atom [structure (D)]:



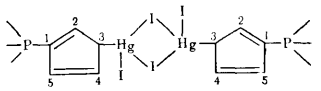
(C) M = Cr, Mo, W . (D)

However, X-ray diffraction analysis of dimethylsulphonium cyclopentadienylide and its π-complexes with chromium and molybdenum carbonyls[17,18] showed that the chromium atom in dimethylsulphonium cyclopentadienylidechromium tricarbonyl is symmetrically coordinated (by an octahedron) with the cyclopentadienyl ring (three coordination sites) and with three carbonyl groups. The distance between the sulphur and chromium atoms (3.478 Å) greatly exceeds the sum of the covalent radii of the chromium and sulphur atoms (2.52 Å). The absence of the Cr...S interaction is also indicated by the deviation of the S atom from the plane of the cyclopentadienyl ring by 0.110 Å towards the opposite chromium atom.

Comparison of the structural parameters of dimethylsulphonium cyclopentadienylide and its π-complex with chromium showed that the π-coordination to the transition metal is not accompanied by sharp changes in the structure of the cyclopentadienylide but leads to an increase of the contribution of the ylide structure. For example, the C–C bond lengths in the cyclopentadienyl ring of the π-complex are somewhat more equalised than in the initial cyclopentadienylide, while the partial double bond character of the sulphur–cyclopentadienyl ring bond is more pronounced in the ylide than in the complex.

The X-ray diffraction analysis of the complex of triphenylphosphonium cyclopentadienylide with cobalt carbonyl was carried out in 1978.[11] The authors noted that the structure of this cationic complex resembles that of the complex of dimethylsulphonium cyclopentadienylide with chromium carbonyl. On the other hand, there is similarity with the $C_5H_5Co(CO)_2$ structure.

The complex of triphenylphosphonium cyclopentadienylide with mercury iodide has a different structure[14]. In the solid state the complex exists as a dimer with two bridging iodine atoms:



The mercury atom is linked by a π-bond to the C(3) carbon atom of the five-membered ring of the ylide. The C(1)–C(2) and C(4)–C(5) bonds are appreciably shorter than the other bonds, which indicates their double bond character. From the ^{13}C NMR spectrum, the authors assume that in solution the mercury atom is linked alternately to the C(2), C(3), C(4), and C(5) atoms.

3. Physicochemical Properties

The complexes of cyclopentadienylides with metal carbonyls are solid crystalline substances. With the exception of pyridinium cyclopentadienylide complexes, they are relatively resistant to the action of atmospheric oxygen. In the solid state the complexes decompose slowly in air, but their solutions are relatively unstable.

Table 1. Parameters of the infrared and ^1H NMR spectra of complexes of cyclopentadienylides.

Cpd.	i.r. spectra			^1H NMR spectra		
	ν(C≡O), cm^{-1}	solvent*	refs	δ(C_5H_5), p.p.m.	solvent	refs
(I)	1913; 1806	$CHCl_3$	[4]	4.92; 4.65	$CHCl_3$	[4]
(II)	1920; 1812	$CHCl_3$	[4]	5.49; 5.23	$CHCl_3$	[4]
(III)	1912; 1802	$CHCl_3$	[4]	5.49; 5.22	$CHCl_3$	[4]
(IV)	1997; 1925	(KBr)	[5]	—	—	—
(V)	1993; 1909	(KBr)	[5]	—	—	—
(VI)	1892	(KBr)	[5]	—	—	—
(VII)	2040; 1963	acetone	[10]	5.83	$(CD_3)_2CO$	[10]
(VIII)	2038; 1950		[10]	6.27	$(CD_3)_2CO$	[10]
(IX)	2109;2082;1890	(KBr)	[11]	—	—	—
(X)	1920; 1813	CH_2Cl_2	[5]	—	—	—
(XI)	1993; 1926	(KBr)	[5]	—	—	—
(XII)	1924; 1830; 1819	(KBr)	[5]	—	—	—
(XIII)	—	—	—	6.33	$CDCl_3$	[12]
(XIX)	—	—	—	6.05; 5.60; 5.75	$CDCl_3$	[12]
(XXII)	1920; 1820	acetone	[19]	5.29; 4.69	$(CD_3)_2SO$	[19]
(XXIII)	1925; 1825	acetone	[19]	6.09; 5.47	$(CD_3)_2SO$	[19]
(XXIV)	1915; 1820	acetone	[19]	5.92; 5.33	$(CD_3)_2SO$	[19]
(XXV)	2042; 1963	acetone	[10]	6.23; 5.47	$(CD_3)_2CO$	[10]
(XXVI)	2022; 1940	acetone	[10]	6.90; 6.15	$(CD_3)_2CO$	[10]
(XXVII)	1919; 1814	CH_2Cl_2	[5]	—	—	—
(XXVIII)	1920; 1820	acetone	[8]	5.55; 4.63	$(CD_3)_2CO$	[8]
(XXIX)	1920; 1820	acetone	[8]	6.20; 5.30	$(CD_3)_2CO$	[8]
(XXX)	—	—	—	8.57	MeCN	[13]
(XXXII)	—	—	—	6.33—6.72	$CDCl_3$	[14]
(XXXV)	—	—	—	7.95	Me_2SO	[15]

*The material used for pressing the specimen discs is indicated in brackets.

(a) *Infrared and NMR spectra.* The parameters of the infrared and ^1H NMR spectra of the cyclopentadienyl complexes of metal carbonyls are presented in Table 1. Evidently, the infrared spectra of these complexes are characterised by intense absorption bands in the region of the vibration frequency of the terminal CO groups. Two signals due to the protons of the five-membered ring and the multiplet due to the protons of the benzene rings can be observed in the ^1H NMR spectra of triphenylphosphonium cyclopentadienylide complexes with Group VIB metal carbonyls. In these complexes the metal is coordinated to the five-membered and not the six-membered ring of the ylide since the signals of the protons in the five-membered ring of the complexes are displaced upfield, relative to the initial ylide, while the chemical shifts of the protons in the benzene rings hardly charge on formation of the complexes[2].

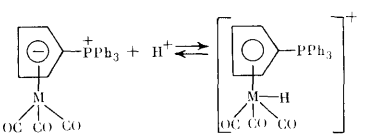
The most interesting information about the influence of coordination to the metal on the physicochemical properties of cyclopentadienylides has been obtained in the study of the ^{13}C NMR spectra[10,20]. Comparison of the $^{13}C\{^1H\}$ spectra of triphenylphosphonium and dimethylsulphonium cyclopentadienylides and their complexes with Group VIB metal carbonyls showed that the π-coordination to the $M(CO)_3$ group (M = Cr, Mo, or W) leads to an appreciable equalisation of the electron density in the five-membered ring of the coordinated cyclopentadienylide[20].

It has also been shown[20] that the shielding of the nuclei of all the carbon atoms of the cyclopentadienyl fragment of the ligand increases on π-coordination, the degree of shielding depending on the nature of the central metal atom and varying in the sequence Cr > W > Mo.

(b) *Electrical conductivity and degree of dissociation.* The complexes of cyclopentadienylides with Group VII and VIII metals are saltlike compounds. Solutions of complexes of triphenylphosphonium and diphenylsulphonium cyclopentadienylides with manganese and rhenium carbonyls in acetone conduct electricity; the molar conductances Λ_M are close to the average value for binary electrolytes formed by coordination compounds[10]. The degrees of dissociation α of these complexes in solution have been calculated from the molecular weights determined ebullioscopically in ethyl methyl ketone[10]. Comparison of the values of α for different complexes showed that the cyclopentadienylide complexes of rhenium are weaker electrolytes than the analogous manganese compounds and that, for the same central metal atom, the triphenylphosphonium cyclopentadienylide complexes are more dissociated in solution than the dimethylsulphonium cyclopentadienylide complexes. The electrical conductivities of the saltlike complexes of palladium with triphenylphosphonium cyclopentadienylide have also been measured[12], but the results are not discussed by the authors.

4. Chemical Properties

(a) *Protonation.* It was shown in 1970 that the complexes of triphenylphosphonium cyclopentadienylide with chromium, molybdenum, and tungsten carbonyls dissolve rapidly in trifluoroacetic acid, forming pale-blue solutions. The infrared and ^1H NMR spectra of the solutions (Table 2) indicate the reversible protonation of the complexes at the metal atom:



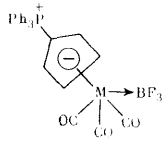
Thus the high-field signal (δ in the range between −5 and −8 p.p.m.) in the ^1H NMR spectra of these solutions is characteristic of the proton linked to the metal atom, as in the corresponding hydrides $C_5H_5M(CO)_3H$. The signal of this proton in the spectrum of the tungsten complex is split owing to the interaction with the ^{183}W nucleus; the spin–spin coupling constant (36 Hz) is close to the value of $J_{^{183}W-^1H}$ for $C_5H_5W(CO)_3H$ and $[(C_5H_5)_2W_2(CO)_6H]^+$.

The stretching vibration frequencies of the carbonyl groups of the protonated complexes were found to have undergone a hypsochromic shift relative to the non-protonated complexes by more than 100 cm^{-1} (Table 2). This fact indicates an increase of the C–O bond order in the protonated complexes as a consequence of the appearance of a positive charge on the metal atom. The study of the parameters of the ^1H NMR spectra of the protonated complexes of triphenylphosphonium cyclopentadienylide with various central metal atoms showed[14] that the basicity of the cyclopentadienylide complexes of Group VIB metals increases with increase of the atomic weight of the metal.

Table 2. Parameters of the ^1H NMR and infrared spectra of the protonated complexes $[(Ph_3PC_5H_4)M(CO)_3H]^+$.[4]

M	δ(C_5H_4), p.p.m.	δ(M–H), p.p.m.	ν(C≡O), cm^{-1}
Cr	5.42; 5.20	−5.09	2042; 1962
Mo	5.91; 5.69	−5.34	2048; 1970
W	6.00; 5.73	−7.15	2042; 1958

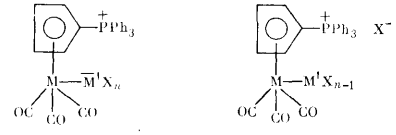
(b) *The formation of adducts with Lewis acids.* The cyclopentadienylide complexes of Group VIB metals form adducts with Lewis acids. Triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and its tungsten analogue form solid dark-red adducts with BF_3, which have been investigated by elemental analysis and infrared spectroscopy[4]:



M = Mo, W.

The chromium complex also reacts with BF_3, but the adducts could not be isolated in a solid state owing to their dissociation. The boron trifluoride in these adducts forms a bond with the metal, which follows from the infrared spectra; the basicity of the complexes relative to BF_3 increases with increase of the atomic number of the metal.

A study has also been made of the interaction of triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and its tungsten analogue with other Lewis acids: CdI_2, $HgCl_2$, $HgBr_2$, HgI_2, $GaBr_3$, and $InBr_3$.[5] The products were 1:1 adducts, moderately resistant to the action of air but sensitive to light. No 1:2 adducts were detected although an excess of Lewis acids was used. Since all the vibration frequencies of the carbonyl groups of the adducts have undergone a bathochromic shift relative to the initial complexes, it was concluded that the central metal atom is the site of attack by the Lewis acid. The authors[5] were unable to make a choice between two structures of the adducts:



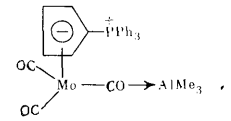
M = Mo, W $\quad$ M^1X_n = CdI_2, $HgCl_2$, $GaBr_3$ etc.

They believe that the ready formation of the adducts indicates the presence of a negative charge on the metal atom in the cyclopentadienylidemetal tricarbonyl complexes and also that the interaction of the metal with the phosphonium centre in these complexes is weak and does not prevent the reaction with the Lewis acid.

The study of the reactions of Group VIB metal complexes of triphenylphosphonium cyclopentadienylide in methylene chloride with strong Lewis acids such as $AlCl_3$ and $TiCl_4$[21] also demonstrated the occurrence of interaction via the metal atom.

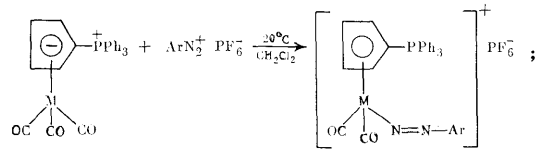
The formation of an adduct via the metal atom between triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl and liquid SO_2 has been decribed[5].

In contrast to the interaction with Lewis acids described above, trimethylaluminium reacts with triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl to form an adduct having a different structure[22]:



Tensimetric titration of the resulting compound with trimethylamine indicates the formation of a 1:1 adduct. The infrared spectrum contains bands at 1932, 1845, and 1665 cm^{-1} in the region corresponding to the vibrations of the CO group. Thus the stretching vibration frequencies of one CO group diminish markedly (by more than 100 cm^{-1}) due to the coordination to $AlMe_3$, while the stretching vibration frequencies of the two non-coordinated CO groups increase by ~15–30 cm^{-1}.

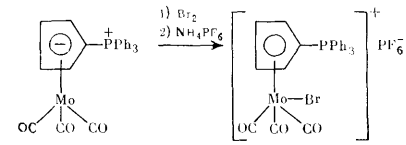
(c) *Reactions with arenediazonium salts.* *p*-Methoxybenzenediazonium hexafluorophosphate readily reacts with molybdenum and tungsten complexes of triphenylphosphonium cyclopentadienylide, giving rise to quantitative yields of products of the substitution of one carbonyl groups by the areneazo-group[5]:



M = Mo, W; Ar = *p*-$MeOC_6H_4$.

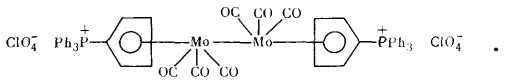
The corresponding chromium complex decomposes under the same conditions. The reaction is analogous to that of $[C_5H_5Mo(CO)_3]^-$ with $ArN_2^+X^-$.[5]

(d) *Reactions with halogens.* Triphenylphosphonium cyclopentadienylidemolybdenum tricarbonyl reacts with chlorine, bromine, or iodine at room temperature, the halogen adding to the metal[5]:

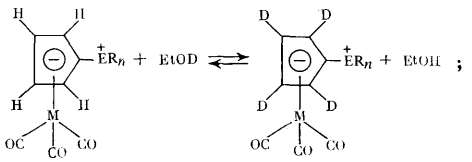


The reaction takes place more smoothly when the intial complex (or its tungsten analogue) is treated with carbon tetrachloride or tetrabromide in CF_3COOH. The halogen adds to the metal atom of the complex $(Ph_3PC_5H_4)Mo(CO)_3$ also on treatment with $SbCl_5$ or $C_5H_5Co(CO)I_2$.[5]

(e) *Oxidation.* The effect of one-electron oxidants, namely tri(*p*-bromophenyl) ammonium salts, has been investigated in relation to the molybdenum complex of triphenylphosphonium cyclopentadienylide[5]. Treatment with $[(BrC_6H_4)_3N]^+ \cdot [SbCl_6]^-$ results in the formation, analogously to the reaction involving halogens, of the salt $[Ph_3PC_5H_4Mo(CO)_3Cl]^+ \cdot [SbCl_6]^-$. On the other hand, on treatment with the substituted ammonium perchlorate, the complex is oxidised with formation of a dimer:



(f) *Hydrogen isotope exchange.* It has been recently observed that the complexes of cyclopentadienylides with Group VIB metal carbonyls can undergo the hydrogen isotope exchange (HIE) reaction with deuteroethanol in neutral media [19,23]:



M = Cr, Mo, W; ER_n = Me_2S, Ph_3P.

Table 3. The rate constant for hydrogen isotope exchange involving cyclopentadienylides and their π-complexes with Group VIB metals (in acetone at 50 °C).[19,23]

Compound	k, s^{-1}	Compound	k, s^{-1}
$(Me_2SC_5H_4)$	$7.0 \cdot 10^{-5}$	$Ph_3PC_5H_4$	$6.7 \cdot 10^{-5}$
$(Me_2SC_5H_4)Cr(CO)_3$	$2.1 \cdot 10^{-7}$	$(Ph_3PC_5H_4)Cr(CO)_3$	No exchange
$(Me_2SC_5H_4)Mo(CO)_3$	$2.9 \cdot 10^{-5}$	$(Ph_3PC_5H_4)Mo(CO)_3$	$8.2 \cdot 10^{-6}$
		$(Ph_3PC_5H_4)W(CO)_3$	$7.1 \cdot 10^{-7}$

The authors used the hydrogen isotope exchange method to compare the reactivities of cyclopentadienylide complexes containing various metals and various onium atoms. Table 3 presents the rate constants for the HIE of cyclopentadienylides and their π-complexes with EtOD in acetone. The results show that the influence of π-coordination to a transition metal on the reactivity of cyclopentadienylides is determined to a large extent by the nature of the central metal atom. For example, the rate constants for the hydrogen isotope exchange under identical conditions are similar in magnitude for dimethylsulphonium cyclopentadienylide and its π-complex with $Mo(CO)_3$, whereas the rate constants for triphenylphosphonium cyclopentadienylide and its complex with $Mo(CO)_3$ differ only by an order of magnitude. On the other hand, the influence of π-coordination to the $Cr(CO)_3$ group is manifested much more intensely and the rate of HIE involving the chromium complex of dimethylsulphonium cyclopentadienylide diminishes by a factor greater than two compared with the non-coordinated ylide. The $W(CO)_3$ group occupies an intermediate position between $Cr(CO)_3$ and $Mo(CO)_3$ as regards its influence on the HIE of cyclopentadienylides.

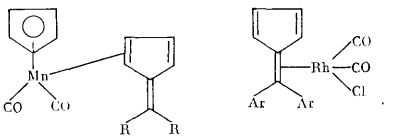
Thus the reactivity of the cyclopentadienyl ring in isotope exchange between cyclopentadienylides and their π-complexes with Group VIB metal carbonyls varies in the sequence S- or P-cyclopentadienylide ≥ Mo complex of ylide > W complex of ylide > Cr complex of ylide.

It has also been shown for the π-complex of dimethylsulphonium cyclopentadienylide with $Mo(CO)_3$ [20] that the π-coordination to the transition metal leads to the abolition of the differences between the rates of exchange in the α- and β-positions of the five-membered ring of the π-ligand, in contrast to the non-coordinated cyclopentadienylide, where the α-position is more reactive.

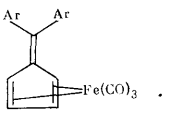
III. TRANSITION METAL COMPLEXES OF PENTAFULVENES

Pentafulvenes can be coordinated to transition metals in various ways:

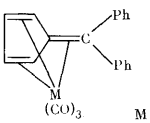
1. Via one double bond[25,27]:



2. Via two double bonds[26]:

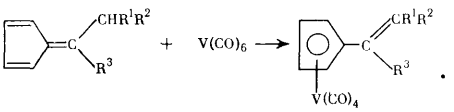


3. Via three double bonds[28,40]:

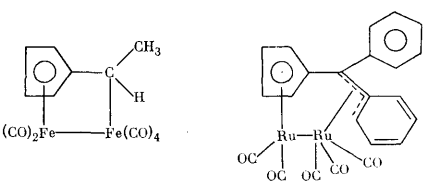


M = Cr, Mo, W.

4. To the cyclopentadienyl ring as the donor of five electrons[29]:

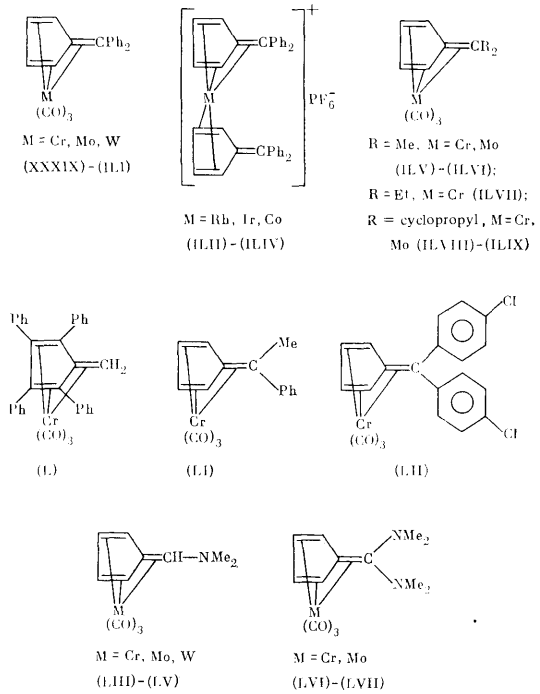


5. In a complex manner[30,31]:



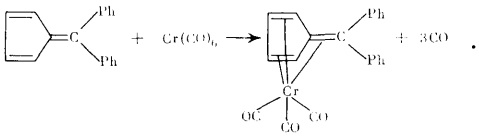
Pentafulvenes are structural units of molecules of compounds such as calicenes, fulvalenes, azulenes, etc. Some of these compounds form complexes with transition metals; for example, the complex of azulene with $Cr(CO)_3$ was described in 1978.[24] However, in this review we shall not consider the complexes of such compounds. We shall deal only with the complexes of pentafulvenes in which the coordination to the metal takes place via three double bonds of the pentafulvene, i.e. the pentafulvene is a six-electron ligand. Such π-complexes of pentafulvenes are comparable

to the π-complexes of cyclopentadienylides with metal carbonyls. All the pentafulvenes with six-electron coordination described in the literature hitherto are presented below:

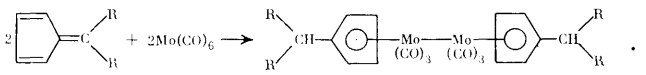


1. Synthesis

The complex of 6,6-diphenylfulvene with chromium carbonyl was first obtained in 1961 by the reaction of fulvene with $Cr(CO)_6$ in hydrocarbon solvents[32]:

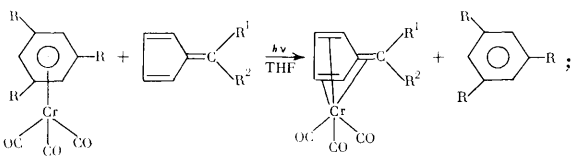


The analogous reactions of the metal carbonyls $Mo(CO)_6$ and $W(CO)_6$ with pentafulvenes in solvents of the type of ethers or in the absence of a solvent form only dimeric complexes (with breakdown of the fulvene structure)[33,34]:



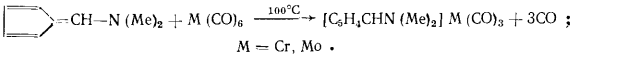
However, it was shown in 1977 that the reactions of 6,6-dialkyl- and 6,6,-diarylpentafulvenes with acetonitrile derivatives of chromium, molybdenum, and tungsten carbonyls in tetrahydrofuran (THF) lead to the formation of fulvene complexes in the case of all three metals[28].

It has been found recently that pentafulvene can substitute the π-arene ligand in arenechromium tricarbonyl complexes with formation of pentafulvene complexes[35]:



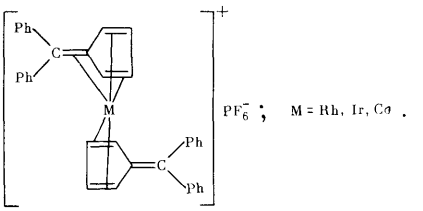
R = H, Me; R^1 = Me, R^2 = Ph; $R^1 = R^2 = C_6H_4Cl$.

Complexes of 6-(*N*,*N*-dimethylamino)- and 6,6-bis(*N*,*N*-dimethylamino)-fulvenes with chromium and molybdenum carbonyls can be obtained by the direct reaction of the fulvenes with $Cr(CO)_6$ and $Mo(CO)_6$ in cyclohexane[36]:



Under these conditions, $W(CO)_6$ does not react with 6-(*N*,*N*-dimethylamino)fulvene and the acetonitrile derivative of tungsten is used to obtain the fulvene complex[37].

Sandwich complexes of 6,6-diphenylfulvene with rhodium, iridium, and cobalt salts were obtained[38] as early as 1967:

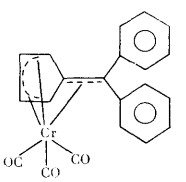


These charged complexes were obtained by the reaction of 6,6-diphenylfulvene, the metal salt, and isopropylmagnesium bromide followed by ultraviolet irradiation, hydrolysis of the reaction mixture, and oxidation with atomospheric oxygen. The yield of the complexes is very low: 6, 0.8, and 0.04% in the case of $CoCl_2$, $RhCl_3$ and $IrCl_3$ respectively. Only charged biscyclopentadienyl complexes of the metals have been isolated after the analogous reaction of 6,6-dimethylfulvene with $RhCl_3$ and $CoCl_2$, i.e. the fulvene structure of the ligand decomposed as a result of the addition of hydrogen to the exocyclic double bond.

2. Structure

It was postulated previously[32] that in the reaction of 6,6-diphenylfulvene with chromium carbonyl the complex formation process involves the benzene ring of the fulvene. However, later the same investigators[39] established by ^1H NMR that the five-membered and not the six-membered ring of 6,6-diphenylfulvene is coordinated to the chromium atom.

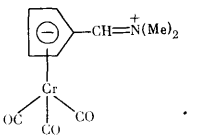
Complete X-ray diffraction analysis of 6,6-diphenylfulvene chromium tricarbonyl confirms the coordination to the five-membered ring[40,41]. It was shown that in the molecule of the complex the chromium atom is linked to all six carbon atoms of the pentafulvene ligand and to the three carbonyl groups, assuming a distorted octahedral coordination. The planarity of the fulvene system is then appreciably disturbed as a result of the deviation of the exocyclic carbon atom towards the chromium atom. Thus the coordination of the chromium atom in 6,6-diphenylfulvenechromium tricarbonyl can be represented as coordination to the butadiene system of the cyclopentadienyl ring and to the exocyclic double bond of the fulvene:



Theoretical analysis[42] of the preferred conformation of the complex (fulvene)$Cr(CO)_3$ showed that the calculated angle of the deviation of the exocyclic carbon atom from the plane of the five-membered ring is close to the experimental value[41].

Comparison of the structure of 6,6-diphenylfulvenechromium tricarbonyl with that of dimethylsulphonium cyclopentadienylidechromium tricarbonyl shows that they differ sharply. In the case of the fulvene complex the exocyclic carbon atom is involved in coordination to the metal, while in the case of the cyclopentadienylide complex the sulphur atom is displaced from the plane of the five-membered ring in the direction opposite to that of the chromium atom and is not linked to the latter.

From X-ray diffraction data for 6-(*N*,*N*-dimethylamino)-fulvenechromium tricarbonyl, it has been concluded[43] that the molecule of this complex contains the fulvene ligand in a dipolar form stabilised by the complex formation reaction between the negatively charged five-membered ring and the $Cr(CO)_3$ group. Thus it has been shown that complex formation results in a significant equalisation of the C–C bond lengths in the cyclopentadienyl ring of the ligand and an increase of the multiplicity of the bond between the nitrogen atom and the exocyclic carbon atom:



3. Infrared and NMR Spectra

The infrared spectra of the metal carbonyl complexes of pentafulvenes with six-electron coordination are characterised by intense absorption bands in the same region of absorption by terminal CO groups as in the spectra of the metal carbonyl complexes of cyclopentadienylides (Table 4). The ^1H NMR spectra of pentafulvene complexes (Table 4) exhibit under the usual conditions two signals due to the α- and β-protons of the five-membered ring, the signals having undergone an upfield displacement relative to the non-coordinated pentafulvene, as in the case of the cyclopentadienylide π-complexes.

The study of the ^{13}C NMR spectra of the chromium tricarbonyl complexes of 6,6-diphenylfulvene and 6-(*N*,*N*-dimethylamino)fulvene[44] showed that the π-coordination of pentafulvenes to the $Cr(CO)_3$ group is accompanied by an increase of the energy of the shielding of the nuclei of all the carbon atoms of the cyclopentadienyl ring, as in the cyclopentadienylide complexes, the effect being observed to a more marked extent in systems with a more pronounced ylene structure. It has also been found that the coordination of 6,6-diphenylfulvene to the chromium atom entails an appreciable increase of the shielding of the exocyclic carbon atom (there is an upfield shift of the signal due to the ^{13}C atom by 26 p.p.m.), while the coordination of 6-(*N*,*N*-dimethylamino)fulvene to the $Cr(CO)_3$ group is accompanied by the deshielding of the exocyclic carbon atom (there is a downfield shift of the signal due to the ^{13}C atom by 6 p.p.m.). The authors[44] explained these facts by a difference between the structures of the complexes. According to X-ray diffraction analysis, the exocyclic double bond of 6,6-diphenylfulvene is involved in coordination to the chromium atom, which leads to an increase of the shielding of the nuclei of the carbon atoms in this bond. On the other hand, if the coordination of 6-(*N*,*N*-dimethylamino)fulvene to the $Cr(CO)_3$ group is accompanied by an increase of the contribution of the ylide structure, one would expect the deshielding of the nucleus of the C_{ex} atom adjoining the onium nitrogen atom and also an increase of the barrier to rotation about the $C_{ex}=N^+Me_2$ bond. The authors found confirmation of this hypotheis in the observation that, apart from the deshielding of the $^{13}C_{ex}$ nucleus, two signals also appear in the ^{13}C NMR spectra due to the CH_3 groups at the nitrogen atom (in contrast to the initial fulvene). The hypothesis of an increase of the contribution of the ylide structure on π-coordination of 6-(*N*,*N*-dimethylamino)fulvene to $Cr(CO)_3$, based on the study of the ^{13}C NMR spectra, was subsequently confirmed by X-ray diffraction[43].

4. Chemical Properties

The chemical properties of the π-complexes of pentafulvenes have been studied extremely little. It has been shown[39] that 6,6-diphenylfulvenechromium tricarbonyl is readily reduced by sodium tetrahydroborate with formation of an anionic cyclopentadienyl complex of chromium:

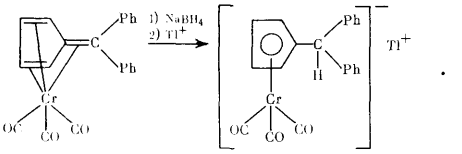
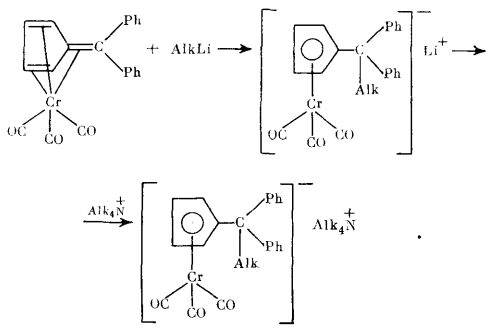


Table 4. Parameters of the infrared and ^1H NMR spectra of π-complexes of pentafulvenes with six-electron coordination.

Compound	i.r. spectra		^1H NMR spectra		
	ν(C≡O), cm^{-1}	refs	δ(C_6H_4), p.p.m.	solvent	refs
(XXXIX)	1971; 1907; 1886	[28]	4.60; 4.18	C_6D_6	[28]
(IL)	1974; 1901; 1885	[28]	4.77; 4.53	C_6D_6	[28]
(ILI)	1969; 1882; 1874	[28]	5.60; 5.05	$CDCl_3$	[28]
(ILII)	—	—	5.0; 4.68; 4.3	SO_2 (liq.)	[38]
(ILIV)	—	—	4.79; 4.37; 4.21	SO_2 (liq.)	[38]
(ILV)	1975; 1908; 1880	[28]	4.67; 3.98	C_6D_6	[28]
(ILVI)	1981; 1909; 1875	[28]	4.88; 4.41	C_6D_6	[28]
(ILVII)	1989; 1898	[28]	4.68; 3.98	C_6D_6	[28]
(ILVIII)	1954; 1894; 1863	[28]	4.79; 4.44	C_6D_6	[28]
(ILIX)	1950; 1895	[28]	5.74; 5.23	$CDCl_3$	[28]
(L)	1984; 1919; 1890	[28]	—	—	—
(LI)	1971; 1893	[35]	5.26; 4.60	$CDCl_3$	[35]
(LII)	1985; 1907	[35]	5.44; 4.67	$CDCl_3$	[35]
(LIII)	1909; 1820; 1788 *	[36]	5.09	$(CD_3)_2CO$	[36]
(LIV)	1908; 1815; 1785 *	[36]	5.66; 5.51	$(CD_3)_2CO$	[36]
(LV)	1906; 1810; 1787 *	[37]	—	—	—
(LVI)	1914; 1799; 1777 *	[36]	—	—	—
(LVII)	1914; 1803; 1783 *	[36]	—	—	—

*The infrared spectra were recorded in liquid paraffin; in the remaining cases the spectra were measured using discs with KBr.

An analogous reaction involving the nucleophilic addition of alkyl-lithium was described in 1977 [28]:



The hydrogen isotope exchange involving the molybdenum complex of 6-(*N*,*N*-dimethylamino)fulvene on treatment with deuteroethanol in a neutral medium has been studied recently under the same conditions as for the corresponding molybdenum complexes of triphenylphosphonium or dimethylsulphonium cyclopentadienylide[20]. It has been shown that the rate of isotope exchange in ylide–ylene systems coordinated to a transition metal atom increases with increase of the contribution of the ylide form to the structure of the ligand:

$$[Me_2NCHC_5H_4]Mo(CO)_3 < (Ph_3PC_5H_4)Mo(CO)_3 < [Me_2SC_5H_4]Mo(CO)_3 .$$

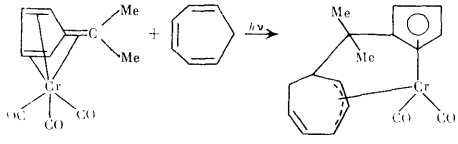
The protonation of complexes of 6-(*N*,*N*-dimethylamino)-fulvene with chromium, molybdenum, and tungsten carbonyls was studied in 1980 by ^{1}H NMR and infrared spectroscopy under the conditions of different acidities in solutions of trifluoroacetic and acetic acid in methylene chloride[45]. It was established that in CF_3COOH the complexes are reversibly protonated at the metal atom and that the rate of protonation varies linearly with the acidity of the medium:

$$(C_5H_4CHNMe_2)M(CO)_3 \underset{Et_2NH}{\overset{H^+}{\rightleftharpoons}} [(C_5H_4CHNMe_2)M(CO)_3H]^+ ;$$
$$M = Cr, Mo, W .$$

Signals are then observed in the ^{1}H NMR spectra in the range of δ values between −3 and −8 p.p.m., which are characteristic of hydrogen atoms linked to a metal. With increase of the atomic number of the metal, the signals are displaced to higher field, which indicates an increase of the degree of shielding of the hydrogen atom attached to the metal. The authors estimated quantitatively the relative basicities of the complexes of 6-(*N*,*N*-dimethylamino)fulvene with Group VIB metal carbonyls and found that the basicity of the complexes increases in proportions of ~1 : 150 : 1800 with increase of the atomic number of the metal from Cr to Mo and then to W.

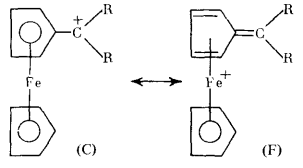
As already stated, previously the qualitative conclusion was reached that the basicity of the complexes of triphenylphosphonium cyclopentadienylide with Group VIB metal carbonyls increases with increase of the atomic number of the metal.

The reaction of 6,6-dimethylfulvenechromium tricarbonyl with cycloheptatriene in hexane under irradiation, which leads to the formation of a complex having a composite structure, has also been described[46]:



5. Metallocenylcarbenium Ions

The metallocenylcarbenium ions, which are readily formed and exhibit an unusual stability, can also be included in the class of pentafulvene complexes with transition metals:

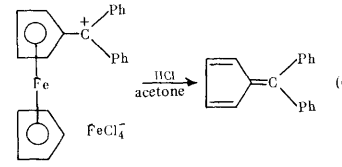


(C) (F)

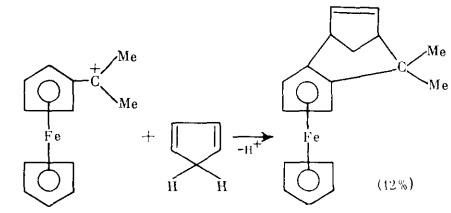
The authors of a review on fulvene complexes[3] regard α-ferrocenylcarbenium ions as complexes with a fulvene ligand. Although the nature of the unusually high stability of the α-ferrocenylcarbenium ions has been the subject of prolonged discussion and there have been many publications on this subject (original and review publications)[47–49], the structure of these species has still not been finally established.

Being unable to consider this question in detail, we shall confine ourselves only to listing the pieces of evidence characterising the interrelation between the fulvene (F) and ferrocenylcarbenium (C) structures and to a discussion of the results of a recent investigation[50] undertaken to determine the structure of the tetrafluoroborate of the diphenylferrocenylcarbenium ion.

One of the pieces of evidence in support of the fulvene structure of the ferrocenylcarbenium ion is the spontaneous formation of fulvenes from the latter in hydrochloric acid solution or under irradiation[51–54], for example:

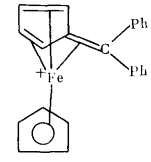


Another important piece of evidence is the ability of ferrocenylcarbenium ions to interact with cyclopentadiene to form a cycloaddition product[55]:



Quantum-chemical calculations on ferrocenylcarbenium ions have shown that a considerable proportion of the positive charge is located at the iron atom[56]. The study of the ^{1}H and ^{13}C NMR spectra (see, for example, Refs.57–59) has shown that the positive charge is distributed throughout the molecule of the complex.

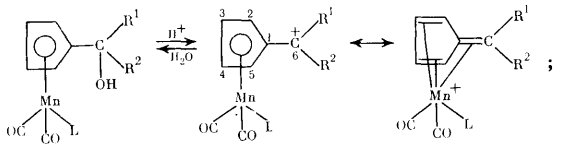
A complete X-ray diffraction analysis of the tetrafluoroborate of the diphenylferrocenylcarbenium ion has been carried out quite recently[50]. The experimental data enabled the author to conclude that the compound is a salt of the fulvene-cyclopentadienyliron cation:



In this system the exocyclic carbon atom is displaced from the plane of the cyclopentadienyl ring in the direction of the iron atom by 20.7°. The exocyclic carbon–carbon bond is appreciably shorter than the simple C–C bond and alternation of bond lengths is observed in the cyclopentadienyl ring, in a manner similar to that established previously for the isoelectronic diphenylfulvenechromium tricarbonyl[40,41]. Analysis of the results led the author[50] to the conclusion that the metallocenylcarbenium ion is stabilised not only as a result of the interaction of the orbital of the exocyclic carbon atom with the molecular orbital of the cyclopentadienyl ring but also as a consequence of the formation of a bond between this carbon atom and the central iron atom.

Like ferrocene, ruthenocene and osmocene greatly stabilise the neighbouring cationic centre[60,61] and therefore α-ruthenocenyl- and α-osmocenyl-carbenium ions can also be regarded as fulvene complexes.

The systematic study of cymantrenylcarbenium ions has been begun comparatively recently[62-69]. Like the ferrocenylcarbenium ions, these ions are formed when the corresponding carbinols are dissolved in acid. Solutions of the cations are extremely stable:



R^1, R^2 = Ph, C_6H_4Me, $C_6H_4CMe_3$, Me, Et etc.,
L = CO, PPh_3, $P(OPh)_3$, PEt_3, $SbPh_3$ etc.

The structure of the cymantrenylcarbenium ions is apparently analogous to that of the corresponding ferrocenyl ions. This is indicated, for example, by the study of the ^1H and ^{13}C NMR spectra, whose results indicate a pronounced delocalisation of the positive charge over the cymantrenyl fragment[65]. Diastereotopy of the protons in the 2- and 5-positions[68,69] similar to that observed earlier for ferrocenyl ions[70], has been observed for cymantrenylcarbenium ions[68,69]; it can be accounted for by the hindered rotation about the C(1)–C(6) bond, which has some double bond character. However, the lack of X-ray diffraction data for carbenium ions stabilised by cymantrenyl residues precludes a final conclusion concerning the full similarity of their structure with that of ferrocenylcarbenium ions.

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The extremely important and interesting available information about the influence of π-coordination to a transition metal atom on the properties of the cyclopentadienyl ring, carrying a full or partial negative charge, cannot as yet be regarded as sufficiently complete. It has been shown from the results of an X-ray diffraction study of dimethylsulphonium cyclopentadienylide (~80% contribution of the dipolar structure) and of its π-complex with the $Cr(CO)_3$ group that the π-coordination of this ylide is not accompanied by sharp changes in the structure of the cyclopentadienylide, but leads to an appreciable equalisation of the C–C bond lengths in the five-membered ring, i.e. to an increase of the contribution of the ylide structure in the π-ligand. In contrast to this, in the case of 6,6-diphenylfulvene, which has the ylene structure, π-coordination to the $Cr(CO)_3$ group leads to the breakdown of the planarity of the fulvene system owing to the deviation of the exocyclic carbon atom in the direction of the chromium atom. In this case the butadiene system of the five-membered ring and the exocyclic double bond are coordinated to the metal. As a result of the coordination of 6-(*N*,*N*-dimethylamino)fulvene (contribution of the dipolar structure ~50%) to the $Cr(CO)_3$ group, the molecule of the complex contains the fulvene ligand in its dipolar form.

The results of the study of the ^{13}C NMR spectra of the complexes of dimethylsulphonium and triphenylphosphonium cyclopentadienylides with Group VIB metal carbonyls showed that the differences between the chemical shifts of the carbon nuclei in the cyclopentadienyl ring diminish sharply on π-coordination to transition metals and an appreciable equalisation of the electron density in the five-membered ring occurs as a result. The observed ability of the π-complexes of cyclopentadienylides with Group VIB metal carbonyls to undergo hydrogen isotope exchange with deuteroethanol in neutral media made it possible to employ the hydrogen isotope exchange method to compare the reactivities of the ylide and their π-complexes.

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Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow