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Cationic and neutral transition metal complexes with a tetramethylfulvene or trimethylallyldiene ligand

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Abstract. Published data on the synthesis and chemical properties of complexes of Group 4 – 10 transition metals (d elements) with η^6-tetramethylfulvene and η^7-trimethylallyldiene ligands, formed from the pentamethylcyclopentadienyl complexes of these metals, are described systematically. A description of the structures of these complexes in terms of a 'specific' resonance hybrid of fulvene and methylenecyclopentadienyl (or allyldiene and dimethylenecyclopentadienyl) structures is proposed. It is noted that similar properties or behaviours of the fulvene and allyldiene complexes can be followed both for compounds formed by metals of the same Group and for compounds of elements of the same transition row with identical electron configurations. The bibliography includes 102 references.

I. Introduction

The discovery of ferrocene in 1951 [1,2] and elucidation of its structure [3,4] and properties [5–7] triggered vigorous development of the chemistry of cyclopentadienyl organometallic complexes. Cyclopentadienyl derivatives have now been synthesised for the vast majority of chemical elements. More than 80% of known organometallic complexes contain either unsubstituted cyclopentadienyl ligand (Cp) or its derivatives (Cp′).[8] In the latter group, a special place is occupied by transition metal complexes with the pentamethylcyclopentadienyl ligand (Cp^*). The chemistry of these complexes started to develop intensively only in recent years, after facile methods for the synthesis of pentamethylcyclopentadiene and some of its derivatives had been proposed.[9] The key feature of metal complexes with pentamethylcyclopentadienyl ligands is the ability to split off one or two hydrogen atoms of methyl groups to be converted into cationic or neutral complexes with the $C_5Me_4CH_2$ or $C_5Me_3(CH_2)_2$ ligands, which are often referred to as tetramethylfulvene and trimethylallyldiene complexes, respectively. The chemistry of these complexes is of substantial interest not only because they have been prepared for many Group 4 – 10 transition metals but also due to the fact that the mode of metal coordination to these ligands depends essentially on the nature of the metal.

Vast experimental information concerning the chemistry of this class of compound has now been accumulated; however, to the best of our knowledge, the data have not been generalised. This stimulated us to compose this review, which covers the synthesis, the reactivity, and the structures of pentamethylcyclopentadienyl complexes of transition metals and quantum chemical calculations of their structures. As follows from the literature, the way of describing the structures of these complexes is debatable; this also calls for systematic consideration of the results of theoretical studies.

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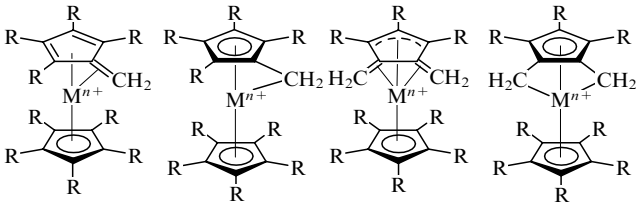
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II. Metal complexes with tetramethylfulvene and trimethylallyldiene ligands

Metal complexes with the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ ligands are formed in various transformations of compounds with the pentamethylcyclopentadienyl ligand. However, before we discuss properties of the coordinated η^5-Cp^* ligand, it is expedient to characterise briefly non-coordinated pentamethylcyclopentadiene. The properties of pentamethylcyclopentadiene (Cp^*H) differ from those of unsubstituted cyclopentadiene (CpH). It is a weaker acid ($pK_a = 26.1$) than CpH ($pK_a = 18.0$);[10] the non-aromatic 5π and 4π species, $C_5Me_5^{\bullet}$ ($Cp^{*\bullet}$) and $C_5Me_5^+$ (Cp^{*+}), it forms are more stable than their non-methylated analogues. The permethylated $Cp^{*\bullet}$ radical has been detected by EPR,[11] and the Cp^{*+} cation has been found as an intermediate [12] in the reactions of the metal Cp^* complexes with nucleophiles (alcohols, alkoxides, amines, organolithium compounds). The transformations of the η^5-Cp^* ligand in the coordination sphere of the metal atom proceed rather easily during a variety of processes.

Theoretically, the fulvene ligand $C_5H_4CH_2$ can be coordinated to a metal according to the η^2-, η^4-, and η^6 -modes. The same mode of coordination is typical of the tetramethylfulvene ligand. η^2-Coordination is encountered very rarely. Complexes with η^4-coordination of the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ ligands are typical only of Groups 9 and 10 metals. Most abundant are neutral and cationic η^6-complexes formed by Group 4 – 8 metals.

When describing the structure of complexes with the $C_5Me_4CH_2$ ligand, researchers use either fulvene (**A**) or methylenecyclopentadienyl (**B**) structures; in some cases, they give preference to structure **A** without good reason. Complexes with the $C_5Me_3(CH_2)_2$ ligand are described by either an allyldiene (**C**) or dimethylenecyclopentadienyl (**D**) structure.



A (η^2,η^4) **B** (σ,η^5) **C** (η^4,η^3) **D** (σ,σ,η^5)

However, it is impossible to give preference to a particular structure without deciding beforehand which parameters characterise each of the structures. Apparently, it should be postulated that complexes with the fulvene structure contain a planar or nearly planar fulvene ligand, while complexes in which the tilt angle of the $C_{Cp}-C_{(\alpha)}H_2$ bond to the metal atom (α) equals 40° should be classified as methylenecyclopentadienyl complexes. It is evident that the deviation of the CH_2 group from the cyclopentadienyl plane by 40° virtually removes this group from conjugation with the ring; therefore, this ligand should not be termed as a fulvene ligand. A similar type of description should be applied to complexes with the $C_5Me_3(CH_2)_2$ ligand. Note that complexes with this extreme type of geometry are seldom encountered; those with an intermediate geometry are more common. The structure of complexes with the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ ligands can be described using a 'specific' resonance hybrid, which takes into account the presence of both forms, $\mathbf{A} \leftrightarrow \mathbf{B}$ and $\mathbf{C} \leftrightarrow \mathbf{D}$, respectively. It should be taken into account that, unlike classical resonance, in this case, not only electrons are displaced but also the geometry changes. Note that in most of original publications, no clear or unambiguous assignment of the structures of transition metal complexes with the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ ligands to forms **A** and **B** ($\eta^2,\eta^4 \leftrightarrow \sigma,\eta^5$) or **C** and **D** ($\eta^4,\eta^3 \leftrightarrow \sigma,\sigma,\eta^5$) has been carried out; therefore, in this review, we describe them as complexes with η^6- and η^7-modes of coordination, respectively.

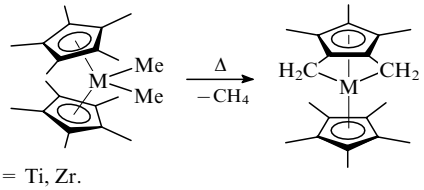
In all studies considered below, the researchers discuss rather comprehensively the structure of each complex they prepare and give numerous facts obtained by chemical, structural, spectral, and quantum-chemical methods supporting one or another structure.

The description of the structures of these compounds in terms of a 'specific' resonance hybrid proposed in this review is underlain by earlier views. As will be shown below, these views were formulated on the basis of systematic research of cationic complexes, but they can also be applied to neutral analogues.

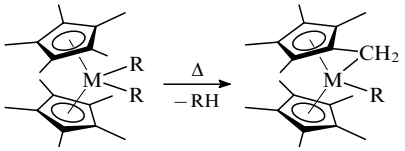
It is worth noting that similar properties or behaviours of complexes can be followed, first of all, for compounds of metals of the same Group. However, in some cases, analogies can also be traced for 16- and/or 18-electron compounds of elements of the same transition row. Therefore, when describing the chemical and spectroscopic properties of complexes, we will emphasise, as far as possible, the analogies found within the Groups or transition rows of elements.

III. The synthesis of complexes with tetramethylfulvene and trimethylallyldiene ligands

Metal complexes with the $C_5Me_4CH_2$ and $C_5Me_3(CH_2)_2$ ligands are often prepared by thermolysis of pentamethylcyclopentadienyl complexes Cp^*ML_n (L_n = Cp, Cp^*) of transition metals. Apparently, the reaction proceeds *via* radical intermediates. For example, heating of 16-electron $(\eta^5\text{-}Cp^*)_2MMe_2$ complexes (M = Ti, Zr) affords η^7-complexes, while the compounds $(\eta^5\text{-}Cp^*)_2MR_2$ (M = Zr, R = Ph; M = Hf, R = Bn) are converted into η^6-complexes.[13–15]

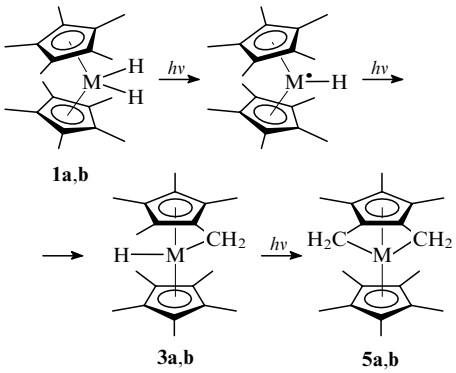


M = Ti, Zr.



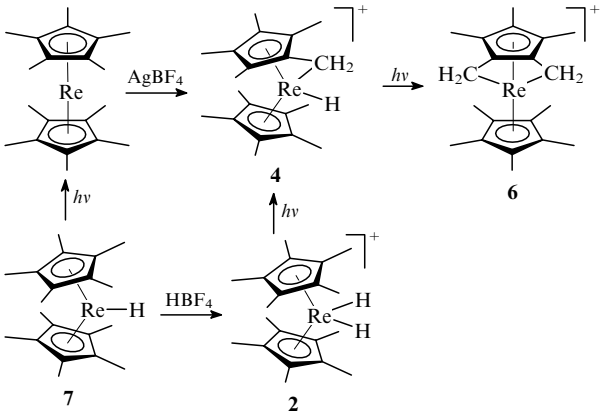
M = Zr, R = Ph; M = Hf, R = Bn.

Usually, $\eta^6\text{-}C_5Me_4CH_2$ complexes are synthesised starting from neutral and positively charged hydride complexes, $[(\eta^5\text{-}Cp^*)_2MH]^+An^-$, which are formed upon protonation of bis(pentamethylcyclopentadienyl) complexes of Group 8 metals or upon the reaction of Cp^*H with vapours of Group 6 and 7 transition metals. Ultraviolet photolysis of solutions of 18-electron metallocenes in acids (*in situ*) or the hydrides $[(\eta^5\text{-}Cp^*)_2MH_m]^{n+}An_n^-$ (M = Mo, W, Re,[16] Ru,[17] Os;[18] n = 0, 1; m = 0, 1, 2), isolated in a pure state, results in the complexes $[(\eta^5\text{-}Cp^*)MH_{m-1}(\eta^6\text{-}C_5Me_4CH_2)]^{n+}$. Thus UV irradiation of 18-electron neutral (**1a**,**b**) and cationic (**2**) η^5-complexes of Group 6 (Mo, W) and 7 (Re) metal hydrides yields successively η^6- (**3a**,**b**, **4**) and η^7-complexes (**5a**,**b**, **6**).[16] Apparently, in the case of Mo, W and Re, the final products are formed *via* 17-electron intermediates, $[\eta^5\text{-}Cp_2^*M^{\bullet}H]^{n+}$ (n = 0, 1), similar to complexes **3a**,**b**.



1a,**b** **3a**,**b** **5a**,**b**

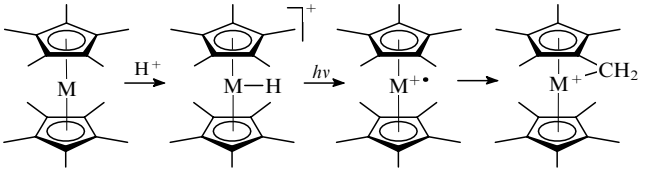
M = Mo (**a**), W (**b**).



7 **4** **2** **6**

The 17-electron complex Cp_2^*Re (unlike the Mo and W analogues) is quite stable and has been isolated. Photolysis of Cp_2^*Re furnishes initially complex **4**, which is then transformed

into complex **6**.[16] The same products are formed from the cationic rhenium dihydrate **2**, resulting from protonation of $(\eta^5\text{-Cp}^*)_2\text{ReH}$ (**7**) (synthesised by co-condensation of Re vapour with Cp^*H)[16] on treatment with HBF_4 . Photolysis of cationic complexes of Group 8 metal hydrides, $[(\eta^5\text{-Cp}^*)_2\text{MH}]^+$ (**9a**,**b**) (M = Ru, Os), prepared from complexes $(\eta^5\text{-Cp}^*)_2\text{M}$ (**10a**,**b**) and a number of acids (CF_3CO_2H, HBF_4, HPF_6 and CF_3SO_3H), proceeds in a similar way (giving rise to η^5-complexes **8a**,**b**).[17,18] A ^{1}H NMR study showed the intermediate formation of the $[(\eta^5\text{-Cp}^*)_2\text{M}]^{+\bullet}$ radical cations (**11a**,**b**), which confirms the radical mechanism of the reaction.



10a,**b** **9a**,**b** **11a**,**b** **8a**,**b**

M = Ru (**a**), Os (**b**).

The difference in the behaviours of neutral and cationic hydrides of Group 6–8 transition metals in the photolysis is manifested in the rate of formation of neutral and cationic products.

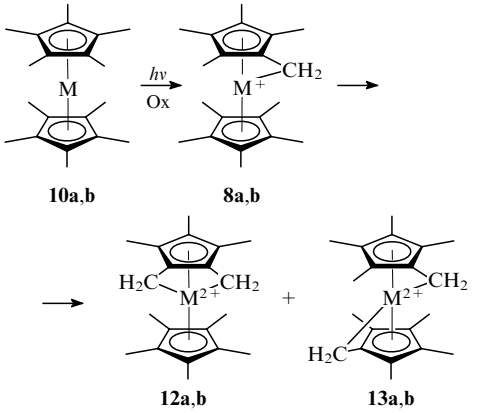
The 4d-metal $[(\eta^5\text{-Cp}^*)\text{MH}_x(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^{y+}$ complexes are formed faster than similar 5d-metal derivatives (Table 1).[16–18] However, for complexes formed by 3d metals, Cr, Mn and Fe, such transformations are unknown.

Table 1. Time (τ) of formation of $[(\eta^5\text{-Cp}^*)\text{MH}_x(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^{y+}$ from $[\text{Cp}_2^*\text{MH}_n]^{m+}$.

M	*n*	*m*	*x*	*y*	τ /h
Mo	2	0	1	0	3
W	2	0	1	0	24
Re	2	1	1	1	1
Ru	1	1	0	1	3
Os	1	1	0	1	15

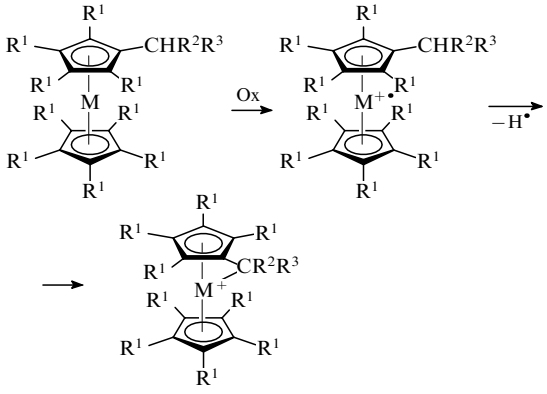
These results are consistent with the data of theoretical calculations of diatomic cations $(\text{MH})^+$; the strength of the M—H bond for elements of the 4d row (Mo and Ru) is lower than that for 5d-row elements (W and Os).[19] Indeed, the $\text{Cp}'_n\text{ML}_m$ compounds (Cp′ = Cp, Cp*) formed by 5d elements tend to have higher basicities than their analogues formed by 4d elements; as a consequence, the dihydride $[(\eta^5\text{-Cp}^*)_2\text{MH}_2]^{n+}$ (M = Re, *n* = 1; M = Os, *n* = 2) or monohydride $[(\eta^5\text{-Cp}^*)\text{MH}.(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^{n+}$ (M = Re, *n* = 1; M = Os, *n* = 2) complexes with the η^6-fulvene ligand are formed in the first stage.[16,20] Note that doubly charged ruthenium complexes, $[(\eta^5\text{-Cp}^*)_2\text{RuH}_2]^{2+}$ and $[(\eta^5\text{-Cp}^*)\text{RuH}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^{2+}$, are not formed under these conditions. (In original publications, doubly and triply charged cations are sometimes referred to as di- and trications, respectively.)

The formation of dimethylene neutral complexes **5a**,**b** and cationic complex **6** upon UV irradiation requires 48, 96 and 20 h, respectively, whereas monomethylene complexes are formed within 3, 24 and 1 h, respectively (see Table 1).[16] For preparing doubly charged Ru- and Os-containing complexes $[(\eta^5\text{-Cp}^*)\text{M}(\eta^7\text{-C}_5\text{Me}_3(\text{CH}_2)_2\text{-1,2})]^{2+}$ (**12a**,**b**) and $[\text{M}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)_2]^{2+}$ (**13a**,**b**), a mere increase in the time of $[\text{Cp}_2^*\text{MH}]^+$ irradiation is insufficient (more than 3 and 15 h, respectively, see Table 1). The reaction medium must also contain an oxidant (Ox) or a substance that promotes oxidation. Indeed, mixtures of complexes **12a**, **13a** and **12b**, **13b** are formed in a high yield only upon UV photolysis in the presence of 20%–25% of oleum in the reaction mixture.[17,18,20–23]



10a,**b** **8a**,**b** **12a**,**b** **13a**,**b**

The key stages in this process include (i) the formation of 16- and 17-electron intermediates of the $[\text{Cp}_2^*\text{Re}]^+$ or $[\text{Cp}_2^*\text{M}]^{+\bullet}$ type (M = Ru, Os) as a result of homolytic cleavage of the M—H bond followed by activation of the C—H bonds and (ii) the transformation of these intermediates into the $[(\eta^5\text{-Cp}^*)\text{ReH}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^+$ and $[(\eta^5\text{-Cp}^*)\text{M}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^+$ complexes (M = Ru, Os), respectively. These intermediates can also be prepared by oxidation of $(\eta^5\text{-Cp}^*)_2\text{M}$ (M = Re, Ru, Os) with one-electron oxidants, AgX (X = CO_2CF_3, BF_4). One-electron oxidation proved to be a versatile approach to the synthesis of a number of complexes of the $\text{LMC}_5\text{R}^1_4\text{CR}^2\text{R}^3$ type [M = Ru, Os; L = Cp, Cp*, η^5-C_9H_7 (indenyl); R^1, R^2, R^3 = H, Me]. Thus it was shown[21] that oxidation of LRuCp^* with $AgBF_4$ yields the complexes $[\text{LRu}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)]^+\text{BF}_4^-$ (L = η^5-Cp, η^5-C_9H_7). A number of publications describe one-electron oxidation of methylated derivatives of ferrocene,[24] ruthenocene[25–27] and osmocene[28] and non-methylated ruthenocene[29,30] to give $[(\eta^5\text{-C}_5\text{R}^1_5)\text{M}(\eta^6\text{-C}_5\text{R}^1_4\text{CR}^2\text{R}^3)]^+\text{An}^-$ (M = Ru, Os; R^1 = H, Me; R^2, R^3 = Alk, Ar; An = BF_4, PF_6) from 17-electron metallocenium derivatives $[(\eta^5\text{-C}_5\text{R}^1_5)\text{M}(\eta^5\text{-C}_5\text{R}^1_4\text{CHR}^2\text{R}^3)]^{+\bullet}$



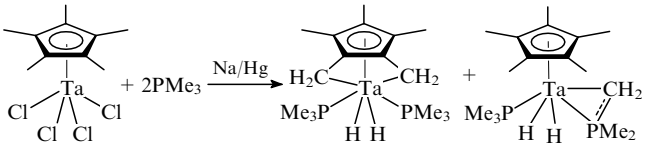
M = Ru, Os; R^1 = H, Me; R^2, R^3 = Alk, Ar.

For iron derivatives, this reaction does not occur and η^6-$C_5Me_4CH_2$ complexes are not formed.

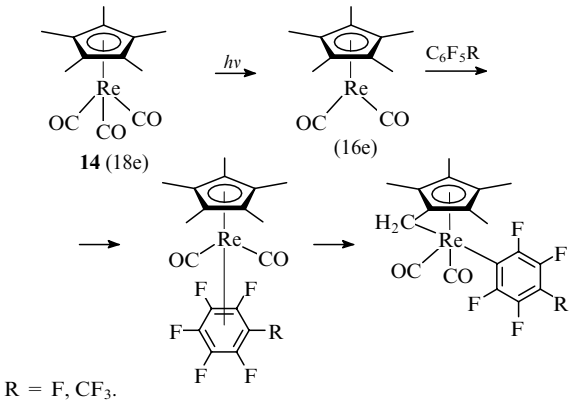
Thus, any 17-electron radical cation, $[\text{LM}(\eta^5\text{-C}_5\text{R}^1_4.\text{CHR}^2\text{R}^3)]^{+\bullet}$ (M = Ru, Os; L = Cp, Cp*, η^5-C_9H_7; R^1 = H, Me; R^2, R^3 = Alk, Ar), having at least one α-C—H bond is capable of being converted into an 18-electron cationic complex,[21] $[\text{LM}(\eta^6\text{-C}_5\text{R}^1_4\text{CR}^2\text{R}^3)]^+$. It was shown that the radical cations add the nucleophile Nu^{n-} (n = 0, 1) giving rise to 19-electron radical cations (n = 0) or radicals (n = 1). The subsequent transformations of these 19-electron species furnish the reaction products. Detailed putative schemes of these reactions are documented.[31,32] It is noteworthy that 19-electron intermediates play a

fairly important role in the transformations of compounds of late transition metals (Groups 9 and 10, see below).

The photolysis, reduction and oxidation of half-sandwich complexes of Group 5–8 metals also occur *via* the formation of 16- and 17-electron intermediates. Thus the reduction of Cp^*TaCl_4 with trimethylphosphine yields two complexes,[33] one containing the η^7-$C_5Me_3(CH_2)_2$ ligand.

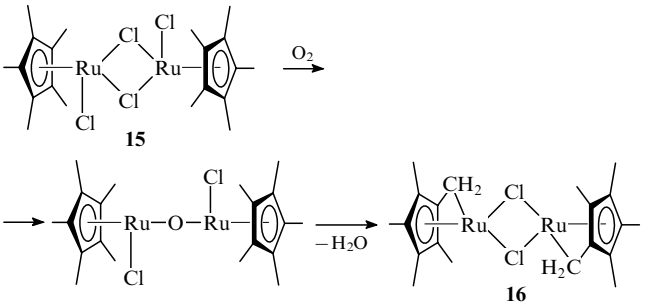


Rhenium complex **14** tends to undergo the following transformations:[34]

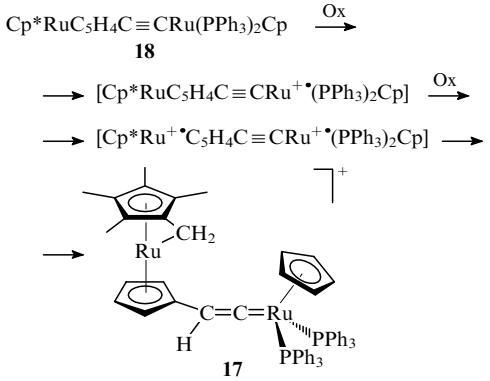


R = F, CF_3.

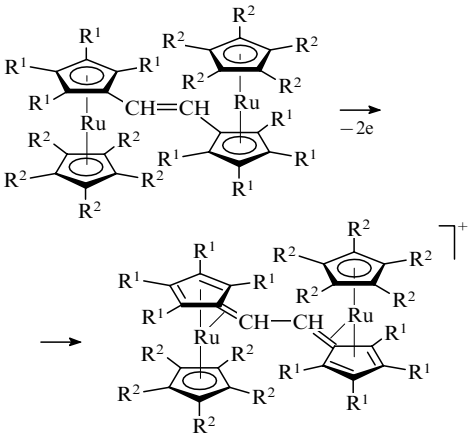
The formation of ruthenium complexes with the η^6-$C_5Me_4CH_2$ ligand is observed in various oxidation processes. For example, oxidation of binuclear halide complex **15** with oxygen involves the intermediate formation of oxide and affords dimeric complex **16**.[35]



The cationic complex **17** is formed upon the oxidation of the binuclear ruthenium complex **18**.[36] In this case, intramolecular interligand transfer of a hydrogen atom takes place in the intermediate 17-electron radical cation.

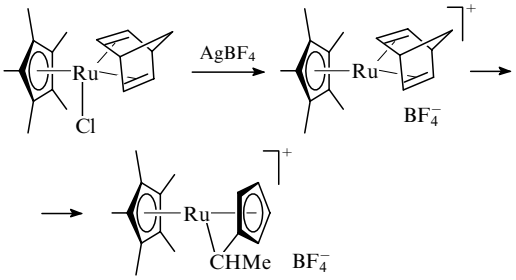


The oxidation of ruthenocene derivatives containing no Me or CHR^1R^2 substituents but having a multiple bond (C=C or C≡C) in the α-position affords compounds with the μ-η^6:η^6-ligand, which is an extensive polyconjugated system.[37]



R^1, R^2 = H, Me.

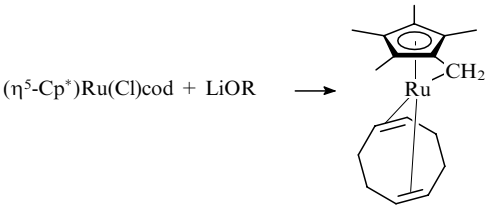
The transformation of a ruthenium complex with the η^4-norbornadiene ligand into a complex with the η^6-$MeCHC_5H_4$ ligand (rather than η^6-$C_5Me_4CH_2$) *via* a 16-electron η^4-complex (activation or cleavage of the C–C bonds) has been reported.[38]

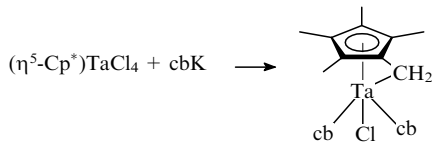


The oxidation of metallocenes Cp^*_2M (**10a**,**b**) in oleum or in the CF_3SO_3H – O_2 system, like photolysis, affords a mixture of η^5:η^7-(**12a**,**b**) and bis-η^6-complexes (**13a**,**b**). Note that the salts $[(\eta^5\text{-}Cp^*)M(\eta^6\text{-}C_5Me_4CH_2)]^+An^-$ (**8a**,**b**, An = BF_4 , PF_6) are preferred over metallocenes as the starting compounds for the preparation of the mixture of doubly charged cations; in this case, the product yield is higher and the reaction proceeds under milder conditions.[18,23]

The most interesting feature of the oxidation of metallocenes **10a**,**b** and cations **8a**,**b** on treatment with molecular oxygen in CF_3SO_3H is the fact that the reaction can proceed further and end in the formation of complexes containing three CH_2 groups, $[(\eta^6\text{-}C_5Me_4CH_2)M\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{3+}$, which have no analogues among organometallic compounds. The properties and the possible structure of these compounds[20,39] are discussed below.

η^6-Fulvene complexes are also formed on treatment of the corresponding precursors with strong bases (for example, lithium alkoxides Pr^iOLi, Bu^tOLi or carbazolyl potassium).[40,41]



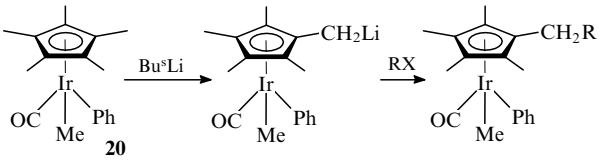


19

cod is 1,5-cyclooctadiene, cb is carbazolyl.

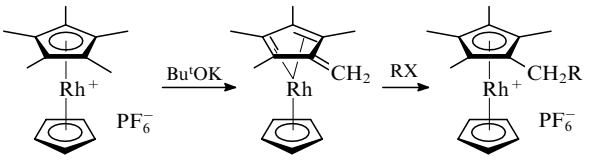
The reaction of chloride **19** with $LiCH_2SiMe_3$ or BnMgCl involves replacement of Cl by CH_2SiMe_3 or Bn without cleavage of the $Ta-CH_2$ bond.[41]

Deprotonation of cationic complexes under the action of strong bases is fairly typical of Group 9 metal derivatives. Generally, this gives rather labile complexes with the η^4-fulvene ligand with a non-coordinated exocyclic double bond. These complexes cannot be isolated due to high reactivity; their formation is indicated by the products of their reactions with various electrophiles. Thus deprotonation of iridium complex **20** followed by the reaction with electrophiles RX gives complexes with the ligands $C_5Me_4CH_2R$ (R = $SiMe_3$, All, Bn, CPh_2OH, CPh(Me)OH, CO_2Li).[42]



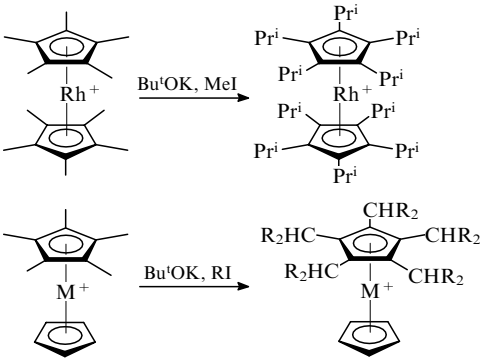
20

For penta- and decamethylrhodocenium and pentamethylcobaltocenium, deprotonation and the reaction with RX (X = Cl: R = Me_3Si, Bn; X = I: R = Me, Et) proceed by an elimination–addition mechanism *via* hypothetical intermediate η^4-fulvene complex **21**, the reaction involving all five (or ten) methyl groups. Treatment with alkyl iodides results in replacement of two hydrogen atoms at each Me group.[43, 44]



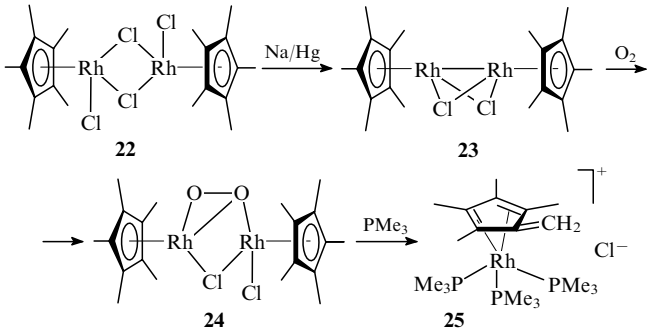
21

R = $SiMe_3$, Bn.



M = Rh, Co; R = Me, Et.

For compounds of Group 9 metals, η^4-fulvene complexes may also arise in oxidation and reduction processes. The reduction of the dimeric rhodium complex **22** and subsequent oxidation of the resulting compound **23** through intermediate complex **24** afford cationic η^4-complex **25**[45] rather than η^6-complexes, as in the case of Group 4–8 metals.

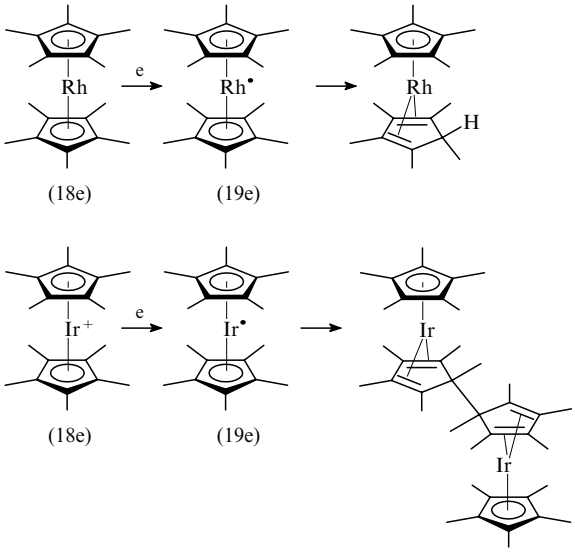


22 **23** **24** **25**

X-Ray diffraction analysis of complex **25** has shown that the CH_2 group and the carbon atom of the cyclopentadienyl ring attached to it are not involved in coordination with the Rh atom and that the methylene group is deflected from the metal atom by 23°.[45]

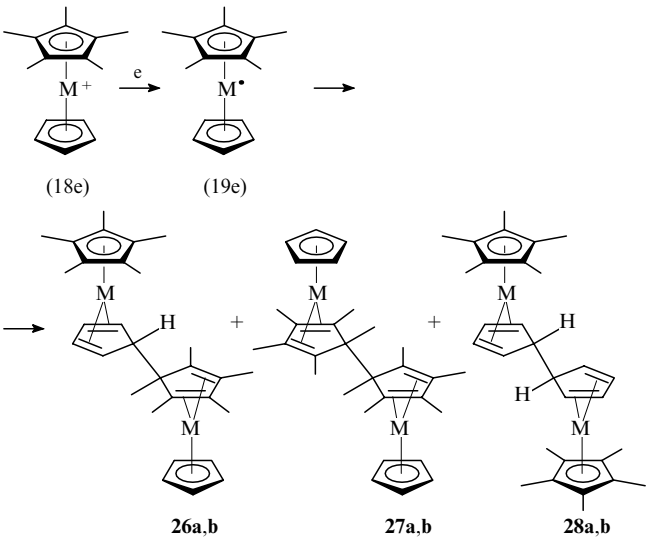
It is noteworthy that transformations of the η^5-cyclopentadienyl complexes of Group 9 metals (Co, Rh, Ir) do not often give mononuclear η^4-coordinated fulvene or cyclopentadiene complexes. For example, the reduction of 18-electron cationic complexes $[Cp^*_2M]^+X^-$ and $[Cp^*MCp]^+X^-$ (M = Rh, Ir, X is an anion) gives, in the first stage, extremely reactive 19-electron radicals, which either trap a hydrogen atom or react with the initial 18-electron cations to give bi- or polynuclear complexes with μ-η^4:η^4-ligands. Nevertheless, it is expedient to consider these transformations for obtaining the general picture of the reactivity of Cp^* compounds of Group 4–10 d-elements.

It is worth noting that the 19-electron intermediates resulting from reduction of complexes formed by Group 9 and 10 metals show more substantial differences between the behaviours of the derivatives of the second (4d) and third (5d) transition row metals than the 17-electron intermediates. Thus the reduction of $[Cp^*_2Rh]^+X^-$ gives rise to mononuclear η^5:η^4-complex, while that of its Ir analogue affords η^5 :η^4-dimer.[46, 47]



(18e) (19e)

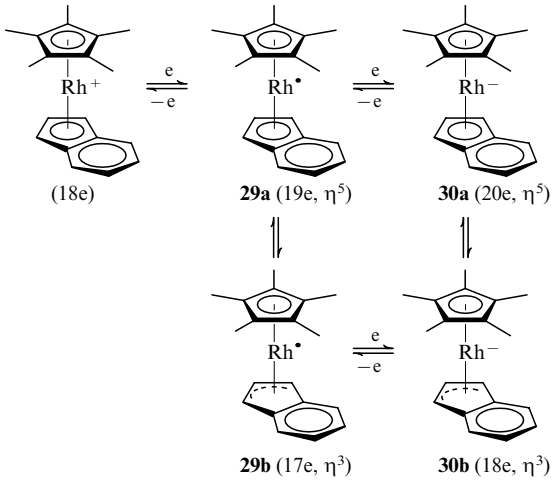
The rhodium and iridium complexes having one pentamethyl-substituted and one unsubstituted Cp ligand are converted into dimers with different contents of spatial isomers. The formation of only one Rh-containing complex (**26a**) and predominance of one isomer for the Ir analogue (**26b**) (isomer ratio **26b** : **27b** = 2 : 1) with total absence of the third isomer **28b** (which is spatially the less hindered isomer with the μ-η^4:η^4-$C_5H_5C_5H_5$ ligand) attests to a reaction of the 19-electron radical with the initial 18-electron cation, because dimerisation of radicals would have yielded a random mixture (1 : 1 : 1) of all three spatial isomers.[47]



M = Rh (**a**), Ir (**b**).

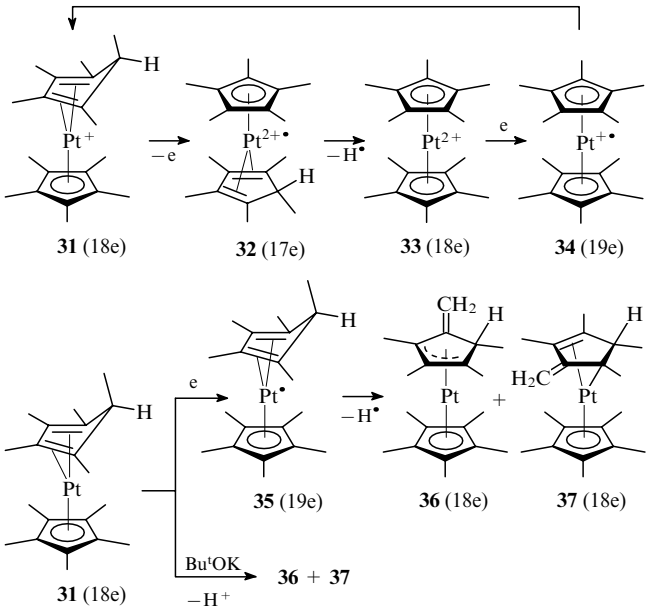
Metal	Compound	Isomer content (%)
Rh	**26a**	100
	27a	0
	28a	0
Ir	**26b**	66
	27b	33
	28b	0

The reduction of Rh and Ir complexes containing η^5-Cp* and η^5-C_9H_7 ligands proceeds in a different way. For instance, electrochemical reduction of the 18-electron rhodium complex is a two-step process, each step being reversible.[46] The reaction gives mononuclear 19-electron radical **29a** and 20-electron anion (**30a**), respectively (or their 17- and 18-electron η^3-isomers **29b** and **30b**, respectively) (*i.e.*, a decrease in the hapticity of the indenyl ligand is involved).

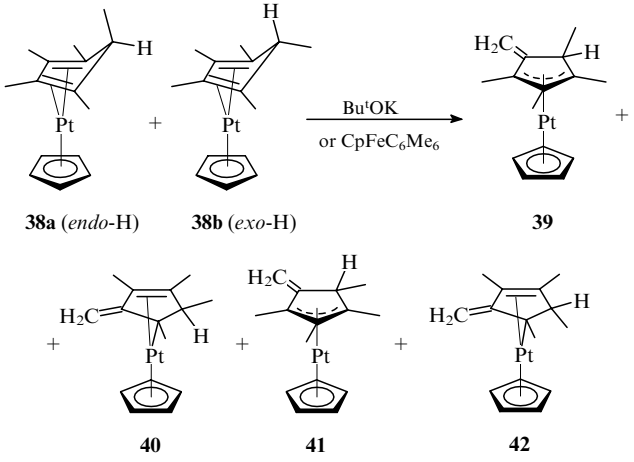


Chemical (1% Na amalgam in THF) or electrochemical reduction of $[(\eta^5\text{-Cp}^*)\text{Ir}(\eta^5\text{-C}_9\text{H}_7)]^+$ proceeds irreversibly, giving rise to a large tetranuclear splayed six-decked complex $[(\eta^5\text{-Cp}^*)\text{Ir}(\mu\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\mu\text{-}\eta^4\text{:}\eta^4\text{-C}_5\text{Me}_5\text{C}_5\text{Me}_5)\text{Ir}(\mu\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}.(\eta^5\text{-Cp}^*)]$.[47] Presumably, the reduction of the initial cation results in a 19-electron radical (analogous to the Rh-containing radical **29**), which splits off an indenyl ligand to give the solvate $[(\eta^5\text{-Cp*})\text{Ir}(\text{THF})_x]$. This complex then reacts with the initial cation yielding the cationic dimer $[(\eta^5\text{-Cp}^*)\text{Ir}(\mu\text{-}\eta^5\text{-C}_9\text{H}_7)\text{Ir}(\eta^5\text{-Cp}^*)]^+$. The reduction of this cation results in the final tetranuclear reaction product.

The electrochemical properties of some Cp* complexes of Group 10 metals (M = Pd, Pt) have been studied in detail.[48–51] For example, it was shown that oxidation of cationic 18-electron complexes $[(\eta^5\text{-Cp}^*)\text{M}(\eta^4\text{-Cp}^*\text{H})]^+$ (**31**) through 17-electron doubly charged radical cations (**32**) furnishes previously unknown 18-electron doubly charged pallado- and platinocenes **33**.[48,51] The electrochemically reversible reduction of platinocene *via* 19-electron radical cation **34** gives the initial complex **31**. Meanwhile, the successive reduction of the Pd analogue reversible in each one-electron stage gives no identifiable products. Further reduction of Pt complex **31** *via* 19-electron radical **35** or its reaction with a strong base (Bu^{t}OK) yields a mixture of η^3- (**36**) and σ:η^2-complexes (**37**).[51] It should be noted that in the intermediate 19-electron complex $(\eta^5\text{-Cp}^*)\text{Pt}(\eta^4\text{-Cp}^*\text{H})$, it is the C—H bond in the methyl group of the η^4-C_5Me_5H ligand that is cleaved rather than the C—H bond in the C(Me)H fragment of this ligand. No transformations of this type are known for Pd complexes.[48]

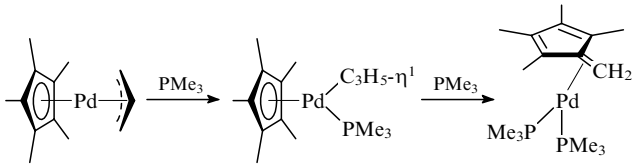


Deprotonation with potassium *tert*-butoxide or reduction with 19-electron $CpFeC_6Me_6$ of dienic Pt complexes containing simultaneously the C_5Me_5H and Cp ligands (**38a**,**b**) yields a mixture of compounds **39**, **40** and **41**, **42**, respectively.[48]



It should be noted that in the reactions listed above, the ligand hapticity decreases as follows: $\eta^5 \rightarrow \eta^4$ and $\eta^4 \rightarrow \eta^3$. Cases of $\eta^5 \rightarrow \eta^2$ transition are also known. For example, the reaction of $(\eta^3\text{-}C_3H_5)\text{Pd}(\eta^5\text{-Cp}^*)$ with PMe_3 affords $(Me_3P)_2\text{Pd}(\eta^2\text{-}$

$CH_2C_5Me_4$), in which the Pd atom is coordinated at the exocyclic double bond of the fulvene ligand.[52]



Apparently, the reaction of the Rh complex with isonitriles under UV radiation follows the same pattern to give 1,2,3,4-tetramethylfulvene *via* intermediate η^5-Cp*, η^3-Cp* and η^1-Cp* complexes.[53]

$$(\eta^5\text{-Cp}^*)\text{Rh(CNR)}_2 \xrightarrow{\text{RNC, } h\nu} (\eta^3\text{-Cp}^*)\text{Rh(CNR)}_3 \xrightarrow{\text{RNC, } h\nu}$$

$$\longrightarrow (\eta^1\text{-Cp}^*)\text{Rh(CNR)}_4 \longrightarrow C_5Me_4CH_2$$

R = CH_2Bu^t.

IV. The reactivity of neutral and cationic complexes

The reactivities of neutral and cationic fulvene complexes towards nucleophiles are fairly similar. Neutral complexes of Group 4–8 metals can also react with electrophilic reagents.[34] In some cases, the reactions of η^6-fulvene complexes with electrophiles (strong acids) proceed without rupture of the M–C_α bond to yield a singly or doubly charged cationic complex. For example, the neutral Re complex [16] and the cationic Os complex [23] react in this way.

$$\text{Cp*Re}(\eta^6\text{-}C_5Me_4CH_2) + HBF_4 \longrightarrow$$

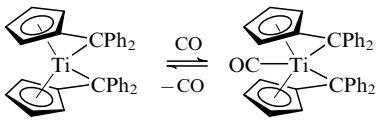
$$\longrightarrow [\text{Cp*ReH}(\eta^6\text{-}C_5Me_4CH_2)]^+BF_4^-,$$

$$[\text{Cp*Os}(\eta^6\text{-}C_5Me_4CH_2)]^+BF_4^- + CF_3SO_3H \longrightarrow$$

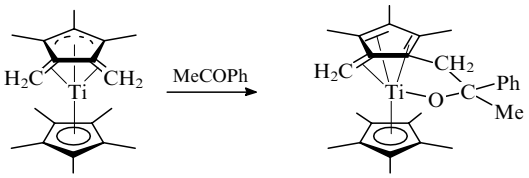
$$\longrightarrow [\text{Cp*OsH}(\eta^6\text{-}C_5Me_4CH_2)]^{2+}An_2^-.$$

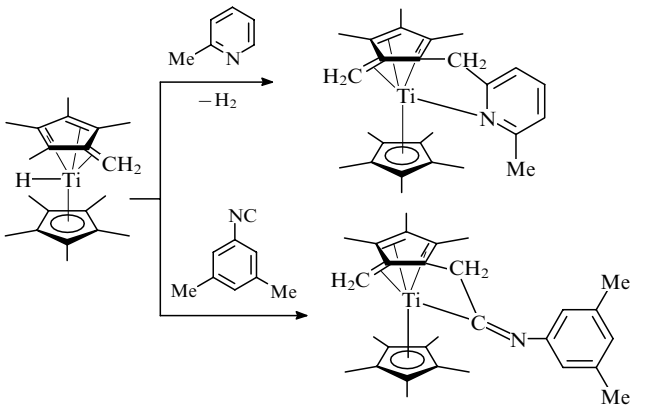
An = BF_4, CF_3SO_3.

For a 16-electron titanium complex containing two fulvene ligands,[54] reversible CO addition without rupture of the Ti– C_α bonds is also possible.



In addition, the 16-electron complexes of Group 4 metals (Ti, Zr, Hf) tend to undergo insertion into the M–CH_2 bonds with extension of the chelate ring and formation of a metal–hetero-atom bond.[55–57]





However, more often, reactions of cationic and neutral η^6-fulvene complexes with electrophiles are accompanied by rupture of the M–CH_2 bond, as for example, in the case of Re complexes.[34]

$$[(C_6F_5)(CO)_2\text{Re}(\eta^6\text{-}C_5Me_4CH_2)] + HHal \longrightarrow$$

$$\longrightarrow \textit{cis}\text{-}[(C_6F_5)(CO)_2\text{Re(Hal)}(\eta^5\text{-Cp}^*)] \longrightarrow$$

$$\longrightarrow \textit{trans}\text{-}[(C_6F_5)(CO)_2\text{Re(Hal)}(\eta^5\text{-Cp}^*)],$$

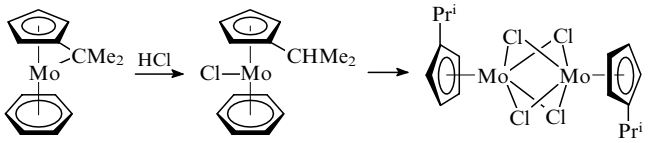
$$[(C_6F_5)(CO)_2\text{Re}(\eta^6\text{-}C_5Me_4CH_2)] + Hal_2 \longrightarrow$$

$$\longrightarrow \textit{cis}\text{-}[(C_6F_5)(CO)_2\text{Re(Hal)}(\eta^5\text{-}C_5Me_4CH_2Hal)] \longrightarrow$$

$$\longrightarrow \textit{trans}\text{-}[(C_6F_5)(CO)_2\text{Re(Hal)}(\eta^5\text{-}C_5Me_4CH_2Hal)].$$

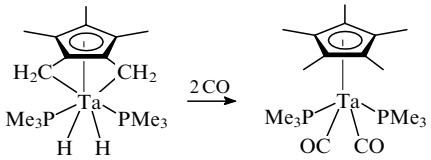
Hal = Cl, Br, I.

In the reaction of neutral molybdenum complex **43** with HCl, the M–C_α bond is also cleaved to give binuclear complex **44** with halide bridges.[58]

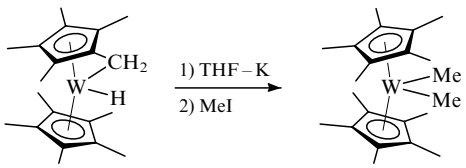


43 **44**

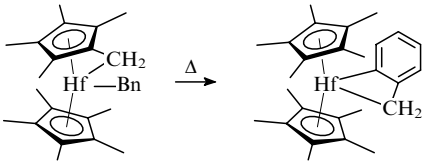
The rupture of two M–C_α bonds also takes place in the reaction of Ta complex with CO.[33]



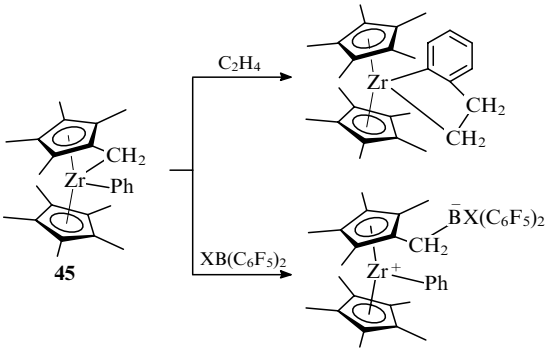
Rupture of the M–C_α bonds can also occur during the reduction of complexes.



In some cases, the reactions of fulvene complexes involve not only the M–C_α bonds but also the bonds of the metal atom with other ligands;[15, 16, 59] in this case, rather unusual transformations, for example *ortho*-metallation, can occur in the metal coordination sphere.

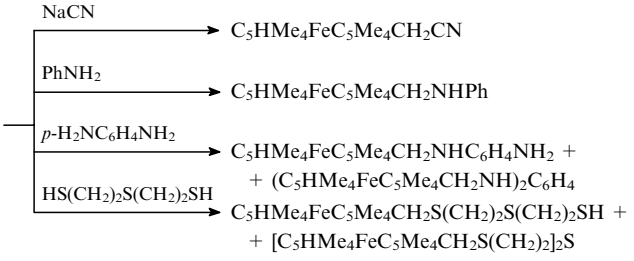


The neutral zirconium fulvene complex **45** reacts with ethylene and electrophilic boranes $XB(C_6F_5)_2$ (X = H, C_6F_5) with cleavage of the $M-C_\alpha$ bond. In the latter case, the reaction gives a zwitterionic complex, which has found use in homogeneous catalysis.[60, 61]



The reactivity of the non-methylated cationic fulvene complexes $[CpMC_5H_4CR^1R^2]^+X^-$ (M = Fe, Ru, Os) has been studied in detail (mainly in relation to ferrocene derivatives) in numerous studies by Russian and foreign researchers (see the reviews [62, 63] and references cited therein). Methylated derivatives are much less studied. Only a few papers dealing with the properties of cationic metal complexes containing the η^6-$C_5Me_4CH_2$ ligand have been published. The reactions of $[C_5HMe_4FeC_5Me_4CH_2]^+BF_4^-$ with a number of nucleophiles accompanied by rupture of the $Fe-CH_2$ bond have been studied.[64]

$[(\eta^5\text{-}C_5HMe_4)Fe(\eta^6\text{-}C_5Me_4CH_2)]^+BF_4^- \longrightarrow$

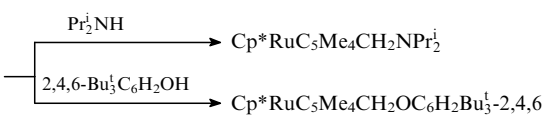


The reactions of salts of nonamethylruthenocenylmethyl cations with nucleophiles have been studied by Kölle *et al.*[25, 65] and Rybinskaya *et al.*[17]

$[Cp^*M(\eta^6\text{-}C_5Me_4CH_2)]^+An^- + KOH \longrightarrow Cp^*MC_5Me_4CH_2OH$

M = Fe, Ru; An = PF_6, CF_3SO_3.

$[Cp^*Ru(\eta^6\text{-}C_5Me_4CH_2)]^+PF_6^- \longrightarrow$



In cationic complexes, the M–CHR bond is easily cleaved under the action of $NaBH_4$, the complexes being reduced to metallocenes.

$[Cp^*M(\eta^6\text{-}C_5Me_4CHR)]^+An^- \xrightarrow{NaBH_4} Cp^*M(\eta^5\text{-}C_5Me_4CH_2R)$

M = Fe: R = H, Ph, Mes; M = Ru, Os: R = H; An = BH_4, PF_6.

The reactions of cationic complexes with the most typical nucleophiles have been studied.[27, 66]

$[Cp^*M(\eta^6\text{-}C_5Me_4CH_2)]^+An^- + MeONa \longrightarrow Cp^*MC_5Me_4CH_2OMe,$

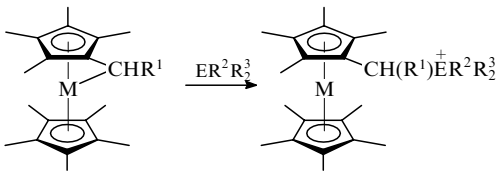
M = Fe, Ru; An = BF_4, PF_6.

$[Cp^*Fe(\eta^6\text{-}C_5Me_4CH_2)]^+An^- + PhSH \longrightarrow Cp^*FeC_5Me_4CH_2SPh,$

An = BF_4, PF_6.

The C–O and C–S bonds in the resulting neutral ethers and thioethers are easily cleaved on treatment with acids yielding the initial cationic compounds.

The salts containing metallocenylmethyl (metallonium) cations readily react with amines and phosphines to give ammonium and phosphonium salts (onium exchange reactions).[67, 68]



M = Os: R^1 = H, $ER^2R^3_2$ = $PPhMe_2$, PPh_3, NMe_3;
M = Ru: R^1 = H, $ER^2R^3_2$ = $PPhMe_2$; R^1 = Ph, $ER^2R^3_2$ = PPh_3.

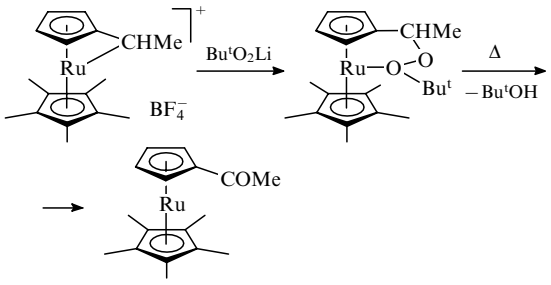
Unlike neutral ethers and thioethers, in cationic metallocenylmethylammonium and -phosphonium cations, the C–N or C–P bonds are not cleaved in the reaction with CF_3SO_3H; instead, protonation at the metal atom to give dications takes place.[67]

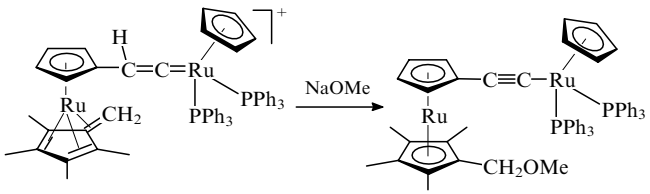
$Cp^*MC_5Me_4CH_2P^+PhMe_2 \xrightarrow{CF_3SO_3H}$

$\longrightarrow Cp^*M^+H(C_5Me_4CH_2P^+PhMe_2)$

M = Ru, Os.

The reaction of $[Cp^*RuC_5H_4CHMe]^+$ with Bu^tOOLi [38] and the reaction of the cationic binuclear Ru complex with MeONa [36] have been studied.





These reactions can be used to prepare functional derivatives of methylated metallocenes and their analogues.

V. Structural characteristics of metal complexes with a fulvene or allyldiene ligand

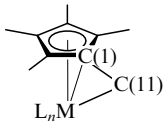
When discussing the structural characteristics of the complexes considered in this review, one should follow first of all the effect of the covalent radii of Group 4–10 transition metal atoms on the structure of compounds and, in particular, on the interatomic distances and bond angles. The covalent radii of Group 4–10 metals have been derived [69] from plenty of experimental data (Table 2). It can be seen from Table 2 that the radii of metal atoms of the 4th Period (3d metals) are much smaller, irrespective of the Group, than the radii of metal atoms of the 5th and 6th Periods (4d and 5d metals †). By following the variation of the radii over the Periods, one can see that the greatest values are found for Group 4 elements, then they smoothly decrease to reach the smallest values for Group 9 elements, and for Group 10 elements, they again somewhat increase.

Table 2. Covalent radii of transition metals (Å).[69]

Period	Group						
	4	5	6	7	8	9	10
4	Ti	V	Cr	Mn	Fe	Co	Ni
	1.56	1.49	1.46	1.38	1.34	1.29	1.35
5	Zr	Nb	Mo	Tc	Ru	Rh	Pd
	1.76	1.66	1.58	1.53	1.49	1.46	1.49
6	Hf	Ta	W	Re	Os	Ir	Pt
	1.77	1.66	1.59	1.51	1.50	1.47	1.43

When considering the structural characteristics of the neutral $L_nM(\eta^6\text{-}C_5R^1_4CR^2R^3)$ (M = Ti, Zr, Hf, Ta, Cr, Mo, W, Re, Ru; L = Cp, Cp*, Ar, CO; R^1 = H, Me; R^2, R^3 = H, Me, Ph) and cationic $[Cp'M(\eta^6\text{-}C_5R^1_4CR^2R^3)]^+$ An^- (Cp′ = Cp, Cp*; M = Fe, Ru, Os; R^1 = H, Me; R^2, R^3 = H, Ph) transition metal complexes with a fulvene ligand (metallocenylmethyl cations) studied to date (Tables 3, 4), one cannot but notice that they are closely similar. Only a few structurally characterised neutral allyldiene (or dimethylenecyclopentenyl) complexes with the $\eta^7\text{-}C_5Me_3(CH_2)_2$ ligand have been reported. Indeed, only one publication has been devoted to the X-ray diffraction study of the Ta complex — $(Me_3P)_2H_2Ta[\eta^7\text{-}C_5Me_3(CH_2)_2]$,[33] and one study [82] reports the structures of three related Ti complexes (see below).

Table 3 presents the X-ray diffraction characteristics of neutral and cationic η^6-fulvene metal complexes $[L_nMC_5R^1_4CR^2R^3]^{m+}An^-_m$ (M are Group 4–10 metals; L_n = Cp, Cp*, Ar, CO, PR^3_3, H; R^1 = H, Me; R^2, R^3 = H, Me, Ph; m = 0, 1, 2) studied to date.



The data for Ti complexes have been collected in a separate Table (Table 4), as they require separate consideration. It can be seen from Table 3 that, despite the different ligand environments of the metal M (L_n ligands) and the substituents in the cyclopentadienyl ring, the M–C(11) and M–C(1) distances are usually commensurable. For compounds of elements of the third transition row (5d), they are somewhat smaller than the distances in complexes formed by metals of the second transition row (4d).

The shortest M–C(11) and M–C(1) distances were found for the 18-electron cationic complex $[Cp^*Os(C_5Me_4CH_2)]^+BPh^-_4$.

† The radii of 5d-metal atoms differ little from one another due to lanthanide contraction.

Table 3. X-Ray diffraction characteristics of transition metal complexes with the $\eta^6\text{-}C_5R^1_4CR^2R^3$ and $\eta^7\text{-}C_5R^1_3(CR^2R^3)_2$ ligands.

Compound	M–C(11) /Å	M–C(1) /Å	The angle α /deg [a]	Ref.
$[Cp^*Os(C_5Me_4CH_2)]^+$	2.224	2.069	41.8	68
$(Me_3SiCH_2)(cb)_2Ta(C_5Me_4CH_2)$	2.246	2.206	–	41
$(PhCH_2)(cb)_2Ta(C_5Me_4CH_2)$	2.254	2.203	–	41
$Cl(cb)_2Ta(C_5Me_4CH_2)$	2.258	2.207	–	41
$[CpRu(C_5£_4CH_2)]^+$	2.272	2.080	42.6	70
$[CpRu(C_5Me_4CH_2)]^+$	2.267	2.071	41.5	71
$[Cl(\mu\text{-}Cl)(C_5Me_4CH_2)Ru]_2$	2.268, 2.271	2.166, 2.172	– –	35
$[Cp^*Ru(C_5Me_4CH_2)]^+$	2.270	2.066	40.3	72
$(cyclo\text{-}C_8H_{12})ClRu(C_5Me_4CH_2)$	2.323	2.072	36	40
$Cp^*Hf(CH_2Ph)(C_5Me_4CH_2)$	2.320	2.258	37	59
$(CO)_2(C_6F_5)Re(C_5Me_4CH_2)$	2.36	2.14	39.6	34
$Cp^*ZrPh(C_5Me_4CH_2)$	2.388	2.282	37	15
$(Me_3P)_2H_2Ta\{C_5Me_3(CH_2)_2\}$	2.394	–	33.4	33
$[Cp^*Os\{C_5Me_4CH(C_6F_5)\}]^+$	2.401	2.094	–	73
$[CpOs(C_5H_4CPh_2)]^+$	2.387	2.088	–	74
$(C_6H_6)W(C_5H_4CPh_2)$	2.33	2.11	39	54
$(CO)_3Cr(C_5H_4CH_2)$	2.352	2.044	35	75
$[Cp^*Ru(C_5Me_4CHPh)]^+$	2.506	2.097	–	73
$[CpRu(C_5H_4CPh_2)]^+$	2.482	2.098	–	76
$(C_6H_5Me)Mo(C_5H_4CPh_2)$	2.374	2.125	38	54
$(CO)_3Cr(C_5H_4CPh_2)$	2.548	–	31	77
$[Cp^*Fe(C_5Me_4CH_2)]^+$	2.567	1.968	23.6	78
$[CpFe(C_5H_4CPh_2)]^+$	2.715	2.009	20.7	79

[a] Here and below, α is the tilt angle of the $C_{Cp}-CR^2R^3$ bond toward the metal.

Table 4. X-Ray diffraction parameters of the Ti complexes with the $\eta^6\text{-}C_5R^1_4CR^2_2$ and $\eta^7\text{-}C_5R^1_3(CR^2_2)_2$ ligands.

Compound	M–C(11) /Å	M–C(1) /Å	The angle α /deg	Ref.
$Cp^*Ti(C_5Me_4CH_2)$	2.281	2.093	35	80
ansa-$(C_5Me_4SiMe_2)Ti(C_5Me_3PhCH_2)$	2.328	2.156	–	81
$Cp^*Ti\{C_5Me_3(OCMePh)CH_2\}$	2.317	2.281	36.3	56
$(BnC_5Me_4)Ti\{C_5Me_3(CHPh)CH_2\}$	2.298,[a] 2.228	2.086, 2.072	44.0	82
$(BnC_5Me_4)Ti\{C_5Me_2Bn(CH_2)_2\}$	2.316, 2.252	2.117, 2.107	43.0	82
$Ti(C_5H_4CPh_2)_2$	2.347, 2.348	2.256, 2.264	36 (37)	54

[a] The Ti–CHPh bond length.

These distances are somewhat longer in 16-electron neutral 'primary' (η^6-6,6-H,H-fulvene) tantalum complexes. Attention is attracted by somewhat greater (and virtually equal to each other) Ru–C(11) distances in the $[Cp'Ru(C_5R_4CH_2)]^+An^-$ cationic complexes (Cp′ = Cp, Cp*; R = H, Me) and the neutral Ru complex, $[\{Cl(\mu\text{-}Cl)C_5Me_4CH_2\}Ru]_2$. In the $[(cyclo\text{-}C_8H_{12})ClRu(C_5Me_4CH_2)]$ complex, the Ru–C(11) distance is somewhat longer.

The data of Table 3 indicate that for 16-electron compounds of Group 4 metals, $[Cp^*ZrPh(C_5Me_4CH_2)]$ and $[Cp^*Hf(CH_2Ph)(C_5Me_4CH_2)]$, and for 18-electron compounds of Group 6 metals, $[(C_6H_5Me)Mo(C_5H_4CPh_2)]$ and $[(C_6H_6)W(C_5H_4CPh_2)]$, the M–C(11) distance tends to increase on going up along the group (5d → 4d). An increase in the M–C(11) and M–C(1) distances in the 18-electron complexes

of Group 8 metals is observed on passing from 4d (Ru) to 3d metals (Fe), despite the smaller covalent radius of the iron atom.

A similar pattern is observed for the 18-electron η^6-6,6-diphenylfulvene cationic complexes of Group 8 metals $[CpM(C_5H_4CPh_2)]^+$ (M = Os, Ru, Fe), neutral complexes of Group 6 metals, $(C_6H_6)W(C_5H_4CPh_2)$, (C_6H_5Me).$Mo(C_5H_4CPh_2)$, $(CO)_3Cr$-$(C_5H_4CPh_2)$, and for two η^6-6-H,6-Ph-fulvene cationic complexes, $[Cp^*M(C_5Me_4CHAr)]^+$ (M = Os, Ar = C_6F_5; M = Ru, Ar = Ph). Thus, most often, for 18-electron complexes of Group 6 and 8 metals and for 16-electron compounds of Group 4 metals, the M–C(11) distances tend to decrease in the sequences Cr > Mo > W; Fe > Ru > Os; and Zr > Hf (5d → 4d → 3d). These regularities clearly attest to the increase in the degree of interaction of the lone electron pair (LEP) of the metal atom with the carbocationic centre in cationic complexes or with the appropriate vacant orbital of the fulvene ligand in neutral complexes along these sequences. It can also be seen from the data of Table 3 that for compounds of Group 8 metals and for Cr-containing complexes, the M–C(11) distance tends to increase with enhancement of steric restrictions in the fulvene ligand (the bulk or the size of substituents), *i.e.*, on passing from primary $[Cp^*M(C_5Me_4CH_2)]^+An^-$ cations to tertiary $[CpM(C_5H_4CPh_2)]^+$ An^- cations (M = Fe, Ru, Os). The corresponding neutral complexes behave in a similar way: the M–C(11) distance increases on passing from $(CO)_3Cr(C_5H_4CH_2)$ to $(CO)_3Cr(C_5H_4CPh_2)$.

More detailed analysis of structural data, both presented in Table 3 and absent from the Table but contained in original publications shows that in all neutral and cationic η^6-$C_5R_4CH_2$ complexes of Group 4 (Zr, Hf), 6 (Mo, W) and 8 (Ru, Os) metals of the second and third transition rows, the M–C(11) bond length barely differs from the lengths of the bonds between the metal and other atoms of the cyclopentadienyl ring of the fulvene ligand. Quantum-chemical calculations (see below) indicate that in the cationic $[Cp^*M(C_5Me_4CH_2)]^+An^-$ complexes (M = Ru, Os), the positive charge is concentrated almost entirely on the metal atom. In any of these compounds, one LEP of the metal atom (Fe and, especially, Ru and Os) is involved in substantial donor–acceptor interaction with the carbocationic centre. In the doubly charged Group 8 metal complexes, donor–acceptor interaction takes place between two LEP of the metal atom (Ru and Os and, to a lesser extent, Fe) and two carbocationic centres. Cationic compounds of this type have been termed metallonium compounds.[83] Apparently, the term 'neutral metallonium complexes' is applicable to neutral fulvene or allyldiene complexes in which the M–C(11) bond length does not differ much from the bond lengths between the metal atom and the carbon atoms of the Cp or Cp^* ring and which are characterised by a substantial donor–acceptor interaction between one or two LEP of the metal atom (Ti, Zr, Hf, Ta, Mo, W, Ru and, to a lesser extent, Cr) and one or two vacant orbitals of the fulvene or allyldiene ligand (see below). Their formation from the starting cyclopentadienyl complexes is actually accompanied by an increase in the hapticity of the metal atom ($\eta^5 \rightarrow \eta^6 \rightarrow \eta^7$). The structure of these complexes is best described by resonance forms **B** (σ,η^5) and **D** (σ,σ,η^5), respectively. Recall that the formation of cationic onium complexes, ER_n^+ (E = N, P, As, O, S, I; R = H, Me), anionic ('inverted') onium complexes, ER_n^- (E = B, Al; R = H, F, Cl), or neutral 'onium' $Me_3N\cdot BH_3$ or $Et_3N\cdot BF_3$ complexes (these are also characterised by interaction of the donor LEP with an acceptor vacant orbital) of organic or organoelement compounds of non-transition elements from the corresponding precursors is also accompanied by an increase in the coordination number of the central atom by unity.

In the case of Ti complexes, it is possible to compare directly structures with the η^6-$C_5R_4^1CR_2^2$ and η^7-$C_5R_3^1(CR_2^2)_2$ ligands. The first characteristic feature that can be noted when comparing the data of Tables 3 and 4 is the shorter M–C(11) distances for Ti complexes compared to similar Zr and Hf complexes; apparently, this is a consequence of the smaller covalent radius of Ti. The Ti–CH_2 bond length in the 15-electron $Cp^*Ti(C_5Me_4CH_2)$ complex is virtually equal to or even somewhat greater than that in the 16-electron complexes with the η^7-$C_5Me_3(CH_2)_2$ and η^7-$C_5Me_3(CHPh)CH_2$ ligands. In the $Ti(C_5H_4CPh_2)_2$ complex, the Ti–CPh_2 bonds (as in the Cr, Fe, Ru and Os complexes) are longer than the Ti–CH_2 bonds in other compounds. An increase in the Ti–CH_2 distance in the *ansa*-$(C_5Me_4SiMe_2)Ti$.$(C_5Me_3PhCH_2)$ complex and the $Cp^*Ti\{C_5Me_3(OCMePh)CH_2\}$ complex containing a TiC(Me)(Ph)O fragment should also be noted.

VI. Spectral characteristics of complexes

1. Chemical shifts

The number of fulvene and allyldiene complexes studied by NMR spectroscopy is much greater, as this does not require growing the crystals. In view of the fact that preparation of suitable crystals for some compounds is either difficult or impossible, the significance of the NMR spectroscopy can hardly be overestimated. The NMR spectral data are complementary to X-ray diffraction data. These data allow one (subject to some restrictions) to elucidate the same features as X-ray diffraction data.

The degree of interaction between the metal atom and the carbocationic centre or a vacant orbital in all the cationic and neutral complexes studied can be estimated by analysing the ^{13}C NMR chemical shifts (δ) of the C(11) nuclei. Of course, certain regularities of the variations of chemical shifts can also be followed in the ^1H NMR spectra but they are usually much less vivid than the corresponding changes in the ^{13}C NMR spectra and are not considered in this review. Tables 5–7 present the chemical

Table 5. Chemical shifts $\delta(^{13}C)$ of the C(11) nuclei in the 'primary' neutral and cationic η^6-6,6-H_2-fulvene and η^7-allyldiene metal complexes.

Compound	δ (^{13}C) /ppm	Ref.
$[Cp^*Fe(C_5Me_4CH_2)]^+$	90.7	84, 85
$Cl(cb)_2Ta(C_5Me_4CH_2)$	90.7	41
$(PhCH_2)(cb)_2Ta(C_5Me_4CH_2)$	89.6	41
$[CpFe(C_5H_4CH_2)]^+$	88.6	86
$[Cp^*Ru\{C_5Me_3(CH_2)_2\}]^{2+}$	88.4	87
$(Me_3SiCH_2)(cb)_2Ta(C_5Me_4CH_2)$	88.4	41
$(BnC_5Me_4)Ti\{C_5Me_3(CHPh)CH_2\}$	81.0	82
$[Cp^*Ru(C_5Me_4CH_2)]^+$	74.6	72
$(C_5HMe_4)TiMe(C_5HMe_3CH_2)$	74.4	88
$[(\eta^5\text{-}C_9H_7)Ru(C_5Me_4CH_2)]^+$	73.9	89
$(PhC_5Me_4)Ti\{C_5Me_2Ph(CH_2)_2\}$	71.3; 73.2	82
$(4\text{-}FC_6H_4C_5Me_4)Ti\{C_5Me_2(C_6H_4F\text{-}4)(CH_2)_2\}$	71.3; 72.7	82
$Cp^*TiMe(C_5Me_4CH_2)$	73.9	55
$(CO)_3Cr(C_5H_4CH_2)$	73.4	73
$[Cp(PPh_3)_2Ru{=}C{=}CHC_5H_4Ru(C_5Me_4CH_2)]^+$	71.7	36
$Cp^*Hf(CH_2Ph)(C_5Me_4CH_2)$	71.2	59
$[Cp^*Os\{C_5Me_3(CH_2)_2\}]^{2+}$	71.1	87
$[CpRu(C_5Me_4CH_2)]^+$	69.4	89
$(BnC_5Me_4)Ti\{C_5Me_2Bn(CH_2)_2\}$	68.19; 68.29	82
$Cp^*Ti\{C_5Me_3(CH_2)_2\}$	67.7	55
$[Cp^*OsH(C_5Me_4CH_2)]^{2+}$	66.5	23
$Cp^*Zr(Ph)(C_5Me_4CH_2)$	63.5	15
$Cp^*Zr\{C_5Me_3(CH_2)_2\}$	56.5	55
$Cp^*Mo\{C_5Me_3(CH_2)_2\}$	56.2	16
$[Cp^*Os(C_5Me_4CH_2)]^+$	55.4	68
$[Cp^*Re\{C_5Me_3(CH_2)_2\}]^+$	53.8	16
$Cp^*WCl(C_5Me_4CH_2)$	51.1	90
$Cp^*W\{C_5Me_3(CH_2)_2\}$	45.9	16
$(Me_3P)_2H_2Ta\{C_5Me_3(CH_2)_2\}$	45.0	33
$[Cp^*ReH(C_5Me_4CH_2)]^+$	45.0	16
$Cp^*Re(C_5Me_4CH_2)$	36.9	16
$Cp^*WH(C_5Me_4CH_2)$	35.3	16

Table 6. Chemical shifts $\delta(^{13}C)$ of the C(11) nuclei in the 'secondary' neutral and cationic η^6-6-R-6-H-fulvene metal complexes.

Compound	$\delta(^{13}C)$ /ppm	Ref.
$[CpFe(C_5H_4CHMe)]^+$	119.5	86
$[Cp^*Ru(C_5H_4CHMe)]^+$	100.1	38
$[(CO)_3Mn(C_5H_4CHPh)]^+$	144.5	91
$[Cp^*Fe(C_5Me_4CHPh)]^+$	132.1	92, 93
$[CpFe(C_5H_4CHPh)]^+$	122.2	94
$[Cp^*Ru(C_5Me_4CHPh)]^+$	104.4	96
$[CpRu(C_5H_4CHPh)]^+$	101.2	94
$[Cp^*Os(C_5Me_4CHPh)]^+$	83.9	93
$[CpOs(C_5H_4CHPh)]^+$	79.0	94
$[Cp^*Fe(C_5Me_4CHMes)]^+$	137.5	92
$[Cp^*Ru(C_5Me_4CHMes)]^+$	134.5	93
$[Cp^*Os(C_5Me_4CHMes)]^+$	102.4	93
$[Cp^*Ru(C_5Me_4CHC_6F_5)]^+$	83.9	93
$(BnC_5Me_4)Ti\{C_5Me_3(CHPh)CH_2\}$	90.2	82
$[Cp^*Os(C_5Me_4CHC_6F_5)]^+$	55.4	93

shifts in neutral and cationic $[L_nM(\eta^6\text{-}C_5R^1_4CR^2R^3)]^{m+}$ and $[L_nM\{\eta^7\text{-}C_5Me_3(CH_2)_2\}]^{m+}$ complexes ($m = 0, 1$).

It can be seen from the data of Tables 5–7 that for most primary, secondary and tertiary cationic and neutral complexes, shielding of ^{13}C nuclei in the CR^1R^2 (CH_2, CHMe, CHPh, CHMes, CHC_6F_5, CMe_2 and CPh_2) groups increases (δ values decrease) from top to bottom along the Groups. Thus, the results obtained by NMR are correlated with X-ray diffraction data, which attest to a decrease in the M–C(11) distance and an increase in the angle α along the same sequences (*i.e.*, Ti–Zr–Hf, Cr–Mo–W and Fe–Ru–Os). Thus, both physical methods provide the same conclusion: the donor–acceptor interaction of the LEP of the metal atom with the carbocationic centre or with the vacant orbital increases on going from top to bottom along the Groups of elements.

The effect of the metal atom [an increase in the shielding (a decrease in the δ values) of the C(11) carbon nuclei from top to bottom along the Group] is often manifested in the fact that the δ values for elements of different Groups but of the same Period are fairly similar. The effect of the metal often counterbalances not only the influence of the charge (see below) but also the degree of substitution at C(11).

The similarity of the δ values for Ru and, especially, Os cationic complexes to those for neutral fulvene complexes with a similar structure (Ti, Zr, Mo, W, *etc.*), apparently, indirectly confirms the conclusion based on extended Hückel (EHT) calculations,[97] according to which the major positive charge in these complexes is concentrated on the metal atom rather than on the CR^1R^2 group. However, it should be noted that the comparison of the carbon δ values for the CR^1R^2 groups is more or less legitimate only in the case of isostructural compounds or compounds with similar structures, because in the general case, the influence of other ligands (ligand environment) cannot be neglected.

Table 7. Chemical shifts $\delta(^{13}C)$ of the C(11) nuclei in the 'tertiary' neutral and cationic η^6-6,6-R_2-fulvene metal complexes.

Compound	$\delta(^{13}C)$ /ppm	Ref.
$[CpFe(C_5H_4CMe_2)]^+$	158.6	86
$[(CO)_3Mn(C_5H_4CPh_2)]^+$	201.0	91
$[CpFe(C_5H_4CPh_2)]^+$	171.6	94
$[CpRu(C_5H_4CPh_2)]^+$	139.6	94
$(CO)Ti(C_5H_4CPh_2)_2$	132.1	54
$(CO)_3Cr(C_5H_4CPh_2)$	126.0	77
$(C_6H_6)Mo(C_5H_4CPh_2)$	103.0	54
$[CpOs(C_5H_4CPh_2)]^+$	95.7	94

Table 8. Chemical shifts $\delta(^{13}C)$ of the C(11) nuclei in the complexes $[(\eta^5\text{-}Cp^*)M\{\eta^7\text{-}C_5Me_3(CH_2)_2\}]^{n+}$ ($n = 0, 1, 2$).

M	$\delta(^{13}C)$ /ppm	Charge	Ref.
Mo	56.2	0	16
Ru	88.4	2+	87
W	45.9	0	16
Re	53.8	1+	16
Os	71.1	2+	87

It can be seen from Table 5 that in the case of 18-electron complexes of Group 6, 7 and 8 metals with η^7-dimethylenecyclopentadienyl ligands, the δ values decrease with a decrease in the overall charge of the complex, *i.e.*, in the series: doubly charged > singly charged > neutral. This can be seen in Table 8.

Therefore, for 18-electron complexes of Group 6, 7 and 8 metals (W, Re, Ru, Os), deshielding (an increase in the δ values) is typically observed on passing from η^6-monomethylene (neutral or singly charged) complexes to η^7-dimethylene compounds (singly or doubly charged). However, for neutral 16-electron Ti complexes, no regularities in the variation of chemical shifts on passing from η^6-monomethylene to η^7-dimethylene compounds, nor changes in the X-ray diffraction characteristics can be revealed.

It should be noted that for primary CH_2 derivatives, it is easier to elucidate regular features in the variation of the δ values depending on the nature of the metal atom, the charge or other electronic effects than for secondary CHR^1 and tertiary CR^1R^2 complexes due to the spatial and electronic effects of the substituents R^1 and R^2. The observed decrease in the δ values following the migration from top to bottom along the Groups appears to be quite natural, because the diffuseness of atomic orbitals of transition metals tends to increase from top to bottom along the Subgroups. On the basis of EHT calculations[95] for the cationic complexes of Group 8 metals, $[Cp^*M(C_5Me_4CH_2)]^+$ (M = Fe, Ru, Os), it was shown that the M–C(11) bond order increases ($0.01 < 0.16 < 0.22$) in the sequence Fe $\ll$ Ru < Os. It is common knowledge that the bond length increases following a decrease in the bond order. The shielding constant σ (or its paramagnetic component σ_p, which makes the greatest contribution to this constant), is a function of a charge density and the M–C(11) bond order. This clarifies the observed decrease in the δ values of the C(11) nuclei for the $[Cp^*M(C_5Me_4CH_2)]^+$ cations in the sequence Fe > Ru > Os. Apparently, similar regularities are also typical of cationic and neutral $\eta^6\text{-}C_5R^1_4CR^2R^3$ complexes formed by metals of other Groups.

2. The spin–spin coupling constants $^1J_{CH}$ for η^6 and η^7 neutral and cationic complexes

Apart from the data on chemical shifts, the spin–spin coupling constants ($^1J_{CH}$) of the carbon atom of the CHR groups are often used to determine the structures of cationic and neutral fulvene complexes. Unfortunately, no systematic research into the spin–spin coupling constants of isostructural cationic and neutral η^6-complexes of Group 4–8 metals has been carried out. A fairly large number of scattered $^1J_{CH}$ values have been reported in the literature. They are summarised in Table 9.

It can be seen that the spin–spin coupling constants ($^1J_{CH}$) for the CH_2 group in the series of the primary $[Cp^*M(C_5Me_4CH_2)]^+$ (M = Fe, Ru, Os) and for the CHR group in the series of the secondary $[Cp^*Os(C_5Me_4CHC_6F_5)]^+$ and $[CpM(C_5H_4CHPh)]^+$ (M = Ru, Os) cationic nonmethylated complexes of Group 8 metals and their neutral analogues barely depend on the nature of the metal.

Meanwhile, the coupling constants of the studied doubly charged dimethylene complexes, $[Cp^*M\{C_5Me_3(CH_2)_2\}]^{2+}$ (M = Ru, Os), and their neutral analogues (Table 10) show that these values increase somewhat on passing from neutral complexes to doubly charged ones. However, generally, the presented

Table 9. Spin–spin coupling constants ($^1J_{CH}$) for the C(11) atom.

Compound	$^1J_{CH}$ /Hz	Ref.
$C_6F_5(CO)_2Re(C_5Me_4CH_2)$	162.0	34
$Cp^*Re(C_5Me_4CH_2)$	157.7	16
$Cp^*WH(C_5Me_4CH_2)$	151.3	16
$Cp^*ZrPh(C_5Me_4CH_2)$	144.8	15
$Cp^*Hf(CH_2Ph)(C_5Me_4CH_2)$	142.0	59
$[Cp^*Fe(C_5Me_4CH_2)]^+$	164.7	84, 85
$[Cp^*Ru(C_5Me_4CH_2)]^+$	164.2	72
$[Cp^*Os(C_5Me_4CH_2)]^+$	166.0	68
$[(\eta^5\text{-}C_9H_7)Ru(C_5Me_4CH_2)]^+$	167.2	89
$[CpRu(C_5Me_4CH_2)]^+$	167.0	89
$[CpRu(C_5H_4CHPh)]^+$	163.2	94
$[CpOs(C_5H_4CHPh)]^+$	164.9	94
$[Cp^*Os(C_5Me_4CHC_6F_5)]^+$	167.9	93
$[Cp^*Ru(C_5Me_4CHMe)]^+$	163.6	93
$Cp^*ReH(C_5Me_4CH_2)$	162.4	16
$[CpFe(C_5H_4CH_2)]^+$	165	86
$[CpFe(C_5H_4CHMe)]^+$	165	86
$[CpFe(C_5H_4CHPr^i)]^+$	163	86
$[CpFe(C_5H_4CHBu^t)]^+$	158	86
$[CpFe(C_5H_4CHPh)]^+$	160	86

Table 10. Spin–spin coupling constants ($^1J_{CH}$) of the doubly charged complexes and their neutral analogues.

Compound	$^1J_{CH}$ /Hz	Ref.
$Cp^*Ti\{C_5Me_3(CH_2)_2\}$	160.0	55
$Cp^*Zr\{C_5Me_3(CH_2)_2\}$	148.0	55
$Cp^*Mo\{C_5Me_3(CH_2)_2\}$	154.0	16
$Cp^*W\{C_5Me_3(CH_2)_2\}$	152.0	16
$[Cp^*Ru\{C_5Me_3(CH_2)_2\}]^{2+}$	171.2	87
$[Cp^*Os\{C_5Me_3(CH_2)_2\}]^{2+}$	172.3	87

data indicate that the spin–spin coupling constants for cationic and neutral compounds, unlike the tilt angles of the $C_{Cp}-CHR$ bond relative to the metal (α), the $M-C_\alpha R$ distances, or the chemical shifts δ, are little dependent on the degree of interaction of the metal with the carbocationic centre or a vacant orbital.

VII. Quantum-chemical description of complexes

The electronic structure of the α-ferrocenylmethyl cation (the cationic fulvene complex), $[CpFe(C_5H_4CH_2)]^+$, was first calculated by the EHT method with charge self-consistence.[96] Gleiter and Seeger[96] have predicted the most typical feature of the structure of complexes of this type, namely, distortion of the planarity of the fulvene ligand, which is manifested as a deviation of the carbon atom of the CH_2 group toward the metal atom (the angle α) through 40°. The researchers also showed that the charge on the Fe atom in this monocation is 0.5, while the rest of the charge (0.5) is delocalised over all carbon atoms of the ligands. Subsequently, it has been shown that neutral and cationic complexes, $[L_nM(C_5H_4CR^1R^2)]^{m+}$ [$L_nM = (CO)_3Cr$, $m = 0$; L_nM = CpFe, $m = 1$] with a fulvene ligand have a similar structure.[97] In a more recent study,[95] EHT calculations for a number of monocations, $[Cp'M(C_5R_4CH_2)]^+$ (M = Fe, Ru, Os; Cp′ = Cp, Cp^*; R = H, Me), were used to calculate the angles α, the energy gaps ($\Delta E = E_{LUMO} - E_{HOMO}$), the charges on the metal atoms (Q) and the CH_2 groups (q), and Mulliken bond orders (Table 11).

It is of interest that the minimum total energy (*i.e.*, the most effective $Mo-CH_2$ interaction) in the neutral fulvene complex $(C_6H_6)Mo(\eta^6\text{-}C_5H_4CH_2)$ corresponds to the angle $\alpha = 35°$ (see Ref. 54), which is well correlated with the experimental values for the angle α (37–39°) found for $(C_6H_5R^1)M(\eta^6\text{-}C_5H_4CR^2_2)$ (M = Mo, W; R^1 = H, Me; R^2 = Me, Ph). Similar calculations for the neutral fulvene complex, $(CO)_3Cr(\eta^6\text{-}C_5H_4CH_2)$, give $\alpha = 21°$ (according to X-ray diffraction data, the angle α in this complex equals 35°).[75]

Table 11. Energy and charge characteristics of the $[(C_5R_5)M(C_5R_4CH_2)]^+$ cations according to EHT calculations.[95]

R	M	α /deg	ΔE /eV	Q(M)	q(CH_2)
H	Fe	5.0	1.28	0.25	0.36
H	Ru	41.5	1.68	1.48	0.04
H	Os	35.0	0.85	0.85	0.12
Me	Fe	26.0	1.33	0.10	0.31
Me	Ru	40.3	2.53	1.35	−0.13
Me	Os	41.8	3.32	0.84	−0.08

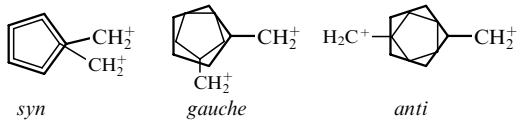
The molecular orbital energies for a number of neutral Ti complexes, $(\eta^5\text{-}Cp^*)TiMe(\eta^6\text{-}C_5Me_4CH_2)$, $(\eta^5\text{-}C_5HMe_4).TiMe(\eta^6\text{-}C_5HMe_3CH_2)$, $(\eta^5\text{-}Cp^*)Ti(\eta^6\text{-}C_5Me_4CH_2)$ and $(\eta^5\text{-}Cp^*)TiMe\{\eta^7\text{-}C_5Me_3(CH_2)_2\}$ have been calculated by the EHT method.[98] For the cationic complexes, $[(\eta^5\text{-}Cp)Os(\eta^6\text{-}C_5H_4CH_2)]^+$ and $[(\eta^5\text{-}Cp)Os\{C_5Me_3(CH_2)_2\text{-}\eta^7\}]^{2+}$, the angles α (40 and 35°, respectively) calculated by EHT[87] were compared with the values obtained experimentally for the $[(\eta^5\text{-}Cp^*)Os(\eta^6\text{-}C_5Me_4CH_2)]^+$ complex ($\alpha = 41.8°$).[95] The calculated $Os-CH_2$ bond length in the $[CpOs\{C_5Me_3(CH_2)_2\}]^{2+}$ complex is 2.33 Å.[99]

The M–C(11) and M–C(1) bond lengths and the tilt angles α in 18-electron singly and doubly charged cationic $\eta^6\text{-}C_5Me_4CH_2$ and $\eta^7\text{-}C_5Me_3(CH_2)_2$ complexes of Group 8 metals calculated using the density functional theory (DFT)[100] are listed in Table 12. It can be seen that the calculated M–C(11) bond lengths tend to increase on passing from η^6-complexes to η^7-complexes. This is indicative of some decrease in the metal–carbocation centre interaction in doubly charged complexes with respect to similar singly charged ones. Comparison of the data of Tables 3 (X-ray diffraction data) and 12 (DFT calculations) shows that the structures of the complexes in the crystal and in the gas phase are somewhat different. A more detailed consideration of the data published in original publications[100,101] permits the conclusion that transition from the gas phase to a condensed (crystalline) state induces the most pronounced change in the M–C(11) bond length, while the lengths of the metal bonds with other atoms of the ligand change insignificantly. Similar conclusions were drawn in another study[70] in which X-ray diffraction analysis and DFT calculations for the $[CpRu(C_5H_4CH_2)]^+$ cationic complex have been performed. Doubly and especially triply charged complexes (see below) also tend to undergo structural changes on passing from the gas phase into a condensed state (solution).

Table 12. Calculated geometric parameters in the cationic complexes of Group 8 metals with the $\eta^6\text{-}C_5Me_4CH_2$ and $\eta^7\text{-}C_5Me_3(CH_2)_2$ ligands.[23,100]

Compound	M–C(11) /Å	M–C(1) /Å	The angle α /deg
$[Cp^*Fe(C_5Me_4CH_2)]^+$	2.324	2.020	34.0
$[Cp^*Fe\{C_5Me_3(CH_2)_2\}]^{2+}$	2.504; 2.511	2.064; 2.063	25.03; 24.58
$[Cp^*Ru(C_5Me_4CH_2)]^+$	2.410	2.156	32.4
$[Cp^*Ru\{C_5Me_3(CH_2)_2\}]^{2+}$	2.456; 2.456	2.200; 2.192	24.62; 24.30
$[Ru(C_5Me_4CH_2)_2)]^{2+}$	2.586; 2.547	2.194; 2.187	25.91; 27.87
$[Cp^*Os(C_5Me_4CH_2)]^+$	2.341	2.158	36.9
$[Cp^*Os\{C_5Me_3(CH_2)_2\}]^{2+}$	2.401; 2.395	2.195; 2.182	31.24; 31.11
$[Os(C_5Me_4CH_2)_2]^{2+}$	2.441; 2.441	2.180; 2.180	32.5; 32.5

The angles α and other geometric parameters, charge characteristics and the rotation energies for the *syn*, *gauche*- and *anti*-conformers of the $[M(C_5Me_4CH_2)_2]^{2+}$ cationic complexes (M = Fe, Ru, Os) have been reported.[99, 100] The EHT calculations showed [99] that of the three possible conformers (*syn, gauche* and *anti*), *gauche*-conformers are thermodynamically most stable in the gas phase and in solutions.



syn *gauche* *anti*

The calculated α values for the *gauche*-conformers of the Fe, Ru and Os complexes are 30, 40 and 40° (EHT data [99]), and the M–C(11) bond lengths are 2.43, 2.20 and 2.22 Å, respectively.

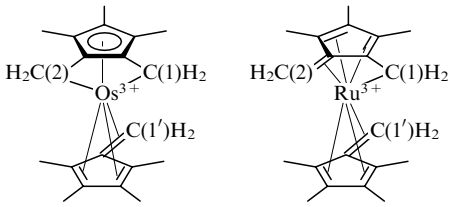
In the *gauche*-conformer, the overlap energy of the corresponding orbitals of the metal atom and the ligands exceeds the Coulomb repulsion energy (which is the lowest in the *anti*-conformer). This is not surprising, because, according to the same calculations, the CH_2 groups bear virtually no positive charge, the charge being concentrated almost entirely on the metal atom. The results of EHT calculations for the structures of doubly charged complexes (predominance of *gauche*-conformers) were confirmed by ^{1}H NMR spectra.[99]

The higher thermodynamic stability of the *gauche*-conformers for the ruthenium complexes was confirmed by subsequent calculations (DFT *ab initio*).[100] Meanwhile, for the osmium analogue, the energies of the *anti*- and *gauche*-conformers are equal.[23] Density functional theory calculations indicate higher thermodynamic stability of 1,2-dimethylene complexes compared to 1,1′-dimethylene complexes.[100] It follows from the results of the same calculations (see Table 12) that in the $[Cp^*Ru\{C_5Me_3(CH_2)_2\}]^{2+}$ and $[Os(C_5Me_4CH_2)_2]^{2+}$ complexes, the distances from the metal atom to both carbocation centres are identical, while in $[Cp^*Os\{C_5Me_3(CH_2)_2\}]^{2+}$ and $[Ru(C_5Me_4CH_2)_2]^{2+}$, these distances are different. In the condensed state (in solution), the interaction of the metal atom with both carbocation centres is the same in any of the four complexes, as indicated by the ^{13}C NMR data [the presence of only one signal from C(11) nuclei]. Thus, in this case, too, the structures of the cationic species in the gas phase and in solution are somewhat different.

VIII. Trimethylene complexes

The representation of η⁶-fulvene and η⁷-allyldiene complexes as a 'specific' resonance hybrid of structures **A** ↔ **B** or **C** ↔ **D** (see Section II) is especially significant for describing the structures of complexes containing three methylene groups in the molecule. It is noteworthy that the whole set of chemical, structural and calculated data available until recently did not allow one to distinguish clearly and unambiguously the structures of mono- and dimethylene complexes. Apparently, it should be stated that forms **B** (σ,η⁵) and **D** (σ,σ,η⁵) are characterised by more substantial donor–acceptor interaction between the metal LEP and the vacant orbitals of carbon atom(s) and, hence, by shorter M–C(11) bonds and greater tilt angles of the C(1)–C(11) bond toward the metal atom than forms **A** and **C**. These shorter bonds can be called metallonium.[101]

The complexes containing three methylene groups in the molecule have been prepared by oxidation of decamethylmetallocenes or monocations **8** (M = Ru, Os) with molecular oxygen in a CF_3SO_3H solution.[20, 39] Their structure has been described in the literature.[22, 101] The Group 8 metal atoms (Fe, Ru, Os) are known to contain three lone electron pairs in three non-bonding orbitals. The LEP are able to interact with three vacant orbitals of the carbon atoms of three carbocation centres or, in other words, they can stabilise the compounds containing three CH_2 groups. According to calculations, in these compounds, the major portion of the positive charge is concentrated on the metal atom.[22, 101] However, it should be noted that, as shown by DFT calculations, in the $[Cp^*M\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{2+}$ and $[M(\eta^6\text{-}C_5Me_4CH_2)_2]^{2+}$ dimethylene complexes (M = Ru, Os), the lengths of both M–CH_2 bonds in the gas phase are either equal or do not differ much (see Table 12).[100] However, in trimethylene osmium complex **46**, the Os–C(1′)H_2 bond length is much longer (2.768 Å) than the other two lengths, Os–C(1)H_2 and Os–C(2)H_2 (2.431 and 2.435 Å , respectively) and the angles α are 27.2, 26.2 and 20.4°, respectively, *i.e.*, this complex can be described by structure **D**(σ,σ,η⁵),**A**(η²,η⁴). For the Ru analogue **47**, the Ru–C(1)H_2 bond is markedly shorter (2.442 Å) than the Ru–C(2)H_2 and Ru–C(1′)H_2 bonds (2.925 and 2.950 Å, respectively) and the angles α are 20.8, 13.4 and 11.7°, respectively, *i.e.*, the trication has structure **C**′(σ,η²,η⁴),**A**(η²,η⁴). In other words, osmium complex **46** is characterised by the presence of two metallonium bonds and one fulvene fragment, and the ruthenium analogue **47** has only one metallonium bond and two fulvene fragments. The spatial structure of both complexes is similar to that for the *gauche*-conformers of the corresponding complexes **13**.



46 (**D**,**A**) **47** (**C**′,**A**)

Thus, according to DFT calculations, the trimethylene ruthenium and osmium complexes have different structures in the gas phase, the Os compound having two short bonds and the Ru analogue containing one short bond. This circumstance indicates that the interaction between the metal atom and the carbocation centres is enhanced from top to bottom along the Group. This trend has been noted above for mono- (**8**) and dimethylene (**12**) complexes; however, in the case of complexes **46** and **47**, it is most pronounced.

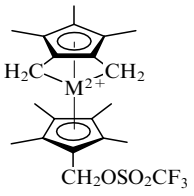
The presence of three methylene groups in the molecules of complexes **46** and **47** was proved unambiguously by ^{1}H and ^{13}C NMR spectroscopy (Table 13).[20, 22, 39, 101] According to NMR

Table 13. ^{1}H and ^{13}C NMR spectral data for mono-, di- and trimethylene complexes of ruthenium and osmium.

Compound	δ(^{1}H) /ppm	$^2J_{HH}$ /Hz	δ(^{13}C) /ppm	$^1J_{CH}$ /Hz
$[Cp^*Ru(\eta^6\text{-}C_5Me_4CH_2)]^+$ (**8a**)	4.75s		74.6t	164–167
$[Cp^*Os(\eta^6\text{-}C_5Me_4CH_2)]^+$ (**8b**)	4.42s		55.4	
$[Cp^*Ru\{\eta^7\text{-}C_5Me_3.$	4.82d	1.9	88.4t	170–172
$.(CH_2)_2\text{-}1,2\}]^{2+}$ (**12a**)	5.27d			
$[Cp^*Os\{\eta^7\text{-}C_5Me_3.$	4.90d	2.4	71.1	
$.(CH_2)_2\text{-}1,2\}]^{2+}$ (**12b**)	5.52d			
$[(\eta^6\text{-}C_5Me_4CH_2)Ru.$	5.03d	1.9	88.6t	170–172
$.\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{3+}$ (**48a**)	(2H)		(2C)	
	5.51d	1.9	65.7t	157
	(2H)		(1C)	
	5.50s			
	(2H)			
$[(\eta^6\text{-}C_5Me_4CH_2)Os.$	5.04d	2.3	71.3	
$.\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{3+}$ (**48b**)	(2H)		(2C)	
	5.66d	2.3	65.8	
	(2H)		(1C)	
	5.49s			
	(2H)			

Note. s is singlet, d is doublet, t is triplet.

spectral data, the structures of Ru- and Os-containing derivatives are similar. It should be noted that the DFT calculations also confirm the existence of three methylene groups in these compounds. The enthalpies of formation (ΔH) of complex **8a** from Cp^*_2Ru, complex **12a** from **8a** and complex **47** from **12a** in the gas phase are -232.2, -124.5 and -13.6 kcal mol^{-1}, respectively,[101] *i.e.*, complex **47** is thermodynamically stable, although its stability is an order of magnitude lower than that for complex **12a**. Thus, according to these calculations, there is a certain probability that trimethylene complexes would be formed in solutions. Indeed, upon the reaction of metallocenes or monomethylene complexes with oxygen in a solution of a strong acid (superacid), three methyl groups are oxidised to give three carbocation centres. However, the ways of stabilisation and, correspondingly, the forms of existence of these unusual species in solution may differ from those of the previously studied analogues **8** and **12**, which have a smaller charge. Thus the ^{1}H and ^{13}C NMR spectra of trimethylene compounds exhibit a number of specific features, which call for discussion. Table 13 presents the chemical shifts (δ) and the spin–spin coupling constants observed in the ^{1}H and ^{13}C NMR spectra of compounds $[Cp^*M(\eta^6\text{-}C_5Me_4CH_2)]^+$ (**8a**,**b**), $[Cp^*M\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{2+}$ (**12a**,**b**) and $[(\eta^6\text{-}C_5Me_4CH_2)M\{\eta^7\text{-}C_5Me_3(CH_2)_2\text{-}1,2\}]^{3+}$ (**48a**,**b**) formed in solution.



48a,**b**

M = Ru (**a**), Os (**b**).

The ^{1}H NMR spectra of trimethylene cations **48a**,**b** exhibit two doublets and one singlet (the ratio of integral intensities is 1 : 1 : 1). Thus, the species obtained in solution really have three methylene groups and a plane of symmetry[20,39] that passes through one of these groups half way between the other two. Presumably, the structure of molecules in solution is analogous, to an extent, to the structure in the gas phase. Meanwhile, the data of the ^{13}C NMR spectra clearly indicate that in Ru- and Os-containing molecules, the metal atom interacts differently with the three carbocation centres and that in both species, the interaction with two of these centres markedly differs from the interaction with the third one. Thus, the structure of the osmium complex in solution does not contradict its structure in the gas phase (according to DFT calculations), whereas the structures of the Ru analogue in solution and in the gas phase are different, *i.e.*, transition from the gas phase to a solution induces more pronounced structural changes in the case of less stable Ru species.

It follows from the data of Table 13 that on passing from compounds **8a**,**b** to **12a**,**b**, the resonance carbon signals substantially shift downfield and the spin–spin coupling constants slightly decrease. Conversely, in the ^{13}C NMR spectra of complexes **48a**,**b**, the δ values and spin–spin coupling constants of the signals for the CH_2 groups of the η^7-$C_5Me_3(CH_2)_2$-1,2 ligand virtually coincide with those for complexes **12a**,**b**. However, the signals for the CH_2 groups of the η^6-$C_5Me_4CH_2$ ligand are shifted upfield, this signal for ruthenium complex **48a** being located in even higher field than in compound **8a**. The coupling constants of the CH_2 group in the trimethylene complex also decrease somewhat with respect to those observed for the monomethylene complex. In addition, the δ values for the carbon nuclei of the CH_2 groups of the η^7-$C_5Me_3(CH_2)_2$-1,2 ligand in complexes **12** and **48** decrease substantially on passing from Ru to Os (higher shielding), whereas the signals for the CH_2 groups of η^6-$C_5Me_4CH_2$ in complexes **48a**,**b** almost coincide (*i.e.*, the chemical shift does not depend on the nature of the metal).

Of course, it cannot be stated with full confidence that on passing from dimethylene complexes to trimethylene complexes, the NMR spectra should show the same trends (a decrease in shielding) as those observed (as has been shown above for numerous examples) on passing from neutral fulvene complexes to singly and doubly charged ones. In the general case, there is no direct correlation between the charge on the carbon atom and the ^{13}C NMR chemical shift of this atom; however, for singly, doubly and triply charged compounds (almost isostructural or with similar structures), the regularities we found in the variation of spectral characteristics allow one to ascribe structures **46** and **47** to the trimethylene species in the gas phase.

The stabilisation of the trimethylene complexes formed in solutions differs from that for complexes **8a**,**b** and **12a**,**b**. Apparently, complexes **8** and **12** in solutions of acids tend to form solvent-separated ion pairs and the nature of the anion (counterion) virtually does not influence the structure of the cations. For the triply charged trimethylene complexes, the interion (cation–anion) interaction is so pronounced that it seems to result in contact ion pairs or, more likely, a covalent bond. According to X-ray diffraction data (see above), the monomethylene cations **8a**,**b** and the BPh_4^- anions[68,72] are arranged in the crystal lattice fairly far from each other. The mono- (**8a**,**b**) and dimethylene cations (**12a**,**b** and **13a**,**b**) occur in solutions of CF_3SO_3H as kinetically independent species with the $CF_3SO_3^-$ anion, and trimethylene species **46**, **47** are partially esterified (at one methylene group) under these conditions to give esters **48a**,**b**.[22] In the ^{13}C NMR spectra, the signals of the CH_2 groups linked covalently to the O_3SCF_3 group are manifested as triplets (δ 65.7 and 65.8, J 157 Hz), while the ^{1}H NMR signals (δ 5.50 and 5.49) are singlets. The observed spin–spin coupling constants and chemical shifts are typical of CH_2 groups linked to two electron-withdrawing substituents, $[Ru]^{2+}$ and $CF_3SO_3^-$, which implies structure **48a**,**b**.[102]

IX. Conclusion

The data presented in this review show that the chemistry of neutral and cationic tetramethylfulvene and trimethylallyldiene complexes of transition metals is of substantial interest. These complexes have been obtained for almost any of Group 4–10 transition metals; they contain a non-planar six- (η^6) or seven-electron (η^7) ligand with a substantial deviation of one or two carbon atoms from the plane of the Cp ring toward the metal atom. This is indicative of the interaction of the LEP of the metal atom with the carbocation centre in cationic complexes or with the corresponding vacant orbital of the fulvene ligand in neutral complexes. The degree of this interaction increases from top to bottom along the Subgroups of the Periodic Table. These structural features (relatively low symmetry) of tetramethylfulvene and trimethylallyldiene complexes determine their properties and distinguish them from η^6-arene or η^7-cycloheptatrienyl complexes with a higher symmetry. The tetramethylfulvene and trimethylallyldiene transition metal complexes are characterised by (i) general methods for the synthesis (mainly, from η^5-pentamethylcyclopentadienyl precursors); (ii) essential similarity in the chemical behaviour [many reactions involving these complexes occur *via* the formation of odd-electron (17- and 19-electron) intermediates]; (iii) rupture of the M–C(11) bond on treatment with nucleophiles (more rarely, electrophiles) to give η^5-derivatives with the C(11)–Nu bond; (iv) similarity of the structural and spectral characteristics, which often do not depend on whether or not the complex is charged. Apparently, these properties allow one to classify tetramethylfulvene and trimethylallyldiene complexes, to a certain approximation, as a separate class of chemical compounds.

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