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The η^5-Indenyl and η^5-Fluorenyl Complexes of Transition Metals and Their Comparison with the η^5-Cyclopentadienyl Compounds

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Data on the synthesis, structure, and reactivity of the η^5-indenyl and η^5-fluorenyl complexes of transition metals are examined and discussed. A comparison with the η^5-cyclopentadienyl analogues is made.
The bibliography includes 187 references.

CONTENTS

I. Introduction 967
II. Methods of synthesis and properties of the η^5-indenyl and η^5-fluorenyl complexes of transition metals 967
III. Conclusion 977

I. INTRODUCTION

The first η^5-indenyl complex (di-indenyliron)[1] was obtained almost simultaneously with ferrocene,[2] while difluorenylzirconium dichloride—the first compound with the η^5-fluorenyl ligand—was synthesised in 1965.[3] Nevertheless the chemistry of the indenyl and fluorenyl complexes of transitional metals has so far been little investigated, in contrast to the cyclopentadienyl complexes. However, the presence of a five-membered ring coordinated to the metal and of non-coordinated six-membered rings in the η^5-indenyl and η^5-fluorenyl complexes makes them of interest for the study of the influence of coordination to the metal on the distribution of π-electron density throughout the condensed system of the ligand. Indene and fluorene complexes are of interest also because different types of coordination to the transition metal (η^6, η^5, η^3, and η^1) are possible in such compounds and metallotropic rearrangments, widely investigated at the present time, are therefore characteristic of them. The η^5-indenyl and η^5-fluorenyl complexes of transition metals are more reactive than their cyclo-pentadienyl analogues in ligand exchange reactions because of their tendency to metallotropic rearrangements. The ease of ligand exchange in these complexes can be used in the synthesis of new organometallic compounds and also of catalysts of certain chemical processes.

II. METHODS OF SYNTHESIS AND PROPERTIES OF THE η^5-INDENYL AND η^5-FLUORENYL COMPLEXES OF TRANSITION METALS

1. Methods of Synthesis

The methods of synthesis of the η^5-indenyl and η^5-fluorenyl complexes of transition metals are usually analogous, with slight modifications, to those used in the synthesis of the η^5-cyclopentadienyl derivatives. The differences in the methods concern the reaction temperature and time, which is frequently associated with the lower stability of the η^5-indenyl and η^5-fluorenyl compounds.

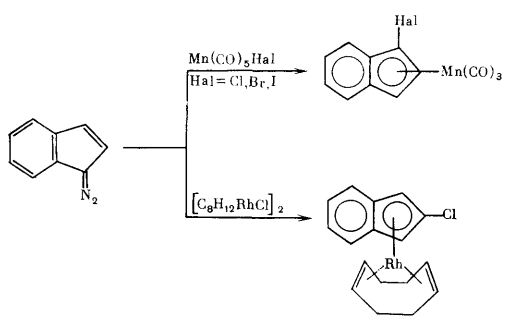
The commonest method of synthesis of these compounds involves the interaction of indenyl and fluorenyl derivatives of alkali metals, more rarely organotin compounds or Grignard reagents, with transition metal salts, carbonyls, or halogen-containing complexes:[3-44]

$$3C_9H_7K + MCl_4 \rightarrow (C_9H_7)_3MCl + 3KCl,\ M = U,\ Th;$$
$$C_9H_7K + W(CO)_6 \rightarrow [C_9H_7W(CO)_3]^{\ominus}K^{\oplus} + 3CO;$$
$$C_{13}H_9Li + [CrCl(NO)(CO)_2] \rightarrow C_{13}H_9Cr(CO)_2NO + LiCl.$$

In order to obtain mixed indenyl sandwich compounds, the transition metal salt is acted upon by alkali metal derivatives of indene and a second ligand:[45-47]

$$TiCl_4 + C_9H_7Na + C_8H_8K_2 \rightarrow C_9H_7TiC_8H_8.$$

A novel method of synthesis of the η^5-indenyl complexes with a halogen substituent in the π-ligand is based on the interaction of diazoindene with halogen-containing transition metal derivatives:[48,49]



One of the most general methods of synthesis of new compounds in organo-metallic chemistry involves the exchange of the carbonyl or halogen groups in metal complexes for *n*- and π-donor ligands (phosphines, olefins, acetylenes, etc.). This method is used widely also for the synthesis of η^5-indenyl and η^5-fluorenyl complexes which have not been described hitherto:[35,38,50-76]:

$$C_9H_7W(CO)_3(CH_3) + C_2H_4 \rightarrow C_9H_7W(CO)_2(CH_3)(C_2H_4) + CO,$$
$$(C_{13}H_9)_2MCl_2 + Na(S_2CNR_2) \rightarrow (C_{13}H_9)_2M(S_2CNR_2)Cl + NaCl,$$
$$M = Ti,\ Zr;\ R = CH_3,\ C_2H_5,\ iso\text{-}C_3H_7.$$

Polymetallic heteronuclear clusters containing the η^5-indenyl ligand have been obtained from the highly reactive η^5-indenylrhodium complexes.[77–83]

2. The Nature of the Metal–π–ligand Bond in the η^5-Indenyl and η^5-Fluorenyl Complexes. The Stability of the Complexes

In the study of the properties of the η^5-indenyl and η^5-fluorenyl complexes of transition metals, it has been frequently noted that these complexes are less stable than their η-cyclopentadienyl analogues.[26,27,32,84–86] According to modern ideas, the π electrons of the ligand are mainly involved in the bond between the π-ligand and the metal.[87] Consequently, the strength of the metal–π-ligand bond should be influenced by substituents in the π-ligand which alter its π-electron density. Theoretical calculations[88] for the indenyl and fluorenyl anions (in alkali metal salts) have shown that the six-membered aromatic rings participate, together with the five-membered ring, in the distribution of π-electron density (including the negative charge) in these anions. Presumably, in the η^5-indenyl and η^5-fluorenyl complexes of transition metals, in which only the five-membered ring is linked directly to the metal, there is also interaction of the π-electron clouds of the six- and five-membered rings, which can weaken the donor–acceptor interaction between the five-membered ring and the transition metal. Indeed, the study of titanium and zirconium complexes has shown that the strength of the metal–π-ligand bond is sensitive to the donor and acceptor characteristics of the substituents in the π-ligand. Thus the resistance of compounds of the type L_2MCl_2 (M = Ti or Zr; L = $C_5H_4CH_3$, C_9H_7, or C_9H_{11}) to decomposition and hydrolysis is correlated with the nature of the substituents in the five-membered ring: the η^5-indenyl derivatives are less stable while the η^5-tetrahydroindenyl derivatives are more stable than the unsubstituted η^5-cyclopentadienyl analogue. This has been attributed[84] to the fact that the six-membered ring in the η^5-indenyl complexes behaves as an electron-accepting substituent in relation to the five-membered ring bound to the metal, which leads to a lower stability of these compounds in polar organic solvents. On the other hand, the saturated cyclohexane ring, which is an electron-donating substituent, increases the stability of the η^5-tetrahydroindenyl complexes of titanium and zirconium. A lower stability of the indenyl complexes compared with the cyclopentadienyl complexes has been established for compounds of Group VII metals. Thus the interaction of η^5-$C_9H_7Re(CO)_3$ with nitrogen-containing bases (pyridine or urotropine) entails the cleavage of the metal–π-ligand bond and the formation of dinuclear complexes with bridging hydroxy- or alkoxy-groups.[89] On the other hand, the reactions of η^5-$C_5H_5Re(CO)_3$ with these bases lead only to substitution of the CO group by the *n*-donor ligand.[90]

Further weakening of the bond between the π-ligand and the metal in the η^5-fluorenyl complexes compared with the indenyl complexes is due to the increase in the number of benzene rings condensed with the five-membered ring, such rings withdrawing the π-electron density from the cyclopentadienyl ring. Indeed, difluorenyl derivatives have not been obtained for metals of the iron triad, which form the most stable dicyclopentadienyl complexes.[32]

Calculations of the force constants for the C≡O bonds in the complexes $C_5H_5Mn(CO)_3$, $C_9H_7Mn(CO)_3$, and $C_{13}H_9Mn(CO)_3$ [26] failed to indicate appreciable changes in these quantities on passing from η^5-$C_5H_5Mn(CO)_3$ to η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_{13}H_9Mn(CO)_3$, which indicates the retention of the same effective charge on the metal atom in all three complexes. The authors suggested that the decrease in the strength of the bond between the five-membered ring and the metal after its successive condensation with benzene rings is a consequence of the weakening of both donor–acceptor and dative metal–ring bonds.

A comparative quantitative estimate of the strength of the π-ligand–metal bond in the indenyl, fluorenyl, and cyclopentadienyl complexes was first made in relation to the carbonyl derivatives $LM(CO)_3$ (M = Mn or Re; L = η^5-C_5H_5, η^5-C_9H_7, or η^5-$C_{13}H_9$) or Group VII metals.[91] The authors used mass spectrometry for this purpose, which makes it possible to study the compounds with exclusion of the influence of the medium. The ratio of the sum of the intensities of the metal-containing ions (after subtracting the intensity of the metal ion) I_1 to the sum of the intensities of all the hydrocarbon ions and the metal ion I_2 was adopted as the measure of the strength of the metal–π-ligand bond. According to the results obtained by this method (see Table), the strength of the binding of the metal to the π-ligand diminishes greatly on passing from rhenium to manganese and diminishes appreciably in the sequence η^5-cyclopentadienyl > η^5-indenyl > η^5-fluorenyl complexes.

Mass-spectrometric data for the metal–π-ligand bond strengths.

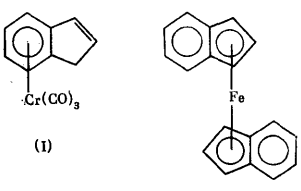
Compound	I_1/I_2	Compound	I_1/I_2
$C_9H_5Re(CO)_3$	87	$C_5H_5Mn(CO)_3$	1.9
$C_9H_7Re(CO)_3$	64	$C_9H_7Mn(CO)_3$	0.51
		$C_{13}H_9Mn(CO)_3$	0.34

3. The Structure of the η^5-Indenyl and η^5-Fluorenyl Complexes of Transition Metals

Three types of coordination are known for the π-complexes of indene and fluorene with transition metals: η^6-coordination [as in the complex (I)], η^5-coordination [as in the complex (II)], and η^3-coordination [as in the complex (III)]. A compound of type (I) belongs to the class of π-arene complexes and the η^5- and η^3-indenyl derivatives are analogues of the cyclopentadienyl and allyl complexes respectively. However, for the indenyl and fluorenyl complexes there apparently exists also a transitional type of coordination between η^5- and η^3-coordinations, for example, in the π-complexes of the lanthanides and the actinides.

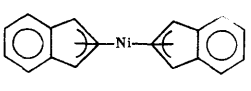
In the present review, we shall consider only η^5-coordination complexes and shall compare them with their cyclopentadienyl analogues.

The structure of the η^5-indenyl and η^5-fluorenyl complexes has been studied by IR spectroscopy,[68,92–94] mass spectrometry,[95] NMR spectroscopy,[96–100] and X-ray diffraction analysis (XDA).[27,57,59,101–102]



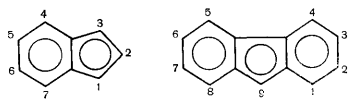
(I)

(II)



(III)

Important information about the type of coordination of the π-ligand in transition metal complexes can be obtained from study of the ^1H and ^{13}C NMR spectra. This is due to the fact that the proton and ^{13}C signals in the NMR spectra of the organic fragments π-coordinated to the metal undergo an appreciable upfield shift compared with the non-coordinated organic compound. Indeed, in the chromium(I) complex with η^6-coordinated indene, all the signals of the carbon atom nuclei in the six-membered ring undergo a 30 p.p.m. upfield shift, while the signals of the non-bridging carbon atoms in the five-membered ring hardly change compared with the non-coordinated indene.[97] On the other hand, in the case of the di-η^5-indenyl complex of iron(II), there is an appreciable upfield shift of the carbon atom signals of the five-membered rings, including bridging carbon atoms, while the signals of the other four carbon atoms in the six-membered rings remain in the same range as for the non-coordinated indene.[97] In the ^{13}C NMR spectrum of the nickel(III) complex in which the π-ligand is η^3-coordinated to the metal atom, only the signals due to the carbon atoms in the 1-, 2-, and 3-positions are appreciably displaced, the signal of the nucleus of the C(3) atom being displaced downfield and those of the nuclei of the C(1) and C(2) atoms being displaced upfield compared with free indene.[97] Here and henceforth the following numbering of the atoms is used:



It is believed[99] that the chemical shifts of the quaternary bridging carbon atoms of the indenyl ligand in the ^{13}C NMR spectra are a good indicator for the determination of the η^5- or η^3-coordination of the π-ligand. Thus the relatively small chemical shifts of the bridging carbon atoms in the dimer $[C_9H_7Mo(CO)_2]_2$ (111.5 p.p.m.) agree with the XDA data indicating the η^5-coordination of the indenyl ligands.

Valuable information about the distortion of the η^5-coordination of the indenyl and fluorenyl ligands has been obtained from ^1H and ^{13}C NMR spectra. Thus a slight distortion of the η^5-type of coordination towards η^3-binding was manifested in the ^1H NMR spectrum of the compound $C_9H_7Rh(C_2H_4)_2$.[19] Only the proton signal in the 2-position in the π-indenyl ligand was split as a result of the interaction with the ^{103}Rh nucleus of the kind observed for the η^3-allyl complexes of rhodium. However, signals of all the carbon atoms of the five-membered ring of this complex appear as doublets in the ^{13}C NMR spectrum as a consequence of the interaction of the ^{13}C nuclei with the ^{103}Rh atoms, which indicates the binding of the rhodium atom to all five carbon atoms.[19] An analogous distortion of the η^5-coordination was reflected in the ^1H and ^{13}C NMR spectra of the complex $C_9H_7Co[P(OR)_3]_2$.[17]

Judging from the NMR spectra, there is some contribution of η^1-type coordination in the fluorenyl complex η^5-$C_{13}H_9Co[P(OR)_3]_2$: the signal of the proton in the 9-position of the π-ligand is at stronger field than for the complexes η^5-$C_{13}H_9Mn(CO)_2L$ (L = CO or PPh_3) and $(\eta^5$-$C_{13}H_9)Zr(\eta^3$-$C_{13}H_9)Cl_2$. Furthermore, the spin–spin coupling constant (SSCC) of the carbon nucleus in the 9-position in the π-ligand to the phosphorus nucleus in phosphite is manifested in the ^{13}C NMR spectrum of the cobalt complex.[17]

The most complete idea about the structure of the η^5-indenyl and η^5-fluorenyl complexes of transition metals is provided by XDA. The first X-ray diffraction studies on η^5-indenyl complexes were performed at the end of the 1950's. The XDA data for di-indenyliron[101] indicated a great similarity between its structure and that of ferrocene. In the planar indenyl ligand, the C–C bond lengths are equalised (1.43 Å) and the C–C–C angles are 120 ° in the six-membered ring and 108° in the five-membered ring, which corresponds to a fully conjugated aromatic system. Di-indenylruthenium has an analogous structure.[102] Subsequently, in the study of the structure of the η^5-indenyl complexes, it was established that they have a number of characteristic features distinguishing them from their η^5-cyclopentadienyl analogues. A slight departure from planarity of the π-ligand as well as a difference in the metal–carbon bond lengths has been observed for the η^5-indenyl complexes: the length of the bonds between the metal and the bridging carbon atoms is somewhat greater than that of the bonds with the remaining three atoms. Thus there is a slight distortion of the η^5-coordination of the indenyl ligand to the metal in the direction of η^3-binding.[57,59,103–105] The mechanism of this distortion involves the movement of the metal atom parallel to the plane of the indenyl ligand. In recent years, the "slip parameter" Δ has been used to estimate this effect.[107–109] The parameter Δ represents the length of the vector between the centre of the five-membered ring and the projection of the metal atom onto the plane of the ring. For η^5-indenyl complexes, the "slip parameter" is usually $\Delta < 0.3$.[107] All the characteristic features of the indenyl complexes have been observed in a study of the structure of bis(1,3-dimethylindenyl)iron hexafluorophosphate: the distortion from planarity of the π-ligand was 0.049 Å and the difference between the Fe–C (five-membered ring) bond lengths was 0.08 Å.[103]

Comparison of the structures of the Group IVB metal complexes $(C_9H_7)_2M(CH_3)_2$ (M = Ti, Zr, or Hf) showed that the difference between the metal–carbon (five-membered ring) bond lengths depends on the nature of the metal: it is 0.19 Å for the titanium compound, 0.12 Å for the zirconium compound, and 0.13 Å for the hafnium compound.[111]

Undistorted η^5-coordination of the indenyl ligand has been observed only in exceptional cases. Such an example is provided by the complex $(CO)(\eta^5$-$C_9H_7)Mo \equiv Mo(C_9H_7$-$\eta^5)(CO)$.[112] The indenyl ligands in this complex are planar and their five-membered rings are linked almost symmetrically to the molybdenum atoms: the difference between the Mo–C(C_5H_3) bond lengths is only 0.06 Å.[112]

A rare example of structural comparison of analogous η^5-indenyl, η^5-fluorenyl, and η^5-cyclopentadienyl complexes has been described.[27,113] For $C_9H_7Cr(CO)_2NO$, $C_{13}H_9Cr(CO)_2NO$, and $C_5H_5Cr(CO)_2NO$, which have in the main similar structures, an increase has been observed in the distance between the chromium atom and the centre of the five-membered ring in the following series of complexes: η^5-cyclopentadienyl, η^5-indenyl, η^5-fluorenyl (1.845, 1.866, and 1.884 Å respectively), and also a decrease in the Cr–N bond lengths with the simultaneous increase in the Cr–CO distances for the indenyl and fluorenyl complexes.

Complexes where the fluorenyl and indenyl ligands are involved in different types of coordination to the same metal atom are of special interest: $(\eta^5$-$C_9H_7)W(\eta^3$-$C_9H_7)(CO)_2$,[114] $(\eta^5$-$C_9H_7)V(\eta^3$-$C_9H_7)$. $.(CO)_2$,[109] and $(\eta^5$-$C_{13}H_9)Zr(\eta^3$-$C_3H_9)Cl_2$.[115,116] In the tungsten complex, one of the indenyl ligands is linked to the metal atom almost symmetrically, the W–C (five-membered ring) bond lengths oscillating from 2.27 to 2.37 Å but remaining within the limits usual

for Group IVB metal complexes. This ligand is planar overall, the C–C bond lengths [1.41(3) Å] indicating the delocalisation of the π-electrons over the aromatic system. For the second indenyl ligand, the W–C (five-membered ring) bond lengths are 3.22(2) and 3.12(2) Å for the bridging carbon atoms and 2.26(2), 2.46(2), and 2.44(2) Å for the non-bridging atoms. This indenyl ligand has lost its planarity as a consequence of η^3-coordination: its five-membered ring is bent at an angle of 26°. For the vanadium complex, large differences between the η^5- and η^3-indenyl ligands have also been observed. For the η^5-coordinated ligand, the V–C (five-membered ring) bond length varies from 2.261(3) to 2.388(3) Å and the "slip parameter" Δ is 0.17. In the η^3-indenyl ligand, the dihedral angle between the planes of the η^3-allyl fragment and the six-membered ring is 12.0(3)°. The V–C (five-membered ring) bond lengths are 2.379, 2.184, and 2.359 Å for the carbon atoms of the allyl fragment and 2.857 and 2.876 Å for the bridging carbon atoms; Δ = 0.56.[109]

The zirconium complex $(\eta^5\text{-}C_{13}H_9)Zr(\eta^3\text{-}C_{13}H_9)Cl_2$ is one of the few compounds with fluorenyl ligands bound in different ways. The difference between the coordinations of the fluorenyl ligands in this complex follows from a comparison of the average Zr–C (five-membered ring) bond lengths. For one of these ligands, the bond length 2.56(7) Å is comparable to the bond length found for $(\pi\text{-}C_5H_5)_2Zr.Cl_2$, while for the other the average value of this distance is 2.52(8) Å for the three non-bridging carbon atoms and 2.80(1) Å (absence of a bond) for the two bridging atoms.[115,116] The authors believe that fundamental geometry of the molecule and the type of bond between zirconium and the π-ligands are determined by the steric requirements imposed by the bulky fluorenyl groups.

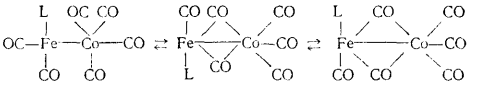
In the π-indenyl complexes of the lanthanides and actinides, distortion in η^5-coordination to the metal atom reaches a higher level than in the complexes of other transition metals. On the other hand, the changes in the bond length and in the planarity of the indenyl ligand in these complexes are smaller than for the η^3-coordinated indenyl ligand. As a result of this, some workers classify the indenyl complexes of the lanthanides and the actinides as η^5-derivatives, while others regard them as η^3-derivatives. XDA has been carried out for a series of samarium,[117] thorium,[118] and uranium[119–122] compounds. Having to choose betweeen the η^5- or the η^3-coordination of the indneyl ligand in $[1,4,7\text{-}(CH_3)_3C_9H_4]_3UCl$, Goffart et al.[120] decided on the η^5-type of binding on the basis of not only XDA data but also on the basis of a qualitative comparison of magnetic susceptibilities, vibrational spectra, and ^1H NMR spectra of this compound and its cyclopentadienyl analogue. The U–C (five-membered ring) bond lengths are 2.91 Å for the bridging carbon atoms and 2.72 Å for the non-bridging atoms. In the analogous thorium complex $[1,4,7\text{-}(CH_3)_3C_9H_4]_3.ThCl$, the Th–C (five-membered ring) bond lengths vary from 2.721(3) to 2.845(4) Å for the non-bridging carbon atoms and from 2.931(3) to 2.946(3) Å for the bridging carbon atoms. However, the authors[118] believe on the basis of these data that the indenyl ligands in the thorium complex are η^3-bound and that there is only a very weak interaction between the metal and the bridging carbon atoms in the five-membered rings.

Thus X-ray diffraction studies on the η^5-indenyl and η^5-fluorenyl complexes and the analogous η^5-cyclopentadienyl complexes have shown that the molecular structures of these compounds are in many respects similar: the η^5-coordinated ligand is planar with equalised C–C bonds, while in the carbonyl derivatives the metal–CO and C–O bond lengths are comparable. However, in contrast to the η^5-cyclopentadienyl complexes, in the η^5-indenyl and η^5-fluorenyl derivatives the bond lengths between the metal and the carbon atoms of the five-membered ring are different: for the three-non-bridging carbon atoms in the $\eta^5\text{-}C_9H_7$ ligand the metal–carbon bond lengths are smaller compared with the two bridge bonds. Some breakdown of the planarity of the η^5-indenyl and η^5-fluorenyl ligands is observed.

4. Stereochemical Non-Rigidity of the η^5-Indenyl Complexes

Comparison of analogous η^5-indenyl and η^5-cyclopentadienyl complexes of transition metals makes it possible to elucidate the influence of the η-ligand on the physicochemical properties and reactivity, in particular, on the properties of the other ligands. The nature of the π-ligand influences the dynamic equilibrium of isomers and conformers in solutions and barriers to the rotation of ethylene and acetylene ligands.

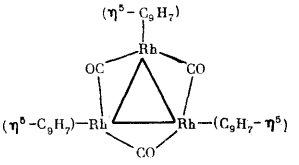
The IR spectra of the complexes $\pi\text{-}LFe(CO)_2Co(CO)_4$ (L = C_5H_5, $CH_3C_5H_4$, or C_9H_7), established that these compounds exist in solutions in the form of equilibrium mixtures of two isomers containing bridging CO groups [the isomers (B) and (C)] and one isomer having only terminal CO ligands [the isomer (A)]:



(A) (B) (C)

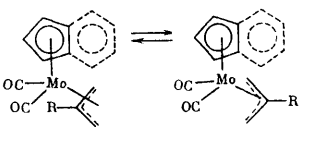
The fraction of the isomer (A) diminishes with decrease in temperature, with increase in solvent polarity, and in the sequence of ligands $\eta^5\text{-}C_9H_7 > \eta^5\text{-}CH_3C_5H_4 > \eta^5\text{-}C_5H_5$.[123] According to XDA data, in the solid state the complex $\eta^5\text{-}C_9H_7Fe(CO)_2Co(CO)_4$ has the structure (B).[124]

An analogous CO group migration process has been investigated for the η^5-indenyl cluster (IV). It was observed that the indenyl cluster exists in the form of only one isomer with bridging CO groups and that the ^{13}C NMR spectrum does not exhibit a temperature dependence in the carbonyl region, in contrast to its η^5-cyclopentadienyl analogue:[59]



(IV)

A series of studies have been devoted to the investigation of the stereochemistry of a number of η^5-indenyl and η^5-cyclopentadienyl complexes of molybdenum[125–127] and iron[128,129] by ^1H NMR. It was established in this way that in solution the compounds $\eta^5\text{-}LMo(CO)_2(\pi\text{-}C_3H_4R)$ (L = $\eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) exist as a mixture of two forms (D) and (E):[126]



(D) (E)

For the η^5-indenyl derivatives of molybdenum with R = CH_3, Cl, or Br, the equilibrium is displaced to the left, while in the case of the

η^5-cyclopentadienyl complexes the substitution of the hydrogen atoms at the central carbon atom in the π-allyl group shifts the equilibrium to the right.[126] The analogous iron and ruthenium compounds η^5-LM(CO)(π-C_3H_4R) (M = Fe or Ru; L = C_5H_5 or C_9H_7) have been isolated in the form of only one isomer (E).[128]

In the study of the temperature variation of the ^{1}H NMR spectra of the rhodium complexes $LRh(C_2H_4)_2$ (L = η^5-C_5H_5 or η^5-C_9H_7), an appreciable influence of the π-ligand on the barrier to the rotation of ethylene was observed.[19,130] The barrier to the rotation of the ethylene ligand in the η^5-indenyl compound (10.5 ± 0.4 kcal mol^{-1}) is much lower than in the η^5-cyclopentadienyl compound (15.0 ± 0.2 kcal mol^{-1}). The coalescence temperature is −90° for the former complex and −19° for the latter.[19] The authors[19] draw a parallel between the lower barrier to the rotation of the olefin in the η^5-indenyl complex and the greater ease of the substitution of the C_2H_4 group in the same compound compared with η^5-C_5H_5Rh. .$(C_2H_4)_2$.

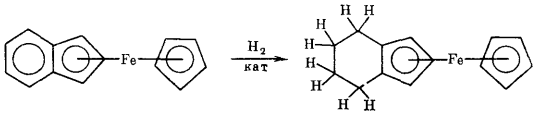
In the cationic complexes of molybdenum with dimethylacetylene of the type $LMo[P(OCH_3)_3]_2(CH_3C{\equiv}CCH_3)^+BF_4^-$ (L = η^5-C_5H_5 or η^5-C_9H_7), the influence of the π-ligand on the barrier to the rotation of acetylene has also been observed: the coalescence temperature is −40° for the indenyl complex and below −90° for the cyclopentadienyl complex.[50]

However, the influence of the indenyl ligand is not always manifested. For example, although the ^{1}H NMR spectra of the ethylene and acetylene complexes of tungsten $LW(CO)_2(CH_3)(C_2H_4)$ and $LW(CO)(CH_3)(CH{\equiv}CR)$ (L = η^5-C_5H_5 or η^5-C_9H_7; R = H or CH_3) do in fact exhibit a temperature dependence, apparently associated with the hindrance of rotation of the π-olefin and π-acetylene ligands, about the metal−ligand bond, the barriers to rotation of the η^5-cyclopentadienyl and η^5-indenyl compounds are approximately equal.[35,52,53,131] In contrast to the tungsten compounds, in the cationic iron complexes $[LFe(CO)_2(C_2H_4)]^+BF_4^-$ (L = η^5-C_5H_5 or η^5-C_9H_7) there is free rotation of the ethylene group regardless of the nature of the π-ligand.[129]

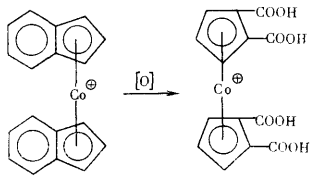
In certain studies, the barriers to rotation of the η^5-indenyl and η^5-cyclopentadienyl ligands have been compared qualitatively in analogous complexes. Thus in the π-allyl complexes of molybdenum η^5-$LMo(CO)_2$(π-C_3H_4R) (L = C_5H_5 or C_9H_7), the η^5-coordinated ligand rotates freely about the Mo−L bond, but the barrier to rotation of the indenyl ligand is higher than for the cyclopentadienyl ligand. As a result, there exists a preferred conformation of the indenyl complexes in which the six-membered ring is arranged above the π-allyl ligand.[126] The hindered rotation of the π-indenyl ligand has also been observed for the dinuclear complex η^5-C_9H_7Rh. .$(CO)_3Cr(CO)[(CH_3)_2C_6H_3]$ in a study of the temperature variation of the ^{13}C NMR spectra.[132]

5. Chemical Shifts

(a) *The reduction and oxidation of the η^5-indenyl complexes.* Hydrogenation with hydrogen in the presence of catalysts (Adams catalyst, platinum dioxide, etc.) has been investigated for a series of indenyl complexes such as di-indenyliron,[133] di-indenylruthenium,[16] cyclopentadienyl(indenyl)iron,[46] ethylenedi-indenyltitanium dichloride,[9,25] di-indenyltitanium dichloride,[32] di-indenylzirconium dichloride,[32] and the dimer of dicarbonylindenyliron.[134] It was found that **in all cases only the double bonds of the six-membered rings of the π-ligand are hydrogenated, which apparently indicates the olefinic** nature of these bonds:



In contrast to the indenyl complexes, the hydrogenation of the six-membered rings of the fluorenyl ligands in $(\eta^5$-$C_{13}H_9)(\eta^3$-$C_{13}H_9)Zr$. .Cl_2 could not be achieved.[32] An example of the oxidation of a six-membered ring, not coordinated to the metal, on treatment of a cationic cobalt complex with potassium permanganate is also known:[135]

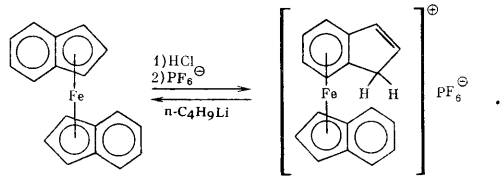


The oxidation-reduction processes in η^5-indenyl and η^5-fluorenyl complexes have also been investigated by electrochemical methods. The majority of these studies have shown that the condensed six-membered rings in the η^5-indenyl and η^5-fluorenyl ligands possess electron-accepting properties, diminishing the electron density on the metal. Thus the replacement of the η^5-cyclopentadienyl ligand by the η^5-indenyl ligand lowers appreciably the reduction potential of cobaltocenium salts: −1.16 V for $(\eta^5$-$C_5H_5)_2Co^+$ and −0.5 V for $(\eta^5$-$C_9H_7)_2Co^+$.[6] The same effect has been observed in the polarographic reduction of rhodium complexes with duroquinone: −1.76 and 2.03 V for $(\eta^5$-$C_5H_5)$Rh(duroquinone) and −1.43 and 1.76 V for $(\eta^5$-$C_9H_7)$Rh(duroquinone).[136] As a result of a study of the electrochemical oxidation of the 17-electron titanium complexes η^5-LTi. .$(\eta^8$-$C_8H_8)$ (L = $CH_3C_5H_4$, C_5H_5, C_9H_7, or $C_{13}H_9$), the authors concluded that the influence of the six-membered condensed rings in these complexes is opposed to that of the CH_3 group.[137] However, data have been published on the electrochemical oxidation of iron compounds [0.49 V for $(\eta^5$-$C_5H_5)_2Fe$, 0.35 V for $(\eta^5$-$C_5H_5)$ $(\eta^5$-C_9. .$H_7)Fe$, and 0.21 V for $(\eta^5$-$C_9H_7)_2Fe$], from which it follows that the replacement of the η^5-cyclopentadienyl ligand by the η^5-indenyl ligand as well as the introduction of the electron-donating substituent into the π-ligand facilitates the oxidation of the central metal atom.[138]

(b) *Metallotropic rearrangements.* In the complexes of transition metals with polycyclic condensed aromatic ligands, the metal is capable of migrating from one ring to another under the influence of various reagents, altering thereby the character of the binding to the π-ligand. These metallotropic rearrangements are characteristic of the indenyl and fluorenyl complexes.

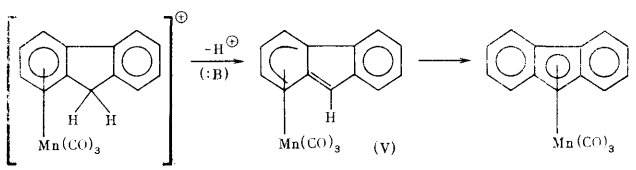
The first example of such inter-ring rearrangement was reported in 1971.[139] In a study of the interaction of di-indenyliron with boron trifluoride etherate, an analogous rearrangement was observed simultaneously.[140] In 1976, the protonation of di-indenyliron and cyclopentadienyl(indenyl)iron was investigated.[141] Under the influence of CF_3COOH and HCl, the iron atom migrated in the

η^5-indenyl complexes from the five-memberd ring to the six-membered ring and η^6-indene complexes of iron were obtained:

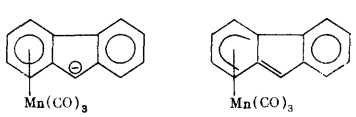


In order to elucidate the stereochemistry of the protonation reaction, the authors studied the interaction of $(\eta^5\text{-}C_9H_7)_2Fe$ with DCl and of $(\eta^5\text{-}1,1,3,3\text{-}C_9H_3D_4)_2Fe$ with HCl. Analysis of the ^1H NMR spectra of the products obtained in these reactions showed that the protonation is stereospecific. It has been suggested[141] that the iron atom is protonated initially and the hydrogen is then transferred to the five-membered ring so that *endo*-addition should result from such "ricochet reaction". Treatment of the η^6-indene complex with n-butyl-lithium regenerated $(\eta^5\text{-}C_9H_7)_2Fe$ in 23% yield. The study of the deprotonation of compounds partly labelled with deuterium and analysis of the mass spectra of the products obtained enabled the authors to conclude that the deprotonated reaction is non-stereospecific. Examples of metallotropic rearrangements of the π-complexes of other Group VIII metal atoms, for example rhodium and iridium, have also been described in the literature.[142-144]

The first metallotropic $\eta^6 \rightarrow \eta^5$-rearrangement of the π-complexes of Group VII metals was observed in a study of the deprotonation of tricarbonylfluorenemanganese:[145]



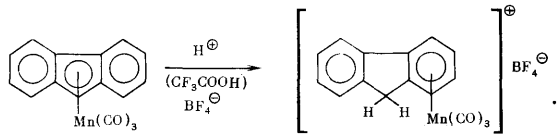
The complex $\eta^6\text{-}C_{13}H_9Mn(CO)_3$ (V) formed initially was converted on heating into the thermodynamically more stable $\eta^5\text{-}C_{13}H_9Mn.(CO)_3$. Two limiting structures were proposed initially for compound (V): the zwitter-ionic structure (Va) and the methylenecyclohexadienyl structure (Vb):[146]



(Va) (Vb)

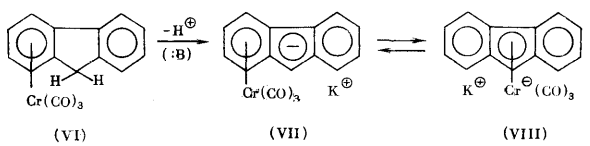
Subsequently XDA showed that the manganese complex (V) has the structure typical of cyclohexadienyl derivatives.[147] Theoretical calculations for the $\eta^6 \rightarrow \eta^5$ rearrangement of the fluorenyl complexes of manganese showed that the η^6-isomer is more stable than the η^5-isomer and that the activation energy for the rearrangement is 25 kcal mol^{-1}.[148] Subsequently kinetic studies on the $\eta^6 \rightarrow \eta^5$ rearrangements of three fluorenyl complexes of manganese, namely $\eta^6\text{-}C_{13}H_9Mn(CO)_3$, $\eta^6\text{-}C_{13}H_9Mn(CO)_2P(C_4H_9\text{-}n)_3$, and $\eta^6\text{-t-}C_4H_9.C_{13}H_8Mn(CO)_3$, confirmed these quantum-chemical calculations.[149] Since the activation energies for the $\eta^6 \rightarrow \eta^5$ rearrangements of $\eta^6\text{-}C_{13}H_9Mn(CO)_3$ and $\eta^6\text{-}C_{13}H_9Mn(CO)_2P(C_4H_9\text{-}n)_3$ proved to be similar and bearing in mind that the replacement of the CO group by the electron-donating phosphine ligand greatly increases the basicity of the central metal atom, the authors concluded that the basicity of the metal does not influence the rate of the rearrangement.

The reverse $\eta^5 \rightarrow \eta^6$ rearrangement was discovered in a study of the protonation of η^5-fluorenyltricarbonylmanganese with trifluoroacetic acid:[150]



In this case, the acid proton apparently adds directly to the fluorenyl ligand. In the η^5-indenyltricarbonylmanganese complexes of manganese and rhenium, the analogous $\eta^5 \rightarrow \eta^6$ rearrangement is observed only on treatment with stronger acids, namely $HFSO_3$ and $AlCl_3$.HCl, which is probably due to the lower basicity of the indenyl ligand compared with the fluorenyl ligand.[151] The increase in the basicity of the central metal atom in the complexes $\eta^5\text{-}C_9H_7.Mn(CO)_2PPh_3$, $\eta^5\text{-}C_9H_7Re(CO)_2PPh_3$, and $\eta^5\text{-}C_{13}H_9Mn(CO)_2PPh_3$ compared with the metal tricarbonyl leads to the protonation of the metal atom in the $CF_3COOH-CH_2Cl_2$ medium and there is no metallotropic rearrangement under these conditions.[151] On the other hand, it has been reported[149] that $\eta^5\text{-}C_{13}H_9Mn(CO)_2.P(C_4H_9\text{-}n)_3$ reacts rapidly with hydrogen chloride, affording the rearrangement product $[\eta^6\text{-}C_{13}H_{10}Mn(CO)_2P(C_4H_9\text{-}n)_3]^+X^-$ and the reaction is non-stereospecific. Hence the authors conclude that the acid proton adds directly to the carbon atom in a 9-position in the fluorenyl ligand.

The inter-ring metallotropic rearrangements of the indenyl and fluorenyl complexes of Group VIB transition metals have been widely investigated by Nesmeyanov's school. In relation to the fluoride anion coordinated to the $Cr(CO)_3$ group, Nesmeyanov and co-workers[152,153] observed the first instance of metallotropic tautomerism where both the initial complex and the product of its metallotropic rearrangement are in equilibrium. Treatment of $\eta^6\text{-}C_{13}H_{10}.Cr(CO)_3$ (VI) with an excess of potassium t-butoxide in tetrahydrofuran (THF) at -70 °C led to its complete conversion into $\eta^6\text{-}C_{13}H_9Cr(CO)_3^-K^+$ (VII), whose isomerisation to $\eta^5\text{-}C_{13}H_9Cr.(CO)_3^-K^+$ (VIII) was observed even at 0 °C and equilibrium was attained after 1 h at 25 °C:



(VI) (VII) (VIII)

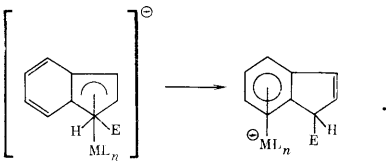
An equilibrium mixture of the same composition was obtained from the mercury derivative:

$$[\eta^5\text{-}C_{13}H_9Cr(CO)_3]_2Hg \xrightarrow{K/Na} (VIII) \rightleftarrows (VII).$$

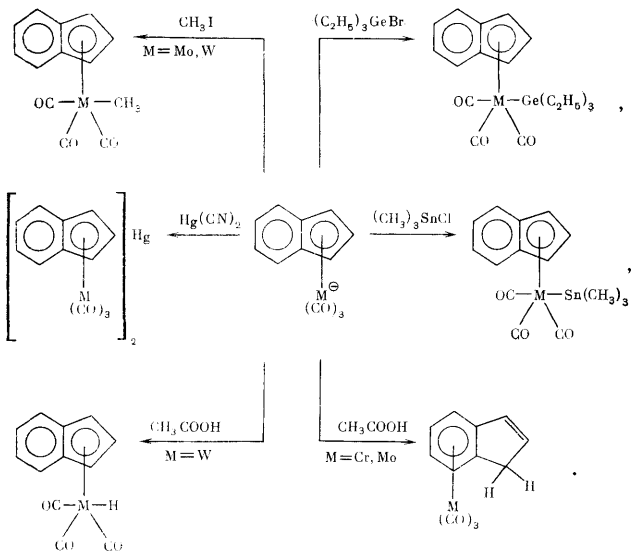
The kinetics of this equilibrium rearrangement have been studied by IR spectroscopy and also by ^1H and ^{13}C NMR.[152-156] The equilibrium constant was shown to depend on the nature of the cation, the solvent, and the concentration of the compound. It was also demonstrated that the rearrangement proceeds via an intramolecular mechanism.[157]

In contrast to η^6-fluorenechromium tricarbonyl, the deprotonation of η^6-fluorenemolybdenum tricarbonyl and η^6-indenechromium tricarbonyl leads to only one isomer of type VIII—$\eta^5\text{-}C_{13}H_9(CO)_3.Mo^-$ and $\eta^5\text{-}C_9H_7(CO)_3Cr^-$ respectively.[33,158]

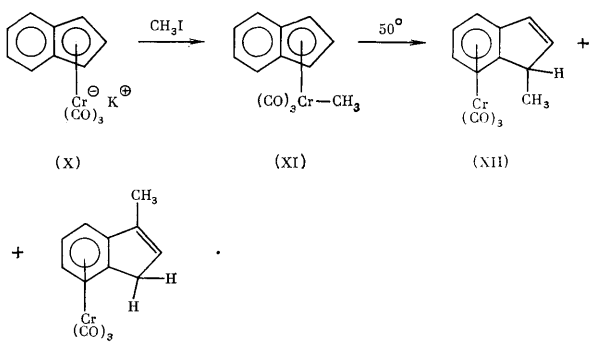
The study of the reactions of the η^5-indenyl and η^5-fluorenyl anionic complexes of Group VIB metals with electrophiles demonstrated a difference between these derivatives and their η^5-cyclopentadienyl analogues. This is associated primarily with the fact that, in contrast to the η^5-cyclopentadienyl systems, the polycyclic systems have an additional pathway leading to the stabilisation of the intermediate (IX)—as a result of the shift of the organometallic group to the six-membered ring of the π-ligand. This process may be thermodynamically preferable to the dissociation of the C—H and C—E bonds:[159]



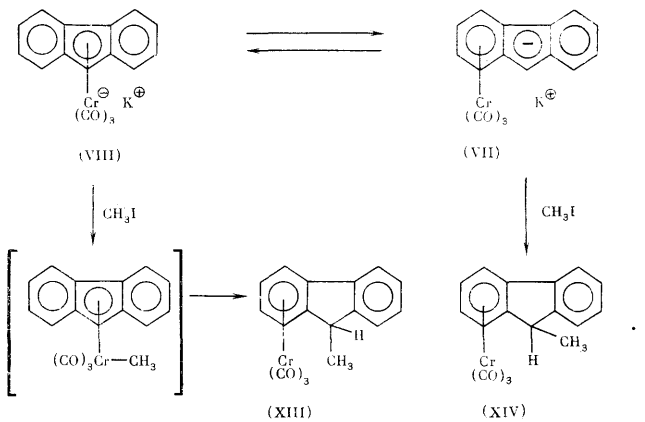
The nature of the metal and the reagent influence appreciably the direction of the reactions of anionic η^5-indenyl complexes of Group VIB metals with electrophiles and determine the feasibility of the $\eta^5 \rightarrow \eta^6$ rearrangements:[33,160]



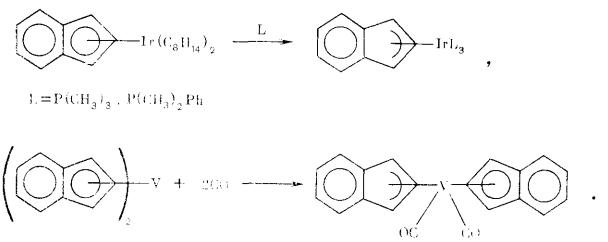
As a rule, the η^6-structures are thermodynamically preferable for chromium derivatives. The stability of the η^5-compounds increases in the sequence Cr < Mo < W.[33] The authors studied in detail the stereochemistry of the interaction of the anion η^6-$C_9H_7Cr(CO)_3^-$ (X) and the tautomeric mixture of compounds (VII) and (VIII) with alkyl halides. Investigations demonstrated the rigorous stereospecificity of these reactions: the "ricochet process" with the initial attack on the metal leads only to the *endo*-isomer, while direct attack on the carbon atom of the five-membered ring affords the *exo*-isomer. Thus the reaction of the complex (X) with CH_3I, which has been shown to proceed via the "ricochet mechanism" [compound (XI) has been isolated and characterised], leads to the *endo*-isomer (XII):[33,159]



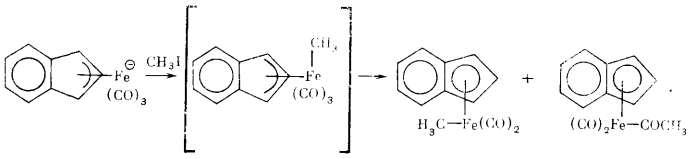
The interaction of the tautomers (VII) and (VIII) with CH_3I proceeds stereoselectively via two different mechanisms with formation of the isomers (XIII) and (XIV):[153,160,161]



The first examples of the $\eta^5 \rightarrow \eta^3$ rearrangements of indenyl complexes in the course of ligand exchange reactions were published for the first time in 1986:[109,162]



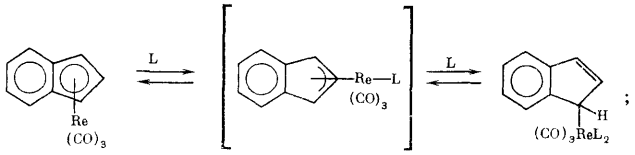
The $\eta^3 \rightarrow \eta^5$ rearrangement was described in 1987 for the reaction of an anionic iron complex with CH_3I:[163]



$\eta^5 \rightarrow \eta^1$ metallotropic rearrangements in which the type of binding of the ligand to the metal changes significantly are also known for the η^5-indenyl and η^5-fluorenyl complexes of transition metals. The ligand, previously coordinated to the metal via the π-electrons of the polycyclic system, forms a bond with the metal via the σ-electrons of one of the carbon atoms. Such rearrangements

have been described also for η^5-cyclopentadienyl compounds, but the presence of condensed benzene rings in the indenyl and fluorenyl ligands greatly facilitates these processes.

The $\eta^5 \rightarrow \eta^1$ rearrangements of carbonyl derivatives of rhenium have been reported recently.[164,165] The interaction of η^5-indenyltricarbonylrhenium with trimethylphosphine at room temperature results in the formation of a stable η^1-indenylbisphosphinerhenium complex:



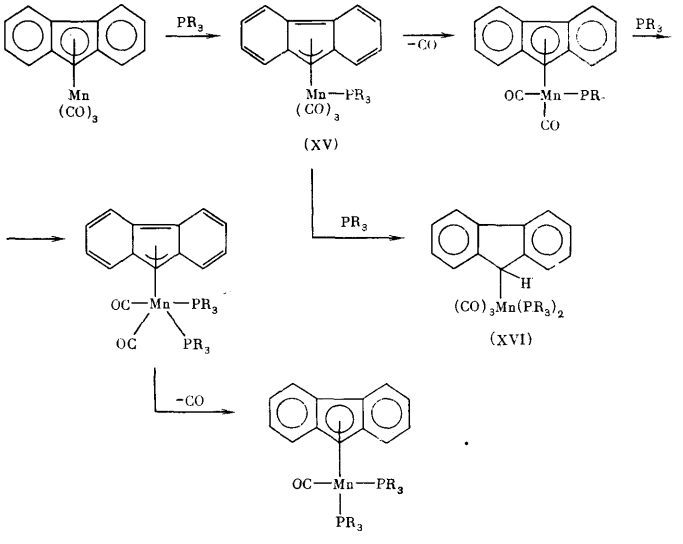
$L = P(CH_3)_3$.

A structure with η^3-linked ligand has been proposed for the intermediate compound. An analogous rearrangement has been described for η^5-cyclopentadienyltricarbonylrhenium, but the rearrangement of the η^5-indenyl complex is 10^8 times faster than for the cyclopentadienyl complex. The $\eta^5 \rightarrow \eta^1$ rearrangement of the indenyl ligand also takes place on treatment of a η^5-indenyl complex of rhodium with an excess of t-butyl isocyanate.[130]

The reverse $\eta^1 \rightarrow \eta^5$ rearrangement of the indenyl ligand has been observed in a photochemical reaction of an iron complex:[166]

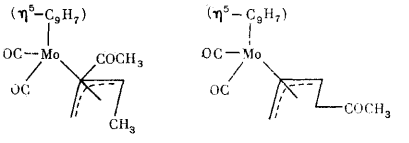
$$(\eta^5\text{-}C_9H_7)\,Fe\,(CO)_2\,(\eta^1\text{-}C_9H_7) \xrightarrow{h\nu} Fe\,(\eta^5\text{-}C_9H_7)_2 + 2CO.$$

The first instance of the $\eta^5 \rightarrow \eta^1$ rearrangement of the fluorenyl ligand has been noted in the reaction of η^5-fluorenyltricarbonylmanganese with an excess of tributyl phosphine:[167]



It has been suggested that the rearrangement proceeds as for the indenyl ligand—via the intermediate complex (XV) with the η^3-type of coordination. The structure of compound (XVI) with the η^1-fluorenyl ligand has been proposed on the basis of the ^{13}C NMR spectrum.

(c) *Ligand exchange reactions in η^5-indenyl and η^5-fluorenyl complexes of transition metals.* Extensive data have now accumulated in the literature concerning the influence of the η^5-indenyl ligand on the rate of exchange of carbonyl, olefinic, and acetylenic groups in the π-complexes of transition metals in thermal reactions. As early as 1965, it was noted that the decarbonylation of the η^5-indenyl complexes of molybdenum $RMo(CO)_3(\eta^5\text{-}C_9H_7)$ proceeds much more readily than that of the corresponding cyclopentadienyl complexes.[34] Subsequently, other studies were published in which the accelerating effect of the η^5-indenyl ligand had been observed. For example, it was noted that $[(\eta^5\text{-}C_9H_7)Mo(CO)_2(CH_3)_2C_2]^+BF_4^-$ reacts faster with PPh_3 [53] and $\eta^5\text{-}C_9H_7Mo(CO)_3CH_3$ reacts faster with but-2-yne[54] faster than their cyclopentadienyl analogues. It has also been established that methylenecyclopropane and buta-1,3-diene are inserted more readily in the $Mo-CH_3$ bond in $\eta^5\text{-}C_9H_7Mo(CO)_3CH_3$, which leads to the formation of the π-allyl complexes (XVII) and (XVIII) respectively with the simultaneous migration of a terminal CO group:[54]

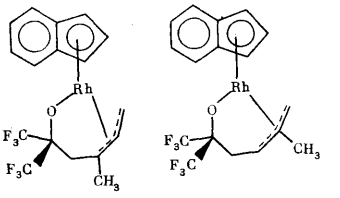


(XVII) (XVIII)

The accelerating effect of the η^5-indenyl ligand compared with the cyclopentadienyl ligand is manifested in the π-complexes of not only Group VI but also of Group VII and VIII transition metals. Especially many examples are known for rhodium derivatives. For instance, $\eta^5\text{-}C_5H_5Rh(C_2H_4)_2$ does not react with carbon monoxide, while the η^5-indenyl analogue reacts rapidly with CO at room temperature, affording $\eta^5\text{-}C_9H_7Rh(CO)_2$ in a quantitative yield.[130] The high reactivity of $\eta^5\text{-}C_9H_7Rh(C_2H_4)_2$ is also manifested in the considerable ease of the exchange of ethylene for phosphines, cycloocta-1,5-diene, 2,3-dimethylbuta-1,3-diene,[19] methylcyclopropane, acrylonitrile, t-butyl isocyanate, isoprene, cyclohexadiene, and cyclohepta-1,3,5-triene.[20,130] Similar reactions are unknown for the analogous complex with the η^5-cyclopentadienyl ligand. The substitution of the Group L in the rhodium complexes $\eta^5\text{-}C_9H_7RhL_2$ (L = CO or PPh_3) for other ligands takes place very readily (20 °C, benzene).[19] The corresponding η^5-cyclopentadienyl compounds are difficult to obtain.

Whereas only prolonged photolysis of $\eta^5\text{-}C_5H_5Rh(CO)_2$ leads to two isomeric clusters $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$ and in a low yield, η^5-indenyl dicarbonylrhodium is converted selectively and with a high yield into the trimer (IV) on refluxing in heptane.[59,130]

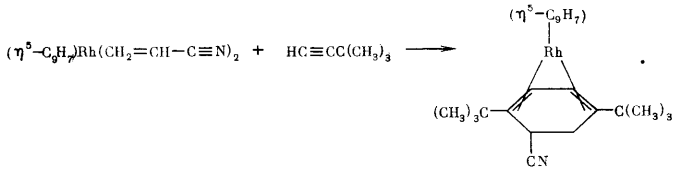
η^5-Indenyl complexes of rhodium with diene ligands exhibit an enhanced reactivity. Thus, in contrast to its η^5-cyclopentadienyl analogue, $\eta^5\text{-}C_9H_7Rh$(isoprene) reacts with $(CF_3)_2CO$ at room temperature with formation of the two isomeric products (XIX) and (XX):[168]



(XIX) (XX)

The reactions of the η^5-indenyl complexes of rhodium $\eta^5\text{-}C_9H_7RhL_2$ (L = isoprene, acrylonitrile, or 2,3-dimethylbuta-1,3-diene) with alkynes, which result in the cyclisation of acetylenes with the olefins

in the coordination sphere of the metal, are remarkable:[20,130]

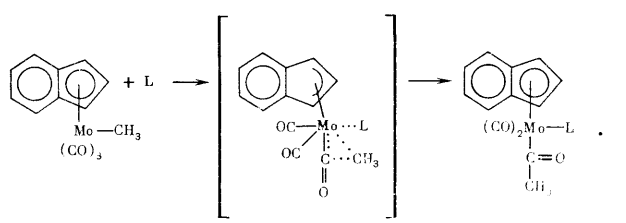


The initial stage in this reaction is the coordination of the acetylene molecule to the metal, which is facilitated by the slip of the rhodium atom along the plane of the indenyl ligand.[20]

The ready carbonylation of the $Fe-CH_3$ bond in the complexes η^5-$C_9H_7Fe(CH_3)(CO)L$ (L = CO or PPh_3) has also been described.[169]

There are many fewer examples of the accelerating effect of the η^5-fluorenyl ligand compared with the η^5-indenyl ligand. For example, it has been noted that η^5-$C_{13}H_9Co[P(OR)_3]_2$ absorbs carbon monoxide more readily than η^5-$C_9H_7Co[P(OR)_3]_2$.[17]

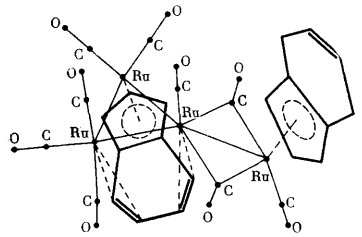
All the examples described above concern the observation of the accelerating influence of the η^5-indenyl or η^5-fluorenyl ligands on the rates of ligand exchange reactions. The first studies designed to estimate quantitatively the comparative reactivities of the η^5-indenyl and η^5-cyclopentadienyl complexes of transition metals in thermal reactions were performed in the 1970's.[170,171] The authors first explained the accelerating influence of the η^5-indenyl ligand. They carried out a kinetic study on the thermal reactions involving the substitution of CO groups by phosphines and phosphites in the molybdenum complexes η^5-$C_9H_7Mo(CO)_3X$ and η^5-$C_5H_5Mo(CO)_3X$ (X = CH_3, Cl, Br, or I) and showed that the ligand exchange proceeds via two competing mechanisms: associative and dissociative. An appreciable accelerating influence of the η^5-indenyl ligand compared with the cyclopentadienyl ligand (at least by a factor of tens and at most by a factor of hundreds of thousands) was observed in both cases. In the associative mechanism, the accelerating effect of the indenyl ligand is caused, according to the authors, by the transition to a π-allyl system, which frees an orbital of the molybdenum atom for the interaction with the nucleophile and ensures thereby the easy occurrence of the reaction via the S_N2 mechanism:



The capacity of the cyclopentadienyl ligand for π-allyl type coordination to the metal is smaller, since in the change from the η^5-coordination to the η^3-coordination in the indenyl complex the six-membered ring retains its total resonance energy, while in the case of the cyclopentadienyl ligand an isolated double bond is formed.[170] The dissociative mechanism has been studied in detail for halogeno-derivatives of η^5-indenyl and η^5-cyclopentadienyl complexes.[171] In this case, the reaction rate constants were found to undergo very pronounced changes on transition to the η^5-indenyl complexes and a dependence of the rate constants on the nature of the halogen was observed:

	$C_5H_5Mo(CO)_3Cl$	$C_5H_5Mo(CO)_3Br$	$C_5H_5Mo(CO)_3I$
$k_{rel}^{10^\circ}$	1	23	614
	$C_9H_7Mo(CO)_3Cl$	$C_9H_7Mo(CO)_3Br$	$C_9H_7Mo(CO)_3I$
$k_{rel}^{10^\circ}$	6600	211 000	3 580 000

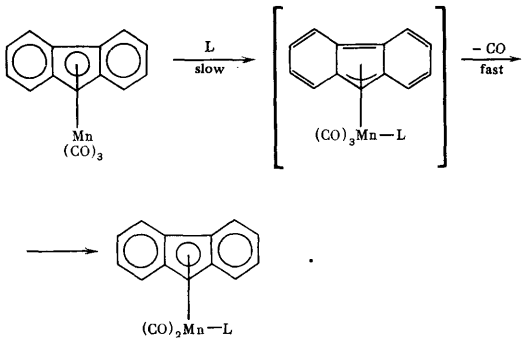
Since the absorption frequencies of the carbonyl groups in the IR spectra of the isostructural complexes η^5-$C_9H_7Mo(CO)_3X$ and η^5-$C_5H_5Mo(CO)_3X$ are almost identical, the differences between the rates of reaction are associated, according to the authors, with the appreciable change in the stability of the transition state. It has been suggested that the stabilisation of the transition state in the dissociative mechanism is achieved by the partial binding of the benzene ring of the π-ligand to the metal. In order to elucidate the role of the aromatic six-membered ring, the kinetic data for the η^5-cyclopentadienyl, η^5-indenyl, and η^5-tetrahydroindenyl complexes of molybdenum[172] and iron[173] were compared. It was found that the activation parameters and the rate constants for the tetrahydroindenyl complex η^5-$C_9H_{11}Mo(CO)_3Cl$ and η^5-$C_5H_5Mo(CO)_3Cl$ are very similar. On the other hand, the reaction rate constant for η^5-$C_9H_7Mo(CO)_3Cl$ is 6000 times greater than for the η^5-cyclopentadienyl analogue. Thus the hydrogenated six-membered ring of the tetrahydroindenyl ligand does not increase the rate of exchange of the CO groups, while the π-electron system of the condensed benzene ring participates in the stabilisation of the transition state. This is confirmed indirectly by the synthesis of the tetranuclear ruthenium cluster (XXI), since the metal atom is involved not only in η^5-type coordination to the five-membered ring but also in η^2,η^2-diene type coordination to the six-membered ring of the indenyl ligand:[174]



(XXI)

In the course of the further development of the kinetic studies on the thermal CO ligand substitution reactions in η^5-indenyl complexes of transition metals, it was shown that the rates of reaction of the indenyl complexes of rhodium η^5-$C_9H_7Rh(CO)_2$ and η^5-$(CH_3)_7C_9Rh(CO)_2$ with PPh_3 are respectively 3.8×10^8 and 6.1×10^5 times greater than for η^5-$C_5H_5Rh(CO)_2$.[175,176] The tendency of the rhodium atom to form π-allyl complexes facilitates the $\eta^5 \rightarrow \eta^3$ transitions in the associative reaction mechanism and leads to a very pronounced increase in rate, which is not observed for other metals. The quantitative effect of the η^5-fluorenyl ligand relative to the η^5-indenyl ligand in the thermal reactions of manganese carbonyl complexes with phosphines and phosphites was estimated in this connection.[167,176] It was shown that the rate of reaction with $P(OC_2H_5)_3$ in decalin is 388 times greater for η^5-$C_{13}H_9Mn(CO)_3$ than for η^5-$C_9H_7Mn(CO)_3$. The increase in the rate of substitution for the η^5-fluorenyl complex compared with the η^5-indenyl and η^5-cyclopentadienyl complexes has been explained[167] by the stabilisation of the η^3-intermediate as a result of the delocalisation of the π-electrons over all three rings, i.e. a high delocalisation energy

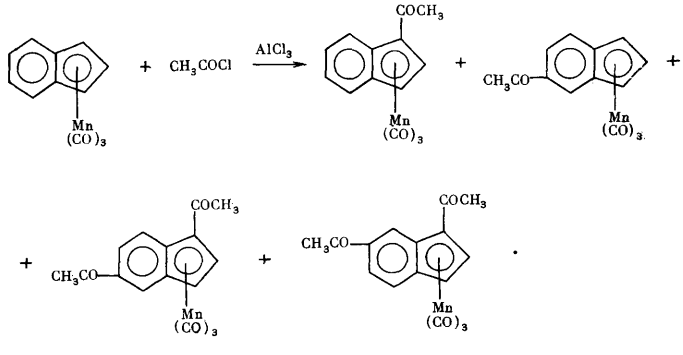
obtains in this instance.



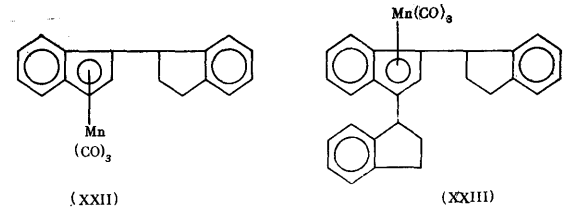
However, the accelerating effects of the η^5-indenyl and η^5-fluorenyl ligands is not always maintained. Thus the effect has not been observed in the photochemical substitution of the carbonyl groups in manganese complexes for triphenylphosphine.[177] The rate constants for the complexes $LMn(CO)_3$, where L = η^5-C_5H_5, η^5-C_9H_7, and η^5-$C_{13}H_9$ are 6.0×10^{-3}, 5.2×10^{-3}, and 3.8×10^{-3} min^{-1} respectively.

(d) *The hydrogen substitution reactions in η^5-indenyltricarbonyl and η^5-fluorenyltricarbonyl complexes of manganese and rhenium.* The hydrogen substitution reactions in the π-ligands of neutral η^5-indenyl and η^5-fluorenyl complexes of transition metals have been little investigated. Attempts to benzoylate η^5-cyclopentadienyl (η^5-indenyl)-iron with benzoyl chloride in the presence of $AlCl_3$ and also to metallate it by n-butyl-lithium were reported in 1964.[47] However, acylation led to the decomposition of the complex and treatment with n-C_4H_9Li and subsequently with D_2O led to the isolation of the non-deuteriated initial compound.

A series of studies[178–180] on the electrophilic and protophilic substitution η^5-indenyl and η^5-fluorenyl ligands of manganese and rhenium complexes were published in 1982–1985. It was shown that, in the interaction of η^5-$C_9H_7Mn(CO)_3$ with an excess of CH_3COCl in the presence of $AlCl_3$ in methylene chloride, hydrogen is substituted by $COCH_3$ in both the five-membered and six-membered rings of the η^5-indenyl ligand:[178]



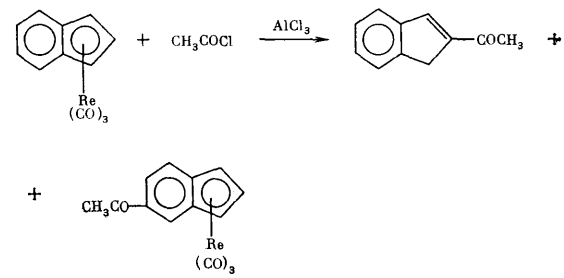
Similarly, in the isotope exchange of hydrogen involving η^5-C_9H_7.$Mn(CO)_3$ on treatment with a mixture of the acids CF_3COOD and D_2SO_4 in CH_2Cl_2, hydrogen is replaced by deuterium in both rings of the π-ligand, although the substitution in the five-membered ring predominates. Apart from the deuteriated derivative, the deuterium-containing complexes (XXII) and (XXIII) were isolated in this reaction. These complexes are apparently formed as a result of the alkylation of the initial compound by the indene protonated in the acid medium, produced as a result of the cleavage of the metal–π-ligand bond.



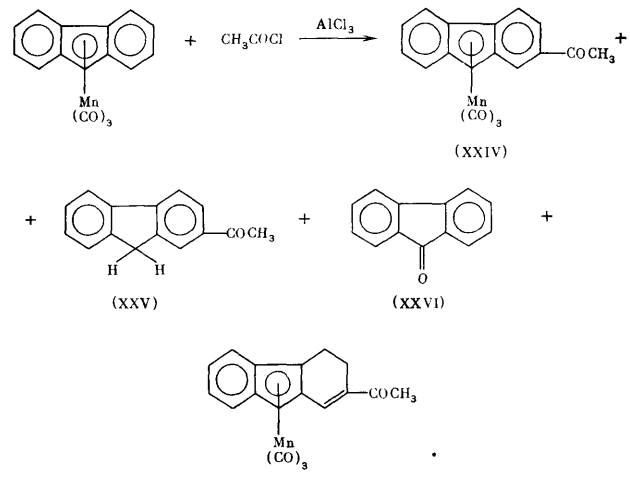
(XXII) (XXIII)

In order to compare the reactivities of the η^5-indenyl and η^5-cyclopentadienyl ligands, the competitive acetylation of η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Mn(CO)_3$ was carried out.[180] It was established as a result that the reactivity of the η^5-indenyl ligand is on the whole much higher than that of the η^5-cyclopentadienyl ligand. However, when the reactivity of only the five-membered ring of the η^5-indenyl ligand is compared with that of the η^5-cyclopentadienyl ligand, then the differences are insignificant.

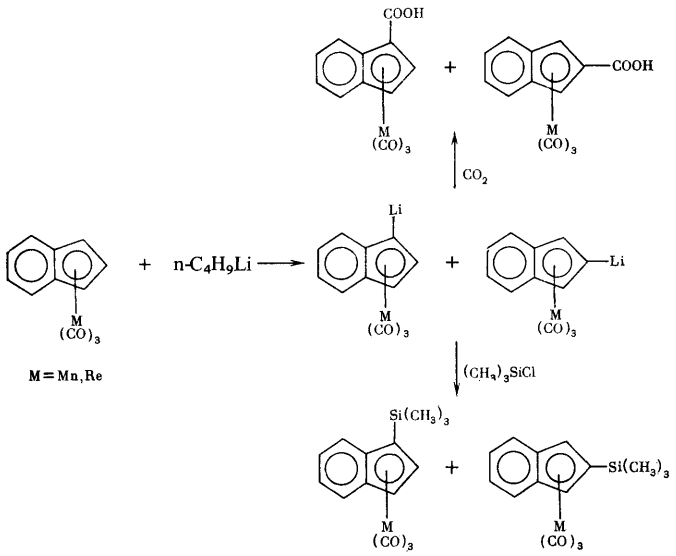
In contrast to η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$, the acetylation of η^5-$C_9H_7Re(CO)_3$ [4] takes place mainly with abstraction of the π-ligand. Thus, after treatment with acetyl chloride in the presence of $AlCl_3$ in CH_2Cl_2, the complex (5-$CH_3COC_9H_6$)$Re(CO)_3$ (5%) and 2-acetylindene (17%) were isolated:[178]



The acetylation of η^5-$C_{13}H_9Mn(CO)_3$ takes place only in the six-membered ring of the π-ligand and is also accompanied by the dissociation of the metal–π-ligand bond. The acylated complex (XXIV) (40%), the products (XXV) and (XXVI) resulting from the elimination of the π-ligand, and the partly hydrogenated complex (XXVII) (6%) are formed:



Metallation of η^5-indenyl complexes of manganese and rhenium with n-butyl-lithium in THF involves only the five-membered ring of the indenyl ligand with formation of a mixture of the 1- and 2-isomers:[179]

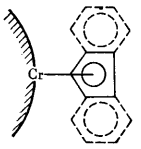


For the quantitative estimation of the comparative reactivities of the η^5-indenyl and η^5-cyclopentadienyl complexes, Lobanova et al.[180] carried out the competitive metallation with n-butyl lithium of mixtures of the following pairs of compounds: η^5-$C_9H_7MnCO_3$ and η^5-$C_5H_5Mn(CO)_3$; η^5-$C_9H_7Re(CO)_3$ and η^5-$C_5H_5Re(CO)_3$; η^5-$C_9H_7Mn(CO)_3$ and η^5-$C_9H_7Re(CO)_3$; η^5-$C_5H_5Mn(CO)_3$ and η^5-$C_5H_5Re(CO)_3$. It was established that the η^5-indenyl complexes are somewhat more reactive than the corresponding η^5-cyclopentadienyl complexes, although the differences are slight. It was also discovered that the rhenium complexes are metallated much more readily than the manganese complexes, which has been explained by the greater tendency of the rhenium compounds to undergo protophilic substitution reactions.[180]

(e) *Catalytic properties of η^5-indenyl and η^5-fluorenyl complexes of transition metals.* The "coordination flexibility" of the η^5-indenyl and η^5-fluorenyl ligands, which accelerates the ligand exchange reactions in transition metal complexes, may be important when they are used as homogeneous catalysts of chemical processes where the lability of the ligands at the metal atom is significant.

The catalytic activity of η^5-indenyl complexes of transition metals has been reported in a number of studies. For example, the interaction of η^5-$C_9H_7Rh(C_2H_4)_2$ with an excess of acetylenes leads to the catalytic cyclotrimerisation of 3,3-dimethylbut-1-yne to 1,2,4-tri-t-butylbenzene, while but-2-yne is cyclotrimerised to hexamethylbenzene.[130] Furthermore, η^5-$C_9H_7Rh(C_2H_4)_2$ is a catalyst of the isomerisation of allyltrimethylsilanes to *trans*-propenyltrimethylsilanes.[181] Dinuclear rhodium complexes with indenyl ligands are also effective catalysts in the trimerisation of acetylenes.[182] The high catalytic activity of η^5-indenyl derivatives of Group IVB metals $(\eta^5\text{-}C_9H_7)_2M$ (M = Ti, Zr, or Hf) in the polymerisation of α-olefins has been noted.[183]

Studies have been made on the catalytic properties of di-indenyl- and difluorenyl-chromium complexes deposited on silica gel.[184] Like chromocene, these complexes exhibited a catalytic activity in the polymerisation of ethylene. It is believed that the polymerisation proceeds via an anionic mechanism and that the catalyst active centre is the chromium centre (XXVIII):



The increased thermal stability of the indenyl catalyst compared with the cyclopentadienyl catalyst has been noted. It has been indicated in patents[185,186] that η^5-$C_9H_7Mn(CO)_3$, η^5-$C_{13}H_9Mn(CO)_3$, as well as η^5-$C_5H_5Mn(CO)_3$ can be used as anti-knocking agents. It has been shown that the η^5-indenyl and η^5-fluorenyl derivatives of titanium L_2TiCl_2 (L = η^5-C_9H_7 or η^5-$C_{13}H_9$) as well as their η^5-cyclopentadienyl analogues exhibit an anticancer activity.[187]

III. CONCLUSION

Thus the data examined above show that η^5-indenyl and η^5-fluorenyl complexes of transition metals have a number of characteristic features apart from their great similarity to their cyclopentadienyl analogues. Thus the strength of the π-ligand–metal bond varies in the sequence η^5-cyclopentadienyl > η^5-indenyl > η^5-fluorenyl, which leads to a decrease in the stability of the indenyl and fluorenyl compounds. Furthermore, some distortion of the η^5-type coordination is observed for the η^5-indenyl and η^5-fluorenyl complexes, which is reflected in the difference between the lengths of the bonds linking the metal to the carbon atoms of the five-membered ring. On treatment of the η^5-indenyl and η^5-fluorenyl derivatives with certain reagents, a change in the type of coordination to the transition metal from η^5- to η^6-coordination and from η^3- to η^1-coordination has been observed, i.e. intramolecular metallotropic rearrangements are characteristic of such compounds. The fact that the rates of thermal ligand exchange reactions of the η^5-indenyl and η^5-fluorenyl complexes exceed by several orders of magnitude the rates of reaction of the η^5-cyclopentadienyl compounds may be of special interest from the practical point of view.

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