U. D. C. 547.402.: 547.482

Chemical Reactions of Cobaltocene and Nickelocene

E.V.Leonova and N.S.Kochetkova

This review deals with the comparative chemical characteristics of metallocenes containing Group VIII metals in the Third Period of the Periodic System, namely cobaltocene, nickelocene, and their derivatives. The common features of their chemical properties and the differences between them have been elucidated. The capacity of cobaltocene and nickelocene to form complexes with electron-accepting agents is discussed.
The bibliography includes 200 references.

CONTENTS

I.	Introduction	278
II.	Substitution reactions of the carbon atoms of cobaltocene and nickelocene	278
III.	Reactions in the side chains of substituted cobalticenium salts	279
IV.	Reactions involving addition to the cyclopentadienyl ligand of cobaltocene and nickelocene	279
V.	Ligand exchange reactions in cobaltocene and nickelocene	284
VI.	Electron-donating properties of cobaltocene and nickelocene	287

I. INTRODUCTION

π Complexes with a sandwich structure, the first representative of which is ferrocene, have been a truly inexhaustible store of interesting problems and puzzles for a generation of investigators. The similarity of the structures and similar principles of the formation of chemical metal – cyclopentadienyl (CP) ligand linkages are responsible for the similarity of the physicochemical properties of metallocenes. However, the nature of the central metal atom should have a significant influence on the metal – ligand bond, causing a corresponding change in the properties of the "sandwich".

In the Third Period, Group VIII of the Periodic System contains three elements (iron, cobalt, and nickel) each of which forms the corresponding "sandwich" compound. The variation of the physicochemical properties of these complexes on passing from iron to nickel is interesting. In view of the large number of reviews and monographs on the chemistry of ferrocene and other π complexes with a sandwich structure[1–10], this review deals mainly with experimental studies on the chemistry of nickelocene, cobaltocene and the cobalticenium cation (up to 1972), the chemical properties of ferrocene being considered only for the purposes of comparison.

The review does not discuss the catalytic properties of these metallocenes and their other possible applications.

II. SUBSTITUTION REACTIONS OF THE CARBON ATOMS OF COBALTOCENE AND NICKELOCENE.

One of the simple chemical proofs of the non-benzenoid aromatic nature of metallocenes is the absence of Diels – Alder reactions with maleic anhydride and reactions with iron(II) chloride as well as the resistance of these compounds to hydrolysing agents. Another important piece of chemical evidence for the aromaticity of these systems is the capacity to undergo substitution reactions.

Neither cobaltocene nor nickelocene form ferrocene by reacting with $FeCl_2$.[11] However, nickelocene is not decomposed by water and cobaltocene is converted into the stable cobalticenium cation[11]. However, whereas electrophilic substitution reactions are typical for ferrocene[1–10], all attempts to acylate, arylate, and metallate nickelocene[10] and also to sulphonate, nitrate, acylate, and arylate cobalticenium picrate[10] under conditions close to those of the analogous ferrocene reactions were unsuccessful. Hitherto, the only known substitution reaction involving the hydrogen atoms of the cyclopentadienyl rings of the cobalticenium cation and nickelocene is the protophilic hydrogen isotope exchange reaction[12]:

$$(C_5H_5)_2M \rightarrow (C_5D_5)_2M\ (M=Fe;\ Co;\ Ni).$$

When nickelocene is treated with *N*-deuteriodiethylamine in the presence of lithium diethylamide, hydrogen isotope exchange takes place with the cyclopentadienyl ring of nickelocene[13, 14]. The rate of hydrogen isotope exchange involving nickelocene depends on the concentration of lithium diethylamide and, when the latter is 0.09 *N* in solution in *N*-deuteriodiethylamine at 25°C, the isotope exchange rate constant is 6×10^{-5} s^{-1}:

$$(C_5H_5)_2Ni \xrightarrow[Et_2NLi]{Et_2ND} (C_5D_5)_2Ni.$$

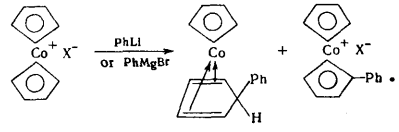
It is noteworthy that the protophilic hydrogen isotope exchange in ferrocene takes place under more severe conditions — in liquid ammonia in the presence of potassamide[15]. The rate constant for the replacement of deuterium in deuterioferrocene by protium in 0.02 *N* potassamide solution in liquid ammonia at 13°C is 9×10^{-4} s^{-1}. Under the same conditions, the rate constant for the exchange of deuterium in benzene is 3×10^{-5} s^{-1}. The data quoted show that in ferrocene and in benzene hydrogen atoms possess a much lower protophilic mobility than in nickelocene[12].

The kinetics of hydrogen isotope exchange between cobalticenium hydroxide and 10% sodium methoxide solution in *O*-deuteriomethanol at 50°C were also investigated and it was established that the rate constant for this reaction is 6.4×10^{-5} s^{-1}. [16] The degree of exchange is 80 – 90% of equilibrium value:

$$(C_5H_5)_2Co^+X^- \xrightarrow[MeONa]{MeOD} (C_5D_5)_2Co^+X^-.$$

The fact that a substitution and not an addition reaction occurs follows from a comparison of the ^1H NMR and infrared spectra of the initial and deuteriated compounds. The ^1H NMR spectrum shows in both cases a singlet with δ = = 5.85 p.p.m., and the infrared spectra of the deuteriated and the initial compounds are extremely similar[16].

It was also shown that in the reaction with phenyllithium or with phenyl-magnesium bromide, cobalticenium salts form, together with addition products, also a certain amount of a phenyl-substituted product[17]:



Other cobalt-containing metallocenes exhibit the chemical properties of aromatic systems. These compounds include cyclopentadienyl(tetraphenylcyclobutadienyl)cobalt[18,19] and its unsubstituted analogue[20]. While the acylation reactions of these compounds have low yields (less than 1%[18,19] and 5%[20] respectively), mercuration[20], the Mannich and Vilsmeier reactions[20], and substitution with lithium[20] take place readily. It is noteworthy that substitution of $C_5H_5CoC_4H_4$ takes place preferentially in the cyclobutadienyl ring[20].

The krypton electronic configuration obtains in these compounds. Analogous organonickel compounds, in particular (cyclopentadienyl-R_3-cyclopropenyl)nickel, exist. The three-membered ring can contain both aromatic[21] and aliphatic substituents[22]. An X-ray diffraction study of the compound $C_5H_5Ni(C_3Ph_3)$ has been carried out[23]. Possibly these compounds, like the cobalt-containing metallocenes, will show a tendency to undergo electrophilic substitution reactions.

III. REACTIONS IN THE SIDE CHAINS OF SUBSTITUTED COBALTICENIUM SALTS

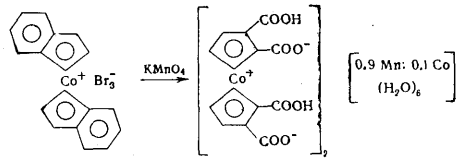
The possibility of carrying out reactions involving the side chains of substituted metallocenes (cobaltocene and nickelocene), other conditions being equal, arises primarily from the strength of the metal – ring bond. Nickelocene is known to enter readily into ligand exchange reactions. On the other hand, the nickelicenium cation and dication are extremely labile and are readily decomposed by atmospheric oxygen. No ligand exchange in aqueous solution at pH 1.99 takes place between cobalticenium perchlorate $(C_5H_5)_2CoClO_4$ and $^{60}Co(ClO_4)_2$.[24]

The cobalticenium cation is not decomposed by concentrated sulphuric and nitric acids[25,26], but is ozonised when ozone is passed through its solution in acetic acid over a period of many hours[27]. These factors permitted a series of side chain reactions of substituted cobalticenium cations. Similar reactions are not known for the cation and dication derived from nickelocene.

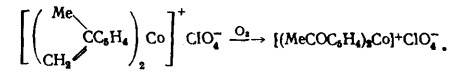
1, 1′-Dimethylcobalticenium perbromide was oxidised at 100°C with an aqueous alkaline solution of potassium permanganate[28]:

$$[Co(C_5H_4Me)_2]^+Br_3 + MnO_4^- \rightarrow [Co(C_5H_4COOH)_2]^-Br^+.$$

The dicarboxylic acid formed in this process was isolated as the bromide. A similar reaction was carried out with bis(indenyl)cobalt(III). 1, 2, 1′, 2′-Tetracarboxycobalticenium has been obtained as a mixed salt:



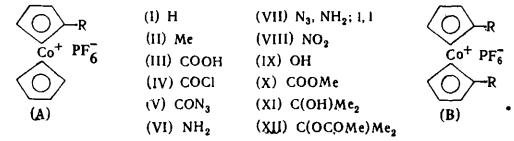
1, 1′-Di-isopropenylcobalticenium perchlorate has been ozonised[29]:



1, 1′-Diacetylcobalticenium has been characterised as the tetraphenylborate and the derivative with the anion of the Reinecke salt.

A mixture of cobalticenium (Ia), methylcobalticenium (IIa), and 1, 1′-dimethylcobalticenium (IIb) has been oxidised[30] with an alkaline solution of sodium permanganate to the corresponding carboxylic acids (III, A, B). The carboxy group was further converted into the acid chloride group (IV, A, B), an ester, an amide, and finally an acid azide (V, A, B). The Curtius rearrangement of the azide gave an amine (VI, A, B) and the 1-amino-1′-azido-compound (VII, B). Similar reactions are also known for ferrocenes[31]. However, in contrast to ferrocenylamine, the aminocobalticenium salt can be oxidised to the nitro-derivative (VIII, A)[30]. Moreover, the aminocobalticenium salt can be diazotised and azo-coupled[30]. Under these conditions, aminoferrocene is converted into the corresponding arylferrocenes[1].

The reaction of dicarboxycobalticenium hexafluorophosphate with alcohol in an acid medium leads to the corresponding ester (X, B)[30]. Moreover, 1,1′-di-(α-hydroxy-α-methylethyl)cobalticenium hexafluorophosphate (XI, B)[32] and the corresponding diacetate (XII, B)[32] were obtained from 1, 1′-di-isopropylcobalticenium hexafluorophosphate:



The infrared spectra of mono-substituted cobalticenium salts with the COOH, CON_3, and NO_2 substituents do not contain frequencies in the region of 1000 and 1100 cm^{-1},[30] while homoannular homologues of cobalticenium salts have spectra with frequencies in this region, resembling in this respect ferrocene derivatives[33].

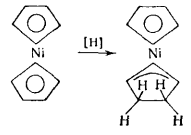
IV. REACTIONS INVOLVING ADDITION TO THE CYCLOPENTADIENYL LIGAND OF COBALTOCENE AND NICKELOCENE

1. Reductive Addition of Hydrogen.

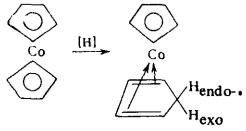
Ferrocene does not react with maleic anhydride[34] and is not hydrogenated in the presence of platinum[27] and Raney nickel[27,35]. The hydrogenation of ferrocene was achieved under very severe conditions — in the presence of Raney nickel at 280 atm and 340°C,[36] but the iron—cyclopentadienyl ring bond was cleaved. For nickelocene †, this process takes place at 50°C in tetrahydrofuran (THF)

† The calculated standard free energies of formation of the biscyclopentadienyl compounds of iron, ruthenium, nickel, and manganese show that the reduction of these metallocenes by hydrogen with formation of the free metal and cyclopentadiene (CPH) or its hydrogenation products is more typical for nickelocene and ruthenocene than for ferrocene[37].

at 27 atm.[38] The reduction results in the formation of cyclopentadienylcyclopentenylnickel:



Nickelocene can also be reduced by sodium amalgam in ethanol[39,40]. Cobaltocene is reduced under similar conditions[41] with formation of cyclopentadienylcyclopentadienecobalt:



Its polarographic study showed[42] that cobaltocene is reduced more readily than nickelocene (-1.92 and -1.74 V respectively). It was established that the above electrochemical reaction of the π complexes is irreversible and that solvent protons are involved in it.

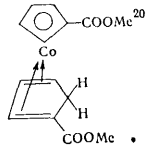
The conversion of $[(C_5H_5)_2Co]^+$ into $C_5H_5CoC_5H_6$ cannot be achieved by electrolysing neutral or alkaline aqueous solutions of a cobalticenium salt or by reduction with sodium amalgam, Devardov's alloy, and sodium dithionite[43]. $LiAlH_4(LaAlD_4)$ or $NaBH_4$ have been used for this purpose[43-47]. Probably attack by the hydride ion is a necessary condition for the conversion of the cobalticenium cation into cyclopentadienylcyclopentadienecobalt. Further interaction of cyclopentadienylcyclopentadienecobalt with lithium aluminium hydride does not entail a change in the structure and properties of the organocobalt compound[44]. It has been shown[42] that the reduction of the cobalticenium cation involves the initial reversible addition of an electron:

$$[(C_5H_5)_2Co]^+X^- + e \rightleftarrows (C_5H_5)_2Co,$$

and then the irreversible addition of hydrogen:

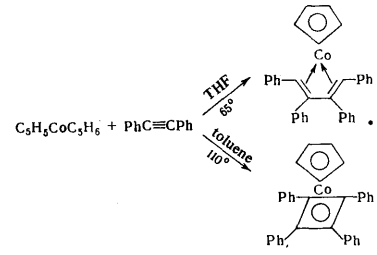
$$(C_5H_5)_2Co + \bar{e} + H^+ \rightarrow C_5H_5CoC_5H_6.$$

All the foregoing considerations apply to substituted cobalticenium salts. Treatment of 1, 1′-dimethoxycarbonylcobalticenium with $NaBH_4$ resulted in the formation of the corresponding organocobalt compound[20]:



If the last compound is not isolated and the reaction mixture formed is sublimed over a period of five days after removing the solvent, it is possible to isolate 1, 1′-dimethoxycarbonylcobaltocene in 47% yield[20]. By treating cyclopentadienylcyclopentadienecobalt with *N*-bromosuccinimide or benzaldehyde, it is possible to obtain cobalticenium salts[44]. The possibility of similar reactions involving nickelocene has not been investigated.

$C_5H_5CoC_5H_6$ and $C_5H_5NiC_5H_7$ are relatively unstable diamagnetic crystalline compounds. $C_5H_5NiC_5H_7$ decomposes on heating in nitrogen. The C_5H_6 group in $C_5H_5CoC_5H_6$ does not enter into the ligand exchange reaction with the cobalticenium cation in acetone solution[24]. When $C_5H_5CoC_5H_6$ is treated with diphenylacetylene[48] in THF at 65°C, the product is cyclopentadienyl-1, 2, 3, 4-tetraphenylbutadienecobalt, while in toluene at 110°C cyclopentadienyltetraphenylcyclobutadienylcobalt ‡ is formed[48,49]:



It is interesting to compare the results of the study of $C_5H_5CoC_5H_6$ and $C_5H_5NiC_5H_7$ by the ^1H NMR method.

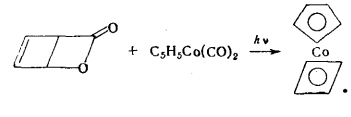
The authors[38] believe that the *endo*-protons are located in the region of the *d* orbitals of the nickel atom, so that they are strongly screened and there is a shift towards high fields (δ = 0.67 p.p.m.). The validity of this assignment has been confirmed by the appreciable broadening of the signal in a high field, which cannot be a consequence, as believed by the authors, of only the spin – spin splitting but suggests an interaction between the *endo*-protons and the nickel atom. If the suggested assignments are adopted, the disappearance of the 0.67 p.p.m. signal from the ^1H NMR spectrum of $C_5H_5NiC_5H_5D_2$ is evidence that the hydrogen adds to the cyclopentadienyl ligand and occupies the *endo*-position[38].

Green et al.[43], who were the first to analyse the ^1H NMR spectrum of $C_5H_5CoC_5H_6$, concluded that the signal in a higher field should be assigned to protons in the *endo*-position. The absence of this signal from the ^1H NMR spectrum of $C_5H_5CoC_5H_5D$ was regarded as evidence supporting the *endo*-addition of the hydrogen atom to the cyclopentadienyl ligand in the reduction of cobaltocene. This assignment is not inconsistent with the analogous interpretation of the infrared spectrum of this compound. The infrared spectra of compounds with similar structures ($C_5H_6CoC_5H_5$, $C_5H_6RhC_5H_5$, and $C_5H_6IrC_5H_5$) have an intense band due to the stretching vibrations of the CH group in the region of 2750 cm^{-1}. Such marked decrease of the frequency is caused, as suggested by Green et al.[43], by the interaction between the metal atom and a hydrogen atom in a favourable position, i.e. in the *endo*-position relative to the metal. The second absorption band of the CH group at 2950 cm^{-1} was assigned to an *exo*-hydrogen atom. The disappearance of the low-frequency band from the infrared spectra of substituted $R-C_5H_5CoC_5H_5$ derivatives was regarded as another piece of evidence supporting the above assignments.

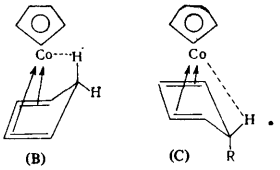
However, X-ray diffraction studies on benzoyl[52] and phenyl[53] derivatives of the above organocobalt compound showed that the group added occupies the *exo*-position, which the authors believe is not in conflict with the above interpretation of the infrared and ^1H NMR spectra[43].

The changes in the infrared and ^1H NMR spectra of $R-C_5H_5CoC_5H_5$ are associated with the differences in the

‡ The corresponding unsubstituted compound was obtained in a moderate yield on photolysing solutions of 2-oxabicyclo[2, 2, 0] hex-5-en-3-one and cyclopentadienyldicarbonylcobalt[20,50]:

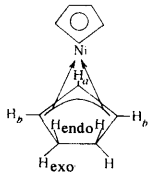
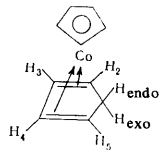


direction in which the methylene group deviates from the plane of the cyclopentadiene ligand. Whereas in the unsubstituted complex the methylene group is bent towards the metal (C), in the substituted derivative it is ben in the opposite direction[54] (D), The angular position of the CHR group greatly increases the distance from the metal to the formally *endo*-hydrogen atom (about 3.0 Å) and the Co – H interaction is weakened:



(B) (C)

Table 1. Parameters of the ^{1}H NMR Spectra of $C_5H_5CoC_5H_6$ and $C_5H_5NiC_5H_7$.

	δ, p.p.m.	Multiplicity	Relative intensity	Assignment	Solvent
a 	5.12	1	5	C_5H_5	C_6D_6
	4.98	3	1	H^a	
	3.83	1	2	H^c	
	1.15	multiplet		H_{exo}	
	0.67[b]	multiplet		H_{endo}	
c 	4.59	1	5	C_5H_5	C_6D_6
	5.25	3	2	H_3H_4	cyclohexane
	2.45	5—6	2 1/4	H_2H_5	
	2.68	3	1/4	H^d_{endo}	
	2.01[e]	2	1	H_{exo}	

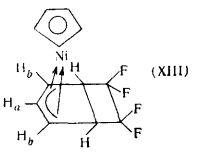
[a] 100 MHz.[38]
[b] There is no signal in the $C_5H_5NiC_5H_5D_2$ spectrum[38].
[c] 40 MHz.[43]
[d] The assignment has been made by analogy with that in Fischer's monograph[51].
[e] There is no signal in the $C_5H_5CoC_5H_5D$ spectrum.[43]

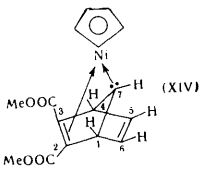
However, an alternative solution of the problem is possible. The methylene group in the substituted and unsubstituted compounds can deviate in the same direction (away from the metal) but to different extents from the plane of the butadiene fragment of the cyclopentadiene ligand. Then the ^{1}H NMR signal of $C_5H_6CoC_5H_5$ in a high field may be a consequence of the screening of one of the protons of the aliphatic group by the π electrons of the cyclopentadiene ligand in the complex[55]. In this case the high-field doublet should correspond to the *exo*-methylene hydrogen atom. The changes in the infrared spectra of the substituted and unsubstituted compounds are then determined by the changes in the angle between the plane of the butadiene fragment and the plane of the methylene group in the ligand. However, all these hypotheses require further X-ray diffraction study.

2. Addition of Alkyls, Alkenes, and Alkynes

The capacity of cobaltocene and nickelocene to add one and two hydrogen atoms respectively to the cyclopentadienyl ligand determines the type of interaction between these metallocenes and saturated and unsaturated compounds. Similar reactions are unknown in the chemistry of ferrocene. The degree of electronic unsaturation of the diene has a significant influence on the nature of its interaction with nickelocene.

The interaction of nickelocene with ethylene led to the isolation of cyclopentadienylcyclopentenylnickel[56]. Subsequent introduction of fluorine into the ethylene molecule reduces the yield of $C_5H_5NiC_5H_7$. The reaction with tetrafluoroethylene gives rise to a compound with the general formula $C_{10}H_{10}NiC_2F_4$, [56] to which structure (XIII) was attributed[56, 57]:

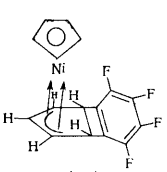

(XIII)

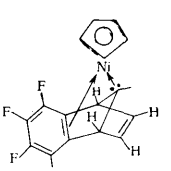

(XIV)

When the dimethyl ester of acetylenedicarboxylic acid is employed as the dienophile, its electron-withdrawing groups favour the addition of the ester via a Diels – Alder reaction, which results in a 68% yield of [2, 3-bis-methoxycarbonyl)-2 π, 5-norbornadien-7-yl](π-cyclopentadienyl) nickel (II) (XIV)[58].

Its structure was confirmed by X-ray diffraction analysis[59]. ^{1}H NMR spectra are also satisfactorily consistent with the proposed structure. Apart from the singlets due to the protons in the cyclopentadienyl ring and the methoxycarbonyl group, the spectrum of (XIV) contains three groups of signals two of which have equal intensities and the third has an intensity smaller by a factor of two. This last signal is in the region of the highest field, which can be accounted for have an effect of the anisotropy of the central metal atom (nickel) on the single proton of the 7-C carbon atom of the norbornadiene ligand[57, 59]. The ^{1}H NMR spectrum of compound (XIII) also has three groups of signals with intensity ratios of 2 : 2 : 1, but the signal with the lowest intensity is observed in the region of the lowest field. This is evidence for the presence of a π-allyl system in the molecule[40, 57, 60]. All these hypotheses have not so far been confirmed by X-ray diffraction studies.

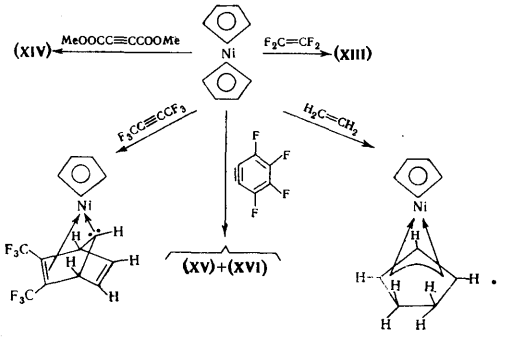
When nickelocene was allowed to react with tetrafluorodehydrobenzene[61], different amounts of both structural isomers with the general formula $(C_5H_5)_2NiC_6F_4$ were isolated:


(XV)


(XVI)

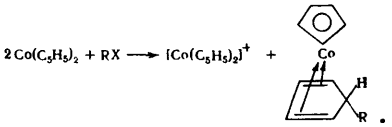
Thus the cyclopentadienyl ligand can combine with olefinic and acetylenic derivatives having electron-accepting groups

in the 1, 2- and 1, 4-positions. This results in the formation of a π-allyl or pseudobutadiene system: §



The addition of olefins, alkyl halides, polyhalogenoalkanes, acyl halides, α-halogenoketones, etc, to cobaltocene takes place with retention of the diene system of the cyclopentadiene fragment. Cobaltocene reacts with tetrafluoroethylene[62]. The infrared spectrum of the products contains ν_{C-H} bands at 3085 and 2940 cm^{-1}. The ^1H NMR spectrum of the compound shows four signals with intensity ratios of 5 : 2 : 2 : 1. On the basis of a detailed analysis of these data[63], the authors concluded that the compounds formed have the structure $C_5H_5CoC_5H_5(CF_2)_2C_5H_5CoC_5H_5$.

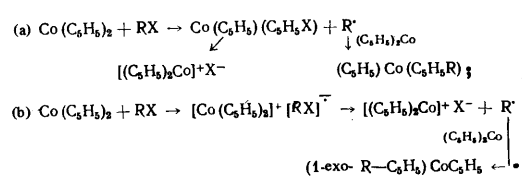
The reaction of cobaltocene and the cobalticenium cation with different organohalogen compounds takes place similarly[43, 64]:



(XVII)

The products have the structure (XVII), where R = CH_2Cl, CH_2Br, $CHCl_2$, $CHBr_2$,[65] etc.[55]. The interaction of cobaltocene with allyl, benzyl, and propargyl halides (R = = $C_6H_5CH=CHCH_2$, $C_6H_5CH_2$, and $C_6H_5C\equiv CCH_2$) was also investigated[66]. Benzoyl chloride[28], α-halogenoketones, and α-halogeno-esters react similarly[65, 67]. Cobaltocene dissolves in chloroform and chlorobenzene without change[65]. However, when the reaction is carried out in the presence of oxygen, a high yield of a compound (XVII), where R = = CCl_3, is formed[68]. Under these conditions, cobaltocene also reacts with acetonitrile, propionitrile, phenylacetylene, and acetone[68], forming the corresponding compounds (XVII). The reaction with acetone gives rise to the dinuclear complex $(C_5H_5CoC_5H_5CH_2)_2CO$.[68]

Two alternative mechanisms of the reaction between cobaltocene and organohalogen compounds have been considered[65, 66, 69]:



§ Nickelocene reacts with perfluorobutyne not only by an addition mechanism but also via a ligand exchange mechanism. A small amount of $(C_5H_5Ni)_2(C_4F_6)$ was isolated[56].

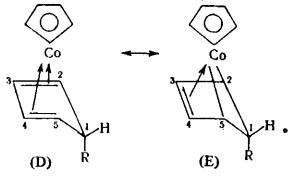
A kinetic study of the reaction did not permit an unambiguous choice. However, the authors are inclined to favour the second mechanism[69] in view of the following qualitative findings: firstly, the rate of reaction of benzyl bromide derivatives is much higher for electron-accepting substituents (p-CN, p-COOEt) and, secondly BBr_3 is known to react with cobaltocene at a temperature as low as -80°C, while $(CH_3)_3NBBr_3$ does not react at 60°C. BBr_3 has more pronounced electron-accepting properties and a higher B – Br bond energy than $(CH_3)_3NBBr_3$. Evidently the reactivity is determined by the electron-accepting properties and not the dissociation energy of the B – Br bond. This conclusion is confirmed also by the finding that the reactivity of $CHBr_3$ in relation to cobaltocene is much lower than that of boron bromide, while the energy of the C – Br bond is also significantly lower than that of the B – Br bond [D(B – Br) = 87.4 kcal $mole^{-1}$; D(C – Br) = 55.5 kcal $mole^{-1}$][69].

The data for the decomposition of azoisobutyronitrile in the presence of cobaltocene are consistent with the proposed radical reaction mechanism[70]. The product is compound (XVII), where R = $C(CH_3)_2CN$. On the other hand, the reaction of chlorotriphenylmethane with cobaltocene results only in the oxidation of the latter to cobalticenium ions[71]. It was suggested that the reaction proceeds according to the equation:

$$(C_5H_5)_2Co + Ph_3C^+ \rightarrow [(C_5H_5)_2Co]^+ + [Ph_3C^\cdot].$$

It is believed[71] that the reaction of nickelocene with the carbonium ion also results in the formation of the nickelicenium cation. However, the low stability of this compound and its paramagnetic properties give rise to the possibility of further interaction between $[(C_5H_5)_2Ni]^+$ and the $(C_6H_5)_3C^\cdot$ radical with formation of the complex. $C_5H_5NiC_5H_5C(C_6H_5)_3$. By virtue of its instability, the latter decomposes into $NiCl_2$ and $C_5H_5-C(C_6H_5)_3$.[71]

The study of *exo*-phenylcyclopentadienecyclopentadienylcobalt[53] showed that the $C_{(1)}$ carbon atom deviates from the plane of the cyclopentadiene ligand by 36° and the bond lengths in the "butadiene" fragment are non-uniform (the $C_{(3)}-C_{(4)}$ distance is a minimum, amounting to 1.38 Å):



(D) (E)

Therefore it was suggested that the carbon atoms in the 2- and 5-positions be regarded as sp^3-hybridised, which would imply that the complex is predominantly in form (F). However, X-ray diffraction study of *exo*-benzoylcyclopentadienecyclopentadienylcobalt showed that the bond order in the "butadiene" system of cyclopentadiene is relatively constant[53]. The authors are inclined to attribute these contradictions to differences between the inductive effects of the benzoyl and phenyl substituents.

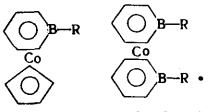
The bond between the substituent and the cyclopentadiene fragment of an *exo*-substituted organocobalt compound is known to be fairly labile. *Exo*-(trichloromethyl)cyclopentadiene(cyclopentadienyl)cobalt splits off a CCl_3 group and is converted into the cobalticenium cation on acid hydrolysis or on standing in acetone. $C_5H_5CoC_5H_5CCl_2COOCH_3$ behaves similarly[67]. On the other hand, although chlorine exchange between LiCl and $(exo\text{-}CCl_3-C_5H_5)Co(C_5H_5)$ is not observed, the C – X bond in compounds of the type $(exo\text{-}XCH_2-C_5H_5)Co(C_5H_5)$[55, 72, 73] or the B – X bond in the

compound (exo-$C_6H_5BXC_5H_5$)CoC_5H_5 (Herberich et al.[74]) is thermally unstable and undergoes heterolysis extremely readily.

Thus whereas $(C_5H_5)Co(C_5H_5CF_2CF_2C_5H_5)Co(C_5H_5)$ sublimes *in vacuo* at 125°C and $C_5H_5CoC_5H_5 - CHCl_2$ and $C_5H_5CoC_5H_5 - CH_2Cl$ are still stable at 70°C, the bromo-compounds decompose appreciably already at room temperature and $C_5H_5CoC_5H_5CH_2I$ decomposes in the solid state at 0°C. The heterolysis of the C – X bond in these compounds terminates in a ring expansion reaction and the formation of cyclohexadienylcyclopentadienylcobalt halide. The reaction with the pseudocarbonium ions derived from organocobalt compounds leads to the formation of a new class of paramagnetic cobalt complexes[75]. The unsubstituted borabenzene

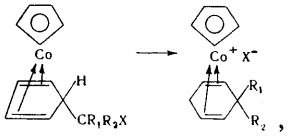


is unknown. However, the reaction of cobaltocene with substituted boron dibromide and subsequent heterolysis of the C – B bond in the resulting compound [exo-Br(R)BC_5H_5]CoC_5H_5 and then the formation of a six-membered ring leads to cobalt complexes of substituted borabenzene ¶ [74,75]:



The compounds have one unpaired electron, the magnetic moment of which is 1.8 ± 0.1 Bohr magnetons[75]. The ionisation potentials of these compounds are higher than that of cobaltocene, which indicates more pronounced electron-accepting properties of the group C_5H_5BR compared with C_5H_5.

The reaction of the pseudocarbonium cation,



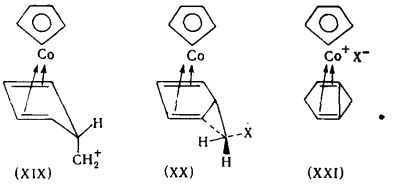
(XVIII)

discovered by Herberich and coworkers[55,65,72] resembles the solvolysis of alkyl halides.

Compounds (XVIII) react under very mild solvolytic conditions[72], such that their structural analogues isobutyl and neopentyl halides hardly ionise. The rate of reaction depends on the medium and the positions of the substituents in the cyclopentadiene ligand (*endo*- and *exo*).

In non-polar solvents, the rate is insignificant, while in acetone, methanol, or their mixture with water the reaction proceeds smoothly and virtually without side products. The reactivity of compounds (XVIII) decreases in the series I > Br > Cl. The effect of substituents on the rate of reaction is the same as for the solvolysis of alkyl halides which has an S_N1 mechanism. Thus the bromo-derivative (XVIII), where $R_1 = R_2 = CH_3$, is much more labile than the secondary bromo-substituted derivative (XVIII), where $R_1 = CH_3$ and $R_2 = H$. Moreover, this reaction is observed only when the substituent occupies the *exo*-position[77].

Thus the authors believe that the order of the reaction (S_N1), the solvolytic effect, which is somewhat weaker than in the solvolysis of t-butyl halides[78], and the entropy of activation[72] indicate the heterolysis of the C – X bond in compounds (XVIII) as the rate-determining stage of the reaction. It is noteworthy that the reaction of primary alkyl chlorides (XVIII) ($R_1 = R_2 = H$, X = Cl) in methanol is faster than the solvolysis of t-butyl chloride[79]. This enhanced reactivity of primary alkyl halides is believed[72] to be evidence in support of the stabilisation of the intermediate ion (XIX) by the entire electron system of the $C_5H_5CoC_5H_5$ group. It is suggested that two processes take place synchronously — heterolysis of the C – X bond and rearrangement of the cyclopentadiene ligand. The authors believe [72] that the six-membered ring is formed either via the complex (XX) or via a short-lived intermediate (XXI):

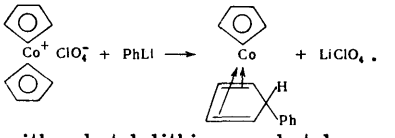


(XIX) (XX) (XXI)

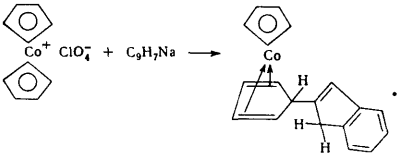
The kinetic study of the process is consistent with either of the two mechanisms proposed.

3. Reactions with Nucleophilic Agents

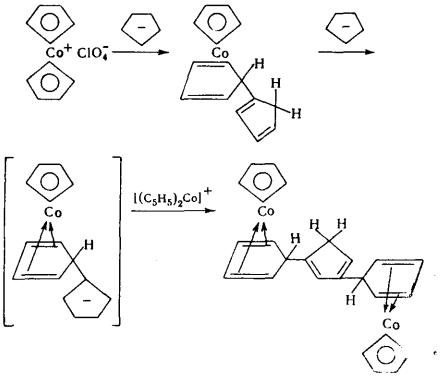
Reactions involving nucleophilic addition to the cyclopentadienyl ligand of nickelocene, where organometallic compounds are employed as the attacking agents, are so far unknown. The cobalticenium cation readily reacts with organolithium or organomagnesium compounds[28] and also with sodium hydroxide and sodamide[80]:



The reaction with n-butyl-lithium, n-butylmagnesium bromide, and methylmagnesium iodide takes place similarly. The reaction of cobalticenium perchlorate with indenylsodium also gives rise to a "normal" addition product — indenylcyclopentadienecyclopentadienylcobalt[81]:



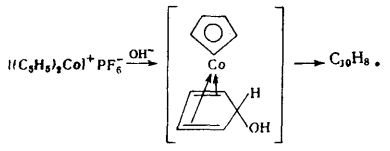
Sodium cyclopentadienide and its methyl derivative react with cobalticenium salts to form dinuclear complexes[81]. The suggested reaction mechanism can be represented as follows in a general form:



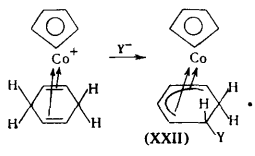
¶ 1, 1'Bis(methoxyborabenzene)cobalt has been investigated by X:ray diffraction[76].

The central ring may be hydrogenated. Initially two hydrogen atoms are added readily and then a further two but with greater difficulty. The compound does not react with maleic anhydride, probably owing to steric factors[81].

The reaction between the cobalticenium cation and sodium hydroxide with formation of azulene has been carried out[80]. The authors believe that it proceeds via the following mechanisum:



Nucleophilic agents such as sodium borohydride[72], ammonia, aliphatic amines, and sodium methoxide[82] add readily to the cyclohexadienyl ligand of the cyclohexadienylcyclopentadienylcobalt cation; the product is cyclopentadienylcyclohexa-1, 3-dienecobalt (XXII):



(XXII)

There is an analogous reaction of the cyclohexadienyltricarbonyliron cation[83, 84].

Thus the numerous addition reactions characteristic of cobaltocene and nickelocene distinguish these compounds from ferrocene. The ferrocene system, like the benzene system, is extremely passive in relation to reactions involving the addition of hydrogen, alkyl halides, alkenes, alkynes, and other reagents[1, 2].

V. LIGAND EXCHANGE REACTIONS IN COBALTOCENE AND NICKELOCENE

The ligand exchange reaction is characteristic of all three types of sandwich compounds discussed in the present review. However, the nature of the ligand capable of replacing the cyclopentadienyl group in ferrocene, nickelocene, and cobaltocene is different. In the first case the ligands can be benzene[85-87], cyclopentadiene[88], their substituted derivatives, and many others. The ligand exchange reaction has been investigated most extensively in nickelocene. The cobalticenium system is more passive in ligand exchange processes.

The reaction of cobaltocene with $Fe(CO)_5$ gives rise to dicobalticenium tridecacarbonylferrate[89]. Under analogous conditions, nickelocene enters into a ligand exchange reaction and is converted into (cyclopentadienyliron)cyclopentadienylnickel tricarbonyl[90, 91]. This is not fortuitous either. Whereas ligand exchange reactions are extremely characteristic of nickelocene and many experimental data have been accumulated in this field, under these conditions cobaltocene is usually converted into a cation or undergoes no change whatever. Similarly, when a triphenylphosphonium halide is allowed to react with nickelocene, the phosphine ligand is coordinated to the nickel atom and a cyclopentadienyl fragment is split off[92], while cobaltocene is oxidised with formation of cobalticenium halide[93]. Mass-spectrometric studies on the dicyclopentadienyl compounds of cobalt and nickel[94, 95] have shown that the energy required to form metallocenium ion $[(C_5H_5)_2M]^+$ is much lower for cobaltocene than for nickelocene (6.21 eV and 7.16 eV † respectively). The stability of the cobalt–cyclopentadienyl linkage in the cobalticenium cation is well known[11, 24-27]. Moreover, the formation of the $[C_5H_5M]^+$ fragment takes place more readily in the case of nickelocene. The energies of ionisation of cobaltocene and nickelocene, resulting in the formation of $[C_5H_5M]^+$, are 14.00 and 12.59 eV respectively. Probably this can explain the finding that nickelocene reacts readily with various nucleophilic agents under mild conditions, exchanging one or two cyclopentadienyl rings. Thus, whereas nickelocene reacts with PF_3 at 60°C and normal pressure to form tetrakis(trifluorophosphine)nickel[98], the complex $(C_5H_5)Co(PF_3)_2$ was obtained from cobaltocene and PF_3 at 170°C and a pressure of 300 atm.[99]. Under analogous conditions, cobaltocene and its derivatives react with carbon monoxide, which results in the isolation of the extremely labile cyclopentadienylcobalt dicarbonyl[20, 100]:

$$(RC_5H_4)_2Co \xrightarrow{CO} RC_5H_4Co(CO)_2.$$

[R = H (Fischer and Jira (Ref.100) or $COOCH_3$ (Rosenblum et. al. (Ref.20)]

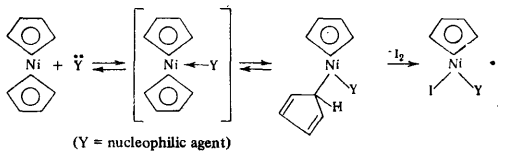
1. SUBSTITUTION OF BOTH CYCLOPENTADIENYL LIGANDS

The capacity of nickelocene to exchange readily a cyclopentadienyl ligand resulted in the formation under mild conditions of various nickel complexes. The analogous reaction with $Ni(CO)_4$ or nickel halides takes place under more severe conditions. Various phosphorus- and nitrogen-containing nickel complexes were obtained in this way[101-103]. The substitution of both cyclopentadienyl ligands in the cobaltocene molecule take place under more severe conditions (on refluxing in dioxan for a week)[104]. The product is formed in low yield:

$$(C_5H_5)_2Co + P(OPh)_3 \rightarrow (Co[P(OPh)_3]_4)_n.$$

2. SUBSTITUTION OF ONE CYCLOPENTADIENYL LIGAND

When equimolar amounts of nickelocene and triphenylphosphine react in benzene at 50°C, one cyclopentadienyl ring is substituted. Further treatment with iodine or hydrogen chloride leads to the formation of $(C_5H_5)Ni(R_3P)X$, where X = Cl or I.[105]. It is believed[105] that the nucleophilic agent is initially coordinated to the nickel atom. Simultaneously with or after the coordination, a $\pi-\sigma$ rearrangement of one of the cyclopentadienyl rings takes place. The final stage of the process involves the stabilization of the unstable σ complex by the substitution of the σ-linked cyclopentadienyl ligand:

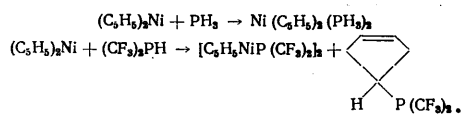


(Y = nucleophilic agent)

The results obtained in the study of the kinetics of the reaction of nickelocene with mercaptans are consistent with the mechanism proposed[106]. Reactions of nickelocene

† The ionisation potential quoted is consistent with other published values: 6,8 eV,[96] 7.06 eV,[94] and 6.75 eV.[97]

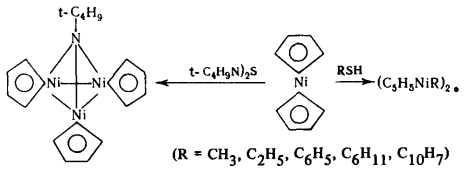
with phosphine[107] and bis(trifluoromethyl)phosphine are known[108]:



In both cases the ease with which the phosphine forms a cluster or interacts with unsaturated hydrocarbons is striking. It is interesting that the reaction between an olefin and a phosphine takes place only following irradiation with ultraviolet light[108]. Therefore it has been suggested [108] that the nickel atom behaves at a catalyst in the addition of a phosphine to the cyclopentadienyl ligand. On heating a 4 – 6-fold excess of $P(OR)_3$ (R = C_6H_5, CH_3, or C_2H_5) with cobaltocene for 3 – 7 days at 100°C, one cyclopentadienyl ligand is also exchanged[104]. The stability of the product $C_5H_5CoL_2$ depends on the nature of the substituent in the ligand L. Analysis of the complexes known so far makes it possible to arrange these compounds in the following series in terms of the decrease of their resistance to the action of oxidising agents: L = $P(OC_6H_5)_3$ > > $PF_3 \simeq P(OCH_3)_3 \simeq P(OC_2H_5)_3 > CO > P(C_6H_5)_3$.[104]

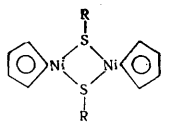
a. Reactions Yielding Polynuclear Complexes

Reactions of nickelocene and 1, 1′-dimethylnickelocene with thioalcohols[106, 109, 110] and the di-imide of sulphurous acid[111] are known. They result in the formation of organonickel compounds containing sulphur[109, 110] or nitrogen[111] bridge atoms:



(R = CH_3, C_2H_5, C_6H_5, C_6H_{11}, $C_{10}H_7$)

The reactions have been carried out with equimolar amounts of the initial compounds in benzene at room temperature. The dark-brown compounds are diamagnetic and stable in air. It has been suggested[109] that the sulphur atoms are sp^3-hybridised and the compounds have the following structure:

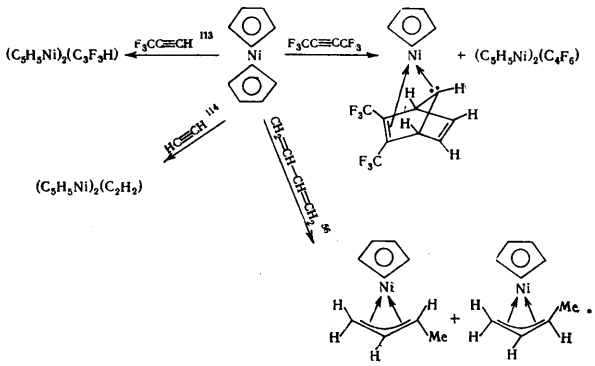


In a study of the polymerisation of cyclohexyl isocyanide in the presence of catalytic amounts of nickelocene, the compound $(C_5H_5NiCNC_6H_{11})_2$ was isolated[112]. $(C_5H_5NiCO)_2$ and $(C_5H_5Ni)_2C_2H_2$ were also used as catalysts. It was shown that nickelocene is the most effective catalyst of the process[112].

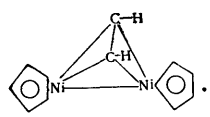
b. Reactions with Unsaturated Compounds

Earlier it was noted that, depending on the electron-accepting properties of the substituents at the unsaturated carbon atom, the reactions of nickelocene with unsaturated hydrocarbons involve addition to the 1, 2- or 1, 4-positions. As the triple bond becomes more nucleophilic, the ligand exchange becomes the dominant process in the reactions of nickelocene with unsaturated compounds.

Thus, whereas the reaction of nickelocene with perfluorobut-2-yne[56] leads to a mixture of products of addition to the 1, 4-positions and of ligand exchange, the reaction with trifluoropropyne[113] results in the formation of a green complex the elemental analysis and mass spectra of which correspond to the formula $(C_5H_5Ni)_2(C_3F_3H)$. A compound of a similar type was obtained from nickelocene and acetylene[114]:



X-ray diffraction analysis of $(C_5H_5Ni)_2(C_2H_2)$ showed[115] that acetylene occupies a bridging position between two nickel atoms:

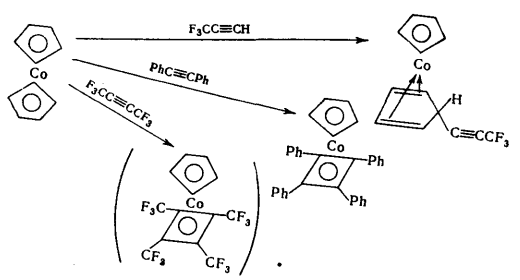


It is noteworthy that cobaltocene can also react with trifluoropropyne[113], but this leads to the formation of a compound with the general formula $(C_5H_5)Co(C_5H_5C \equiv CCF_3)$. ^1H and ^{19}F NMR spectra showed that this is a product of the "normal" addition to the cobaltocene molecule[113]. The reaction of perfluorobut-2-yne with cobaltocene results in the formation of traces of the stable complex $(C_5H_5)CoC_8F_{12}$,[116] and the reaction with tolane terminates with formation of a high yield of the aromatic complex $(C_5H_5)Co[C_4(C_6H_5)_4]$[116] (see scheme on p. 286). The complexes $(C_5H_5)Co(C_4R_4)$, where R = $Si(CH_3)_3$, CoCh3, etc, can be obtained similarly[145].

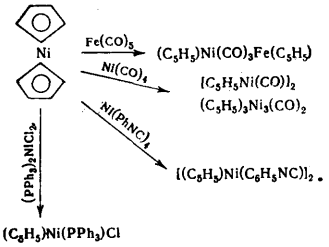
c. Disproportionation Reactions

The ease with which nickelocene exchanges its cyclopentadienyl rings promotes its involvement in disproportionation reactions. Reactions with $Fe(CO)_5$,[90, 91] $Ni(CO)_4$,[117–120] $Ni(C_6H_5NC)_4$,[121] and $[(C_6H_5)_3P]_2NiCl_2$[121, 122] are known.

Schematic representation of the interactions of cobaltocene with unsaturated compounds.



The disproportionation and synproportionation reactions of ferrocene homologues take place in the presence of aluminium chloride[88]:

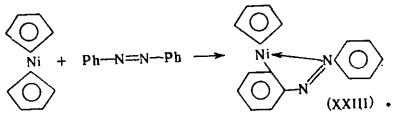


The only disproportionation reaction of cobaltocene known hitherto is the reaction with cyclobutadienyltetraphenylpalladium dibromide[123]:

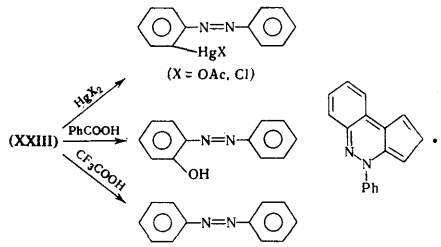
$$(C_5H_5)_2Co + (C_4Ph_4)PdBr_2 \rightarrow (C_5H_5)Co(C_4Ph_4).$$

d. Reactions Involving the Formation of Complexes with an M – C σ Bond.

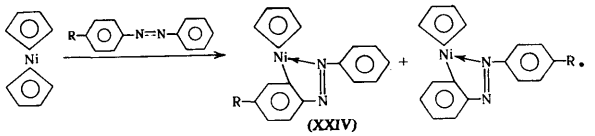
The reaction of nickelocene with azobenzene was described for the first time by Kleiman and Dubek[124]:



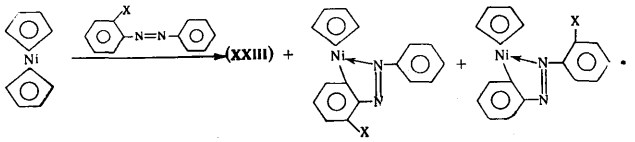
The study of the reactions and the ^1H NMR spectra of (2-azophenyl)phenylcyclopentadienylnickel (XXIII) demonstrated the existence of an Ni – C σ bond with the *ortho*-carbon atom of one of the benzene rings[125]:



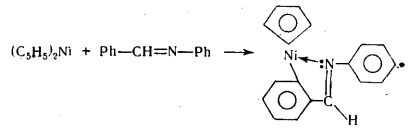
Examination of the influence of various *ortho*- and *para*-substituents in azobenzene on the nature of the compounds formed in the reaction[126] showed that *para*-substituted azobenzenes [$(CH_3)_2N$, CH_3O, CH_3, F, Cl, $COOCH_3$, CN, or NO_2] react with nickelocene to form the complexes (XXIV):



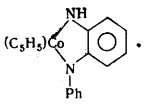
The reaction of ortho-substituted halogenoazobenzenes with nickelocene takes place anomalously:



The rate of formation of compounds (XXIII) increases in the series azobenzene < *o*-chloroazobenzene < *o*-bromoazobenzene. Benzylideneaniline reacts with nickelocene like azobenzene[127]:



Cobaltocene also reacts with azobenzene[128]. However, here the product is a complex to which the following structure has been assigned:



The yield of the reaction is 2.4%.

When nickelocene is treated with an alky- or alkynylmagnesium iodide in the presence of triphenylphosphine[129], nickel complexes also containing an Ni – C σ bond are formed:

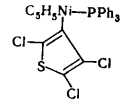
$$(C_5H_5)_2Ni + Ph_3P \xrightarrow{RMgI} C_5H_5Ni(Ph_3P)\sigma\text{-}R.$$
$$(R‡ = Me \text{ or } C\equiv CR').$$

Another convenient procedure for the preparation of these compounds involves the reaction between $(C_5H_5)Ni[(C_6H_5)_3P]Cl$ and various organolithium or organomagnesium compounds[122, 131, 132]:

$$C_5H_5Ni(Ph_3P)Cl + RMgX \rightarrow C_5H_5Ni(Ph_3P)\sigma\text{-}R,$$

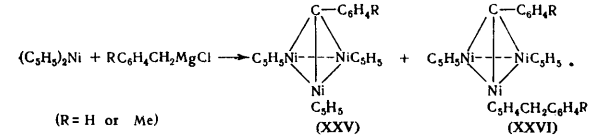
where R = aliphatic and aromatic substituents.

The above organonickel compounds consist of dark-green diamagnetic crystals which are fairly stable in air. The stability of complexes of the type $(PR_3)_2NiR'_2$ or $(PR_3)_2NiR'X$ is known to increase in the following sequence depending on the nature of the substituent: alkyl < ethynyl or substituted ethynyl ≃ *o*-aryl[133]. This sequence is probably determined by the possibility of the formation of a $d_\pi - p_\pi$ bond between the nickel atom and σ - R and also by the inhibition of the rotation of the *ortho*-substituted phenyl group about the Ni – C bond, which likewise promotes the interaction of the ligand π orbitals with the *d* orbitals of the nickel atom[133]. In this connection, it is interesting to note that, in contrast to the stable complex



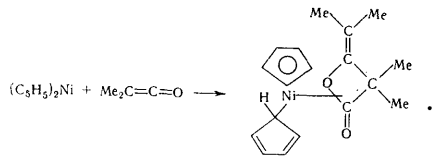
a thiophen derivative without chlorine atoms has not been isolated at all[132].

‡ On the other hand, the reaction of nickelocene with benzylmagnesium chloride at room temperature results in the formation of nickel cluster compounds[130]:



It is suggested[130] that compound (XXVI) is formed owing to an unusual alkylation process: (XXVI) + $RC_6H_4CH_2MgCl$ → (XXVI), which has been confirmed experimentally.

The interaction of a ketone with nickelocene[134] gives rise to a compound in which one of the cyclopentadienyl ligands is linked to the nickel atom via a σ bond:



VI. ELECTRON-DONATING PROPERTIES OF COBALTOCENE AND NICKELOCENE

Analysis of the chemical reactions of cobaltocene and nickelocene reveals significant differences between the chemical behaviour of each compound. This is a consequence of the electronic structures of these π complexes. Moreover, the different stabilities of their cations, $[(C_5H_5)_2CO]^+ > [(C_5H_5)_2Ni]^+$ and $[(C_5H_5)_2Ni]^{2+}$, play a significant role.

1. CONDITIONS GOVERNING THE FORMATION OF THE METALLOCENIUM CATION.

The oxidation-reduction potentials of the metallocenes (Fe, Co, Ni) were determined initially in 90% ethanol using 0.1 M sodium perchlorate solution as the electrolyte. The results were $E_{1/2}$ = +0.30 V for ferrocene, $E_{1/2}$ = = -1.16 V for cobaltocene[135], and $E_{1/2}$ = -0.08 V for nickelocene[136]. Further studies in this field led to a revision of these values[42, 45].

The polarographic reduction of substituted cobalticenium salts at a mercury electrode in an aqueous alcoholic medium was also investigated[32]. The half-wave potentials $E_{1/2}$ are independent of the pH of the medium. The effect of substituents on $E_{1/2}$ is of the usual type[32]. Table 2 lists for comparison the oxidation-reduction potentials of the unsubstituted metallocenes and certain π acceptors.

Table 2. Oxidation-reduction potentials of the metallocenes (Fe, Co, Ni) and certain π aceptors*.

Donor	$E°$, V	Refs.	π Acceptor	$E°$, V	References
$(C_5H_5)_2$ Fe	+0.30	137	*p*-benzoquinone	−0.50	138
	+0.42	42	*p*-chloranil (CA)	+0.01	138
$(C_5H_5)_2$ Co	−0.98	42	tetracyanoethylene (TCE)	+0.15	139
$(C_5H_5)_2$ Ni	+0.01	42	2,3-dichloro-5,6-dicyanoquinone (DDQ)	+0.51	138

* All the E values were determined in acetonitrile.

The metallocenes exhibit a high electron-donating capacity, which is reflected in their tendency to form readily salts and charge-transfer complexes.

Interaction with Strong Oxidising Agents (Halogens, Thiocyanogen, and Picric Acid)

The electron deficiency of the π acceptor and the electron-donating properties of the metallocene determine the type of the charge-transfer complex formed. Partial charge separation between the components, $(\text{Don.})^{+\delta}$ $(\text{Acc.})^{-\delta}$, leads to the formation of a π complex of the dative type[140]. In this case the infrared and ultraviolet spectra of the π complex exhibit all the features characteristic of the metallocene and the π acceptor. When the charge separation is more complete, a charge-transfer complex of the ionic type is produced[141]. Further development of this process terminates with the formation of a salt in which the metallocene is converted into the metallocenium cation and the π acceptor behaves as the anion. Treatment of ferrocene with chlorine[142] or bromine[143] is known to result in the formation of a ferricenium halogenoferrate (III) salt $[(C_5H_5)_2Fe]FeX_4$. Thiocyanogen, the oxidising capacity of which is intermediate between those of bromine and iodine, forms the salt $[(C_5H_5)_2Fe]_2Fe(NCS)_4$, but in this case the metal in the anion is in a lower state of oxidation[144]. The series is terminated by iodine[146, 147], which forms polyiodides with ferrocene. When thiocyanogen is allowed to react with cobaltocene, the latter does not decompose like ferrocene. The product is cobalticenium thiocyanate $[(C_5H_5)_2Co](NCS)$.[144]

Iodine reacts similarly with cobaltocene[148], forming cobalticenium tri- or octo-iodide. When iodine reacts with nickelocene, the latter is decomposed[148]. According to its chemical properties, bis(tricarbonylcyclopentadienylchromium) is an analogue of iodine. Its reaction with cobaltocene gives rise to the cobalticenium salt $[(C_5H_5)_2Co][C_5H_5Cr(CO)_3]$.[149] Treatment of cobaltocene with HX (X = Cl, Br, or I) in ether results in the formation of cobalticenium tetrahalogenocobaltates $[(C_5H_5)_2Co]_2CoX_4$.[93] The authors believe[93] that the reaction proceeds in several stages:

$$(C_5H_5)_2Co^{\cdot} + HX \rightarrow [(C_5H_5)_2Co]^+X^- + H^{\cdot}, \quad (1)$$

$$[(C_5H_5)_2Co]^+X^- + HX \xrightarrow{\text{slow}} C_5H_6 + C_5H_5^{\cdot} + CoX_2^{\cdot}, \quad (2)$$

$$2[(C_5H_5)_2Co]^+X^- + CoX_2 \xrightarrow{\text{rapid}} [(C_5H_5)_2Co]_2^+[CoX_4]^-. \quad (3)$$

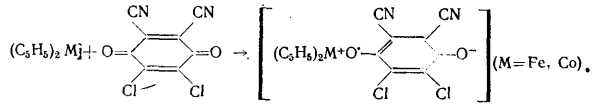
Hydrogen fluoride, being a weak acid, cannot decompose the cobalticenium ion [Eqn. (2)] and therefore the reaction results in the formation of the complex $[(C_5H_5)_2Co]HF_2$.[93] The reaction of the hydrogen halides HX (X = Cl, Br, or I) in the presence of triphenylphosphine with cobaltocene in ethereal solution leads to the formation of $[(C_5H_5)_2Co]^+X^-$ (X = Cl, Br, or I) as the main product and as well as small amounts of $[(C_5H_5)_2Co]_2^+[CoX_4]^-$ and $[(C_5H_5)_2Co][Co(PRh_3)X_3$.[150, 151] Trichloroacetic acid reacts with ferrocene to form a paramagnetic compound with reducing properties[152]. The authors believe that an electron of the ferrocene molecule is bound by the acid proton, as happens in the reaction between an alkali metal and ammonia or an amine[153]. The interaction between trichloroacetic acid and cobaltocene takes place similarly. The product is the paramagnetic compound $[(C_5H_5)_2Co]^+(BH^-)(BH)_2$, where B = CCl_3COO.[154] However, the usual cobalticenium salt is also formed in this case together with the charge-transfer complex, which is fully consistent with the electron-accepting properties of cobaltocene.

Picric acid reacts with ferrocene to form a charge-transfer complex[155, 156], while its reactions with cobaltocene[148] and nickelocene[148] give rise to salts §.

§ However, it has been shown that in the reaction between picric acid and cobaltocene, a charge-transfer complex is formed together with the cobalticenium salt[154].

2. CHARGE-TRANSFER COMPLEXES

Treatment of ferrocene[157] or cobaltocene[157,158] with 2, 3-dichloro-5, 6-dicyanoquinone (DDQ) or 7, 7, 8, 8-tetracyanoquinodimethan results in both cases in the formation of stable complexes with a 1 : 1 component ratio. The infrared spectra of the complexes with DDQ do not contain the ν_{CO} band (1680 cm^{-1}), but a new band appears at 1590 cm^{-1}, which has been assigned to the vibrations of the phenoxy-group[159]; this suggests that these compounds are ionic π complexes[157]:



It is noteworthy that only the addition of a solution containing a 40-fold molar excess of $AgClO_4$ relative to the DDQ – cobaltocene and DDQ – ferrocene complexes results in the appearance in the ultraviolet spectra of these compounds of the band which has been assigned to absorption by the metallocenium cations. It has been shown experimentally[157] that the component ratio in the DDQ – nickelocene complex is not 1 : 1 and the infrared spectrum of this compound differs significantly from those of the corresponding ferrocene and cobaltocene π complexes. It is most probable that, by virtue of its electron-donating properties, nickelocene forms a mixture of salts of the singly and doubly-charged cations, $[(C_5H_5)_2Ni]^+$ and $[(C_5H_5)_2Ni]^{2+}$, in its reaction with DDQ.

Tetracyanoethylene (TCE)[157] and *p*-chloranil (CA)[160] form charge-transfer complexes with cobaltocene and nickelocene, which differ significantly in stability. As a stronger electron acceptor, TCE forms unstable compounds with cobaltocene and nickelocene, which can be kept in an atmosphere of nitrogen or at a low temperature (-80°C). The interaction with CA, which is a weaker electron-acceptor than TCE, leads to the formation of stable complexes. This anomaly can probably be accounted for by the lower "electron capacity" of the tetracyanoethylene system compared with the CA aromatic molecule and also by the higher electron-donating capacity of cobaltocene and nickelocene compared with ferrocene. This explanation has been confirmed by the properties of the TCE–ferrocene[161] and TCE – bis(tetrahydroindenyl)iron[157] complexes. The introduction of an alkyl substituent is known to enhance the electron-donating properties of the ferrocene system, increasing thereby the likelihood of the transfer of electron density to the π acceptor. Presumably the π complex of substituted ferrocene with TCE is less stable than the complex with an aromatic π acceptor. Indeed the TCE–bis(tetrahydroindenyl)iron complex is labile, while the complex with DDQ is quite stable[157]. On the basis of ultraviolet and infrared spectroscopic data, the TCE – ferrocene complex was assigned to the dative type[157,161-163] and the TCE–cobaltocene complex was assumed to be ionic[157], CA, the electron-accepting properties of which differ only slightly from those of TCE, forms similar complexes with ferrocene[157], cobaltocene[157,164], and nickelocene[157,160].

The data presented show that, depending on the relative contributions by the electron-donating and electron-accepting properties of both components of the charge-transfer complexes, the degree of charge separation between the components may be various. Dative complexes are usually formed by ferrocene. The interaction with cobaltocene and nickelocene leads to the formation of ionic complexes.

The capacity to form complexes with electron acceptors is a general property of the three types of compounds considered.

* * *

In conclusion we shall consider the properties of the metallocenes which must be taken into account in their synthesis. The metallocenes can be obtained in the gas phase[165,166] by the reaction between metal salts and cyclopentadiene. However, the yield is not always quantitative. Cyclopentadiene or its dimer are used as the starting materials for the synthesis of the metallocenes by reaction with the corresponding metal carbonyls[136,167]:

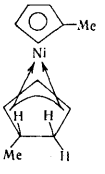
$$C_5H_6 + M_n(CO)_m \rightarrow (C_5H_5)_2M + CO$$

for M=Fe, m=5, n=1; for M=Co, m=8, n=2).

The main product of this type of reaction with nickel carbonyl is cyclopentadienylcyclopentenylnickel. Nickelocene is formed as a side product in an amount not exceeding 5%[136,168,169]:

$$C_5H_6 + Ni(CO)_4 \rightarrow C_5H_5NiC_5H_7 + (C_5H_5)_2Ni.$$

The interaction of $CH_3C_5H_5$ with $Ni(CO)_4$ led to the isolation of a red diamagnetic compound to which the following structure was attributed on the basis of ^1H NMR spectra[170]:



When cyclopentadiene is introduced into the reaction in the form of the anion, the dimer of cyclopentadienylnickel carbonyl $(C_5H_5NiCO)_2$ is isolated[171]:

$$C_5H_5Na + Ni(CO)_4 \rightarrow (C_5H_5NiCO)_2.$$

Probably this compound is obtained by a ligand exchange reaction between the nickel carbonyl and the nickelocene formed, which is extremely typical for the chemistry of the latter[117-120]. It is noteworthy that the interaction of di-μ-carbonyldi(cyclopentadienyl)dinickel(0) $(C_5H_5NiCO_2)$ with a monodentate ligand L {L = CO, $(C_6H_5)_3As$, $(C_6H_5)_3P$, $C_2H_5(C_6H_5)_2P$, $[(CH_3)_2N]_3P$, etc.} leads to the formation of a nickelocene in 30 – 70% yield[172-173]:

$$(C_5H_5NiCO)_2 + 2L \rightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2.$$

The amount of ionic character of cyclopentadiene or its substituted derivative is also significant in the formation of nickelocene. One can employ different bases, the nucleophilic properties of which are sufficient for the formation of the ionised form of cyclopentadiene. A fairly wide range of amines, with $pK_a < 9$, is usually employed for unsubstituted cyclopentadiene[174]. The so called "amine method" was found to be valid in all three cases. Ferrocene[175,176], cobaltocene[176], its cation[175], and nickelocene[176] were obtained in high yields. More powerful nucleophilic agents can also be used. Among these mention may be made of sodium methoxide[177], potassium hydroxide[178], ethylmagnesium bromide[26,136,179,180], and thallium(I) hydroxide[181-183]. In all these cases, the metallocenes were obtained in high yields. Sodium cyclopentadienide can also be employed as a cyclopentadienylating agent. It is synthesised by metallating cyclopentadiene with metallic sodium[184], sodamide[185,186], sodium hydride[187], or sodium acetylide[188].

It is noteworthy that in the synthesis attention should be concentrated on the choice of the transition metal salt. When nickel chloride is replaced by its acetylacetonate in the reaction with cyclopentadienylmagnesium bromide, the yield of nickelocene increases from 8 to 60%.[136] If cobalt chloride is replaced by the bromide, the reaction of the latter with cyclopentadienylthallium results in a quantitative isolation of the cobalticenium salt instead of the 25% yield in the case of cobalt chloride[181]. On the other hand, the yield of nickelocene increases from 0 to 25 and 70% as nickel(II) chloride is replaced in succession by its bromide[181] and then by hexamminenickel(II) chloride[182]. Cobalticenium salts can be obtained in high yields also by the disproportionation reaction of dihalogenocyclopentadienylcobalt[189]:

$$[C_5H_5CoX_2]_n \rightarrow [C_5H_5)_2Co]^+.X^- + CoX_3,$$

where X = I, Br, or Cl. The π complexes of cobalt can be arranged in the following sequence in terms of the decrease of their resistance to disproportionation: $[Co(C_5H_5)I_2] > [Co(C_5H_5)Br_2] > [Co(C_5H_5)Cl_2]$.[189]

Ferrocene derivatives are usually obtained by an electrophilic substitution reaction[1-10]. The direct introduction of a substituent into cobaltocene and nickelocene molecules is complicated by the ready oxidisability of the compounds and their tendency to undergo addition and ligand exchange reactions. This was discussed above in detail. Therefore cobaltocene and nickelocene derivatives can be obtained either from fulvenes[29, 32, 190] or from substituted cyclopentadienes[33, 191-193, 200] and cyclopentenones[30, 194]. Members of the homologous series of metallocenes [29, 32, 191, 193], polysubstituted heterohomologous series of metallocenes[192, 193], chlorometallocenes[200], homoannular homologues of metallocenes[33, 195], and also hydroxy-derivatives of ferrocene and cobaltocene[30, 194] have been obtained in this way. An interesting method involving the employment of ferrocene derivatives, which are widely available, as the starting materials for the synthesis of other metallocenes, in particular cobalticenium salts, has been described[196]:

$$(RC_5H_4)_2Fe \xrightarrow[2.CoCl_2,\ THF]{1.LiEtNH_2} [(RC_5H_4)Co]^+X^-,$$

(a) R = Et; X = $^1/_2PtCl_6$; (b) THF = Pr; X = $HgCl_3$).

If the substituted cyclopentadiene obtained by the reductive cleavage of ferrocene is isolated as an organothallium derivative, it can be converted into other metallocenes[181, 197, 198]:

$$(R_1R_2C_5H_3)_2Fe \xrightarrow[2.\ TlOH,\ H_2O]{1.\ LiEtNH_2} R_1R_2C_5H_3Tl \xrightarrow{MX_2} (R_1R_2C_5H_3)_2M.$$

(M = Co, Ni).

In addition, nickelocene has been converted into ferrocene[199], which may be important for the identification of nickelocene and its derivatives. Thus interconversions of the dicyclopentadienyl derivatives of the metals in the Fe, Co, Ni triad are possible.

Examination of the chemical behaviour of nickelocene and cobaltocene (substitutions, addition, and ligand exchange reactions) showed that information about the reactions of the first type is comparatively scanty. Therefore in the future the efforts of investigators will probably be directed towards research in this field.

REFERENCES

1. A. N. Nesmeyanov, "Izbrannye Trudy" (Selected Works), Izd. Akad. Nauk. SSSR, Moscow, 1959, Vol. 2.
2. A. N. Nesmeyanov, "Khimiya Ferrotsena" (The Chemistry of Ferrocene), Izd. Nauka, Moscow, 1969.
3. M. Rosenblum, Chemistry of the Iron Group Metallocenes, Intersci. Publ., New York, 1965, Part 1.
4. D. E. Bublitz and K. L. Rinehart, Organic Reactions, 17, 1, 1969.
5. I. Motoyama and M. Sato, J. Synth. Org. Chem. Japan., 29, 664 (1971).
6. M. I. Bruce, Organomet. Chem. Rev., 5B, 379 (1969).
7. M. I. Bruce, Organomet. Chem. Rev., 6B, 665 (1970).
8. M. I. Bruce, Organomet. Chem. Rev., 9B, 123 (1972); 10B, 75 (1972).
9. E. G. Perevalova and T. V. Nikitina, "Organometallic Reactions" Wiley Intersc., 1972, Vol. 4, p. 163.
10. A. N. Nesmeyanov and E. G. Perevalova, Uspekhi Khim., 27, 3 (1958).
11. G. Wilkinson, F. A. Cotton and J. M. Birmingham, J. Inorg. Nuclear Chem., 2, 95 (1956).
12. V. N. Setkina and D. N. Kursanov, Uspekhi Khim., 37, 1742 (1968) [Russ. Chem. Rev., No. 10 (1968)].
13. E. V. Bykova and V. N. Setkina, Izv. Akad. Nauk. SSSR, Ser. Khim., 1626 (1967).
14. D. N. Kursanov, E. V. Bykova, and V. N. Setkina, Dokl. Akad. Nauk. SSSR, 184, 100 (1969).
15. F. S. Yakushkin, V. N. Setkina, E. A. Yakovléva, A. I. Shatenshtein, and D. N. Kursanov, Izd. Akad. Nauk SSSR, Ser. Khim., 206 (1967).
16. D. N. Kursanov, V. N. Setkina, N. K. Baranetskaya, G. G. Dvoryantseva, and R. B. Materikova, Dokl. Akad. Nauk SSSR, 161, 847 (1965).
17. C. Furlani and J. Collamati, Chem. Ber., 95, 2928 (1962).
18. M. D. Rausch and R. Genetti, J. Amer. Chem. Soc., 89, 5502 (1967).
19. M. D. Rausch and R. Genetti, J. Org. Chem., 35, 3888 (1970).
20. M. Rosenblum, B. North, D. Wells, and W. P. Giering, J. Amer. Chem. Soc., 94, 1239 (1972).
21. M. D. Rausch, R. M. Tuggle and D. L. Weaver, J. Amer. Chem. Soc., 92, 4981 (1970).
22. W. K. Olander and T. L. Brown, J. Amer. Chem. Soc., 94, 2139 (1972).
23. R. M. Tuggle and D. L. Weaver, Inorg. Chem., 10, 1504 (1971).
24. J. F. Weiher, S. Katz and A. F. Voigt, Inorg. Chem., 1, 504 (1962).
25. E. O. Fischer and R. Jira, Z. Naturforsch., 8B, 1 (1953).
26. G. Wilkinson, J. Amer. Chem. Soc., 74, 6148 (1952).
27. E. O. Fischer, Rec. Trav. chim., 75, 629 (1956).
28. E. O. Fischer and G. E. Herberich, Chem. Ber., 94, 1517 (1961).
29. G. R. Knox, I. D. Munro, P. L. Pauson, G. H. Smith, and W. E. Watts, J. Chem. Soc., 4619 (1961).
30. J. E. Sheats and M. D. Rausch, J. Org. Chem., 35, 3245 (1970).
31. F. S. Arimoto and A. Haven, J. Amer. Chem. Soc., 77, 6295 (1955).
32. N. E. Murr and R. Dabard, Compt. rend., Ser (C), 272, 1989 (1971).
33. A. N. Nesmeyanov, E. V. Leonova, N. S. Kochetkova, and L. Ya. Golovleva, Dokl. Akad. Nauk. SSSR, 191, 1070 (1970).
34. G. Wilkinson, F. A. Cotton, and J. M. Birmingham, J. Inorg. Nuclear Chem., 2, 95 (1956).
35. E. O. Fischer, Angew. Chem., 67, 475 (1955).

36. A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina, and N. A. Simukova, Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk, 739 (1956).
37. A. G. Turnbull, Austral. J. Chem., 20, 2059 (1967).
38. K. W. Barnett, F. D. Mango, and C. A. Reilly, J. Amer. Chem. Soc., 91, 3387 (1969).
39. J. C. Wollensak, US P. 3088960 (1963); Chem. Abs., 59, 10127B (1963).
40. M. Dubeck and A. H. Filbey, J. Amer. Chem. Soc., 83, 1257 (1961).
41. A. H. Filbey, 138th Meeting Amer. Chem. Soc., New York, September, 1960, Abs. 54.
42. S. P. Gubin, S. A. Smirnova, and L. I. Denisovich, J. Organomet. Chem., 30, 257 (1971).
43. M. L. H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc., 3753 (1959).
44. G. Wilkinson, US P. 3088961 (1963); Chem. Abs., 59, 11567H (1963).
45. A. A. Vleck, Coll. Czech. Chem. Comm., 30, 952 (1965).
46. J. C. Brantley, US P. 2988563 (1961); Chem. Abs., 55, 24789i (1961).
47. J. M. Birmingham, A. H. Fischer, and G. Wilkinson, Naturwiss., 42, 96 (1955).
48. A. Nakamura, Met Inst. Sic. Ind. Res., Osaka, Univ., 19, 81 (1962).
49. A. Nakamura and H. Hagihara, Bull. Chem. Soc. Japan, 34, 452 (1961).
50. M. Rosenblum, W. P. Giering, B. North, and D. Wells, J. Organomet. Chem., 28, C17 (1971).
51. E. O. Fischer and H. W. Wehner, "Metal π Complexes" (Translated into Russian), Izd. Mir, Moscow, 1968, p. 48.
52. M. R. Churchill, J. Organomet. Chem., 4, 258 (1965).
53. M. R. Churchill and R. Mason, Proc. Chem. Soc., 112 (1963); Proc. Roy. Soc., A 279, 191 (1964).
54. R. Mason and G. Wilkinson, Experientia, Essays in Coord. Chem., Suppl., 9, 233 (1964).
55. G. E. Herberich, G. Greiss, and H. F. Heil, J. Organomet. Chem., 22, 723 (1970).
56. D. W. McBride, E. Dudek, and F. G. A. Stone, J. Chem. Soc., 1752 (1964).
57. D. W. McBride, P. L. Pruet, E. Pitcher, and F. G. A. Stone, J. Amer. Chem. Soc., 84, 497 (1962).
58. M. Dubeck, J. Amer. Chem. Soc., 82, 6193 (1960).
59. L. F. Dahl and C. H. Wei, Inorg. Chem., 2, 713 (1963).
60. R. F. Heck, J. C. W. Chien, and D. S. Breslow, Chem. Ind., (London) 986 (1961).
61. D. M. Roe and A. G. Massey, J. Organomet. Chem., 20, PI (1969); 23, 547 (1970).
62. K. F. Watterson and G. Wilkinson, Chem. Ind., (London) 1358 (1960).
63. H. Hochn, L. Pratt, K. F. Watterson and G. Wilkinson, J. Chem. Soc., 2738 (1961).
64. S. Katz, J. Weiher, and A. Voight, J. Amer. Chem. Soc., 80, 6459 (1958).
65. G. E. Herberich, E. Bauer, and J. S. Schwarzer, J. Organomet. Chem., 17, 445 (1969).
66. G. E. Herberich and E. Bauer, J. Organomet. Chem., 16, 301 (1969).
67. G. E. Herberich and G. Greiss, J. Organomet. Chem., 27, 113 (1971).
68. H. Kojima, S. Takahashi, H. Yamazaki, and N. Hagihara, Bull. Chem. Soc. Japan, 43, 2272 (1970).
69. G. E. Herberich and J. Schwarzer, J. Organomet. Chem., 34, C43 (1972).
70. G. E. Herberich and J. Schwarzer, Angew. Chem., 82, 883 (1970); Angew. Chem., Intern. Ed., 9, 897 (1970).
71. H. Werner, G. Mattmann, A. Salzer, and T. Winkler, J. Organomet. Chem., 25, 461 (1970).
72. G. E. Herberich and J. Schwarzer, Chem. Ber., 103, 2016 (1970).
73. G. E. Herberich and J. Schwarzer, Angew. Chem., 81, 153 (1969).
74. G. E. Herberich, G. Greiss, and H. F. Heil, Angew. Chem., Intern. Ed, 10, 805 (1970); Angew. Chem., 82, 138 (1970).
75. G. F. Herberich, G. Greiss, H. F. Heil, and J. Müller, Chem. Comm., 1328 (1971).
76. G. Huttner and B. Krieg, Angew. Chem., 84, 29 (1972).
77. G. E. Herberich and H. Müller, Chem. Ber., 104, 2781 (1971).
78. E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 70, 846 (1948).
79. A. R. Olson and R. S. Halford, J. Amer. Chem. Soc., 59, 2644 (1937).
80. C. J. Attridge, S. J. Baker, and A. W. Parkins, Organomet. in Chem. Synthesis, 1, 183 (1971).
81. E. O. Fischer, W. Fellmann, and G. E. Herberich, Chem. Ber., 95, 2254 (1962).
82. G. E. Herberich and R. Michelbrink, Chem. Ber., 103, 3615 (1970).
83. A. J. Birch, P. E. Gross, J. Lewis, D. A. White, and S. B. Wild, J. Chem. Soc., A, 332 (1968).
84. M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, J. Chem. Soc., A, 240 (1967).
85. A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, Dokl. Akad. Nauk SSSR, 149, 615 (1963).
86. A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Shilovtseva, Dokl. Akad. Nauk SSSR, 160, 1327 (1965).
87. A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Isaeva, Dokl. Akad. Nauk SSSR, 176, 106 (1967).
88. D. E. Bublitz, J. Organomet. Chem., 16, 149 (1969).
89. A. G. Razuvaev, P. G. Petukhov, V. I. Ermolaev, and V. P. Beketov, Zhur. Obshch. Khim., 37, 672 (1967).
90. J. E. Tilney-Bassett, Proc. Chem. Soc., 419 (1960).
91. J. E. Tilney-Bassett, J. Chem. Soc., 4784 (1963).
92. M. van den Akker and F. Jellinek, Rec. Trav. chim., 86, 897 (1967).
93. M. van den Akker and F. Jellinek, Rec. Trav. chim., 90, 1101 (1971).
94. L. Friedman, A. P. Irsa, and G. Wilkinson, J. Amer. Chem. Soc., 77, 3689 (1955).
95. J. Müller and L. D'Or, J. Organomet. Chem., 10, 313 (1967).
96. P. Shissel, D. J. McAdoo, E. Hedaya, and D. W. Neil, J. Chem. Phys., 49, 5061 (1968).
97. A. Foffani, S. Pignataro, G. Disterfano, and G. Innerta, J. Organomet. Chem., 11, 571 (1968).
98. J. F. Nixon, Chem. Comm., 34 (1966).
99. Th. Kruck, W. Hieber, and W. Lang, Angew. Chem., Intern. Ed., 5, 247 (1966); Angew. Chem., 78, 208 (1966).
100. E. O. Fischer and R. Jira, Z. Naturlorsch., 10b, 355 (1955).
101. I. R. Olechowski, C. G. McAllister, and R. F. Clark, Inorg. Chem., 4, 246 (1965).
102. H. Behrens and K. Meyer, Z. Naturforsch., 21b, 489 (1966).
103. H. Werner, V. Harber, and E. Deckelmann, Helv. Chim., Acta, 52, 1081 (1969).
104. V. Harder, J. Müller, and H. Werner, Helv. Chim. Acta, 54, 1 (1971).

105. Yu. A. Ustynyuk, T. I. Voevodskaya, N. A. Zharikova, and N. A. Ustynyuk, Dokl. Akad. Nauk. SSSR, 181, 372 (1968).
106. P. C. Ellgen and C. D. Gregory, Inorg. Chem., 10, 980 (1971).
107. F. Klainberg and E. L. Muetterties, J. Amer. Chem. Soc., 90, 3296 (1968).
108. R. C. Dobbie, M. Green, and F. G. A. Stone, J. Chem. Soc. A, 1881 (1969).
109. W. K. Schropp, J. Inorg. Nuclear Chem., 24, 1688 (1962).
110. J. Cooke, M. Green, and F. G. A. Stone, J. Chem. Soc. A, 170 (1968).
111. S. Otsuka, A. Nakamura, and T. Yoshida, Inorg. Chem., 7, 261 (1968).
112. Y. Yamamoto and N. Nagihara, Bull. Chem. Soc. Japan, 39, 1084 (1966).
113. D. A. Harbourne and F. G. A. Stone, J. Chem. Soc. A, 1765 (1968).
114. M. Dubeck, J. Amer. Chem. Soc., 82, 502 (1960).
115. O. S. Mills and B. W. Shaw, Acta Cryst., 18, 562 (1965).
116. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, J. Chem. Soc., 3488 (1962).
117. E. O. Fischer and C. Palm, Chem. Ber., 91, 1725 (1955).
118. T. H. Coffield and K. G. Ihrman, US P. 3086035, (1963); Chem. Abs., 59, 8792B (1963).
119. T. H. Coffield and K. G. Ihrman, US P. 3086036; Chem. Abs., 59, 8791F (1963).
120. T. H. Coffield and K. G. Ihrman, US P. 3086037; Chem. Abs., 59, 8791D (1963).
121. P. L. Pauson and W. Stubbs, Angew. Chem., 74, 466 (1962).
122. H. Yamazaki, T. Nishido, Y. Matsumoto, S. Sumida, and N. Hagihara, J. Organomet. Chem., 6, 86 (1966).
123. P. M. Maitlis and M. L. Lames, J. Amer. Chem. Soc., 85, 1887 (1963).
124. I. P. Kleiman and M. Dubeck, J. Amer. Chem. Soc., 85, 1544 (1963).
125. Yu. A. Ustynyuk, I. V. Barinov, and E. I. Sirotkina, Dokl. Akad. Nauk SSSR, 187, 112 (1969).
126. Yu. A. Ustynyuk and I. V. Barinov, J. Organomet. Chem., 23, 551 (1970).
127. Yu. A. Ustynyuk, V. A. Chertkov, and I. V. Barinov, J. Organomet. Chem., 29, C53 (1971).
128. T. Joh, H. Hagihara, and S. Murahashi, Bull. Chem. Soc., Japan, 40, 661 (1967).
129. H. Yamazaki, Y. Matsumoto, H. Kojima, and N. Hagihara, Mem. Inst. Sci. Ind. Res., 25, 121 (1968).
130. T. I. Voyevodskaya, I. M. Pribytkova, and Yu. A. Ustynyuk, J. Organomet. Chem., 37, 187 (1972).
131. H. Yamazaki and N. Hagihara, Bull. Chem. Soc. Japan, 37, 907 (1964).
132. M. D. Rausch, T. R. Criswell, and A. K. Ignatowicz, J. Organomet. Chem., 13, 419 (1968).
133. J. Chatt and B. L. Shaw, J. Chem. Soc., 1718 (1960).
134. M. Sato, K. Ichibori, and F. Sato, J. Organomet. Chem., 26, 267 (1971).
135. J. Page and G. Wilkinson, J. Amer. Chem. Soc., 74, 6149 (1952).
136. G. Wilkinson, P. Pauson and F. A. Cotton, J. Amer. Chem. Soc., 76, 1970 (1954).
137. J. Tirouflet, E. Laviran, R. Dabard, and J. Komenda, Bull. Soc. Chim. France, 857 (1963).
138. M. E. Peover, J. Chem. Soc., 4540 (1962).
139. O. W. Webster, W. Mahler, and R. E. Benson, J. Amer. Chem. Soc., 84, 3678 (1962).
140. Y. Matsunaga, J. Chem. Phys., 41, 1609 (1964).
141. D. B. Chestnut and W. D. Phillips, J. Chem. Phys., 35, 1002 (1961).
142. A. N. Nesmejanov, E. G. Perewalowa, and L. P. Yurjiwa, Chem. Ber., 93, 2729 (1960).
143. R. Riemschneider and D. Helm, Chem. Ber., 89, 155 (1956).
144. M. F. A. Dove and D. B. Sowerby, Z. Naturforsch., 20b, 394 (1965).
145. J. F. Helling, S. C. Rennison, and A. Merijan, J. Amer. Chem. Soc., 89, 7140 (1967).
146. A. B. Savitskii, Zhur. Obshch. Khim., 30, 3167 (1960).
147. A. N. Nesmeyanov, R. B. Materikova, V. I. Kzenzenko, N. P. Palitsin, N. S. Kochetkova, and T. I. Grigor'eva, Zhur. Org. Khim., 9, 378 (1973).
148. B. Hetnarski, Z. Grabovski and W. Kutkiewicz, Roczniki Chem., 43, 4589 (1969).
149. A. Miyake, H. Kondo, and M. Aoyama, Angew. Chem., 81, 498 (1969); Angew. Chem. Intern. Ed., 8, 520 (1969).
150. M. van den Akker, Dissertation, Groningen, 1970.
151. M. van den Akker, R. Olthot, F. van Dolhuis, and F. Jellinek, Rec. Trav. chim., 91, 75 (1972).
152. M. Aly, R. Bramley, J. Upadhyay, A. Wassermann, and P. Woolliams, Chem. Comm., 404 (1965).
153. M. C. R. Symons, Quart. Rev., 13, 99 (1959).
154. D. V. Banthorpe, B. V. Charlwood, and A. Wassermann, Chem. Comm., 294 (1972).
155. B. Getnarski, Dokl. Akad. Nauk, 156, 604 (1964).
156. B. Getnarski, Bull. Acad. polon. Sci. Ser. Sci. chim., geol., georg., 13, 515, 523, 557, 563 (1965).
157. R. L. Brandon, J. H. Osierki, and A. Ottenberg, J. Org. Chem., 31, 1214 (1966).
158. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and M. E. Mochel, J. Amer. Chem. Soc., 84, 3374 (1962).
159. E. A. Chandross and R. Kreilick, J. Amer. Chem., 85, 2530 (1963).
160. J. C. Goan, E. Berg, and H. E. Podall, J. Org. Chem., Soc., 29, 975 (1964).
161. M. Rosenblum, R. W. Fisch, and C. Bennett, J. Amer. Chem. Soc., 86, 5166 (1964).
162. R. L. Collins and R. Rettig, J. Inorg. Nuclear Chem., 29, 503 (1967).
163. W. H. Baddley, Inorg. Chim. Acta, 2, 7 (1968).
164. H. Watanabe, J. Notoyama and K. Hata, Bull. Chem. Soc. Japan, 39, 850 (1966).
165. R. Riemschneider, US P. 3064020 (1962); Chem. Abs., 58, 11403E (1963).
166. D. C. Freeman, US P. 3032569 (1962); Chem. Abs., 57, 13807C (1962).
167. G. Wilkinson, J. Amer. Chem. Soc., 76, 209 (1954).
168. E. O. Fischer and H. Werner, Chem. Ber., 92, 1423 (1959).
169. E. O. Fischer, U. Zahn, and H. Werner, US P. 3121729 (1964); Chem. Abs., 60, 15913g (1964).
170. E. O. Fischer and H. Werner, Chem. Ber., 95, 695 (1962).
171. H. J. Corder and W. Jaeckh, BRD. P. 1131214 (1962); Chem. Abs., 57, 15157H (1962).
172. P. Ellgen, Inorg. Chem., 10, 232 (1971).
173. R. B. King, Inorg. Chem., 2, 936 (1963).
174. E. H. Morehouse, US P. 3071695 (1963); Chem. Abs., 58, 1260F (1963).
175. A. I. Titov, E. S. Lisitsina, and M. R. Shentova, Dokl. Akad. Nauk SSSR, 130, 341 (1960).
176. H. Watanabe, I. Motogama, and K. Hata, Bull. Chem. Soc. Japan, 38, 853 (1965).

177. J. F. Cordes, Z. Naturforsch., 21, (8), 746 (1966).
178. W. L. Jolly and D. J. Chazan, Inorg. Synt., 11, 122 (1968).
179. G. Wilkinson, P. L. Pauson, J. M. Birmingham, and F. A. Cotton, J. Amer. Chem. Soc., 75, 1011 (1953).
180. A. F. Reid and P. C. Wailes, Inorg. Chem., 5, 1213, (1966).
181. A. N. Nesmeyanov, R. V. Materikova, and N. S. Kochetkova, Izv. Akad. Nauk SSSR, Ser. Khim., 1334 (1963).
182. A. N. Nesmeyanov, R. B. Materikova, N. S. Kochetkova, and R. V. Luk'yanova, Izv. Akad. Nauk SSSR, Ser. Khim., 975 (1969).
183. C. C. Hunt and J. R. Doyle, J. Inorg. Nuclear Chem. Letters, 2, 283 (1966).
184. J. F. Cordes, Chem. Ber., 95, 3084, (1962).
185. E. G. Lindstrom and M. R. Barusch, US P. 2862945 (1958); Chem. Abs., 53, 3240F (1959).
186. C. L. Hobbs, US P. 733129 (1955); Chem. Abs., 50, 7146a (1956).
187. J. J. Bulloff, US P. 303093 (1962); Chem. Abs., 57, 7312e (1962).
188. C. L. Hobbs, US P. 3092647 (1963); Chem. Abs., 59, 11568e (1963).
189. D. M. Roe and P. M. Maitlis, J. Chem. Soc., A, 3173 (1971).
190. E. O. Fischer and B. J. Weimann, J. Organomet. Chem., 8, 535 (1967).
191. H. T. Reynolds and G. Wilkinson, J. Inorg. Nuclear Chem., 9, 86 (1959).
192. R. B. King and M. B. Bisnette, J. Organomet. Chem., 8, 287 (1967).
193. N. A. Nesmeyanov, E. V. Leonova, N. S. Kochetkova, S. M. Butyugin, and I. S. Meisner, Izv. Akad. Nauk SSSR, Ser. Khim., 106 (1971).
194. R. E. Benson and R. V. Lindsey, J. Amer. Chem. Soc., 79, 5417 (1957).
195. R. Markby, H. W. Sternberg, and I. Wender, Chem. Ind. (London) 1381 (1959).
196. A. N. Nesmeyanov, R. B. Materikova, N. S. Kochetkova, and L. A. Tsurgozen, Dokl. Akad. Nauk SSSR, 160, 137 (1965).
197. A. N. Nesmeyanov, R. B. Materikova, E. I. Fedin, N. S. Kochetkova, P. V. Petrovskii, L. A. Fedorov, and E. V. Leonova, Dokl. Akad. Nauk SSSR, 177, 586 (1967).
198. A. N. Nesmeyanov, R. B. Materikova, N. S. Kochetkova, and E. V. Leonova, Dokl. Akad. Nauk SSSR, 177, 131 (1967).
199. E. V. Leonova, Candidate's Thesis, Institute of Organic Derivatives of the Elements, Moscow, 1971.
200. G. Wulfsberg and R. West, J. Amer. Chem. Soc., 94, 6069 (1972).

Institute of Organic Derivatives
of the Elements, USSR Academy
of Sciences, Moscow