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Heterometallic Ferrocene-based Transition Metal Compounds

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The literature data on the synthesis, properties, and applications of ferrocene derivatives containing a *d* element or its inorganic and organic derivatives in the molecule are described systematically and surveyed.
The bibliography includes 293 references.

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I. INTRODUCTION

The practical applications of ferrocene and its derivatives have greatly expanded in recent times[1-4] primarily due to the successful development of synthetic studies on this extremely interesting class of compounds.

Among the wide variety of ferrocene derivatives, compounds containing in the molecule another transition metal, namely dinuclear and polynuclear heterometallic derivatives of ferrocene (HMF), occupy a special place. They have been investigated extremely vigorously in recent years. More than 300 compounds have been synthesised and extensive experimental data on their properties and practical applications have accumulated. It is noteworthy that the principal results for HMF have been obtained in the last ten years and as yet have not been adequately surveyed in the literature. The majority of the studies published up to 1970 are discussed in monographs[5-7]. Individual scattered data on HMF have also been published in annual reviews on ferrocene[8-19] and in Gmelin's handbooks[20-25]. A review devoted to ferrocene-containing metal complexes, in which these compounds have been formally classified on the basis of the nature of the heterometal, was published[26] in 1981. It covers up approximately one-third of the published literature but little attention is devoted to the chemistry of HMF, in particular its synthetic aspects.

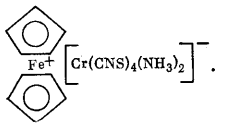
The aim of the present review is to give a systematic account of the literature data, mainly on the synthesis and also on the properties and applications of HMF, and to classify the existing compounds. The generalisations made concerning the methods of synthesis of HMF can be used to develop procedures for the preparation of polynuclear compounds based on other organometallic compounds of transition metals. The literature up to 1980 inclusive and the majority of the publications in 1981 are covered.

II. TYPES OF HETEROMETALLIC DERIVATIVES OF FERROCENE AND METHODS OF THEIR SYNTHESIS

HMF can be most rationally classified taking into account the characteristics of the chemical bond whereby the ferrocene fragment is coupled to a derivative of another metal in the course of the formation of the HMF. This approach takes into account not only the specific features of the bond but also its genesis, reflecting thereby to some extent also the method of synthesis of the compound. The proposed classification of HMF is used in this review and in its subdivision into sections.

1. Salts of the Ferrocenium Cation

One of the most unusual reactions in the chemistry of ferrocene is its oxidation to the ferrocenium cation, which takes place readily in an acid medium[20]. In order to obtain the HMF, the ferrocenium cation may be combined with an anion incorporating the transition metal atom. The first bimetallic salt obtained in this way has been ferrocenium reineckate[20]:



This salt precipitates when an acid solution of ferrocenium sulphate is mixed with a solution of the Reinecke salt. The infrared spectra[27] and thermal decomposition[28] of this compound have been investigated. Ferrocenium molybdate, tungstosilicate[27], metatungstate, and tetravanadate[29,30], which are solid powders insoluble in organic solvents, were obtained similarly to the reineckate. The formula $[FcH]MoO_4$ was attributed[27] to the molybdate†. There is a possibility of the formation of $[FcH]Mo_8O_{26}.2H_2O$, which is associated with the polymerisation of the molybdate ions in an acid medium and the tendency of ferrocenium cations to form precipitates with bulky anions[30]. The reineckates of substituted ferrocenes have also been isolated[21,31].

A series of compounds of the ferrocenium cation with noble metal anions have been obtained: ferrocenium hexachloroplatinate $[FcH]PtCl_6$ [from ferrocenium chloroferrate(III) and chloroplatinic acid][32] and salts with gold-containing anions[33]: $[(FcX)^+(AuCl_4)^-]_3Au$, where X = H, Cl, Br, I, Et, Ph, CN, NO_2, COMe, COPh, or COOMe. These compounds are almost quantitatively precipitated on interaction of ferrocene derivatives with chloroauric acid. In a number of instances (X = H, Cl, CN, COOMe) gold was washed out with aqua regia and the compounds $[FcX]AuCl_4$ were isolated.

Similar complexes of palladium $\{[FcH][PdCl_3]\}$,[34] iridium $\{[FcH][IrCl_4(PMe_2Ph)_2]\}$,[35] vanadium $\{[FcH]VOX_3$(X = Cl or Br)$\}$,[36-39] and titanium $\{[FcH]TiCl_4\}$[38,39] were obtained by the reaction of ferrocene with the corresponding salt in a hydrocarbon medium in the absence of oxidants. The ionic nature of the compounds was confirmed by Mössbauer[34], ultraviolet, and infrared spectroscopy[36,37]. Thermochemical

† Here and henceforth Fc = ferrocenyl ($C_5H_5FeC_5H_4$) and correspondingly FcH = ferrocene.

study of the formation of complexes of ferrocene with Lewis acids[38] showed that an ionic complex is formed if the energy of the donor–acceptor bond exceeds the ionisation energy of ferrocene. There exists also information about the synthesis of a ferrocenium salt with a complex nickel-containing anion: $[FcH][Ni(S_2C_4F_6)_2]$.[20] Single crystals of this compound exhibit a high conductivity.

2. Salts of Ferrocene-containing Acids

Compounds of this type are obtained by the reaction of the corresponding acid with transition metal salts. The copper salts of ferrocenecarboxylic[22,40], ferrocenedicarboxylic[5], and ferrocenylcyanoacrylic acids[24], as well as the uranyl salts of ferrocenemonocarboxylic and ferrocenedicarboxylic acids[41] have bee described. Such salts, which are coloured powders insoluble (with some exceptions[42]) in organic solvents, have been described also for other ferrocene acids; ferrocenemonosulphonic acid $[(Fc{-}SO_3)_2M.4H_2O$, M = Cu or Mn],[43] ferrocenedithiocarboxylic acid $[(Fe{-}CSS)_2M$, M = Cu,[40] Co, Ni, Mn, Cu, Pd,[42] or MoO_2 [44]], ferrocenehydroxamic acid $[(Fc{-}CONHO)_2Cu]$, and ferrocenylacetylhydroxamic acid $[(Fc{-}CH_2CONHO)_2Cu]$.[45,46]

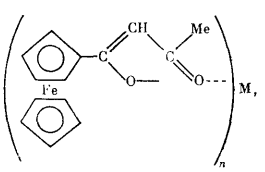
The fairly stable gold-containing derivatives of thioferrocene, which is dimeric in solution and is obtained by the exchange reaction[47]

$$Fc{-}SNa + ClAuPPh_3 \rightarrow Fc{-}SAuPPh_3 ,$$

may be assigned to the same type of HMF. Its interaction with fluoroboric acid results in the formation of the cationic complexes $[Fc{-}S(AuPPh_3)_2]^+BF_4^-$ and $[Fc{-}S(AuPPh_3)_2PPh_3]^+.BF_4^-$.

3. Chelate Compounds

One of the ways of synthesising HMF involves the use of ferrocene-containing β-diketones as chelating ligands. Stable compounds soluble in organic solvents have been obtained from acetoacetyl ferrocene in 70–90% yield:[22,48–57]



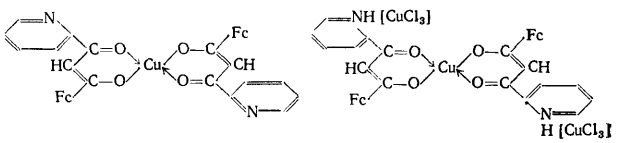
M = Ni, Co, Cu, Mn, Cr, VO, Ru; $n = 2, 3$.

Like metal acetylacetonates, they are capable of forming adducts with electron-donating molecules (pyridine and water)[49–51,56]. Nickel ferrocenoylpivaloylmethanate[58], copper ferrocenoylbenzoylmethanate[53], copper, palladium[53], allylpalladium[59,60], and ruthenium[57] ferrocenoyltrifluoroacetonates, a series of copper[61] and uranyl[41,62] complexes of 1,1′-bis(acetoacetyl)ferrocene and 1,1′-bis(benzoylacetyl)ferrocene, the ethylenediaminenickel complex of 1,1′-bis(acetoacetyl)ferrocene[63] and the cyclopentadienylnickel complex of ferrocenoyltrifluoroacetone (NFTA) [64] have also been described. The metal : iron ratio in these compounds varies with the oxidation state of the metal ion and the number of β-diketone substituents in ferrocene. In contrast to its fluorine-free analogue, in reactions with dichlorometallocenes under mild conditions, NFTA substitutes a chlorine atom and a cyclopentadienyl group with formation of metallocene bis-β-diketonates[60,64]:

$$Cp_2MCl_2 + 2NFTA \rightarrow CpM(FTA)_2Cl,\ M = Ti,\ Zr,\ Hf,\ Nb .$$

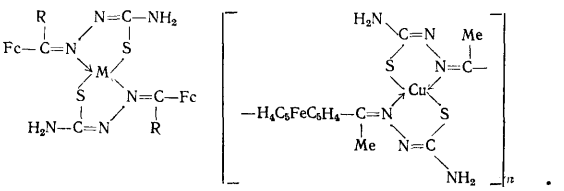
Metallocenes β-diketonates are brightly coloured crystalline substances which are readily soluble in organic solvents, are stable in air, and have relatively high decomposition temperatures.

The isomeric pyridoylferrocenoylmethanates behave unusually in their reactions with copper salts[65]. By virtue of the presence of the pyridine nitrogen atom they form chelates with the ratio Fe : Cu = 1 : 0.6–1 : 3.5 depending on the ratio of the reactants and their concentrations. Several compounds of the type



have been isolated and characterised.

There is also a possibility of the formation of chelates from ferrocene thiosemicarbazones. Copper, nickel, and cobalt chelates based on formylferrocene thiosemicarbazones[66–68], acetylferrocene thiosemicarbazones, and 1,1′-diacetylferrocene bis(thiosemicarbazones) [69] have been obtained:

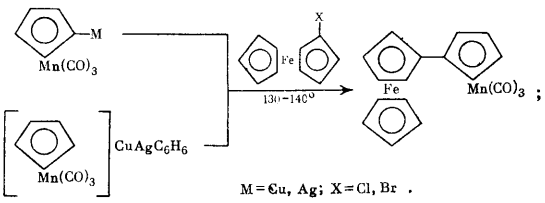


The displacement of the absorption band of the ferrocene fragment in the electronic spectra of these compounds takes place as a consequence of the appreciable mutual influence of the ferrocenyl system and the central metal atom in the complex[67]. Measurements of the magnetic moments have shown that the cobalt complex is a dimer with a Co–Co bond. It has been noted that the coordination of such ligands to metal atoms can occur in the thiol and imine forms[68,70].

Polymeric, infusible, and insoluble in organic solvents chelates of copper, manganese, cobalt, and chromium based on ferrocene-containing β-ketoimines[71–73] and also silver and copper chelate complexes of salicylferrocene[5] have been described. The instability constants of certain organometallic compounds (OMC) of this type have been determined[22].

4. Compounds of the Type Fc–OMC and Fc–R–OMC with σ-Linked Fragments

Various reactions involving the coupling of a cyclopentadienyl ring of ferrocene to groups containing a transition metal entail wide possibilities for the synthesis of HMF. Cymantrenylferrocene—a compound which incorporates the fragments of two of the most thoroughly investigated cyclopentadiene complexes (ferrocene and cymantrene)—has been obtained[74–77]:



M = Cu, Ag; X = Cl, Br .

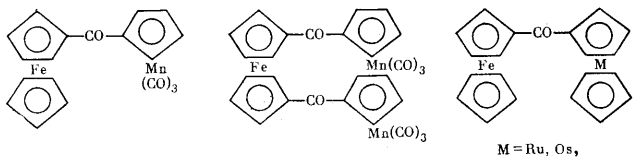
The cymantrenyl substituents can be introduced also into both rings of ferrocene. Cymantrenylferrocene can be obtained by the pyrolysis of diferrocenyl- and dicymantrenylmercury in the presence of silver powder[78]. It has been recently reported[79] that the most convenient method involves the interaction of copper(II) halides with lithiometallocenes. These procedures are also applicable to the synthesis of substituted cymantrenylferrocenes. The yield of the HMF is 30–70%. Cymantrenylferrocene is a stable crystalline substance which is readily soluble in organic solvents and enters into various reactions.

Various HMF can be synthesised similarly from lithio-, sodio-, or other metal-substituted derivatives of one organometallic compound and halogeno-derivatives of another. The synthesis for this procedure of a derivative of tervalent gold, namely dibutylgold thioferrocenolate Fc–SAu–$(n\text{-}Bu)_2$, having a trimeric structure, has been described[47]. Diferrocenyldicymantrenyltin has been obtained by the reaction of cymantrenyl-lithium and dichlorodiferrocenyltin. The reaction between ferrocenyl-lithium and dichlorocymantrenyltin also leads to this compound but with a lower yield[80,81]. Under mild conditions, it was possible to obtain ferrocenylmethyl compounds of molybdenum[82] and tungsten[82,83] according to the scheme

$$Fc{-}COCH_2Cl + NaM(CO)_3Cp \rightarrow Fc{-}COCH_2M(CO)_3Cp .$$

The tungsten-containing ketone is stable on storage and in solution in contrast to molybdenum-containing ketone, which decomposes even in the solid state to the extent of one-third in 24 h. Similar HMF and $Fc{-}CH_2Mn(CO)_5$ have been obtained from chloromethyl- and chlorocarbonyl-ferrocene[84,85]. On heating, the carbonyl derivatives are decarbonylated with formation of $Fc{-}M(CO)_3Cp$.

The Friedel–Crafts alkylation and acylation constitute a convenient method of coupling to organometallic fragments[5,7,20,86–89]. A series of HMF of the type



M = Ru, Os,

have been obtained and characterised. The carbonyl groups of these compounds are readily reduced to CH_2 groups with retention of the HMF structure.

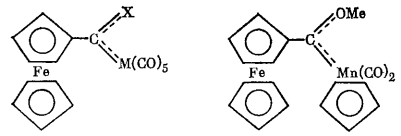
The condensation reactions of aldehyde and ketone derivatives of ferrocene, benzenechromium tricarbonyl, and cymantrene result in almost quantitative yields of the corresponding HMF [90–92] of two types:

RCH=CHCOR′ and RCOCH=CHR′;
R = Fc; R′ = PhCr(CO)3, $C_5H_4Mn(CO)_3$.

Such condensation of ferrocene derivatives has also been achieved with cymantrenylamine and dinuclear ketimines were obtained as a result[22]. The condensation products are crystalline high-melting substances which are soluble in various organic solvents. The manganese derivatives are somewhat less stable in solutions.

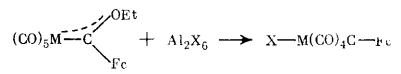
Ferrocenylacetylene can be used to synthesise HMF. Like the synthesis of copper acetylides, the interaction of CuI in aqueous ammonia with ferrocenylacetylene in alcohol[20] leads to copper ferrocenylacetylide (Fe–C≡CCu) in 73–80% yield. Its derivatives dideuterated[93], brominated, and iodinated[94] in the ring have been obtained. Such acetylides can be used successfully in a wide variety of syntheses[13,20,95] including the synthesis of HMF. The exchange reaction of copper ruthenocenylacetylide with iodoferrocene in pyridine gave rise to ferrocenylruthenocenylacetylene[96]: $Fc{-}C{\equiv}CC_5H_4RuC_5H_5$. This compound sublimes *in vacuo* (1 mmHg) at 180 °C without change in its melting point. The reactions of ferrocenylacetylene with *cis*-$PtCl_2(PMe_2Ph)_2$ and $(PPh_3)_2IrCl(CO)$, leading respectively to *trans*-$PtCl(C{\equiv}CFc)(PMe_2Ph)_2$ [97] and a hexacoordinate iridium complex, decomposing on recrystallisation into the initial components, have been described[98].

A series of reactions involving addition to the carbonyl ligand in metal carbonyl have been achieved. The reactions of metal carbonyls with organolithium compounds lead to the conversion of the carbonyl ligand into a carbene ligand. A series of bimetallic ferrocenylcarbene complexes were obtained in the course of studies of a series of ferrocene derivatives[99–101]:



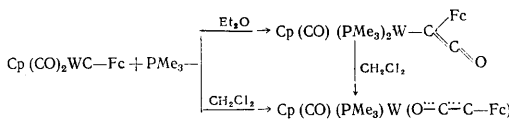
X = OMe, OEt, NH_2, NMe_2, NC_4H_8, $ONMe_4$; M = Cr, W .

These compounds are crystalline, stable in air (with the exception of the manganese complex), and soluble in inorganic solvents. It was not possible to synthesise the analogous cobalt and vanadium complexes. The chromium, molybdenum, and tungsten complexes based on 1,1′-dimethylferrocene were obtained recently[102]. The carbene complexes are the starting materials for the synthesis of new HMF. They react with boron and aluminium halides with elimination of an electron-donating group (one CO ligand), forming carbyne complexes[103,104]:



M = Cr, Mo, W; X = Cl, Br .

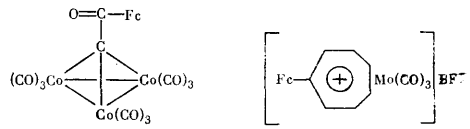
The iodo-homologues have been obtained by the exchange reaction of the above complexes with LiI. The thermal stability of these compounds decreases in the sequence W > Cr > Mo and I > Br > Cl; the chemical stability ranges from that of the iodotungsten derivative, which is stable on storage in air, to the chlorochromium compound, which ignites spontaneously. It has been shown for the tungsten derivative[105] that these complexes react with cyclopentadienylsodium to form dicarbonyl(π-cyclopentadienyl)carbyne complexes, which are readily soluble in organic solvents and whose reactions with phosphines give rise to metal-substituted ketens, which are stable in the solid state[106]:



In CH_2Cl_2 these ketens combine almost quantitatively with CO at 30 atm over a period of 24 h [107] with the formation of $Cp(CO)_2(PMe_3)W{-}C(Fc){=}C{=}O$.

The electrophilic substitution of hydrogen in ferrocene by new acylating agents—carbotricobalt decacarbonyl hexa-

fluorophosphate[108] and the complex $[C_7H_7Mo(CO)_3]BF_4$—has been achieved[7,20], which led to the following HMF:



Other ferrocene cluster compounds have also been obtained: $Fc-CCo_3(CO)_9$ [20,109] and $Fc-CH_2CO_2CCo_3(CO)_9$.[110]

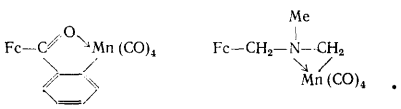
A simple method of synthesis of HMF consists in the addition of organometallic compounds to carbonyl derivatives of ferrocene[21,22,111,112], for example:

$$Fc-CHO \xrightarrow{LiR} Fc-CH(R)OLi \xrightarrow{H_2O} Fc-CH(R)OH,\quad R=C_6H_4Mn(CO)_3;$$
$$Fc-COMe + Cp_2Zr(Cl)H \rightarrow Cp_2Zr(Cl)OCH(Me)-Fc.$$

These compounds are soluble in hydrocarbons but hydrolyse at the metal–oxygen bond with liberation of ferrocene-containing alcohols.

There are literature data concerning polymeric HMF obtained by the copolymerisation of vinyl derivatives of cymantrene and ferrocene[113], (benzyl acrylate)chromium tricarbonyl, and 2-ferrocenylethyl acrylate[114,115]. Polymers of other metal-containing monomers are also known[117–122].

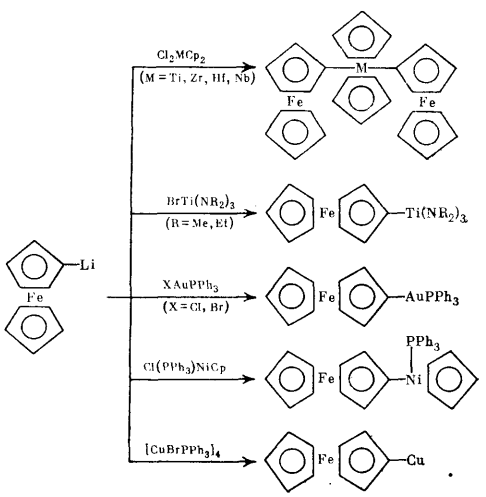
The possibility of the synthesis of HMF by the cyclometallation of substituents in ferrocene derivatives is also noteworthy[127]. Various dinuclear heterometallic derivatives can be obtained by this procedure, but in the case of ferrocene the reaction is known only in a few instances. These involve the metallation of benzoylferrocene and dimethylaminomethylferrocene with methylmanganese pentacarbonyl in the benzene ring and in the methyl group respectively[128]:



Pyrazolines containing the ferrocenyl and cymantrenyl substituents have been described[116,129]. Catalytic thermolysis of such pyrazolines in the presence of KOH and platinum on charcoal leads to the corresponding cyclopropane HMF.[116]

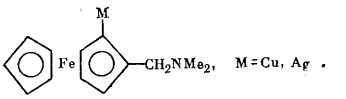
5. Compounds With a Cyclopentadienyl–Metal Bond

HMF of this kind are usually obtained by the exchange reaction between lithioferrocenes and transition metal halides[130–137]:



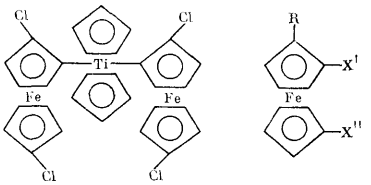
The reaction with $AuCl_3$ terminates with the formation of HMF in satisfactory yield only for the ratio Li : Au = 2 : 1.[133] Only the compound $Fc_2AuClPPh_3$ has been obtained under these conditions.

The thermal stability of HMF of this type varies within wide limits—from the nickel compound which is unstable in a pure form[135,136] to the cyclopentadienyl derivatives of Group IV metals which sublime *in vacuo* at high temperatures[130,131]. However, the latter are unstable in air. Ferrocenylcopper, which in unstable in an inert atmosphere up to 120 °C, also decomposes in air. It is noteworthy that the presence of halogen atoms and of the dimethylaminomethyl group in the cyclopentadienyl rings of ferrocene stabilises the carbon–metal bond and the HMF is also much more stable. Thus the HMF obtained from 1-(dimethylaminomethyl)-2-lithioferrocene and copper and silver iodides (yield more than 60%) are stable in air up to 150–170 °C:[138,139]



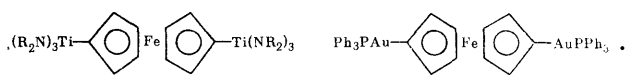
Similar methoxy-substituted HMF are somewhat less stable[140].

Copper and silver derivatives without stabilising substituents were obtained only recently[137,141]. The silver derivative is more stable and persists in air for several hours. A series of derivatives of other metals have been obtained from lithioferrocenes containing stabilising substituents:[142,143]

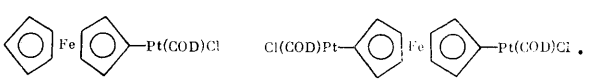


$X^I = X^{II} = Cl$, $R = Mn(CO)_5$, $AuPPh_3$, $Ir(CO)PPh_3$;
$X^I = Cl$, $X^{II} = H$, $R = AuPPh_3$.

If 1,1′-dilithioferrocene is used in the synthesis, HMF substituted in both rings are obtained[132,142,144,145], for example:

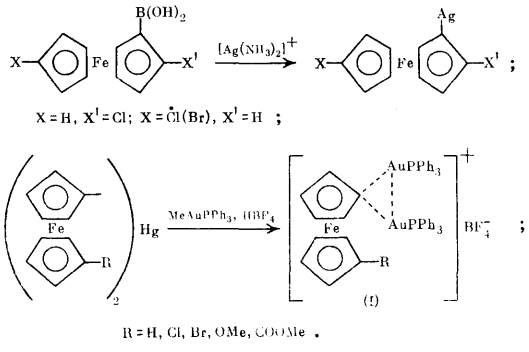


The same results were obtained on incomplete ferrocenylation of the platinum salt $Pt(COD)Cl_2$ (COD = cyclo-octa-1,5-diene) with trimethylstannylferrocene and 1,1′-bis(trimethylstannyl)ferrocene[146]:

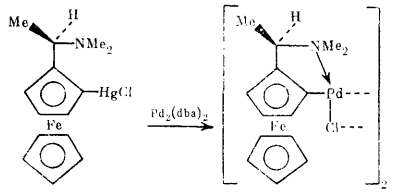


The reaction of 1,1′-dilithioferrocene with cobalt chloride leads to the formation of polyferrocenylenes[147].

Apart from the organolithium and organotin compounds, ferrocene derivatives of boron[148–151] and mercury[152–156] are used for the synthesis of HMF of this type:

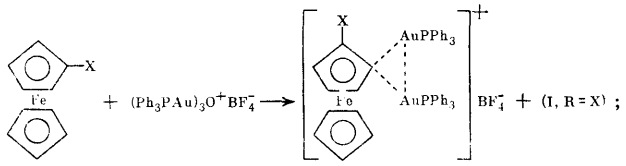


These reactions involving organomercury compounds proceed over a period of several minutes at room temperature with yields of compounds (I) up to 80–90%. The use of the optically pure 2-chloromercuri-derivative of 1-dimethylaminoethylferrocene for the synthesis of an optically active complex with a palladium atom in the ring has been described[157–159]:

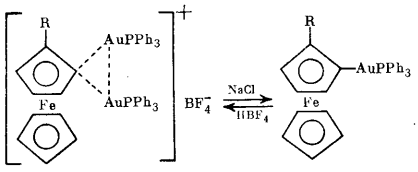


where dba = dibenzylideneacetone.

Other methods of adding a transition metal directly to a cyclopentadienyl ring of ferrocene are also known. Nesmeyanov and coworkers[160–163] were the first to metallate ferrocene and its derivatives by an aurating agent—a gold-containing oxonium salt. Ferrocene is aurated at 20 °C in the presence of HBF_4, giving a 60% yield of a cationic digold complex (I, R = H). Ferrocene derivatives form mixtures of homoannular and heteroannular isomers:

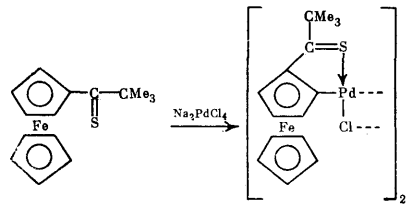


In all cases, except when X = Ph, homoannular 1,2-isomers are formed preferentially. Methoxy- and nitro-ferrocenes give rise to 1,2-disubstituted ferrocenes only. Under the influence of nucleophiles (Cl^-, CN^-, PPh_3), the cationic complexes are converted quantitatively into organomonogold compounds, whose reaction with tetrafluoroboric acid readily reconverts them into ionic complexes[164]:

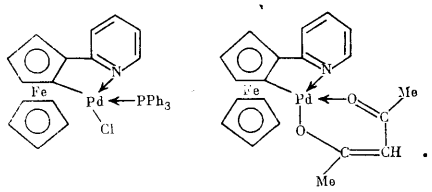


The reaction proceeds from right to left also under the influence of dinuclear organogold complexes $[R(AuPPh_3)_2]BF_4$.[165] In view of the ease of such reactions, it is assumed that it is most convenient to synthesise gold-containing HMF of the type $Fc–AuPPh_3$ from organomercury compounds via the cationic complexes[155]. It is of interest that acetylferrocene is aurated by tris(triphenylphosphinegold)oxonium permanganate not in the cyclopentadienyl ring but in the acetyl group, forming $Fc–COCH_2AuPPh_3$, albeit in a low yield (5%).[161,162]

The first example of the intramolecular orthopalladisation of metallocenes was published in 1974:[166]

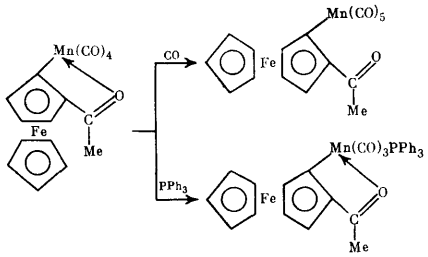


Subsequently this reaction was achieved also for other ferrocene derivatives—dimethylaminomethylferrocene[167], 2-pyridylferrocene[168], acetylferrocene *N,N*-dimethylhydrazone[169], acetylferrocene acetylhydrazones[170], and 1,1′-diacetylferrocene bis(acetylhydrazone).[171] Li_2PdX_4 (X = Cl or Br) are also used as palladising agents. The reaction is carried out in the presence of sodium acetate. The dimeric complexes obtained in a yield exceeding 90% react with electron-donating molecules or metal acetylacetonates to form the corresponding monomeric HMF, for example;



If the palladisation is carried out in the presence of a salt of an optically active acid or an optically active derivative of ferrocene is used, then optically active HMF are obtained. The asymmetric cyclopalladisation of dimethylaminomethylferrocene [172,173] and the optically active *N,N*-dimethylamino-1D-methylferrocene [174] and 1-dimethylaminoethylferrocene[157,158] has been achieved.

The metallation of acetyl- and dimethylaminomethyl-ferrocenes by methylmanganese and methylrhenium pentacarbonyls has also been described[128,175]. In all cases homoannular *ortho*-metallated ferrocenes are formed in 32–50%, yield except in the reaction of dimethylaminomethylferrocene with the manganese compound described in the previous section. The reaction of the manganese derivative with CO is accompanied by ring rupture, which indicates the lability of the Mn ← O bond; however, the reaction with triphenylphosphine proceeds differently—with substitution of one carbonyl group:

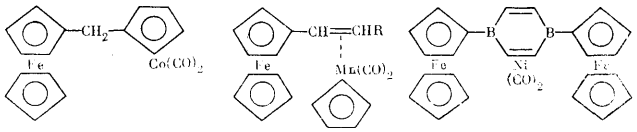


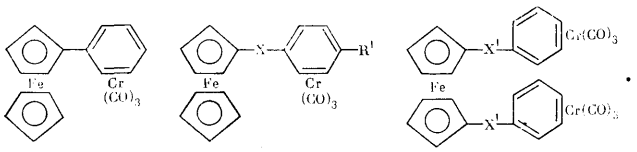
6. π-Complexes of Unsaturated Ferrocene Compounds

Heterometallic derivatives of ferrocene can be obtained from metal carbonyls using the ability of the latter to substitute their CO groups by π-donor ferrocene-containing ligands. Several compounds of this type have been described. Ferrocenylacetylenes readily react with cobalt carbonyl[26,98]:

$$Fc{-}C{\equiv}CR + Co_2(CO)_8 \xrightarrow{C_6H_6,\,25^\circ} Fc{-}C{\equiv}CR\,[Co_2(CO)_6]\ ;$$
$$R=H,\ Fc\ .$$

The following cobalt-, manganese, nickel-, and chromium-containing HMF have been obtained similarly (sometimes with ultraviolet irradiation): [20,85,176–180]

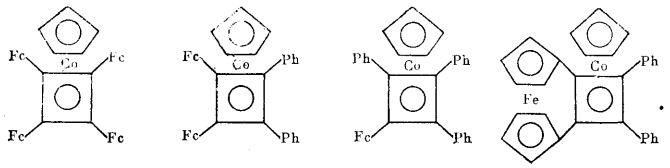




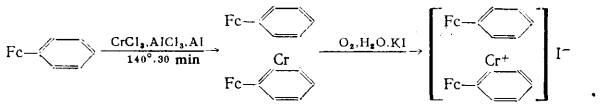
(a) R = H, Me; (b) R' = H, X = CH_2, CO, CH_2CH_2, $COCH_2$, CH(OH)CH_2, CH=CH, CH(OH); (c) R' = Me, X = CO, CH(OH); (d) X' = $COCH_2$, CH(OH)CH_2 .

Cobalt- and manganese-containing HMF of this type are relatively readily fusible compounds (or liquids); the chromium-containing HMF and the nickel complex melt (sometimes with decomposition) in the range 135–230 °C.

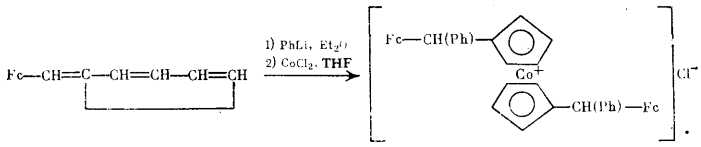
The interaction of the ethynylferrocenes Fc–C≡CPh, Fe–C≡C–Fc, and Fe($C_5H_4C{\equiv}CPh)_2$ with the cyclopentadienylcobalt complexes $CpCo(CO)_2$, $CpCo(PPh_3)_2$, and CpCo(RC≡CR)PPh_3 have been studied by two groups of investigators[181,182]. Mixed cyclobutadiene complexes with different Fe : Co ratios, soluble in hydrocarbons, were isolated:



The group of compounds which are synthesised using arene- or cyclopentadienyl-containing metallocenes, usually ferrocenes, while the other metal is introduced, by the method for the synthesis of metallocene and arene compounds, should be assigned to this type of HMF. Thus, 1,1'-diferrocenyldibenzenechromium, identified as the iodide, has been synthesised under the conditions of the Fischer reaction in 17% yield[123]:



Since the synthesis is complicated by side reactions, an attempt was made to synthesise this compound and its *p*-tolylferrocenyl analogue by the reaction of chromium vapour with phenyl- and *p*-tolylferrocene in a high vacuum (10^{-5} mmHg, 77 K); the yield was approximately 1% relative to the evaporated chromium, which entered the reaction zone[124]. A similar cobaltocenium derivative was obtained from α-ferrocenylfulvene[20]:



The manganese[125] and tungsten[126] derivatives have been obtained analogously.

Dimeric 1-ferrocenyl-π-allylpalladium chloride complexes have been synthesised by the reaction of conjugated dienes (butadiene, isoprene, and 2,3-dimethylbutadiene) with ferrocenylpalladium chloride, obtained *in situ* from chloromercuriferrocene and Li_2PdCl_4.[183] A complex of vinylferrocene and palladium(II) chloride has also been obtained[33].

7. Transition Metal Complexes with Ferrocene Ligands Containing Group V and VI Elements as Donor Atoms

The complex formation reactions of ferrocene derivatives containing electron-donating nitrogen, phosphorus, arsenic, etc. atoms with transition metal compounds constitute a convenient method of synthesis of HMF. Thus, when dimethylaminomethylferrocence is mixed with nickel and cobalt halides and thiocyanates[184] and also with palladium chloride[185], solid coloured adducts are formed:

$$[FcCH_2NMe_2]_2MX_2 \quad M=Co,\ Ni,\quad X=Cl,\ Br,\ I,\ CNS;\quad M=Pd,\ X=Cl\ .$$

The reaction with titanium and zirconium halides gives rise to 1 : 1 complexes[186]. Dimethylaminomethylferrocene hydrochloride reacts with K_2MCl_4 and $Na_2M(CN)_4$, yielding compounds with a different structure[185]: $[FcCH_2NHMe_2]_2MX_4$, where M = Pt or Pd. Nickel, platinum, palladium, ruthenium[187], and rhodium[188] complexes of 1,1'-bis(dimethylarsino)ferrocene[187,188] and 1,1'-bis(diphenylarsino)ferrocene[187], the palladium complex of 2-ferrocenylpyridine[168], the nickel[189], cobalt[190], gold[191], and palladium[192] complexes of ferrocenylphenylphosphines, the cobalt, nickel, and copper complexes of 1,1'-bis(diphenylphosphino)ferrocene[193], the rhodium complexes of ferrocenylphosphinamines[194], the cobalt complex of 1-(dimethylaminomethylmethyl)-2-pyridylferrocene[26], the titanium and zirconium complexes of ferrocenylacetonitrile[186], the silver[39], titanium, and vanadium[39,195] complexes of 1,1'-dicyano-ferrocenes[7,22], and the ruthenium complexes of cyanoferrocene and ferrocenylacrylonitrile[196] have been synthesised and investigated.

Ferrocenylphosphinegold halide complexes are converted into organogold HMF under the influence of organolithium and organomagnesium compounds[197]

$$BrAuL + MeMgI \rightarrow MeAuL\ ;$$
$$L = PFc_3,\ FcPPh_2\ .$$

Oxidants react with these complexes in a way which depends on the nature of the reagent[191], oxidising either gold or the ferrocene system:

$$BrAuFcPPh_2 \xrightarrow{Br_2} Br_3AuFcPPh_2$$
$$BrAuFcPPh_2 \xrightarrow{HAuCl_4} [(BrAuFcPPh_2)^+(AuCl_4)^-]_3Au\ .$$

Triferrocenylphosphine complexes of arylgold compounds are obtained by displacing triphenylphosphine with triferrocenylphosphine, the latter being a stronger electron donor[197]:

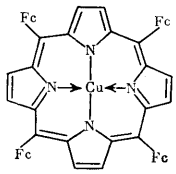
$$ArAuPPh_3 \xrightarrow{Fc_3P} ArAuPFc_3\ ;$$
$$Ar = p\text{-}MeC_6H_4,\ m\text{-}FC_6H_4\ .$$

HMF of this type are also known to include cationic digold complexes[165,197,198], which are formed, like the compounds

aurated in the ferrocene nucleus, via the following mechanisms:

$$R_2Hg + MeAuPFc_3 \xrightarrow{HBF_4} R(AuPFc_3)_2BF_4,$$
$$R=PhCH=CH,\ PhCH=C(COOMe),\ o\text{-}IC_6H_4,\ \alpha\text{-thienyl};$$
$$p\text{-}MeC_6H_4AuPFc_3 \underset{Fc_3P}{\overset{HBF_4}{\rightleftharpoons}} p\text{-}MeC_6H_4(AuPFc_3)_2BF_4.$$

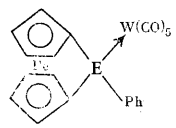
The first heterometallic derivative of ferrocene of the porphyrin series has also been obtained from *meso*-tetraferrocenylporphyrin and copper acetate in dimethylformamide and has been isolated after recrystallisation from chloroform in the form of an adduct with dimethylformamide and $CHCl_3$:[199]



According to Mössbauer spectroscopic data, oxidation of this compound results in the formation of several ferrocenium centres.

A series of HMF have been obtained by the reactions of metal carbonyls with ferrocenylphosphine ligands: $CpMn(CO)_2L$ ($L = PFc_3$, PFc_2Ph, or $PFcPh_2$), $RC_5H_4Mn(CO)_2PFc_3$ (R = Et, C_5H_{11}, MeCO, or C_4H_9CO), $C_6H_6Cr(CO)_2L$ and $(CO)_5ML$ (M = Cr, Mo, or W), $(CO)_4ML_2$ (M = Mo or W), $Fc_3PMn_2(CO)_9$, $[(FcPPh_2)_2Co(CO)_3]^+BPh_4^-$,[190,200–203] and $Fc_3PMn(CO)_4Me$.[128] Similar complexes of chromium, molybdenum, tungsten, vanadium, cobalt, and nickel carbonyls with bifunctional nitrogen-, phosphorus-, and arsenic-containing ferrocene ligands have been described[193,194,204,205].

It is known that coordination to transition metals appreciably stabilises ligands which are relatively unstable under the usual conditions. It is therefore possible to employ in the synthesis of stable HMF of this type even ferrocene compounds which are unstable in air. For example, crystalline complexes stable in air have been obtained from thioketones which readily polymerise and oxidise under the usual conditions and from ferrocenophanes, which are unstable in air[206–208]:



$Fc{-}CS{-}CMe_3Cp_2Mo_2(CO)_4$
$Fc{-}C(R){=}S \rightarrow M(CO)_5$;
R=Ph, M=Cr, Mo, W; R=Me, M=W;
E=P, As.

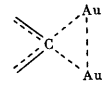
The possibility of synthesising HMF of this type by displacing amine ligands from the Reinecke salt by aminoferrocenes (L) has also been demonstrated[209]. With a 1 : 1 component ratio, the outer-sphere ammonia is displaced with formation of the solid crystalline complex $LH[Cr(SCN)_4(NH_3)_2]$. With increase of the aminoferrocene : Reinecke salt ratio, the inner-sphere ammonia is displaced.

III. STRUCTURE AND PROPERTIES

1. Structure

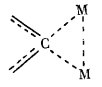
The structural analysis of crystalline HMF has been carried out for certain compounds, which made it possible to discover their structural characteristics. When a metal forms σ-bonds directly with a carbon atom of a cyclopentadienyl ring of ferrocene, there is a possibility of a redistribution of electron density with participation, in particular, of the metal *f* orbitals, which alters the interatomic distances in the Fc fragment[138]. On the other hand, in the case of diferrocenyltitanocene Cp_2TiFc_2, a shortening of the σ-bond between titanium and a carbon atom of the cyclopentadienyl ring of ferrocene and constancy of the bond lengths in the sandwich fragments were observed[210]. The molecular structure of $(Et_2N)_3TiC_5H_4FeC_5H_4Ti(NEt_2)_3$ has been described[211].

There is also a possibility of a more complex bonding of the metal atom to the cyclopentadienyl ring with formation of the structural fragment



in which the two gold atoms linked to one another form a three-centre two-electron bond with one of the carbon atoms with the ferrocene-containing group[154,164]. The presence of the above fragment has been most clearly confirmed by X-ray diffraction data for the compound $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2.(PPh_3)_2]BF_4$.[212,213]

The Au–Au bond (2.77 Å) in such compounds is shorter than in metallic gold (2.88 Å). As a consequence of the presence of the Fe–Au bond (2.82 Å), the planes of the cyclopentadienyl rings are not parallel (the dihedral angle is 16°) and the bridging ring has the envelope configuration. Ultraviolet spectroscopic and ^1H NMR data show that the bridge structure of the compounds is maintained also in solutions[153,214]. The related compound 2-copper(dimethylaminomethyl)ferrocene and its silver analogue have the cluster structure[215,216]. In these substances it is also possible to isolate the fragment



but the distortion of the Fc is smaller probably due to the weaker interaction between M and Fe. A weak interaction between the silver atom and the nitrogen atom of the aminogroup has been noted for the silver derivative.

Direct bonding of the metal to a carbon atom of a cyclopentadienyl ring of ferrocene is not always accompanied by the M–Fe interaction. Apart from the nature of the atom M, the character of the bonds which it forms with the atoms in the immediate environment is of decisive importance. For example, in cyclo-1-(1′-dimethylaminoethylferrocene)-2-(acetylacetonato)palladium the metal is involved in the square planar coordination fairly characteristic of palladium with formation of acetylacetonate and PdC_3N metal-containing rings. The ferrocene fragment has a configuration intermediate between crossed and eclipsed with the usual average bond lengths[159].

In the absence of a direct bond between M and a cyclopentadienyl ring of ferrocene, the mutual influence of the M and Fe atoms on the structural characteristics of their environment is also weakened. However, it is still fairly pronounced, for example, in halogenotetracarbonyl complexes of transition metals bound to the ferrocenyl residue by a linkage of the type $M{\equiv}C{-}Fc$.[104] In these compounds, as in the carbene derivatives which resemble them[102], there is a significant decrease of electron density in the cyclopentadienyl rings of ferrocene as a result of the stronger conjugation than in the usual substituted ferrocenes, caused by the overlap of the π orbitals of the substituted ring by the p_z orbital of the acetylenic carbon. The HMF considered are oxidised more readily than ferrocene; their oxidation-reduction properties are appreciably influenced by the nature of the metal and to a lesser extent the halogen.

The compound of nickel iodide carbonyl with ferrocene-1,1'-bis(dimethylarsine) [217] is of interest because in it the cyclopentadienyl rings of ferrocene form part of a bidentate ligand. The nickel atom has a trigonal bipyramidal coordination with the equatorial and axial dispositions of As. The $FeAs_2$ and $NiAs_2$ planes form an angle of 46.6° and the cyclopentadienyl rings are rotated by 8.8° compared with the eclipsed conformation and are inclined to one another at an angle of ~3°. The Ni–As distances are within the usual limits for nickel complexes with arsenic derivatives, but the equatorial bond is somewhat longer than the axial bond. The interatomic distances in the ferrocene fragment have the usual values. The C–O bond is shorter than in the carbonyl complexes. The bidentate ligand may include also one cyclopentadienyl ring of ferrocene. It has been established by NMR and infrared spectroscopy[204] that 1-(dimethylamino)-methyl-2-(diphenylphosphino)ferrocene behaves as a bidentate ligand in reactions with Group VI metal (Cr, Mo, and W) carbonyls and gives rise to a complex of the type $[CpFeC_5H_3.(PPh_2)CH_2NMe_2]W(CO)_4$.

Polydentate ligands can also be linked with the aid of the ferrocene fragment. This can entail the formation of strained structures. Comparison of the EPR spectra of copper chelate complexes of acetylacetone, ferrocenylacetone, and 1,1'-bis-acetoacetylferrocene showed that only in the latter case does the symmetry of the environment of the copper ion deviate from the acetylacetonate symmetry[50,51]. When the ferrocene nucleus is separated from the M atom by two and more atoms, the mutual influence of the metal-containing fragments on their structure is not observed. In such complexes ferrocene frequently has the eclipsed conformation[182,218]; however, as in the cases discussed above, the conformation may be influenced decisively by the packing in the crystal and not by the electronic structure and geometry of the molecule. Estimation of the mixing coefficients in the molecular orbital of the unpaired electron showed that these coefficients of the $d_{x^2-y^2}$ orbitals of the copper atoms are identical to within 0.04 for the acetylacetonate and ferrocenoylacetonate. This indicates identical distibution of spin density in a type b_1 orbital in both chelates and the absence of an appreciable influence of the ferrocenyl substituent on this orbital[51]. The ferrocenyl residue also does not have a significant influence on the metal atom in the tetraferrocenylporphyrin complex; the EPR spectrum corresponds to the spectra of other copper complexes of porphyrins[199]. The usual structure of the chelate unit has been found also in other metal ferrocenoylacetonates[51,56]. However, a redistribution of electron density can occur in orbitals without unpaired electrons[219,220].

The nature of the localisation of the charge in the ferrocene component is most significant in ionic compounds. If the ferrocene component consists of a ferrocenium type cation, then the Fe–Cp bonds in it are weakened (compared with the corresponding ferrocene derivative) and the absorption bands in the infrared spectrum corresponding to these bonds undergo a bathochromic shift[27,30]. Allowance for this and also for the bathochromic shift of the d–d transition band in the optical spectrum led to an ionic structure for complexes of ferrocene with metal halides[36,37].

2. Solubility

There are no quantitative literature data on the solubilities of HMF (with a rare exception[56]). Only qualitative data are usually quoted, from which it follows that many HMF are appreciably soluble in organic solvents. In order to increase the solubility of compounds based on β-diketones in hydrocarbons, the oleic acid residue is introduced into the molecules of the β-diketonates[221]. The low solubility of salts of nitrogen-containing ferrocene chelates[65,69] and acids[45,46] is apparently associated with intermolecular association in the solid state via the electron-donating nitrogen atoms or with the polymeric structure of the compounds. HMF of other types are apparently also insoluble due to their polymeric structure[5,47,63].

3. Thermal Stability

Polymerisation in the solid state influences appreciably the thermal behaviour of HMF. For example, polymeric chelates of ferrocene thiosemicarbazones and β-ketoimines[66–69,71] do not melt up to 250–300 °C, decomposing in the solid state on further heating. The unusually high stability of ferrocene-silver compared with alkyl- and aryl-silver can also be accounted for by the formation of intermolecular bonds[151].

The thermal decomposition of HMF has been investigated for a few compounds. Thermolysis of ferrocenium salts has been investigated for the reineckate and salts with isopoly-acids[28–30,49]. A characteristic feature of the process is the formation of ferrocene. The thermal stability of salts of ferrocenemonosulphonic acid has been characterised by thermogravimetric and differential thermographic methods[43]. The compounds are unstable in air in the anhydrous state, the copper salt decomposing even before the loss of the entire water of crystallisation.

The thermal decomposition of the copper chelate of ferrocenylacetone has been investigated by derivatographic, mass-spectrometric, and gas-chromatographic methods[49,51]. It has been established that cyclopentadiene, methane, and hydrogen are evolved at 200–260 °C together with a keto-derivative of ferrocene (identified by the infrared spectra); the residue contains metallic copper and iron(II) and iron(III) oxides. The chelates of ferrocene-containing β-ketoimines decompose in the same temperature range (>200–250 °C),[73] their thermal stability being lower than that of the initial β-ketoimines, which the authors attribute to the presence of the unstable ferrocenium form in the polychelates.

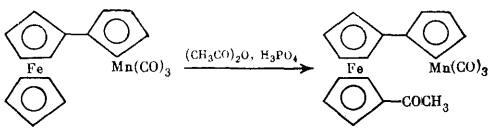
There exist data on the thermal stabilities and decomposition of other compounds, in particular the copper salt of ferrocenecarboxylic acid[22], allylpalladium ferrocenyltrifluoro-acetonate[59,60], 2-copper-1-(dimethylaminomethyl)ferrocene[215], a series of ferrocenesilver compounds[148–150], diferrocenyl-dicyclopentadienyl derivatives of titanium, zirconium, hafnium[130], and niobium[131], and also ferrocenephosphinegold cationic complexes[197]. The majority of HMF lose the ability to sublime on heating which is characteristic of ferrocenes. One of the few exceptions to this rule is ferrocenylruthenocenylacetylene[96] and the dicyclopentadienyldiferrocenyl derivative of zirconium, hafnium, and titanium[130] (the heat capacity of the last compound was measured and its thermodynamic functions were calculated[222]).

4. Chemical Properties

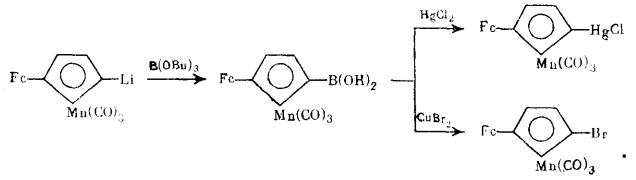
The majority of HMF are resistant to oxygen and atmospheric moisture, except for the compounds mentioned in the appropriate parts of the review. The instability of individual HMF in organic solvents has also been pointed out[33,60,64,102,105,133,161,205].

Many HMF exhibit an important chemical property of ferrocene—the ability to be oxidised to the cation[87–90,178,180,223], which may serve as one of the ways of synthesising trimetallic compounds[128,129]. Both organometallic fragments of HMF are chemically reactive. For example, depending on

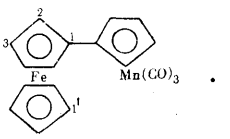
the type of reagents employed, the substitution of a hydrogen atom in cymantrenylferrocene can take place in a cyclopentadienyl ring of either ferrocene or cymantrene. Acylation by acetic anhydride proceeds in accordance with the mechanism[76,77]



In contrast to this, metallation by n-butyl-lithium occurs in the cyclopentadienyl ring of cymantrene. The organolithium derivative obtained is a convenient reagent for the synthesis of various derivatives of ferrocenylcymantrene containing substituents in the cymantrene ring:

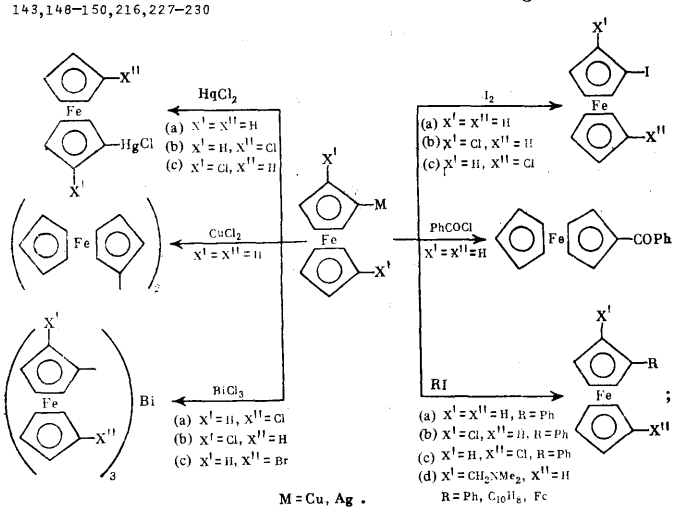


The bromo-derivative of this HMF, containing bromine in a cyclopentadienyl ring of ferrocene, can be obtained from 1,1'-dibromoferrocene and cymantrenylcopper or cymantrenylsilver via the reactions described above (in Section II). Bromine can be substituted by other groups on treatment with bivalent copper salts (acetate and phthalimide)[75,77]. Thus the properties of the σ-linked cymantrenyl and ferrocenyl residues in cymantrenylferrocene differ from those of cymantrene and ferrocene. The difficulty of the exchange of the bromine in 1-bromo-1'-cymantrenylferrocene for different groups, the ease of reduction of the ferrocene derivative to cymantrenylferrocene, the smaller tendency of the latter (compared with ferrocene) to undergo oxidation to the ferrocenium cation, the reduced basicity of 1-amino-1'-cymantrenylferrocene (compared with ferrocenylamine), and also its oxidation to the corresponding azoferrocene, which takes place with difficulty, are associated with the electron-accepting influence of the cymantrenyl group. This has been confirmed by the formal oxidation-reduction potentials[223,254] and data for the isotope exchange of the hydrogen in cymantrenylferrocene with acids[225], from which it follows that the cymantrenyl substituent decreases the rate of the isotope exchange involving the ferrocene nucleus by a whole order of magnitude and that the most reactive positions for electrophilic substitution are 1' and 3:



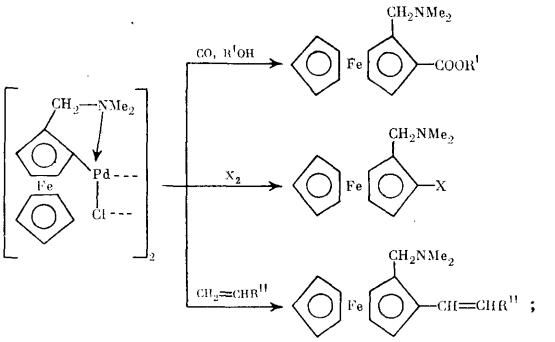
It was established that the 1'-, 3-, and 2-positions are respectively 8 times, 11 times, and 20 times less active than in ferrocene. It is significant that, under the conditions of the hydrogen isotope exchange, the cymantrenyl fragment does not react. The result of the study of the isotope exchange involving benzenedicarbonyldiferrocenylphosphinechromium[226] is unexpected—the hydrogen atoms of the π-benzene and cyclopentadienyl rings are exchanged at almost the same rates, indicating the equalisation of the electron density in the given complex. The hydrogen atoms of the cyclopentadienyl rings in Ph_2PFc, coordinated to the chromium atom, undergo isotope exchange faster almost by three orders of magnitude than the hydrogen atoms of the non-coordinated ferrocenylphosphine.

Many HMF with a metal–carbon σ-bond readily react with various reagents, which can be used for the synthesis of ferrocene otherwise difficult to obtain, including HMF:[137,140,143,148–150,216,227–230]



The reactions of the organonickel σ-complexes $CpFeC_5H_3$·(Cl)Ni(PPh_3)Cp with acids, acetyl chloride, and mercury(II) chloride also take place under mild conditions and with high yields[135,136]. The nickel–π-cyclopentadienyl ring and nickel–triphenylphosphine bonds are not involved in this process. The organogold derivatives Fc–$AuPPh_3$ react with halogens also with formation of halogenoferrocenes and triphenylphosphinegold halides[231,232]. However, reactions involving the electrophilic substitution of the gold atom could not be carried out[233]. The high reactivity of the gold–carbon bond has been used to synthesis the substituted vinylferrocenes Fc–C(CN) = C(CN)R, where R = CN or $AuPPh_3$.[234] Hydrogen sulphide and the acids HX (X = Cl or Br) readily decompose many similar HMF.[42,130,131,141,148–150] Stabilised ferrocenylsilver and ferrocenylcopper condense with cymantrenylcopper and chloroferrocenylsilver above 120 °C, forming dinuclear metallocenes[216].

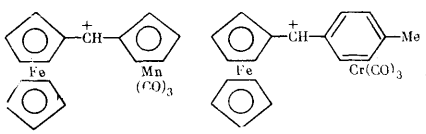
It has been shown for various aminoferrocenes with a Pd atom in the ring that extensive synthetic possibilities are associated with HMF of this type. The reaction conditions depend greatly on the nature of the reagent; the products of the synthesis are 1,2-substituted ferrocenes[168,235,236]:



Such reactions have also been achieved for similar enantiomeric HMF.[172,235,237–239] The latter are planar-chiral compounds and substitution of the metal by some other group takes place with retention of not only the stereochemical configuration but also of the enantiomeric purity. The presence in these HMF of the dimethylamino-group, which tends to

undergo nucleophilic substitution in the form of a quaternary ammonium base, makes it possible to vary within wide limits the nature of the substituents and to obtain a wide variety of 1,2-disubstituted ferrocenes.

The marked influence of the organometallic fragment linked to the ferrocene fragment on the properties of the latter is also illustrated by the behaviour of the α-metallated ketones $Fc-COCH_2M(CO)_3Cp$ (M = Mo or W) in relation to nucleophiles[83,240]. In contrast to acetylferrocene, such HMF do not form derivatives involving the keto-group. This is associated with the low electrophilic activity of the carbon atom of the keto-group, caused by the marked electron-donating properties of the cyclopentadienylmetal carbonyl fragments, and also with the dissociation of the metal–carbon σ-bond in reactions with nucleophiles. Triethyloxonium tetrafluoroborate converts these ketones into the corresponding salts $[Fc-C(OEt)CH_2M(CO)_3Cp]BF_4$, which are convenient reagents for the synthesis of derivatives of α-metallated ketones. α,β-Unsaturated ketones, for example, ferrocenylideneacetylcymantrene, react with methylmagnesium iodide via the 1,2-addition mechanism to form the corresponding ketone and tertiary alcohol[92]. The latter is converted under the influence of HBF_4 in acetic anhydride into a salt of the allyl cation, which alkylates dimethylaniline in the *para*-position with an almost quantitative yield of the derivative $Fc-CH.(C_6H_4NH_2)CH=C(CH_3)C_5H_4Mn(CO)_3$. Secondary and tertiary carbinols of this type readily ionise on treatment with acids, forming intensely coloured carbenium ions[179,241,242]:



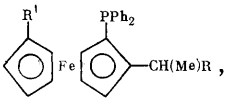
Such cations are extremely stable owing to the delocalisation of the positive charge over both metallocenyl residues.

Finally, the high reactivity of the carbene complexes $(CO)_5CrC(Fc)X$, where X = OMe or NC_4H_8,[218,243] and of ferrocenylpalladium chloride obtained *in situ*,[244,245] which produce various linear and cyclic ferrocene derivatives in reactions with unsaturated compounds, is noteworthy. The reactions involving other types of HMF have been little studied. In contrast to palladium chloride, ferrocenium trichloropalladate reacts with allyl chloride, forming the complex $(C_3H_5)_2Pd_3Cl_4$.[246] Reactions involving the addition of neutral molecules (CO, SO_2, MeSCN) to the rhodium complexes of 1,1′-bis(dimethylarsino)ferrocene (AF) of the type $[Rh(AF)_2]PF_6$ to form the complexes $[Rh(L)(AF)]PF_6$, which in their turn combine with various molecules X (X = H_2, O_2, Br_2, I_2, HCl, HBr, HI, MeI, $MeSO_2Cl$, $F_3CC{\equiv}CCF_3$, or MeSSMe), forming the compounds $[RhX(AF)]PF_6$, have been described[188]. The compound $[Rh(S_2)(AF)_2]PF_6$ has been obtained by the reaction with sulphur, while the reaction of $[Rh(O_2)(AF)_2]PF_6$ with SO_2 yields $[Rh(SO_4)(AF)_2]PF_6$.

IV. APPLICATIONS OF HETEROMETALLIC DERIVATIVES OF FERROCENE

In contrast to ferrocene and benzenechromium tricarbonyl, the ferrocenylcarbene complexes of chromium are catalysts of the hydrogenation of nitriles and amides to amines[100]. The hydrogenation of olefins does not occur under these conditions. The hydrogenation of various unsaturated compounds in the presence of chiral ferrocenylphosphinerhodium complexes is used to obtain optically active compounds[247–251].

Derivatives of the type



R = H, OH, NMe_2; R′ = H, PPh_2

are used as a rule of the chiral ligand.

The hydrogenation of α-acetamidoacrylic acids takes place with a yield of 86–94%.[194,248,252] The process takes place in various solvents with a high stereoselectivity (the optical yield is 89–93%). Acetophenone is hydrogenated rapidly and quantitatively to (*R*)-1-phenylethanol with an optical purity of 40%,[253] which is much higher than in the presence of other known rhodium catalysts of this process. The biologically active 2-amino-1-arylethanols are obtained by the hydrogenation of aryl aminomethyl ketones with 100% conversion and an enantioselectivity up to 95%.[249] Phosphine complexes of rhodium without ferrocenyl substituents exhibit a lower activity (80% conversion) and a lower optical yield (12%).

Dichloro[1,1′-bis(dimethylphosphine)ferrocene]nickel(II) catalyses the hydrosilylation of olefins and acetylenes[254,255]; in some cases this entails the substitution of hydrogen by chlorine. The hydrosilylation reaction is catalysed also by a platinum complex of this type. The asymmetric hydrosilylation of olefins, catalysed by chiral ferrocenylphoephine-palladium complexes[256], is used for the synthesis of optically active alcohols and alkyl bromides. A series of chiral phosphineferrocenerhodium complexes have been used successfully for the asymmetric hydrosilylation of ketones[257]. These HMF can give rise to hydrosilylation products with a higher optical yield than the phosphinerhodium complexes without ferrocene. Ferrocenylphosphinerhodium complexes are also effective catalysts of the hydroformylation of unsaturated compounds[258,259]. For example, the hydroformylation of hex-1-ene to n-hexanol takes place with 100% conversion and 93.2% selectivity.

The complex $(Ph_2PC_5H_4)_2FePdCl_2$ is the most active of the nickel and palladium complexes of phosphines in reactions of s-alkyl Grignard reagents with organic halides[260] and allyl alcohols[261]. The corresponding secondary derivatives are obtained as a result in a high yield (up to 97%). The reactions are not complicated by the isomerisation of the secondary alkyl groups to the primary groups, which is characteristic of other palladium and nickel complexes of phosphine. When chiral aminoalkylferrocenylphosphinenickel complexes are made to undergo this reaction, the corresponding optically active compounds are formed with a high stereoselectivity[262]. The same procedure has been used successfully for the asymmetric synthesis of terpenes[263]. It has also been shown recently that $(Ph_2PC_5H_4)_2FeNiCl_2$ is an effective catalyst of the reactions of t-alkyl Grignard reagents with bromostyrene[264], which results in the selective formation of $PhCH=CHCMe_3$. The application of nickel and cobalt compounds with polyfunctional aminophosphineferrocene ligands as catalysts of the isomerisation of alkyl groups[265] and prochiral allylamines[266] has been described. The initiating effect of the chelate complexes of ferrocenoylacetone in the polymerisation reactions of styrene and methyl methacrylate has also been described[267,268]. There are data concerning the catalytic activity of HMF in the thermolysis of $KClO_4$[269] and as regulators of the combustion of rocket fuels[270]. The advantages of the application of salts of ferrocenesulphonic acid in rocket fuels compared with ferrocene have been noted[270]. It has been suggested that chromium complexes of ferrocenoylacetone be used as antistatic additives to petroleum products[4,48,221]. The application of the Fc–Li + Cp_2TiCl_2 mixture for the fixation of nitrogen[271], of the $TiCl_4$

complex of ferrocene in the photopolymerisation of epichlorohydrin[272], and of the salt $FeCp_2[Ni(S_2C_4F_6)_2]$ in dactyloscopy[20] has also been noted. The effectiveness of HMF in the synthesis of various ferrocene derivatives has been described in previous Sections.

The possibility of oxidising ferrocene to the cationic form and of carrying out the classical reactions of organic chemistry with the latter and the relatively ready availability of ferrocene derivatives permitted a successful development of synthetic studies designed to produce various heterometallic derivatives of ferrocene. A multiplicity of compounds of this type, containing virtually all transition metals, have been obtained. The data described in the review indicate the main pathways leading to the specific synthesis of HMF with specified structures and properties. The specific synthesis is facilitated when the classification of HMF proposed in this review and based on the characteristic features of the bond between the heterometal or its derivative and the ferrocene fragment is used, since such features determine the specific characteristics of the synthetic reactions of HMF of different classes. Because of this, definite possibilities arise in the planned synthesis of new HMF.

The successful development of synthetic studies created a basis for the practical application of HMF but hitherto only a few of them have found such applications. This is apparently because the majority of the compounds have been obtained in recent years and their properties have been inadequately investigated. The available data on HMF suggest that they will exhibit specific properties, particularly in catalysis, in various chemical reactions, and especially in the synthesis of ferrocene derivatives and optically active compounds which are otherwise difficult to obtain. However, at present it is still by no means always clear which characteristics of HMF determine the manifestation of particular useful practical properties of these compounds.

During the preparation of the review for the press, new studies on the synthesis, properties[273–287] and applications[288–293] of HMF were published.

REFERENCES

1. A.N.Nesmeyanov and N.S.Kochetkova, Usepkhi Khim., 1974, **43**, 1513 [Russ.Chem.Rev., 1974(9)].
2. N.S.Kochetkova and Yu.K.Krynkina, Uspekhi Khim., 1978, **47**, 934 [Russ.Chem.Rev., 1978(5)].
3. M.D.Reshetova, "Primenenie Ferrotsena v Promyshlennosti" (Industrial Applications of Ferrocene), Izd. NIITEKhIM, Moscow, 1975.
4. M.D.Reshetova, "Primenenie Ferrotsena" (Applications of Ferrocene), Izd.NIITEKhIM, Moscow, 1976.
5. M.Dub (Editor), "Organometallic Compounds", Springer, Berlin, 1966, Vol.1.
6. M.Dub, "Organometallic Compounds", Springer, Berlin, 1975, Vol.1, First Supplement.
7. E.G.Perevalova and T.V.Nikitina, in "Organometallic Reactions" (Edited by E.I.Becker and M.Tsutsui), Wiley-Interscience, New York, 1972, Vol.4, p.163.
8. A.N.Nesmeyanov (Editor), "Metody Elementoorganicheskoi Khimii. Podgruppy Medi, Skandiya, Titana, Vanadiya, Khroma, Margantsa. Lantanoidy i Aktinoidy" (Methods of Organoelemental Chemistry. The Copper, Scandium, Titanium, Vanadium, Chromium, and Manganese Subgroups. Lanthanides and Actinides), Izd.Nauka, Moscow, 1974, Book 1.
9. A.N.Nesmeyanov (Editor), "Metody Elementoorganicheskoi Khimii. Podgruppy Medi, Skandiya, Titana, Vanadiya, Khroma, Margantsa. Lantanoidy i Aktinoidy" (Methods of Organoelemental Chemistry. The Copper, Scandium, Titanium, Vanadium, Chromium, and Manganese Subgroups. Lanthanides and Actinides), Izd.Nauka, Moscow, 1974, Book 2.
10. M.I.Bruce, Organometal.Chem.Rev., 1972, **B10**, 75.
11. B.W.Rockett and G.Marr, J.Organometal Chem., 1972, **45**, 389.
12. G.Marr and B.W.Rockett, J.Organometal.Chem., 1973, **58**, 323.
13. B.W.Rockett and G.Marr, J.Organometal.Chem., 1974, **79**, 223.
14. G.Marr and B.W.Rockett, J.Organometal.Chem., 1976, **106**, 259.
15. B.W.Rockett and G.Marr, J.Organometal.Chem., 1976, **123**, 205.
16. G.Marr and B.W.Rockett, J.Organometal.Chem., 1978, **148**, 273.
17. B.W.Rockett and G.Marr, J.Organometal.Chem., 1979, **167**, 53.
18. G.Marr and B.W.Rockett, J.Organometal.Chem., 1980, **189**, 163.
19. B.W.Rockett and G.Marr, J.Organometal.Chem., 1981, **211**, 215.
20. Gmelin's Handbuch der anorganischen Chemie, B.14, Eisen-Organische Verbindungen, Teil A, Ferrocen 1, Springer, Berlin, 1974.
21. Gmelin's Handbuch der anorganischen Chemie, B.49, Eisen-Organische Verbindungen, Teil A, Ferrocen 2, Springer, Berlin, 1977.
22. Gmelin's Handbuch der anorganischen Chemie, B.50, Eisen-Organische Verbindungen, Teil A, Ferrocen 3, Springer, Berlin, 1978.
23. Gmelin's Handbuch der anorganischen Chemie, B.41, Eisen-Organische Verbindungen, Teil A, Ferrocen 4, Springer, Berlin, 1977.
24. Gmelin's Handbuch der anorganischen Chemie, B.41, Eisen-Organische Verbindungen, Teil A, Ferrocen 4, Springer, Berlin, 1980.
25. Gmelin's Handbuch der anorganischen Chemie, B 41, Eisen-Organische Verbindungen, Teil A, Ferrocen 7, Springer, Berlin, 1980.
26. W.R.Cullen and J.D.Woollins, Coordination Chem.Rev., 1981, **39**(1–2), 1.
27. I.Pavlik and J.Klikorka, Coll.Czech.Chem.Comm., 1965, **30**, 664.
28. T.P.Adamovich, P.N.Gaponik, A.I.Lesnikovich, V.G.Guslev, I.G.Litvinenko, and V.V.Sviridov, Zhur.Obshch.Khim., 1976, **46**. 826.
29. P.N.Gaponik, A.I.Lesnikovich, Yu.G.Orlik, and V.V.Sviridov, "Vsesoyuznoe Soveshchanie 'Metalloorganicheskie Soedineniya dlya Polucheniya Metallicheskikh i Okisnykh Pokrytii'. Tezisy Dokladov" (All-Union Conference on 'Organometallic Compounds for the Synthesis of Metallic and Oxide Coatings'. Abstracts of Reports), Gorky, 1974, p.40.
30. P.N.Gaponik, A.I.Lesnikovich, and Yu.G.Orlik, Zhur.Neorg.Khim., 1977, **22**, 376 [Russ.J.Inorg. Chem., 1977(2)].
31. R.Epton, M.E.Hobson, and G.Marr, J.Organometal. Chem., 1978, **149**, 231.
32. A.N.Nesmeyanov, "Khimiya Ferrotsena" (The Chemistry of Ferrocene), Izd.Nauka, Moscow, 1969, p.80.
33. A.N.Nesmeyanov, K.I.Grandberg, T.V.Baukova, A.N.Kosina, and E.G.Perevalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1969, 1829.

34. N.S.Nametkin, S.P.Gubin, I.K.Dobrov, V.T.Tyurin, A.V.Nefed'ev, and R.A.Stukan, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1439.
35. D.Mingos, P.Michael, and C.T.Webber, Nouv.j.chim., 1980, **4**, 77.
36. A.V.Savitskii and L.M.Kuznetsov, Zhur.Neorg.Khim., 1970, **15**, 3011 [Russ.J.Inorg.Chem., 1970(11)].
37. D.Nicholls and K.R.Seddon, J.Chem.Soc., Dalton Trans., 1973, 2747.
38. V.G.Tsvetkov, L.M.Dyagileva, M.K.Safonova, and Yu.A.Aleksandrov, Koord.Khim., 1979, **5**, 772.
39. L.M.Dyagileva and Yu.A.Aleksandrov, Khim.Elementoorg.Soed.(Gor'kii), 1980(8), 27.
40. R.D.Bereman and D.P.Nalewajek, J.Inorg.Nuclear Chem., 1981, **43**, 519.
41. P.A.Vigato, U.Casellato, D.A.Clemete, G.Bandoli, and M.Vidali, J.Inorg.Nuclear Chem., 1973, **35**, 4131.
42. S.Kato, M.Wakamatsu, and M.Mizuta, J.Organometal. Chem., 1974, **78**, 405.
43. A.-M.Fouchardiere, Ann.Chim., 1968, **3**, 513.
44. M.Nakamoto, K.Shimizu, and T.Tanaka, Inorg.Chim. Acta, 1981, **53**, 51.
45. T.P.Vishnyakova, I.A.Golubeva, and L.M.Timofeeva, Zhur.Obshch.Khim., 1969, **39**, 2534.
46. A.Ostaszynski, H.Plenkiewiez, B.Hetnarski, and T.Urbanski, Bull.Acad.Polon.Sci., Ser.sci.chim., 1971, **19**(3), 181.
47. E.G.Perevalova, D.A.Lemenovskii, K.I.Grandberg, and A.N.Nesmeyanov, Dokl.Akad.Nauk SSSR, 1972, **203**, 1320.
48. Ya.M.Paushkin, T.P.Vishnyakova, I.D.Vlasova, and F.F.Machus, Zhur.Obshch.Khim., 1969, **39**, 2379.
49. P.N.Gaponik, V.G.Guslev, O.A.Ivashkevich, I.I.Kolbasko, A.I.Lesnikovich, Yu.G.Orlik, and V.V.Sviridov, Symposium, "Kinetika i Mekhanizm Khimicheskikh Reaktsii v Tverdom Tele" (Kinetics and Mechanism of Chemical Reactions in Solids) (Edited by V.V.Sviridov), Izd.Beloruss.Gos.Univ., Minsk, 1975, p.326.
50. P.N.Gaponik, A.I.Lesnikovich, and Yu.G.Orlik, "XII Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii. Tezisy Dokladov" (The XIIth All-Union Chugaev Conference on the Chemistry of Complex Compounds. Abstracts of Reports), Novosibirsk, 1975, p.502.
51. Yu.G.Orlik, P.N.Gaponik, A.I.Lesnikovich, and A.I.Vrublevskii, Zhur.Obshch.Khim., 1978, **48**, 1601.
52. A.M.Shevchik, Yu.P.Losev, and Ya.M.Paushkin, Symposium, "Stroenie, Svoistva i Primenenie β-Diketonatov Metallov" (The Structure, Properties, and Applications of Metal β-Diketonates) (Edited by V.I.Spitsyn), Izd.Nauka, Moscow, 1978, p.136.
53. O.N.Suvorova, Candidate's Thesis in Chemical Sciences, Lobachevskii Gorky State University, Gorky, 1969.
54. H.Imai and T.Shiraiwa, Technol.Repts.Kansai Univ., 1981(22), 107.
55. O.Gurtler and H.Henning, J.Electroanal.Chem., 1971, **30**, 253.
56. H.Imai and T.Ota, Bull.Chem.Soc.Japan, 1974, **47**, 2497.
57. J.-C.Lu, Y.-C.Zhang, J.-H.Bian, and Hua Hsueh Tung Pao, 1981(2), 88; Chem.Abs., 1981, **95**, 24 007.
58. F.Dietze, E.Butter, and E.Uhlmann, Z.anorg.Chem., 1973, **400**, 51.
59. G.B.Kazarinov, O.N.Vylegzhanina, G.A.Domrachev, and G.A.Razuvaev, Symposium, "Metody Polucheniya i Analiza Veshchestv Osoboi Chistoty" (Methods for the Synthesis and Analysis of Specially Pure Substances) (Edited by G.G.Devyatykh and I.M.Korenman), Izd.Nauka, Moscow, 1970, p.123.
60. G.A.Razuvaev, G.A.Domrachev, O.N.Suvorova, and L.G.Abakumova, J.Organometal.Chem., 1971, **32**, 113.
61. C.Hauser and C.Cain, J.Org.Chem., 1958, **23**, 1142.
62. U.Cassellato, M.Vidali, P.A.Vifato, G.Bandoli, and D.A.Clemente, Inorg.Nuclear Chem.Letters, 1973, **9**, 299.
63. M.L.M.Green, "Organometallic Compounds. Vol.2. The Transition Metals" [Chapman & Hall, London, 1968] (Translated into Russian), Izd.Mir, Moscow, 1972, p.203.
64. O.N.Suvorova, V.V.Parutin, and G.A.Domrachev, Symposium, "Stroenie, Svoistva i Primenenie β-Diketonatov Metallov" (The Structure, Properties, and Applications of Metal β-Diketonates) (Edited by V.I.Spitsyn), Izd.Nauka, Moscow, 1978, p.132.
65. L.Wolf and H.Hennig, Z.anorg.Chem., 1965, **341**, 1.
66. D.M.Wiles and T.Suprunchuk, Canad.J.Chem., 1968, **46**, 1865.
67. W.D.Fleischmann, Dissertation, Dokt.Naturwiss, Munich, 1972; 1974, 2B187.
68. W.D.Fleischmann and H.P.Fritz, Z.Naturforsch, 1973, **28B**, 383.
69. Y.Omota, R.Kobayashi, and N.Sugiyama, Bull.Chem. Soc.Japan, 1973, **46**, 2896.
70. A.P.Budhkar, U.N.Kantek, and D.N.Sen, Indian J. Chem., 1978, **16A**, 626.
71. I.A.Eremina, Symposium, "Neft' i Gaz i Ikh Produkty" (Petroleum, Gas, and Their Products) (Edited by V.N.Vinogradov), MINKhGP im.Gubkina, Moscow, 1971, 144.
72. I.A.Eremina and A.A.Zavelova, "Neft' i Gaz i Ikh Produkty" (Petroleum, Gas, and Their Products) (Edited by V.N.Vinogradov), MINKhGP im.Gubkina, Moscow, 1971, p.143.
73. I.A.Eremina, Abstract of Candidate's Thesis in Chemical Sciences, Gubkin Moscow Institute of the Chemical and Gas Industry, Moscow, 1973.
74. A.N.Nesmeyanov, V.A.Sazonova, N.N.Sedova, and L.S.Klimenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 735.
75. A.N.Nesmeyanov, N.N.Sedova, V.A.Sazonova, and L.S.Borodina, Dokl.Akad.Nauk SSSR, 1972, **207**, 617.
76. A.N.Nesmeyanov, N.N.Sedova, V.A.Sazonova, I.F.Leshcheva, and I.S.Rogozhin, Dokl.Akad.Nauk SSSR, 1974, **218**, 356.
77. N.N.Sedova, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1973.
78. R.F.Kovar and M.D.Rausch, J.Org.Chem., 1973, **38**, 1918.
79. A.N.Nesmeyanov, N.N.Sedova, S.K.Moiseev, and V.A.Sazonova, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1171.
80. A.N.Nesmeyanov, T.P.Tolstaya, V.V.Korol'kov, and A.N.Yarkevich, Dokl.Akad.Nauk SSSR, 1975, **221**, 1337.
81. V.V.Korol'ko, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1975.
82. A.N.Nesmeyanov, E.G.Perevalova, L.I.Leont'eva, and S.A.Eremin, Dokl.Akad.Nauk SSSR, 1978, **243**, 1208.
83. S.A.Eremin, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No.3782-79 (1979); Ref.Zhur.Khim., 1980, 21Zh345.
84. K.H.Pannell, J.B.Cassias, G.M.Crawford, and A.Flores, Inorg.Chem., 1976, **15**, 2671.

85. A.N.Nesmeyanov, L.G.Makarova, and V.N.Vinogradova, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 2796.
86. US P.3 138 625, 1964; Chem.Abs., 1964, **61**, 9530.
87. S.P.Gubin, S.A.Smirnova, L.I.Denisovich, and A.A.Lubovich, J.Organometal.Chem., 1971, **30**, 243.
88. S.P.Gubin and A.A.Lubovich, J.Organometal.Chem., 1970, **22**, 183.
89. S.A.Smirnova, S.P.Gubin, A.A.Lubovich, and L.I.Denisovich, Dokl.Akad.Nauk SSSR, 1971, **200**, 605.
90. A.Meyer and R.Dabard, Compt.rend., 1967, **264C**, 1775.
91. A.N.Nesmeyanov, V.A.Sazonova, V.N.Postnov, and A.M.Baran, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 902.
92. A.N.Nesmeyanov, V.N.Postnov, V.A.Sazonova, T.N.Galakhova, and A.A.Kuznetsov, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2172.
93. M.D.Rausch and A.Siegel, J.Organometal.Chem., 1969, **17**, 117.
94. M.Rosenblum, N.M.Brawn, D.Ciappenelli, and J.Tancrede, J.Organometal.Chem., 1970, **24**, 469.
95. A.M.Sladkov and I.R.Gol'ding, Usepkhi Khim., 1979, **48**, 1625 [Russ.Chem.Rev., 1979(9)].
96. M.D.Rausch and S.Siegel, J.Org.Chem., 1969, **34**, 1974.
97. M.H.Chisholm and R.K.Potkul, Synth.React.Inorg. Met.-Org.Chem., 1978, **8**, 65.
98. C.U.Pittman and L.R.Smith, J.Organometal.Chem., 1975, **90**, 203.
99. G.A.Moser, E.O.Fischer, and M.D.Rausch, J.Organometal.Chem., 1971, **27**. 379.
100. J.A.Connor and J.P.Lloyd, J.Chem.Soc., Dalton Trans., 1972, 1470.
101. M.D.Rausch, G.A.Moser, and C.F.Meade, J.Organometal.Chem., 1973, **51**, 1.
102. E.O.Fischer, F.J.Gammel, J.O.Besenhard, A.Frank, and D.Neugebauer, J.Organometal.Chem., 1980, **191**, 261.
103. E.O.Fischer, M.Schluge, and J.O.Besenhard, Angew. Chem., 1976, **88**, 719.
104. E.O.Fischer, M.Schluge, J.O.Besenhard, P.Friedrich, G.Huttner, and F.R.Kreissl, Chem.Ber., 1978, **111**, 3530.
105. E.O.Fischer, T.L.Lindner, G.Huttner, P.Friedrich, F.R.Kreissl, and J.O.Besenhard, Chem.Ber., 1977, **100**, 3397.
106. F.R.Kreissl, K.Eberl, and W.Uedelhoven, Chem.Ber., 1977, **100**, 3782.
107. W.Uedelhoven, K.Eberl, and F.R.Kreissl, Chem.Ber., 1979, **112**, 3376.
108. J.E.Hallegren, C.S.Eschbach, and D.Seyferth, J.Amer. Chem.Soc., 1972, **94**, 2547.
109. D.Seyferth, J.E.Hallegren, R.I.Spohn, G.H.Williams, M.O.Nestle, and P.L.K.Hung, J.Organometal.Chem., 1974, **65**, 99.
110. D.Seyferth and C.L.Nivert, J.Organometal.Chem., 1976, **113**, C65.
111. P.Etievant, B.Gautheron, and G.Tainturier, Bull.Soc. chim.France, pt.2, 1978, 292.
112. P.Etievant, G.Tainturier, and B.Gautheron, Compt. rend., 1976, **283C**, 233.
113. C.U.Pittman and T.D.Rounsefell, Macromolecules, 1976, **9**, 936.
114. C.U.Pittman, R.L.Voges, and J.Elder, Macromolecules, 1971, **4**, 302.
115. C.U.Pittman, in "Organometallic Reactions and Syntheses", Vol.6 (Edited by E.I.Becker and M.Tsutsui), Plenum Press, New York–London, 1977, p.1.
116. A.N.Nesmeyanov, V.A.Sazonova, V.N.Postnov, A.M.Baran, Ya.A.Angelyuk, and B.A.Surkov, Dokl. Akad.Nauk SSSR, 1978, **241**, 1099.
117. C.E.Carraher and J.T.Reimer, Polymer, 1972, **13**(4), 153.
118. C.E.Carraher and J.T.Reimer, J.Polymer Sci., Polymer Chem.Educ., 1972, **10**, 3367.
119. C.E.Carraher and G.F.Burrish, J.Macromol.Sci., 1976, **10A**, 1457.
120. C.E.Carraher and M.J.Christensen, J.Amer.Chem. Soc.Polymer Prepr., 1976, **17**, 530.
121. C.E.Carraher, M.J.Christensen, and J.A.Schroeder, J. Macromol.Sci., 1977, **11A**, 2021.
122. C.E.Carraher and M.J.Christensen, Angew.macromol. Chem., 1978, **69**, 61.
123. A.N.Nesmeyanov, N.N.Zaitseva, L.P.Yur'eva, R.A.Stukan, and V.E.Prusakov, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1420.
124. Yu.A.Shevelev, M.V.Dodonov, L.P.Yur'eva, G.A.Domrachev, and N.N.Zaitseva, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 1414.
125. M.B.Freeman and L.G.Sheddon, Inorg.Chem., 1980, **19**, 1125.
126. H.Brunner, R.Lukas, and A.Woditsch, J.Organometal. Chem., 1978, **161**, C49.
127. M.I.Bruce, Angew.Chem., 1977, **89**, 75.
128. S.S.Crawford and H.D.Kaesz, Inorg.Chem., 1977, **16**, 3193.
129. A.N.Nesmeyanov, A.M.Baran, L.Eggert, V.N.Postnov, and V.A.Sazonova, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1402.
130. G.A.Razuvaev, G.A.Domrachev, V.V.Sharutin, and O.N.Suvorova, J.Organometal.Chem., 1977, **141**, 313.
131. G.A.Razuvaev, V.V.Sharutin, G.A.Domrachev, and O.N.Suvorova, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 2177.
132. H.J.Bürger and C.Kluess, J.Organometal.Chem., 1973, **56**, 269.
133. E.G.Perevalova, K.I.Grandberg, D.A.Lemenovskii, and T.V.Baukova, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 2077.
134. A.N.Nesmeyanov, E.G.Perevalova, D.A.Lemenovskii, A.N.Kosina, and K.I.Grandberg, Izv.Akad.Nauk SSSR, 1969, 2030.
135. A.N.Nesmeyanov, E.G.Perevalova, L.I.Khomik, and L.I.Leont'eva, Dokl.Akad.Nauk SSSR, 1973, **209**, 869.
136. L.I.Khomik, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1975.
137. A.N.Nesmeyanov, N.N.Sedova, V.A.Sazonova, and S.K.Moiseev, J.Organometal.Chem., 1980, **185**, C6.
138. A.N.Nesmeyanov, V.A.Sazonova, N.N.Sedova, Yu.V.Volgin, and O.V.Dudkina, Dokl.Akad.Nauk SSSR, 1976, **226**, 1092.
139. A.N.Nesmeyanov, V.A.Sazonova, N.N.Sedova, and E.N.Stakheeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2354.
140. A.N.Nesmeyanov, N.N.Sedova, S.K.Moiseev, and V.A.Sazonova, Dokl.Akad.Nauk SSSR, 1981, **256**, 98.
141. A.N.Nesmeyanov, V.A.Sazonova, N.N.Sedova, and S.K.Moiseev, Dokl.Akad.Nauk SSSR, 1980, **252**, 361.
142. E.G.Perevalova, D.A.Lemenovskii, O.B.Afanasova, V.P.Dyadchenko, K.I.Grandberg, and A.N.Nesmeyanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2594.
143. A.G.Osborne and R.H.Whiteley, J.Organometal.Chem., 1979, **181**, 425.
144. M.Tsuitsui and N.Ely, J.Amer.Chem.Soc., 1974, **96**, 3650.

145. M.Tsutsui, N.Ely, and A.Gebala, Inorg.Chem., 1975, **14**, 78.
146. Z.Dawoodi, C.Eaborn, and A.Pidcock, J.Organometal. Chem., 1979, **170**, 95.
147. L.Bednarik, K.S.Gohdes, and E.W.Neuse, Transit. Met.Chem., 1977, **2**, 212.
148. A.N.Nesmeyanov and N.S.Sazonova, Dokl.Akad.Nauk SSSR, 1967, **176**, 598.
149. A.N.Nesmeyanov, V.A.Sazonova, N.S.Sazonova, and V.N.Plyuchina, Dokl.Akad.Nauk SSSR, 1967, **177**, 1352.
150. A.N.Nesmeyanov, N.S.Sazonova, V.A.Sazonova, and L.N.Meskhi, Izv.Akad.Nauk SSSR, Ser.Khim., 1969, 1827.
151. N.S.Sazonova, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1969.
152. A.N.Nesmeyanov, E.G.Perevalova, O.B.Afanasova, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 483.
153. A.N.Nesmeyanov, E.G.Perevalova, K.I.Grandberg, D.A.Lemenovskii, T.V.Baukova, and O.B.Afanasova, J.Organometal.Chem., 1974, **65**, 131.
154. O.B.Afanasova, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1975.
155. A.N.Nesmeyanov, E.G.Perevalova, O.B.Afanasova, M.N.Elison, and K.I.Grandberg, Izv. Akad.Nauk SSSR, Ser.Khim., 1975, 477.
156. A.N.Nesmeyanov, E.G.Perevalova, O.B.Afanasova, M.V.Tolstaya, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1118.
157. L.L.Troitskaya, V.I.Sokolov, and O.A.Reutov, Dokl. Akad.Nauk SSSR, 1977, **236**, 371.
158. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, J.Organometal.Chem., 1977, **133**, C28.
159. L.G.Kuz'mina, Yu.T.Struchkov, L.L.Troitskaya, V.I.Sokolov, and O.A.Reutov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1528.
160. A.N.Nesmeyanov, E.G.Perevalova, V.P.Dyadchenko, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2844.
161. V.P.Dyadchenko, Vestnik Moskov.Univ., Khim., 1976, **17**, 358.
162. V.P.Dyadchenko, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1977.
163. A.N.Nesmeyanov, V.P.Dyadchenko, K.I.Grandberg, A.N.Red'kin, and E.G.Perevalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2050.
164. A.N.Nesmeyanov, E.G.Perevalova, K.I.Grandberg, D.A.Lemenovskii, T.V.Baukova, and O.B.Afanasova, Vestnik Moskov.Univ., Khim., 1973, **44**, 387.
165. A.N.Nesmeyanov, E.G.Perevalova, M.V.Ovchinnikov, Yu.A.Snakin, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1925.
166. H.Alper, J.Organometal.Chem., 1974, **80**, C29.
167. J.C.Gaunt and B.L.Shaw, J.Organometal.Chem., 1975, **102**, 511.
168. A.Kasahara, T.Isumi, and M.Maemura, Bull.Chem. Soc.Japan, 1977, **50**, 1878.
169. M.Nonoyama, Inorg.Nuclear Chem.Letters, 1976, **12**, 709.
170. M.Nonoyama and M.Sugimoto, Inorg.Chim.Acta, 1979, **35**, 131.
171. M.Sugimoto and M.Nonoyama, Inorg.Nuclear Chem. Letters, 1979, **15**, 405.
172. V.I.Sokolov and L.L.Troitskaya, Chimia, 1978, **32**, 122.
173. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, J.Organometal.Chem., 1979, **182**, 537.
174. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, Dokl. Akad.Nauk SSSR, 1977, **237**, 1376.
175. S.S.Crawford, G.Firestein, and H.D.Kaesz, J.Organometal.Chem., 1975, **91**, C57.
176. A.N.Nesmeyanov, G.B.Shul'pin, L.M.Korneva, and M.I.Rybinskaya, Dokl.Akad.Nauk SSSR, 1974, **217**, 1091.
177. G.E.Herberich and B.Hessner, J.Organometal.Chem., 1978, **161**, C36.
178. J.Besancon and J.Tirouflet, Rev.Chim.Miner., 1968, **5**, 363.
179. A.Ceccon, A.Gobbo, and A.Venzo, J.Organometal. Chem., 1978, **162**, 311.
180. S.P.Gubin and V.S.Khandkarova, J.Organometal. Chem., 1970, **22**, 449.
181. K.Vasufuku and H.Yamazaki, J.Organometal.Chem., 1977, **127**, 197.
182. M.D.Rausch, F.A.Higbie, G.F.Westover, A.Clearfield, R.Gopal, J.M.Troup, and I.Bernal, J.Organometal. Chem., 1978, **149**, 245.
183. A.Kasahara and T.Izumi, Bull.Chem.Soc.Japan, 1972, **45**, 1256.
184. P.Singh, R.Chand, and R.J.Rivest, Inorg.Nuclear Chem., 1975, **37**, 45.
185. E.B.Moynahan, T.D.Popp, and M.F.Werneke, J.Organometal.Chem., 1969, **19**, 229.
186. S.C.Jain and R.Rivest, J.Inorg.Nuclear Chem., 1970, **32**, 1579.
187. J.Bichop and A.Davison, Inorg.Chem., 1971, **10**, 832.
188. J.T.Mague and M.O.Nutt, Inorg.Chem., 1977, **16**, 1259.
189. N.E.Schore, J.Amer.Chem.Soc., 1979, **101**, 7410.
190. J.Kotz and C.Nivert, J.Organometal.Chem., 1973, **52**, 387.
191. A.N.Nesmeyanov, E.G.Perevalova, O.B.Afanasova, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2166.
192. V.S.Tolkunova, A.Z.Rubezhov, V.I.Bakhmutov, and V.D.Vil'chevskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2228.
193. A.W.Rudie, D.W.Lichtenberg, M.L.Katcher, and A.Davison, Inorg.Chem., 1978, **17**, 2859.
194. W.R.Cullen, F.W.B.Einstein, C.-H.Huang, A.C.Willis, and E.-S.Yeh, J.Amer.Chem.Soc., 1980, **102**, 988.
195. L.M.Dyagileva, O.S.Morozov, N.N.Vyshinskii, V.G.Tsvetkov, and Yu.A.Aleksandrov, Zhur.Obshch. Khim., 1980, **50**, 1859.
196. N.Dowling, P.M.Henry, N.A.Lesis, and H.Taube, Inorg.Chem., 1981, **20**, 2345.
197. A.N.Nesmeyanov, E.G.Perevalova, O.B.Afanasova, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1919.
198. A.N.Nesmeyanov, E.G.Perevalova, Yu.A.Snakin, and K.I.Grandberg, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 1928.
199. R.G.Wollmann and D.N.Hendrickson, Inorg.Chem., 1977, **16**, 3079.
200. A.N.Nesmeyanov, D.N.Kursanov, V.N.Setkina, V.D.Vil'chevskaya, N.K.Baranetskaya, A.I.Krylova, and L.A.Glushchenko, Dokl.Akad.Nauk SSSR, 1971, **199**, 1336.
201. A.N.Nesmeyanov, D.N.Kursanov, V.D.Vil'chevskaya, N.K.Baranetskaya, A.I.Krylova, V.I.Losilkina, and V.N.Setkina, Dokl.Akad.Nauk SSSR, 1978, **241**, 111.
202. C.U.Pittman and G.Evans, J.Organometal.Chem., 1972, **43**, 361.

203. J.C.Kotz, C.L.Nivert, J.M.Lieber, and R.C.Reed, J.Organometal.Chem., 1975, **91**, 87.
204. J.C.Kotz, C.L.Nivert, J.M.Lieber, and R.C.Reed, J.Organometal.Chem., 1975, **84**, 255.
205. J.Bichop and A.Davison, Inorg.Chem., 1971, **10**, 826.
206. D.N.Kursanov, V.N.Setkina, S.P.Dolgova, and M.N.Nefedova, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1886.
207. D.Seyferth and H.P.Withers, J.Organometal.Chem., 1980, **185**, C1.
208. H.Alper, N.D.Silavwe, G.I.Birnbaum, and F.R.Ahmed, J.Amer.Chem.Soc., 1979, **101**, 6582.
209. P.N.Gaponik, A.I.Lesnikovich, and Yu.G.Orlik, Zhur.Obshch.Khim., 1978, **48**, 1177.
210. L.N.Zakharov, Yu.T.Struchkov, V.V.Sharutin, and O.N.Suvorova, Cryst.Struct.Comm., 1979, **8** 439.
211. U.Thewalt and D.Schomburg, Z.Naturforsch., 1975, **30B**, 636.
212. V.G.Andrianov, Yu.T.Struchkov, and E.R.Rossinskaya, Chem.Comm., 1973, 338.
213. V.G.Andrianov, Yu.T.Struchkov, and E.R.Rossinskaya, Zhur.Strukt.Khim., 1974, **15**, 74.
214. D.A.Lemenovskii, M.N.Elinson, O.B.Afanasova, and A.N.Nesmeyanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 2105.
215. A.N.Nesmeyanov, Yu.T.Struchkov, N.N.Sedova, V.G.Andrianov, Yu.V.Volgin, and V.A.Sazonova, J.Organometal.Chem., 1977, **137**, 217.
216. A.N.Nesmeyanov, N.N.Sedova, Yu.T.Struchkov, V.G.Andrianov, E.N.Stakheeva, and V.A.Sazonova, J.Organometal.Chem., 1978, **153**, 115.
217. C.G.Pierpont and R.Eisenberg, Inorg.Chem., 1972, **11**, 828.
218. K.H.Dotz, R.Dietz, and D.Neugebauer, Chem.Ber., 1979, **112**, 1486.
219. G.A.Domrachev and O.N.Vylegzhanina, Zhur.Obshch. Khim., 1968, **38**, 2473.
220. V.G.Osipov, M.D.Reshetova, N.N.Silkina, S.A.Yankovskii, and E.A.Chernyshev, Zhur.Obshch.Khim., 1974, **44**, 599.
221. Ya.M.Paushkin, T.P.Vishnyakova, F.F.Machus, I.D.Vlasova, and I.F.Krylov, Khim.i Tekhnol.Topliv. i Masel, 1969, 22.
222. I.B.Rabinovich, M.S.Sheiman, G.V.Burchalova, G.P.Kamelova, and A.S.Smirnov, Termodinam.Org. Soed.(Gor'kii), 1979(8), 22.
223. L.I.Denisovich and S.P.Gubin, Uspekhi Khim., 1977, **46**, 50 [Russ.Chem.Rev., 1977(1)].
224. A.N.Nesmeyanov, "Khimiya σ- i π-Kompleksov Zheleza, Margantsa i Reniya" (The Chemistry of the σ- and π-Complexes of Iron, Manganese, and Rhenium), Izd. Nauka, Moscow, 1980, p.342.
225. A.N.Nesmeyanov, D.N.Kursanov, V.N.Setkina, V.A.Sazonova, E.I.Fedin, P.V.Petrovskii, N.N.Sedova, and Yu.V.Volgin, Dokl.Akad.Nauk SSSR, 1975, **221**, 854.
226. V.I.Losilkina, D.N.Kursanov, N.K.Baranetskaya, V.D.Vil'chevskaya, V.S.Tolkunova, and V.N.Setkina, Dokl.Akad.Nauk SSSR, 1980, **255**, 883.
227. A.N.Nesmeyanov, N.N.Sedova, Yu.V.Volgin, and V.A.Sazonova, Dokl.Akad.Nauk SSSR, 1976, **228**, 1347.
228. E.G.Perevalova, D.A.Lemenovskii, K.I.Grandberg, and A.N.Nesmeyanov, Dokl.Akad.Nauk SSSR, 1972, **202**, 93.
229. A.N.Nesmeyanov, V.A.Sazonova, N.N.Sedova, and E.N.Stakheeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2141.
230. A.N.Nesmeyanov, N.N.Sedova, Yu.V.Volgin, and V.A.Sazonova, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2831.
231. E.G.Perevalova, D.A.Lemenovskii, K.I.Grandberg, and A.N.Nesmeyanov, Dokl.Akad.Nauk SSSR, 1971, **199**, 832.
232. A.N.Nesmeyanov, K.I.Grandberg, D.A.Lemenovskii, O.V.Afanasova, and E.G.Perevalova, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 887.
233. E.G.Perevalova, D.A.Lemenovskii, T.V.Baukova, E.I.Smyslova, K.I.Grandberg, and A.N.Nesmeyanov, Dokl.Akad.Nauk SSSR, 1972, **206**, 883.
234. E.G.Perevalova, D.A.Lemenovskii, V.P.Alekseev, K.I.Grandberg, and A.N.Nesmeyanov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1869.
235. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, Dokl.Akad.Nauk SSSR, 1979, **246**, 124.
236. T.Izumi, K.Endo, O.Saito, I.Shimizu, M.Maemura, and A.Kasahara, Bull.Chem.Soc.Japan, 1978, **51**, 663.
237. A.Kasahara, T.Izumi, and H.Watabe, Bull.Chem.Soc. Japan, 1979, **52**, 957.
238. T.Komatsu, M.Nonoyama, and J.Fujita, Bull.Chem. Soc.Japan, 1981, **54**, 186.
239. V.I.Sokolov, L.L.Troitskaya, and O.A.Reutov, J.Organometal.Chem., 1980, **202**, C58.
240. A.N.Nesmeyanov, E.G.Perevalova, L.I.Leont'eva, and S.A.Eremin, Dokl.Akad.Nauk SSSR, 1980, **252**, 119.
241. A.G.Ginzburg, V.N.Setkina, Sh.G.Kasumov, G.A.Panosyan, P.V.Petrovskii, and D.N.Kursanov. Dokl.Akad.Nauk SSSR, 1976, **22**, 1368.
242. A.Ceccon, M.Gentiloni, L.Sella, and A.Venzo, Gazzetta, 1977, **107**, 439.
243. J.A.Connor and J.P.Lloyd, J.Chem.Soc., Perkin Trans., 1973, 17.
244. A.Kasahara, T.Izumi, G.Saito, M.Yodono, R.Saita, and Y.Goto, Bull.Chem.Soc.Japan, 1972, **45**, 895.
245. A.Kasahara and T.Izumi, Bull.Chem.Soc.Japan, 1973, **46**, 665.
246. N.S.Nametkin, I.K.Dobrov, A.L.Bykovets, and V.D.Tyurin, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 199.
247. M.Kumada and T.Hayashi, "Symposium on Rhodium Homogeneous Catalysis, Verzprem (Hungary)", p.157; Chem.Abs., 1979, **90**, 121 760.
248. T.Hayashi, T.Mise, S.Mitachi, K.Yamamoto, and M.Kumada, Tetrahedron Letters, 1976, 1133.
249. T.Hayashi, A.Katsumura, M.Konishi, and M.Kumada, Tetrahedron Letters, 1979, 425.
250. T.Hayashi and M.Kumada, in "Fundamental Research in Homogeneous Catalysis", Vol.2 (Edited by Y.Ishii and M.Tsutsui), Plenum Press, New York, 1978, p.159.
251. K.Yamamoto, J.Wakatsuki, and R.Sugimoto, Bull.Chem. Soc.Japan, 1980, **53**, 113.
252. W.R.Cullen and E.-S.Yeh, J.Organometal.Chem., 1977, **139**, C13.
253. T.Hayashi, T.Mise, and M.Kumada, Tetrahedron Letters, 1976, 4351.
254. Japanese P.49-25 649, 1974; Ref.Zhur.Khim., 1975, 5N83.
255. J.Kiso, M.Kumada, K.Tamao, and M.Umeno, J.Organometal.Chem., 1973, **50**, 297.
256. T.Hayashi, K.Tamao, Y.Katsuro, I.Nakae, and M.Kumada, Tetrahedron Letters, 1980, **21**, 1871.
257. T.Hayashi, K.Yamamoto, and M.Kumada, Tetrahedron Letters, 1974, 4405.
258. BRD P.2 617 305, 1976; Chem.Abs., 1976, **86**, 22 369.
259. BRD P.2 834 742, 1979; Chem.Abs., 1979, **90**, 203 487.

260. T.Hayashi, M.Konishi, and M.Kumada, Tetrahedron Letters, 1979, 1871.
261. T.Hayashi, M.Konishi, and M.Kumada, J.Organometal. Chem., 1980, **186**, C1.
262. T.Hayashi, M.Tajika, K.Tamao, and M.Kumada, J.Amer.Chem.Soc., 1976, **98**, 3718.
263. K.Tamao, T.Hayashi, H.Matsumoto, and M.Kumada, Tetrahedron Letters, 1979, 2155.
264. T.Hayashi, M.Konishi, K.Vokota, and M.Kumada, Chem.Letters, 1980, 767.
265. M.Zembayashi, K.Tomao, T.Mise, and M.Kumada, Tetrahedron Letters, 1977, 1799.
266. H.Kumobayashi, S.Akutagawa, and S.Otsuka, J.Amer. Chem.Soc., 1978, **100**, 3949.
267. T.P.Vishnyakova, Ya.M.Paushkin, I.D.Vlasova, and G.I.Biryukova, Vysokomol.Soed., 1968, **B10**, 452.
268. Ya.M.Paushkin, T.P.Vishnyakov, Yu.V.Korshak, I.A.Eremina, and I.D.Vlasova, Dokl.Akad.Nauk Beloruss.SSR, 1974, **18**, 42.
269. V.G.Guslev, K.K.Kovalenko, A.I.Lesnikovich, and V.V.Sviridov, Fiz.Goreniya i Vzryva, 1976, **12**, 441.
270. US P.3 607 471, 1971.
271. A.Dormond, J.C.Leblanc, F.Moigne, and J.Firoujlet, Compt.rend., 1972, **274C**, 1707
272. K.Kaeriyama, J.Polymer Sci., Polymer.Chem.Educ., 1976, **14**, 1547.
273. V.N.Postnov, A.M.Baran, and V.A.Sazonova, Dokl. Akad.Nauk SSSR, 1981, **258**, 124.
274. V.N.Postnov, V.A.Sazonova, Yu.N.Polivin, and V.A.Chertkov, Dokl.Akad.Nauk SSSR, 1982, **264**, 96.
275. A.A.Koridze, N.M.Astakhova, and P.V.Petrovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 957.
276. E.W.Neuse and M.S.Loonat, Transit.Met.Chem., 1981, **6**, 260.
277. H.-H.Wei and D.-M.Horng, Transit.Met.Chem., 1981, **6**, 319.
278. S.Kamiyama, A.Kasahara, T.Izumi, I.Shimizu, and H.Watabe, Bull.Chem.Soc.Japan, 1981, **54**, 2079.
279. L.C.Francesconi, D.R.Corbin, A.W.Clauss, D.N.Hendrickson, and G.D.Stucky, Inorg.Chem., 1981, **20**, 2078.
280. N.E.Schore, L.S.Benner, and B.E.Labelle, Inorg. Chem., 1981, **20**, 3200.
281. O.R.Hughes and D.A.Young, J.Amer.Chem.Soc., 1981, **103**, 6636.
282. N.A.Lewis, Talanta, 1981, **28**, 860.
283. P.V.Petrovskii, V.N.Setkina, S.P.Dolgova, and D.N.Kursanov, J.Organometal.Chem., 1981, **221**, 177.
284. A.A.Koridze, I.T.Chizhevky, P.V.Petrovskii, E.I.Fedin, N.E.Kolobova, L.E.Vinogradova, L.A.Leites, V.G.Andrianov, and Yu.T.Struchkov, J.Organometal. Chem., 1981, **206**, 373.
285. N.N.Sedova, S.K.Moiseev, and V.A.Sazonova, J.Organometal.Chem., 1982, **224**, C53.
286. J.M.Brown, P.A.Chaloner, A.G.Kent, B.A.Murrer, P.N.Nicholson, D.Parker, and P.J.Sidebottom, J.Organometal.Chem., 1981, **216**, 263.
287. G.Marr and B.W.Rockett, J.Organometal.Chem., 1982, **227**, 373.
288. T.Hayashi, M.Konishi, K.Yokota, and M.Kumada, Chem.Comm., 1981, 313.
289. T.Kobayashi and M.Tanaka, Chem.Comm., 1981, 333.
290. M.Kumada, T.Hayashi, T.Mise, A.Katsumura, N.Nagashima, and M.Fukushima, Kenkyu Hokoku–Asahi Garasu Kogyo Gijutsu Shoreikai, 1980(37), 69; Chem.Abs., 1982, **96**, 85 708.
291. J.D.Unruh and J.R.Christenson, J.Mol.Catal., 1982, **14**, 19.
292. T.Kobayashi and M.Tanaka, J.Organometal.Chem., 1982, **231**, C12.
293. T.Hayashi, M.Konishi, M.Fukushima, T.Mise, M.Kagotani, M.Tajika, and M.Kumada, J.Amer.Chem. Soc., 1982, **104**, 180.

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