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Reactions of metallocenes with organocadmium and organomercury compounds *

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Abstract

The results of reactions of 3d-series metallocenes, Cp_2M (M = V, Cr, Mn, Fe, Co, Ni; Cp = C_5H_5, C_5H_4Alk, C_5Me_5, Ind) with organocadmium and organomercury compounds have been summarized and classified. The effect of the nature of the metal and ligand on the reactivity of metallocenes has been discussed.

Introduction

The first reactions of metallocenes with organocadmium and organomercury compounds were carried out about 15 years ago by Razuvaev and colleagues [1–3]. Investigations carried out at that time and later led to the discovery of new types of organometallic compounds including bi- and polynuclear compounds. Organocadmium and organomercury compounds proved to be extremely unique reagents in reactions with metallocenes.

The change in electronic configuration of the central atom in metallocenes and the ligand environment have an important influence on the reactivity in interactions with organocadmium and organomercury compounds.

The reaction systems of metallocenes, organocadmium or organomercury compounds, are similar to Ziegler–Natta systems and can serve as models in the study of several catalytic processes.

Vanadium derivatives

Oxidative addition reactions are typical reactions of metallocenes for an electron-deficient 15-electron complex of vanadium–vanadocene [1]. Reaction of

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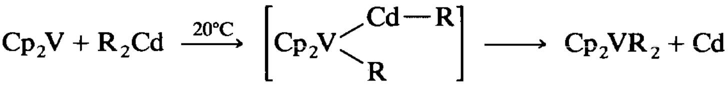
* This paper is dedicated to the memory of Prof. G.A. Razuvaev.

vanadocene with organocadmium compounds was carried out for the first time in 1975. On reacting Cp_2V with $Cd(GeEt_3)_2$, the compound Cp_2VGeEt_3 was isolated [2]. The mechanism of this reaction was interpreted as the insertion of Cp_2V into the cadmium–germanium bond with the subsequent elimination of metallic cadmium, equivalent to oxidative addition. The following experiments on the reaction of Cp_2V with R_2Cd (R = Me, Et, Ph, CH_2Ph) resulted in the synthesis of d^1-vanadocene complexes, Cp_2VR_2 type (Table 1) [3]. The complexes Cp_2VR_2 (R = Me, Et, CH_2Ph) were characterized by the ESR method in solution and one complex, Cp_2VMe_2, was isolated in crystalline form, the composition of which was confirmed by traditional chemical methods. Based on the experimental data, it was suggested that the reaction proceeds via the route of oxidative addition of R_2Cd to Cp_2V through the formation of an intermediate d^1-complex with a V–Cd bond.



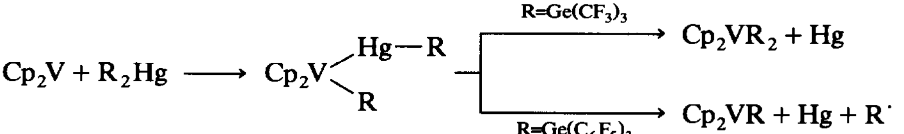
$$Cp_2V + R_2Cd \xrightarrow{20°C} \left[Cp_2V \begin{matrix} \diagup Cd-R \\ \diagdown R \end{matrix} \right] \longrightarrow Cp_2VR_2 + Cd \qquad (1)$$

(I)

The intermediate complex I was not recorded by ESR spectroscopy in the low-temperature reaction. Attempts to register complex I by low-temperature (80 K) IR spectroscopy was unsuccessful. As a result of the reaction of Cp_2V with Me_2Cd on a low-temperature matrix, the absorption bands at 330, 350 and 400 cm^{-1} assigned to the V–Me bond but not to the V–Cd bond were registered [4].

The interaction of Cp_2V with $[(C_6F_5)_3Ge]_2Cd$ gives $Cp_2VGe(C_6F_5)_3$ in 79% yield. The ESR signal ($g = 1.997$, $A_i(^{51}V) = -45$ E) arising in the reaction process is attributed to the primary oxidation product I [5]. Yet, the absence of hyperfine splitting at the cadmium atom in the spectrum points to the indefiniteness of the above assignment of the ESR signal.

Evidence for the mechanism of the oxidative addition reaction was obtained on studying the interaction of vanadocene with organomercury compounds containing fluorinated groups. ESR spectroscopy presented evidence in support of the formation of the primary oxidative addition product in the reaction of Cp_2V with R_2Hg (R = $Ge(CF_3)_3$, $Ge(C_6F_5)_3$) [5,6].



$$Cp_2V + R_2Hg \longrightarrow Cp_2V \begin{matrix} \diagup Hg-R \\ \diagdown R \end{matrix} \begin{cases} \xrightarrow{R=Ge(CF_3)_3} Cp_2VR_2 + Hg \\ \xrightarrow[R=Ge(C_6F_5)_3]{} Cp_2VR + Hg + R^{\cdot} \end{cases} \qquad (2)$$

(II)

Complex II was registered at −40°C, its half-life at 20°C in toluene being 20 min [6]. Demercurization of complex II leads to the formation of d^1- or d^2-derivatives of vanadocene.

The presence of a mercury-containing substituent in complex II was confirmed by "satellite" components in the hyperfine structure of the ESR spectrum arising from the interaction of an unpaired electron with magnetic isotopes of the mercury atom (Table 1).

Comparison of the reactivity of organocadmium compounds with organomer-

Table 1

Parameters of ESR isotropic spectra of d^1-complexes L_2VR_2 formed in reaction of L_2V with R_2M (M = Cd, Hg)

L_2VR_2	g_i	$-A_i(^{51}V)$ (E)	Ref.
Cp_2VMe_2	1.9915	63.0, 4.8 (6H)	3
Cp_2VEt_2	1.9920	62.7	3
$Cp_2V(CH_2Ph)_2$	1.9910	64.0	3
$Cp_2V[Ge(CF_3)_3]_2$	1.9993	56.8	6
$Cp_2V[HgGe(CF_3)_3]Ge(CF_3)_3$	1.9863	50.5, 111 (1 Hg)	6
$Cp_2V[CdGe(C_6F_5)_3]Ge(C_6F_5)_3$	1.997	45	5
$Cp_2V[Hg(C_6F_5)_3]Ge(C_6F_5)_3$	1.9789	52.6, 116 (1 Hg)	5
$Cp^*{}_2VMe_2$	1.9913	64.3, 4.3 (6 H)	15
$Cp^*{}_2VEt_2$	1.9931	58.0	15
$Cp^*{}_2VPr_2$	1.9935	57.6	15
Ind_2VMe_2	1.9860	69.5, 4.4 (6 H)	11
Ind_2VEt_2	1.9855	66.4	11
Ind_2VPr_2	1.9853	66.0	11
Ind_2VPh_2	1.9896	64.9	11

cury derivatives in the oxidative addition reactions indicates the higher activity of organocadmium compounds. The compound R_2Hg (R = Alk, Ph, α-$C_{10}H_7$), unlike R_2Cd, does not react with Cp_2V at 20°C. The reactivity of organomercury compounds increases sharply with fluorine-containing groups. Thus, the reaction of Cp_2V with $(C_6F_5)_2Hg$ proceeds rapidly at room temperature giving $Cp_2VC_6F_5$ in 93% yield [7].

The products of the oxidative addition reactions of organocadmium and organomercury compounds are d^1- and d^2-vanadocene complexes. The conditions for the formation of d^1- and d^2-derivatives of vanadocene should be considered. The primary product of the oxidative addition is always d^1-complex **I** or **II**. A low thermal stability of many d^1-complexes Cp_2VR_2 (R = Alk, R ≠ Me) which are readily transformed into Cp_2VR [3] is responsible for the predominant formation of d^2-complexes in the oxidative addition reactions. However, in most cases, the absence of Cp_2VR_2 complexes in the reaction of vanadocene with R_2M (M = Cd, Hg) cannot be attributed only to their low thermal stability. Thus, attempts to register $Cp_2V(GeEt_3)_2$ in the reaction of Cp_2V with $(Et_3Ge)_2Cd$ failed [2] whereas this complex was obtained by the reaction of Cp_2VCl_2 with R_2M (M = Cd, Hg) [8].

At the same time, it is known that d^1-complexes can undergo reactions with vanadocene to form d^2-derivatives [9]:

$$Cp_2V(X)R + Cp_2V \longrightarrow Cp_2VX + Cp_2VR \qquad (3)$$

It is likely that the reaction of complexes **I** or **II** with initial Cp_2V giving d^2-derivatives

$$\mathbf{I}\ (\mathbf{II}) + Cp_2V \longrightarrow 2\ Cp_2VR + Cd(Hg) \qquad (4)$$

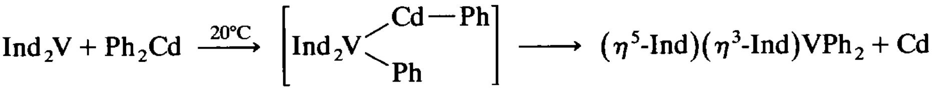
can compete with the reaction of Cp_2VR_2 formation from **I** or **II**.

The difficulty of preparing a number of Cp_2VR_2 compounds through the reaction of Cp_2V with R_2M (M = Cd, Hg) can be explained by reactions 3 or 4.

Phenyl derivatives of vanadocene Cp_2VPh_2 and $Cp_2V(C_6F_5)_2$ were not obtained. The steric obstacles of the location of two phenyl groups at the vanadium atom with a small atomic radius make it impossible to obtain the compounds Cp_2VR_2 not only in the reactions of Cp_2V with Ph_2Cd and $(C_6F_5)_2Hg$ but in other reactions.

These hindrances can be removed partly by changing the π-ligand coordination. This is testified by investigations carried out with bis-indenylvanadium, an analogue of vanadocene. Despite its similarity to vanadocene, bis-indenylvanadium possesses its own special features, in particular, the ability for metallotropic rearrangements [10].

The reaction of R_2Cd ($R = Alk$) with Ind_2V proceeds similarly to the reaction with Cp_2V and results in the isolation of Ind_2VR_2 (Table 1). [11]. Yet, the d^1-complex Ind_2VPh_2 is registered in the reaction mixture of Ind_2V and Ph_2Cd, in contrast to the reaction of Cp_2V. It is suggested [11] that the formation of Ind_2VPh_2 becomes possible due to η^5-η^3-rearrangement, *i.e.* the change in the coordination of one indenyl ligand and the increase in the length of a vanadium–ligand bond.



$$\mathrm{Ind_2V + Ph_2Cd} \xrightarrow{20°\mathrm{C}} \left[\mathrm{Ind_2V}\begin{array}{l}\diagup \mathrm{Cd{-}Ph} \\ \diagdown \mathrm{Ph}\end{array}\right] \longrightarrow (\eta^5\text{-Ind})(\eta^3\text{-Ind})\mathrm{VPh_2 + Cd}$$

(5)

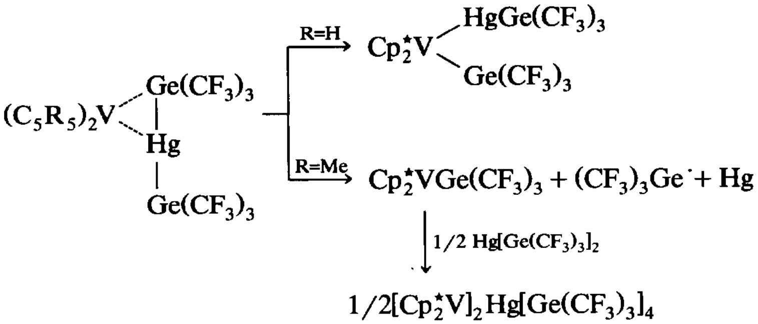
The displacement of cyclopentadienyl ligands by indenyl ligands does not bring about substantial screening of the vanadium atom during the reaction with organocadmium compounds, confirmed by close reaction rates [11].

Considerably large screening of the central atom is observed in a decamethylvanadocene molecule, Cp^*_2V ($Cp^* = C_5Me_5$). In addition, the substitution of hydrogen atoms by methyl groups in the cyclopentadienyl ligand leads to the rise in the vanadium atom basicity [12–14]. The rate of the reaction of Cp^*_2V with R_2Cd ($R = Alk$) therefore, decreases to a great extent in comparison with the unsubstituted analogue [15].

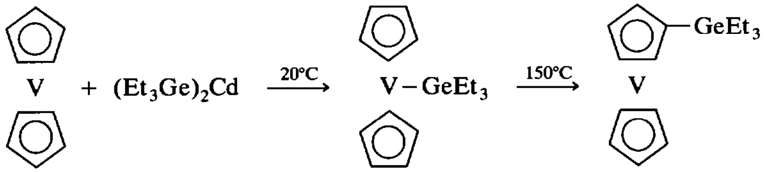
The interaction of Cp^*_2V with R_2Cd ($R = Me, Et, Pr$) gives the compounds $Cp^*_2VR_2$ (Table 1) with properties close to those of Cp_2VR_2. The compounds $Cp^*_2VR_2$ are slightly more thermally stable compared to the unsubstituted analogues. The half-life of Cp_2VEt_2 and Cp_2VPr_2 is some hours at 20°C, for $Cp^*_2VR_2$ and Cp^*_2V it is equal to several days [15].

The steric and electronic effect of methyl substituents in the decamethylvanadocene molecule manifested itself most considerably in the reaction with $[Ge(CF_3)_3]_2Hg$. The reaction of Cp^*_2V with $[Ge(CF_3)_3]_2Hg$ does not give the oxidative addition product expected [11]. As a result of the reaction in toluene, the ionic complex $[Cp^*_2V]_2Hg[Ge(CF_3)_3]_4$ was isolated, its equivalent electric conductivity in dimethoxyethane at 22°C being 50 $ohm^2/cm\ mol$ [6].

A sharp change in direction of the reactions of vanadocenes $(C_5R_5)_2V$ ($R =$ H, Me) with $[Ge(CF_3)_3]_2Hg$ is caused by the increase of basicity in the decamethylvanadocene, which facilitates the stage of one-electron transfer. Moreover, the steric obstacles rule out the possibility of forming a complex with a V–Hg–Ge bond that leads to the fragmentation of the Ge–Hg–Ge chain in the starting molecule of the organomercury compound with the formation of metallic mercury and radicals:



A series of studies on the thermal decomposition of Cp_2VR_n ($n = 1, 2$) showed that the homolysis of the V–R bond is accompanied by the migration of an R group into the cyclopentadienyl ring vanadocene [16–18]. Therefore, by using successively the reactions of synthesis and decomposition, substituted vanadocenes can be obtained.



This method allowed us to obtain a monosubstituted derivative of vanadocene with an Et_3Ge group in the cyclopentadienyl ring that is rather difficult to carry out by another method [18].

Chromocene

Being a 16-electron complex, chromocene like vanadocene is able to undergo the oxidation reactions. It is supposed that the reaction of Cp_2Cr with R_2Cd ($R = Alk$) proceeds in such a direction [4]. The product of oxidative addition is 18-electron complex **III** which decomposes rapidly with the formation of metallic cadmium, alkane and alkene in equimolar quantities and with regeneration of chromocene

$$Cp_2Cr + R_2Cd \xrightarrow[-Cd]{20°C} \underset{\textbf{(III)}}{[Cp_2CrR_2]} \longrightarrow Cp_2Cr + RH + R_{-H} \text{ (or R–R)}$$

The migration of the R group into the cyclopentadienyl ring with the formation of $(C_5H_4R)(C_5H_5)Cr$ is a side process [4].

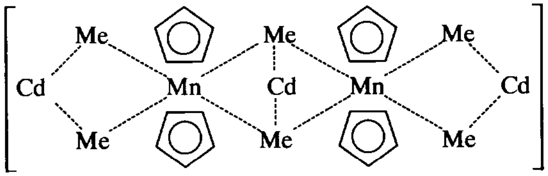
The ability of chromocene to be more easily oxidized into a cation than vanadocene is responsible for the isolation of an ionic complex in the reaction with $[(C_6F_5)_3Ge]_2Hg$ [10]:

$$2\,Cp_2Cr + 3[(C_6F_5)_3Ge]_2Hg \xrightarrow[-Hg]{20°C,\ DME} 2[Cp_2Cr]^+Hg[Ge(C_6F_5)_3]_3^- \cdot DME$$

Manganocene

For manganocene, in contrast to chromocene and vanadocene, the reactions of oxidative addition are not typical. The reaction of manganocene with organocadmium compounds R_2Cd (R = Me, Et, Pr, Bu) proceeds through a concerted mechanism by which the primary coordination of organocadmium compound to the manganese atom leads to the abstraction of one cyclopentadienyl ligand and the addition of three R groups. Monocyclopentadienyl compounds of manganese, $CpMnR_3$, result from reactions of this kind. The primary coordination stage was established from data on the study of the reaction of Cp_2Mn with Me_2Cd by low-temperature (80 K) IR spectroscopy [4,20]

$$2\,Cp_2Mn + 3\,Me_2Cd \xrightarrow[C_5H_{12}]{20^\circ C,}$$



$$\longrightarrow$$

(IV)

$$2\,CpMnMe_3 + 3\,Cd + 2[Cp]$$

The reaction of organocadmium compounds with $(C_5H_4Alk)_2Mn$ (Alk = Me, Et, ${}^iPr$) proceeds in a similar manner [21,22]. However, with bulky cyclopentadienyl ligands (C_5Me_5) and bulky R groups (R = Ph, $GeEt_3$), steric obstacles for the formation of complex **IV** occur and make the reaction route to the formation of $CpMnR_3$ difficult or impossible [20,21].

The reaction of manganocene with organocadmium compounds gives a new type of monocyclopentadienyl compounds of manganese which are isostructural to cymantrene. The composition and structure of the complex obtained are confirmed by IR spectroscopy data and chemical reactions [20–23]. The methyl complex, $CpMnMe_3$, occurs as amber crystals with melting point 87°C, which are readily sublimated at room temperature under vacuum. The other alkyl derivatives, $CpMnR_3$ (R = Et, Pr, Bu), are isolated as liquids with the boiling temperature $50–55°C/10^{-1}$ mmHg. From DTA data, the decomposition of the compounds $CpMnR_3$ (R = Alk) is observed at temperatures above 140–160°C with an exothermic effect. The main direction of the decomposition of $CpMnR_3$ (R = Et, Pr, Bu) is β-disproportion reaction. The decomposition of the methyl derivative involves the stages of α-disproportion and reductive elimination [23].

The reaction of manganocene with organomercury derivatives is studied for $[(C_6F_5)_3Ge]_2Hg$. It was established that in this case, the transport of cyclopentadienyl anions from the manganese atom to the mercury atom with the formation of cyclopentadienylgermylmercury anion takes place.

$$Cp_2Mn + [(C_6F_5)_3Ge]_2Hg \xrightarrow{THF} [Cp_2[(C_6F_5)_3Ge]_2Hg]^{2-}Mn^{2+}\cdot 2THF$$

The thermal decomposition of $[Cp_2[(C_6F_5)_3Ge]_2Hg]^{2-}Mn^{2+}$ under vacuum in the range from 20 to 200°C results in metallic mercury (86%), Cp_2Mn (52%), $[(C_6F_5)_3Ge]_2Hg$ (33%), THF (86%) and C_5H_6 [19].

Table 2

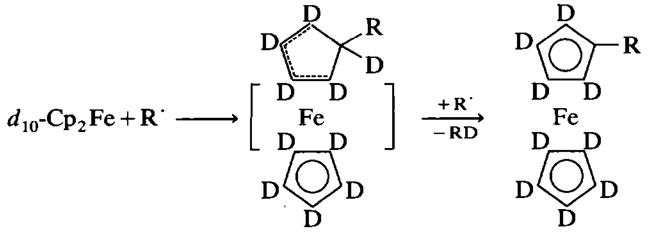
The yield of reaction products of Cp_2Fe with R_2M (M = Cd, Hg) (the yield is given in moles per mole of decomposed R_2M, the reagent ratio is 1 : 1) [24–26]

R_2M	Reaction conditions	$(RC_5H_4)CpFe$	RH	R_{-H}	R–R
Et_2Cd	190°C, 1 h, gas phase	0.01	0.21	0.10	0.82
Me_2Hg	300°C, 11 h, gas phase	0.28	0.84	–	0.07
Me_2Hg	300°C, 5.5 h liquid phase	0.31	1.01	–	0.02
Et_2Hg	230°C, 1 h, gas phase	0.11	0.89	0.16	0.22
Et_2Hg	230°C, 1 h, liquid phase	0.17	0.93	0.88	0.02
Pr_2Hg	220°C, 1 h, gas phase	0.07	0.91	0.40	0.09
Pr_2Hg	220°C, 1 h, liquid phase	0.25	0.85	0.62	0.03

Ferrocene

Ferrocene, an 18-electron complex, is weakly reactive towards organocadmium and organomercury compounds. The interaction of these compounds proceeds only under the thermal decomposition condition of cadmium and mercury alkyl derivatives. The products of such reactions are monoalkylferrocene, alkane, alkene and dimerization products of alkyl radicals. The ratio of the reaction products depends upon the process conditions (Table 2) [24–26].

The reaction of homolytic displacement of ferrocene by the radical generated on the decomposition of the organocadmium and organomercury compounds proceeds in the gas phase. This is confirmed by the experimental data on deuteroferrocene. As a result of the reaction of d_{10}-Cp_2Fe with Et_2Hg (230°C, reagent ratio 1 : 1), ethylnonadeuteroferrocene (0.11 mol) and monodeuteroethane (0.09 mol) are isolated.



When the reaction of the organomercury compound occurs in the presence of liquid phase ferrocene, the yield of alkylferrocene increases and the yield of alkene is close to that of alkane (Table 2). It is suggested [24] that in this case, together with the radical substitution reaction, the molecular reaction of the formation of unstable sandwich-covalent derivatives of ferrocene proceeds to give alkane, alkene, metallic mercury and unsubstituted ferrocene.

The introduction of substituents (ethyl, tert-butyl, acetyl) into the cyclopentadienyl ring leads to suppression of the molecular interaction of dialkylmercury with ferrocene. This is associated with higher steric requirements for the molecular reaction [24] (Table 2).

Cobaltocene

For cobaltocene with a 19-electron shell, the addition reactions accompanied by a decrease in the number of valent electrons, resulting in complexes with an 18-electron shell at the cobalt atom are preferable.

Cobaltocene reacts with R_2Cd ($R = Alk$, Ph, CH_2SiMe_3, $GeEt_3$) at room temperature to form the addition products, cyclopentadiene–cyclopentadienyl complexes $(C_5H_5R)CpCo$, the yield of which is determined by the ratio of the initial reagents [25–28].

The arrangement of an attacking R group relative to the ring plane is important in the addition reaction to the cyclopentadienyl ligand of cobaltocene. The matter of the *exo-endo* position of the substituents can be cleared up on the basis of ^1H NMR data. The values of the constants of spin–spin interaction (CSSI) of protons H_{exo} and H_{endo} with $H_{1,4}$ protons depend little upon the nature of the R group and are equal to 1.9 and 2.4–2.6 Hz respectively; therefore, they are used to identify the position [29]. The CSSI values of protons H_5 with $H_{1,4}$ are 2.4–2.6 Hz for the complexes **a** obtained by the reaction of Cp_2Co with R_2Cd. We can conclude that the attacking R group is in the *exo*-position relative to the ring [28–30].

In the reaction of cobaltocene with the organocadmium compound R_2Cd, two mechanisms of R group insertion are presumed: the direct attack of the cyclopentadienyl ring by the R group and the intermediate formation of the unstable sandwich, covalent complex **VI** [28].

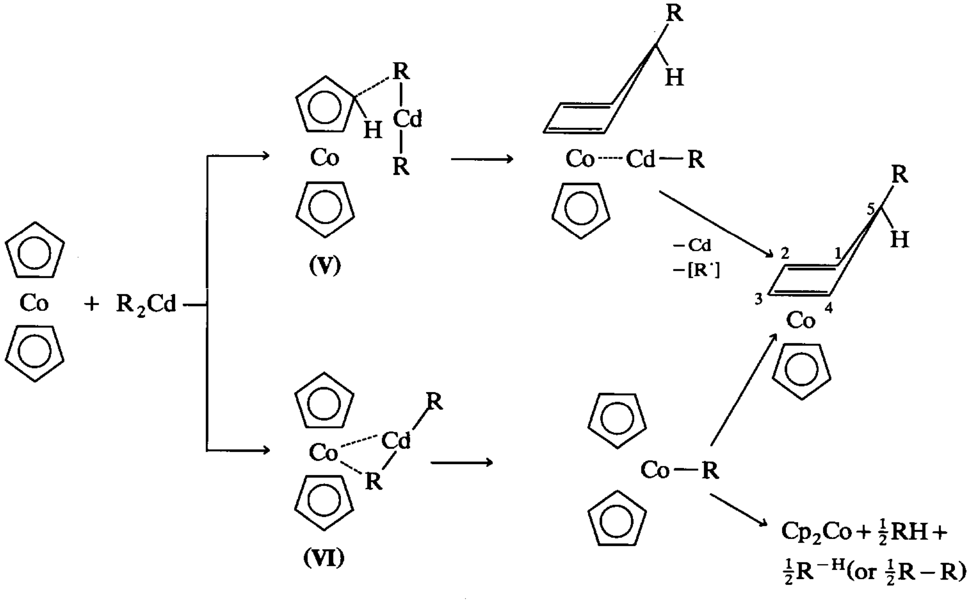
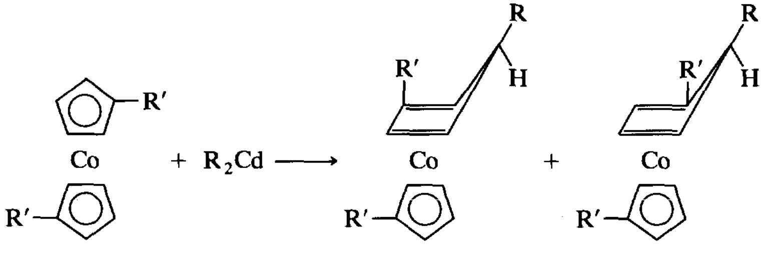


Table 3

Ratio of isomers in reactions of $(C_5H_4R')_2Co$ with R_2Cd (1) and $(C_5H_4R')_2CoX$ with RLi (2)

R′, R Reaction	Et, Me	Et, Ph	^{t}Bu, Me	^{t}Bu, Pr	^{t}Bu, Ph
1	1.3	1.5	5.2	10.0	Trace of **VIII**
2	0.8	1.0	5.6	3.0	Only **VII**

The reaction of substituted derivatives of cobaltocene $(C_5H_4R')_2Co$ (R′ = Et, ^{t}Bu) with R_2Cd results in the isomeric complex [30].



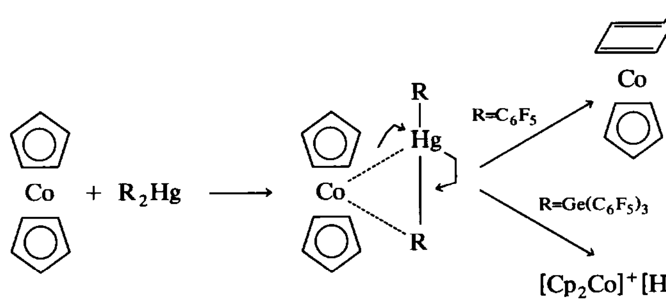
(VII) **(VIII)**

Complexes **VII** and **VIII** are chiral. Diastereotopy of the hydrogen atoms in substituted cyclopentadienyl rings is confirmed by NMR spectroscopy [30]. The ratio of isomers **VII** and **VIII** is mainly determined by steric factors. Similar isomers **VII** and **VIII** are isolated when substituted salts of cobalticinium react with nucleophilic agents where the isomer ratio is determined by both the steric and electronic effects of the substituents [31] (Table 3).

Organomercury compounds R_2Hg (R = Alk, Ph), unlike the corresponding organocadmium compounds, do not react with cobaltocene at room temperature. The compounds $(Et_3Ge)_2Hg$ and $(PhC_2)_2Hg$ react with Cp_2Co to form a cyclopentadiene–cyclopentadienyl complex of cobalt (in low yield) similar to those obtained by interaction of Cp_2Co with R_2Cd [28] and Cp_2CoX with RLi [32]. The introduction of an electronegative substituent at the mercury atom sharply increases the reaction rate. The interaction of $(C_6F_5)_2Hg$ with Cp_2Co (20°C, 48 h) leads to an almost quantitative yield of $(C_5H_5C_6F_5)CpCo$ [33].

From the NMR spectra, in the reaction of cobaltocene with organomercury compounds, the attacking R group is in the *exo*-position relative to the cyclopentadiene ring [33].

The mechanism of R group insertion into the cyclopentadienyl ring on reacting Cp_2Co with R_2Hg is supposed to be similar to the mechanism of Cp_2Co reaction with R_2Cd. In the reaction process, the activation of the R–Hg bond in the coordination sphere of the cobalt atom occurs with the subsequent migration of one R group into the cyclopentadienyl ring. The activation of the Hg–R bond sharply increases with an electronegative C_6F_5 group. This is due to the partial transfer of electron density from the cobalt atom to the mercury atom. Such coordination is facilitated by a strong polarization of the Hg–C_6F_5 bond.

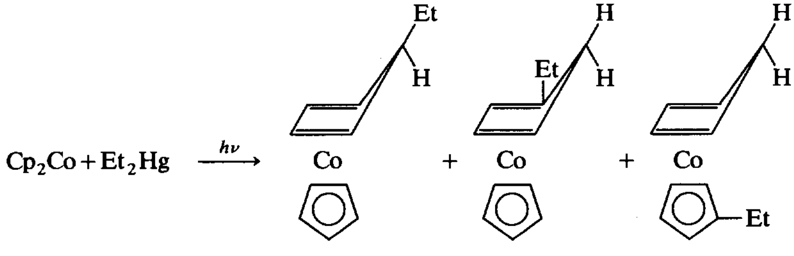


One electron oxidation of cobaltocene and the electron transfer onto R_2Hg is an extreme case of the process. Such direction of the reaction is realized in the interaction of Cp_2Co with $[(C_6F_5)_3Ge]_2Hg$ when a stable organomercury anion is formed [19].

The structure of the complex $[Cp_2Co^+][Hg[Ge(C_6F_5)_3]_3]^-$ is identified. The anion $[Hg[Ge(C_6F_5)_3]_3]^-$ contains an almost plane fragment Ge_3Hg with a trigonal configuration of the hydrogen atom which comes out of the plane of three Ge atoms by 0.2 Å. Valent angles of Ge–Hg–Ge (115.13(5)°, 119.51(5)° and 123.4(5)°) are somewhat distorted in comparison with the ideal values (120°) [19].

The reaction of Cp_2Co with R_2Hg (R = Et, Ph) is initiated by UV radiation. On photolysis of Cp_2Co with Ph_2Hg, the complex $(C_5H_5Ph)CpCo$, similar to that obtained in the reaction with Ph_2Cd, is formed [28].

Under the photolysis conditions, the reaction of Cp_2Co with Et_2Hg results in the formation of a mixture of isomeric complexes **IX**, **X** and **XI** [33].



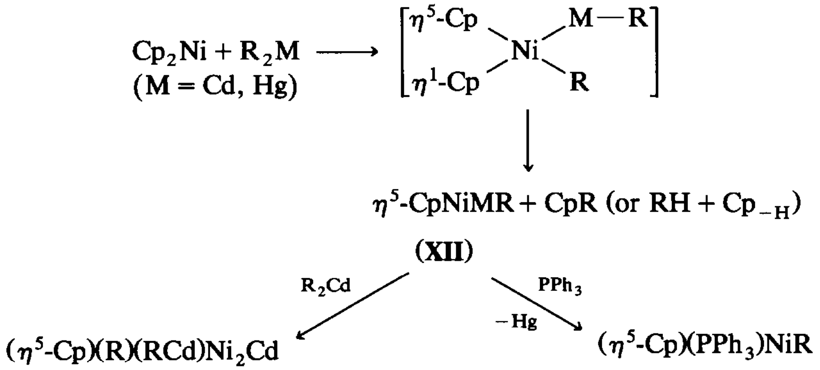
One of the reaction directions for the formation of complexes **X** and **XI** is probably isomerization of complex **IX** in the photolysis process [34].

Nickelocene

For nickelocene, with a 20-electron configuration of the nickel atom, the addition reactions are known to be accompanied by η^5-η^3, η^5-η^1 rearrangement of the cyclopentadienyl ring or its abstraction [35,36]. The reactions of nickelocene with organocadmium and -organomercury compounds proceed in the same direction.

The interaction of Cp_2Ni with R_2Cd ($R = {}^nPr$, Ph_3Ge) in toluene gives the polynuclear complex $[\eta^5\text{-Cp(R)(RGeCd)Ni}]_2Cd$ [37]. The reaction goes in a step-by-step manner. At the first stage, π-σ-rearrangement of one cyclopentadienyl ring occurs in the electron-supersaturated complex. The ring then comes out of the coordination sphere of the complex as a neutral compound and as a result, a coordination unsaturated complex of nickel **XII** is formed. The latter gives an 18-electron polynuclear complex with the Ni–Cd bond in the reaction with the organocadmium compound. In the case $R = GePh_3$, the compound is isolated as an adduct with toluene.

The structure of this compound is established. The nickel atom has the coordination of "a piano stool". The angles of Ge–Ni–Cd and Cd–Ni–Cd are diminished to 86° instead of the ideal magnitude of 90° because of a bulky Cp ligand. The Ni–C(Cp) distance (2.07 Å) is slightly shorter than in the semisandwich cyclopentadienyl complex. Tetragonal coordination of the germanium atoms is distorted: Cd(Ni)–Ge–Ph angles are increased up to 110–120° in comparison with the ideal angle (109°). One of the cadmium atoms, being the symmetry centre, has a linear coordination to neighbouring atoms of nickel.



Although the reaction of nickelocene with $(Et_3Ge)_2Hg$ in the presence of PPh_3 has the initial stage in common with R_2Cd, it then proceeds in another direction. After the abstraction of the mercury atom, the intermediate complex **XII** is stabilized by triphenylphosphine. This reaction results in the compound $\eta^5\text{-Cp(PPh}_3\text{)NiGeEt}_3$ [38].

Types of metallocene reactions

The reactivity of metallocenes in the reactions with organocadmium and organomercury compounds is determined by several factors including the electronic configuration of the metallocene central atom, the character of the cyclopentadienyl ligand and the substituent at the cadmium or mercury atom.

While considering the reactivity of metallocenes it is convenient to apply the Sidgwick's rule, *i.e.* the rule of 18 electrons. According to this rule, the oxidative addition reactions are characteristic of electron-deficient complexes of vanadium and chromium. As a result of these reactions, the electronic shells of the central atom in metallocenes form stable or intermediate 17- or 18-electron complexes. For metallocenes of the iron-triad, the most typical reactions are associated with

Table 4

Reactions of metallocenes with R_2M

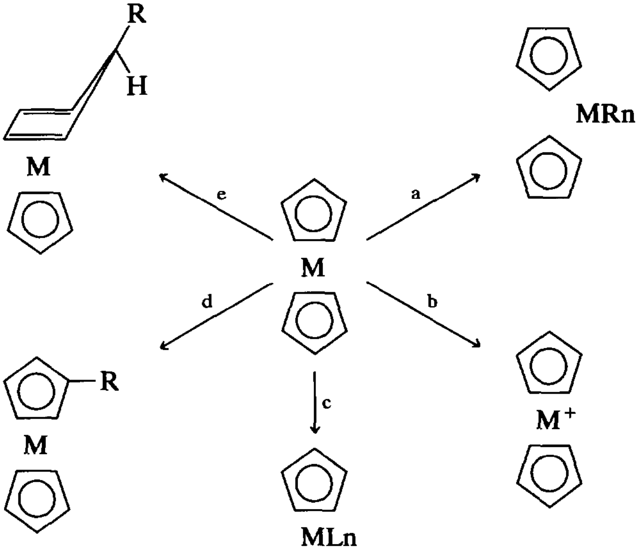
Metallocene	R_2M	Reaction type	Final product
Cp_2V			
$Cp = C_5H_5, C_5H_4Alk, C_5Me$, Ind	R_2Cd (R = Alk, Ph, Et_3Ge)	a	Cp_2VR_n ($n = 1, 2$)
$Cp = C_5H_5$	R_2Hg (R = $(CF_3)_3Ge$, $(C_6F_5)_3Ge$)	a	Cp_2VR_n ($n = 1, 2$)
$Cp = C_5Me_5$	R_2Hg (R = $(CF_3)_3Ge$)	b	$[Cp_2V]^+{}_2[HgR_4]^{2-}$
Cp_2Cr			
$Cp = C_5H_5$	R_2Cd (R = Alk, Ph)	a	Products of catalytic decomposition of R_2Cd
$Cp = C_5H_5$	R_2Hg (R = $(C_6F_5)_3Ge$	b	$[Cp_2Cr]^+[HgR_3]^-$
Cp_2Mn			
$Cp = C_5H_5, C_5H_4Alk$	R_2Cd (R = Alk)	c	$CpMnR_3$
$Cp = C_5H_5$,	R_2Hg (R = $(C_6F_5)_3Ge$	b+c	$[Cp_2(R)_2Hg]^{2-} Mn^{2+}$
Cp_2Fe			
$Cp = C_5H_5, C_5H_4Alk$	R_2Cd (R = Alk)	d	$Cp(C_5H_4R)Fe$
$Cp = C_5H_5, C_5H_4Alk$	R_2Hg (R = Alk)	d	$Cp(C_5H_4R)Fe$
Cp_2Co			
$Cp = C_5H_5, C_5H_4Alk$	R_2Cd (R = Alk, Ph, Et_3Ge, CH_2SiMe_3	e	Cp(CpR)Co
$Cp = C_5H_5$	R_2Hg (R = C_6F_5, C_2Ph_2 Et_3Ge)		Cp(CpR)Co
$Cp = C_5H_5$	R_2Hg (R = $(C_6F_5)_3Ge$	b	$[Cp_2Co]^+[HgR_3]^-$
Cp_2Ni			
$Cp = C_5H_5$	R_2Cd (R = Et, Pr, Ph_3Ge)	c	$[Cp(R)(RCd)Ni]_2Cd$
$Cp = C_5H_5$	R_2Hg (R = Et_3Ge)	c	$Cp(PPh_3)NiR$

the decrease in the number of electrons in the metal atom shell by changing the coordination of the cyclopentadienyl ligand or by its abstraction. The main types of reactions for such complexes are reactions of radical addition and substitution as well as the abstraction of the cyclopentadienyl ligand (Table 4).

The reactions of vanadium derivatives with organocadmium and organomercury compounds proceeding via oxidative addition depend upon the steric factors and the vanadium atom basicity. The increase in steric hindrance brings about a decrease in the reaction rate. For the derivative with indenyl ligands, change of the ligand coordination is possible in the reaction process.

Metallocenes of vanadium, chromium and cobalt take part in one-electron oxidation reactions. Such reactions are observed in the interaction of metallocenes with organomercury compounds containing the GeR^f_3 group. The reaction is little influenced by steric factors and is determined by the localization of the electron density at the metal atom and the facility of electron transfer on generating a stable anion.

The reaction of the cyclopentadienyl ligand abstraction with the simultaneous addition of new groups, which is characteristic of manganocene and nickelocene,



Scheme 1. Types of reactions of metallocenes with organocadmium and organomercury compounds. (a) Oxidative addition; (b) one-electron oxidation; (c) abstraction of Cp ligand and addition of L ligand (through a concerted or successive mechanism); (d) radical displacement; (e) radical addition.

proceeds through an intermediate complex. It is sensitive to steric factors and does not proceed with derivatives containing pentamethylcyclopentadienyl ligands.

The radical substitution reaction on heating ferrocene with organomercury and organocadmium compounds depends upon the spatial volume of an attacking agent substituent in the cyclopentadienyl ring of ferrocene.

The radical addition reaction is less sensitive to steric factors than the radical substitution reaction and it is determined by electron factors to a greater extent.

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