# Chapter 11

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# Study of the smoke-reducing properties of metal-organic compounds and their industrial applications

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**ABSTRACT**

Metal-organic compounds possess environmentally significant properties and fields of application. For ferrocene and cymantrene, as well as some of their derivatives, there are reactions of great environmental importance. One of these is the reaction of ferrocene carbinols with Ba(OH)2 and Ca(OH)2, resulting in the formation of the corresponding carbinolates — reactions that are of considerable industrial relevance. However, the drawback of this process is that the reaction products are not obtained in high yields. Compared to reactions with aliphatic ketones, those involving cyclic ketones proceed rather weakly. To increase the reaction yield, a phase-transfer catalytic medium has been employed. Reactions with aliphatic ketones yield the corresponding ferrocenylcarbinolates with 60–72 % efficiency.

**Keywords:** Ferrocene; Cymantrene; Cyclic Carbinols; Cyclic Ketones; Environment.

## INTRODUCTION

The issue of air pollution remains topical in our country, as it is globally. Reforms based on the implementation of Euro-5 standards have facilitated the use of fuels that are significantly less detrimental to the environment. According to Euro standards, a primary prerequisite is the virtual absence of sulfur and benzene in the fuels utilized. Furthermore, the octane rating of carburetor fuel must not be less than 95, and the fuel must possess a high smoke-suppressant capability. In this context, the antidetonation and smoke-suppressant properties of novel derivatives synthesized from ferrocene and simanthrene have been investigated. As noted, the corresponding derivatives formed by ferrocene and simanthrene—the principal representatives of organometallic compounds—with ketones are already widely employed for their antidetonation characteristics in fuels.[1,2,3]

New mono- and di-substituted derivatives of ferrocene and simanthrene were used to create ecologically clean octane-boosting compositions, and their application features were studied. It was determined that the carbinol complexes and ether derivatives of ferrocene and simanthrene exhibit an effect up to three times greater than ferrocene and simanthrene when used in the same concentration in fuel. It has been confirmed that, depending on the origin and composition of the gasoline, these compositions possess the ability to increase the octane number by 12 to 18 units.

As for ferrocene, it is a $\pi$-complex with a closed cyclic structure — dicyclopentadienyliron, $(C_5H_5)_2Fe$. Ferrocene is a widely distributed industrial product and has been extensively studied in coordination chemistry. It differs from other representatives of its class by its unique properties. Specifically, ferrocene is the only compound among transition metal complexes that

decomposes at temperatures above 500°C, a characteristic that distinguishes it from other metal-organic compounds.

In our study, the alkylation of pyrocondensate was carried out using the Al + CCl4 system. Experimental results showed that the alkylation of ferrocene with pyrocondensate proceeds through substitution occurring only on one of the cyclopentadienyl rings of the ferrocene molecule, resulting in mixtures of alkylferrocenes with different compositions. The melting and boiling points of the variously structured alkylferrocenes obtained in the process were also determined.

Initially, the reaction mixture consisted of an 80 g/L ferrocene solution, 0,5 L of pyrocondensate, and 3 % of the Seyidov catalytic system (Al + CCl4). After five hours of stirring at 50–60 °C, samples were taken every half hour, and it was found that alkylation did not proceed efficiently under these conditions. According to chromatographic analyses, only 10–12 % of alkylferrocene was formed. When the catalyst concentration was increased to 10 %, decomposition of the ferrocene molecule was observed, and the alkylation reaction did not proceed.

Following the discovery of ferrocene's antidetonation properties (resistance to knocking/explosion) in diesel fuels, it attracted significant attention from numerous scientists. Concurrently, ferrocene exhibits considerable chemical reactivity due to its inherent stability, thereby expanding its potential applications within the field of chemistry.

Ferrocene is an orange crystalline solid with a characteristic odor and is more stable compared to cymantrene. It possesses the chemical properties typical of aromatic hydrocarbons and primarily undergoes electrophilic substitution reactions. Its melting point is 174 °C, boiling point is 249 °C, and decomposition temperature is 474 °C. The molecular weight of ferrocene, Mr((C5H5)2Fe), is 186.

## METHOD

The mono- and di-substituted derivatives of ferrocene continue to possess a broad scope of application today.[4,5] Compared to ferrocene itself, these derivatives exhibit a greater capacity to elevate the octane number. The ferrocenyl carbinols, obtained from the reaction of ferrocene with ketones, are capable of undergoing more extensive chemical transformations relative to ferrocene and its alkyl derivatives. This enhanced capability is attributed to the presence of active oxygen within their molecular structure. On the other hand, the derivatives of ferrocene possess a higher molecular weight compared to the parent compound. This increase in molecular weight leads to a reduction in the molar quantity of iron incorporated into the final composition. The lower mass fraction of iron in ferrocene derivatives allows them to be utilized as more effective additives, promoting a slower rate of engine degradation. From this perspective, the application of high-molecular-weight ferrocene derivatives as anti-knock additives in fuels has been deemed environmentally satisfactory.[6]

Concerning the other application areas of ferrocene, it is widely utilized as a colorant, in the preparation of pharmaceutical substances in medicine, in the manufacturing of heat absorbers and radiation shields, as well as in other fields.[7] Ferrocene undergoes reactions characteristic of aromatic hydrocarbons, a property which increases its potential for application in numerous chemical reactions. Furthermore, based on the low oxidation-reduction potential of the iron moiety (0,6 units) within the ferrocene molecule, it behaves as a neutral molecule, thereby enhancing its capacity to react in both acidic and basic media. Reactions conducted primarily in an acidic medium are characteristic of ferrocene, where electrophilic substitutions occur, many

of which possess industrial significance. Ferrocene exhibits good solubility in organic solvents. One of its most crucial properties is its favorable solubility in nonpolar solvents.

Ferrocene can be used in all grades of gasoline at concentrations not exceeding 37 mg/mL. When the mass fraction of iron is too high, the incomplete combustion of fuel in automobile engines leads to the deposition of iron oxides, which ultimately causes engine failure and resin formation in the gasoline. To eliminate these drawbacks, it is advisable to use ferrocene derivatives with higher antiknock properties than ferrocene itself.[8] As the molecular weight of a compound increases, the mass fraction of iron decreases, which helps to prevent the aforementioned issues. Therefore, it becomes feasible to use ferrocene derivatives that possess 1,5–3 times greater antiknock efficiency than ferrocene. Extensive research in this field has been carried out in Russia. In this context, ecologically clean, highly effective anti-detonation additive compositions, branded "Kriskat," based on multifunctional ferrocene and simanthrene, have been developed for motor fuels in Azerbaijan.

Based on the aforementioned points, it is evident that ferrocene and simanthrene derivatives possess high antidetonation properties and constitute industrially significant compounds. The reactions carried out between ferrocene and aliphatic ketones were also conducted identically with simanthrene.

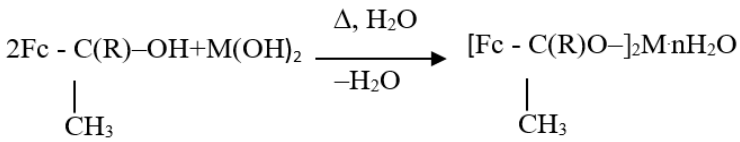
$C_5H_5FeC_5H_5+CH_3COCH_3 \rightarrow C_5H_5FeC_5H_4C(CH_3)_2OH$

Based on the reaction of simanthrene with the corresponding aliphatic ketone (acetone), the derivative simanthrenyldimethylcarbinol was obtained.

## RESULTS AND DISCUSSION

The reactions of ferrocene- and cymantrene-based carbinols with Ba(OH)2 and Ca(OH)2 are of great environmental significance. It has been established that the barium salts (carbinolates) obtained from the interaction of carbinols derived from ferrocene with Ba(OH)2 possess smoke-reducing properties. Compositions prepared by dissolving these carbinolates in gasoline fractions reduce the amount of smoke released into the atmosphere, thereby contributing to environmental protection.

The overall course of the process is as follows:




M=Ca, Ba. The structure of the metal-complex derivatives obtained in the reaction was determined using IR spectroscopy and $^1H$ NMR methods.[9] Specifically, the $\nu_{OH}$ absorption band at 3665 $cm^{-1}$, corresponding to the OH group of ferrocene carbinol, disappeared after interaction with Ba(OH)2. This indicates the absence of the corresponding OH group in the ferrocene carbinolate.

Analysis of the ferrocene carbinol by $^1H$ NMR (spectrum recorded in CDCl3) showed three signals in the 4–5 ppm region. Two signals at 4,85 and 4,33 ppm corresponded to the substituted

cyclopentadienyl ring (C5H4), while one signal at 4,04 ppm was attributed to the unsubstituted C5H5 ring. Additionally, the signal corresponding to the protons of the CH3 group in the ferrocene carbinolate was observed at 2,12 ppm.

The salts of carbinol derivatives obtained from metal-organic compounds—for example, calcium salts of ferrocene carbinols—possess precipitating properties, and these characteristics are utilized in the petroleum industry to remove unwanted substances from residual oil fractions. These reactions are therefore of industrial significance. Additionally, they have environmental advantages.

The reaction of ferrocene carbinols with barium hydroxide was carried out at 250 °C. The same process was attempted with cyclic ketones, but the yields were very low. Compared to Ba(OH)2, using barium chloride (BaCl2) for these reactions is more practical, as barium chloride is insoluble in alcohols but soluble in water. This allows barium ferrocene carbinolates obtained at room temperature to be easily separated from the aqueous phase compared to organic solvents, and then dried in a drying oven. In the wet state, the product appears yellow; upon drying, it transforms into a solid, dark orange crystalline substance with a characteristic odor, and after complete drying, it can be ground into powder.

$2Fc\text{–}C(R, R^1)\text{–}OH + BaCl_2 \rightleftarrows (Fc - C(R,R^1)\text{-}O)_2Ba + 2HCl$
$Fc = C_5H_5FeC_5H_4$;
$R=R^1 = CH_3$; $C_2H_5$.

Barium salts of ferrocene carbinols are highly soluble in alcohols and moderately soluble in hydrocarbon-type organic solvents; for example, they dissolve at concentrations of 20–25 g/L at 20°C.

In our study, the reactions of ferrocene carbinol derivatives with CaCl2were carried out under the same conditions as with BaCl2, at room temperature and 25 °C. These calcium salts are less stable but are environmentally significant compounds. Compared to barium ferrocene carbinolates, they are poorly soluble in both nonpolar and polar solvents. It was possible to isolate these compounds in a pure form from the reaction mixture by extraction with diisopropyl ether.

$2Fc - C(R,R^1)\text{-}OH + CaCl_2 \rightleftarrows (Fc - C(R,R^1)\text{-}O)_2Ca + 2HCl$
$Fc\text{-}\ C_5H_5FeC_5H_4$;
$R=R^1 = CH_3$;$C_2H_5$.

Barium-based ferrocene carbinolates decomposed at temperatures below 97°C, while calcium-based ferrocene carbinolates decomposed at 105°C. During the preparation of calcium ferrocene carbinolate, the yield was found to be in the range of 40–45 %.

Similar to the preparation of the barium dihydrate metal complex of ferrocene carbinolate, $C_{26}H_{30}Fe_2BaO_2 \cdot 2H_2O$, the barium dihydrate metal complex of cymantrene carbinolate, $C_{22}H_{20}Mn_2BaO_{8*}2H_2O$, was synthesized. The reaction was carried out in a THF medium, and the target product was obtained with a yield of 60–68 %.[10]

Microanalysis results confirmed that the complex corresponds to the elemental composition $C_{22}H_{20}Mn_2BaO_8 \cdot 2H_2O$. Overall, barium-based carbinolates exhibit 1–1,5 times higher smoke-reducing efficiency compared to existing smoke suppressants used in gasoline and diesel fuels,

and 0,4–0,6 times higher efficiency compared to ferrocene and cymantrene themselves. Tests of the smoke-reducing properties of metal-organic carbinolates in diesel fuels were conducted at the laboratories of the Azerbaijan State Oil Company, currently the central laboratory of the Heydar Aliyev Oil Refinery.[11]

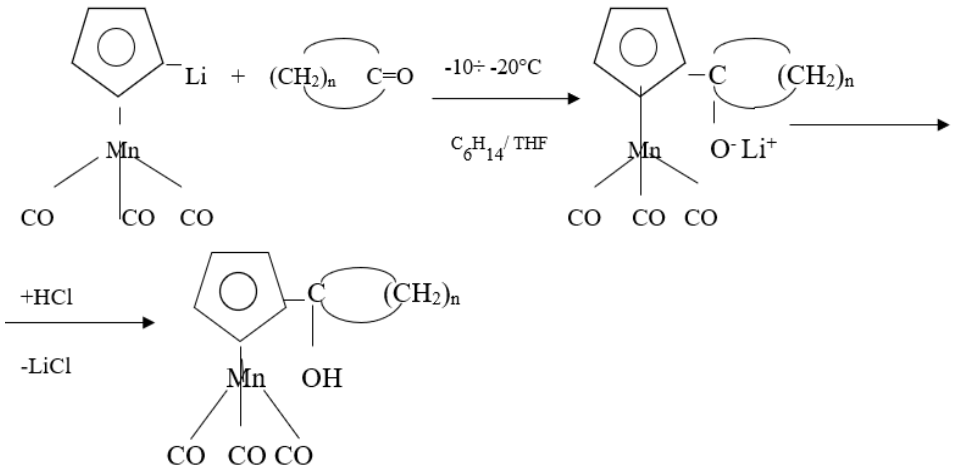
Reactions based on cymantrene were also carried out in a water–alcohol medium.[12] The resulting cymantrene carbinolates varied in color from light to dark blue and were obtained as powders. They were highly soluble in hot water, organic solvents, and various grades of gasoline. Ferrocene carbinolates decomposed at temperatures above 210 °C, whereas cymantrene carbinolates decomposed at much lower temperatures, below –105 °C.

Carbinols obtained from reactions of metal-organic compounds with aliphatic ketones reacted more readily with Ba(OH)2 and gave higher yields compared to carbinols derived from cyclic ketones. The barium salts of carbinols obtained from cyclic ketones also exhibit smoke-reducing properties; however, these reactions are relatively more difficult, and the target products are obtained in lower yields. The reactions were performed in various media.

The composition of the barium carbinolate formed from cymantrene carbinol obtained with cyclohexanone depends on the solvent used in the reaction and can be represented by the following formula:

$(CO)_3MnC_5H_4C\ \ (CH_2)_5O-_{\ 2}\ Ba_{\bullet}(solv)_n$ Complex I

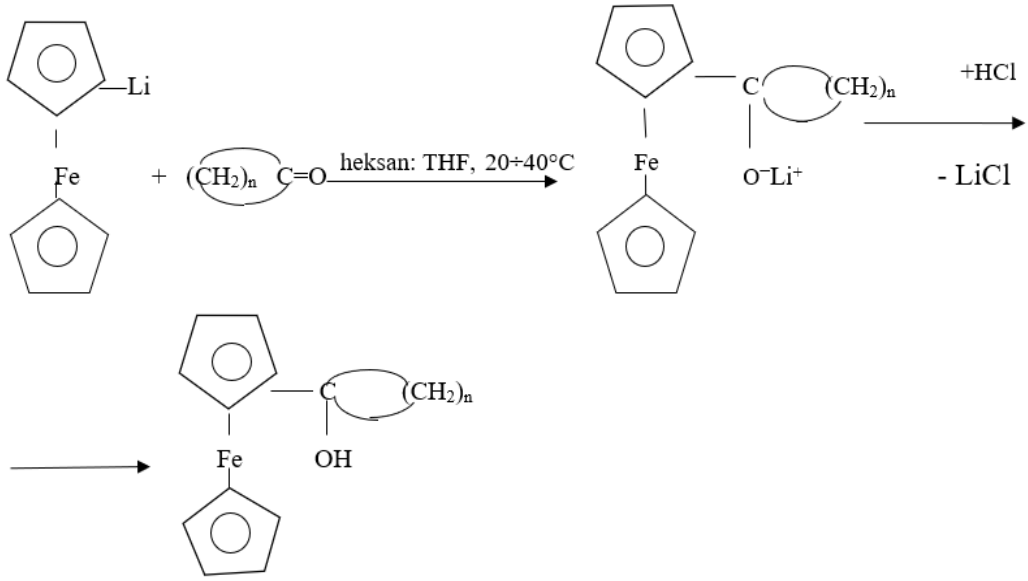
Solv=$H_2O$, THF, ROH; n varies between 2–4. For the preparation of cymantrene cyclocarbinol used in the reaction, the lithium derivative of cymantrene was employed. At low temperature, the cymantrene lithium reacted with the corresponding cyclic ketones. It should be noted that the process was carried out at a temperature around –10 °C, and the reaction proceeded as described below. In this reaction, n = 5.




Regardless of the nature of the reacting ketone, an intermediate compound is initially formed in the reaction. Only upon its subsequent neutralization is the carbinol derivative of the organometallic compound (simanthrene) obtained.[13]

The yield of the resulting simanthrenylcarbinol can vary depending on the specific nature of the reacting ketone. For instance, the yield of the reaction product with aliphatic ketones was high, whereas the yield with cyclic ketones (such as cyclopentanone and cyclohexanone) was low. This difference in yield is explained by the spatial structure (steric hindrance) of the ketone.

The lithium-substituted ferrocene was also used in the preparation of the corresponding salt from the reaction of ferrocene carbinol with Ba(OH)2. The process was carried out at 20–40 °C over 2–3 hours, following the reaction below. During this time, an intermediate product was first obtained, and its reaction with HCl yielded the corresponding ferrocene carbinol derivative. When the lithium derivative of ferrocene is used instead of ferrocene itself, the reaction product can be synthesized in a one-step procedure.




Based on the examined reaction, the yield of the obtained ferrocenylcyclocarbinol derivative was higher than that of the simanthrenylcyclocarbinol derivative. This is explained by the different reactivity of the ferrocene and simanthrene molecules, as well as the tendency of the simanthrene molecule to undergo rapid decomposition. In this case, the value of n in the reaction was n = 5.

The reaction of the ferrocene carbinol obtained from cyclohexanone with Ba(OH)2 was carried out in a THF medium, resulting in the corresponding barium carbinolate being obtained in a very low yield of 14 %.

$C_5H_5FeC_5H_4C(CH_2)_5O\text{-}_2Ba(THF)_2$ Complex II

To increase the yield of the reaction product, instead of ferrocenylcyclohexylcarbinol and simanthrenylcyclohexylcarbinol, their sodium or potassium derivatives ($C_5H_5FeC_5H_4C(CH_2)_5ONa$ /K) were used, and BaCl2 was used instead of Ba(OH)2. The reaction was carried out in a THF medium, which resulted in a significantly higher yield of the product.

$2\ C_5H_5FeC_5H_4C(CH_2)_5O\text{-}Na + BaCl_2$
$C_5H_5FeC_5H_4C(CH_2)_5O\text{-}_2Ba \cdot nTHF$

n=2

During the investigation of Complexes I and II using IR spectroscopy, signals corresponding to the –OH groups in the carbinols of the respective organometallic compounds were not observed. Instead, absorption bands corresponding to the ether group (C–O–) were detected in the $\nu_{C\text{-}O\text{-}}$ region at 1580–1610 $cm^{-1}$. This indicates that the –OH group was replaced by the C–O– group.

When the organometallic complexes synthesized based on ferrocene and simanthrene are utilized as fuel additives, these substances facilitate the combustion process and play a positive role in environmental protection by preventing the formation of smoke. The smoke-free combustion of the fuel does not contribute to air pollution. Considering the scarcity of compounds that promote smoke reduction, substances exhibiting this property are regarded as highly advantageous from an ecological perspective. Specifically, the barium salts of the derivatives obtained from ferrocene and simanthrene ensure the smoke-free combustion of hydrocarbon fuels.

As noted above, carbinols obtained from reactions of ferrocene and simanthrene with aliphatic ketones, unlike those derived from cyclic ketones, react more readily with Ba(OH)2, yielding the target products in high yield. For example, the reaction between ferrocenyl dimethylcarbinol and barium hydroxide carried out in refluxing tetrahydrofuran (THF) resulted in a high product yield. The reaction proceeded with the elimination of two moles of water.

$2Fc\text{–}C(CH_3)_2\text{–}OH + Ba(OH)_2 \rightleftarrows [Fc\text{–}C(CH_3)_2O\text{–}]_2Ba \cdot 2H_2O$
$Fc = C_5H_5FeC_5H_4$

The resulting ferrocenyl isopropylate barium complex was obtained in 62–70 % yield. However, this complex does not possess a sharp melting or boiling point, and it decomposes above 210 °C. The ferrocenyl isopropylate barium complex can be easily washed with low-boiling hydrocarbon solvents such as pentane, hexane, or petroleum ether, then dried, and finally obtained as a solid. During drying, if air remains in the container, the complex turns into a liquid, indicating the hygroscopic nature (water-absorbing property) of the compound. In this state, the isolated complex retains two moles of water and has the following composition:[14]

$[Fc\text{–}C(CH_3)_2O\text{–}]_2Ba \cdot 2H_2O$
$Fc = C_5H_5FeC_5H_4$ .

The obtained $[Fc\text{–}C(CH_3)_2O\text{–}]_2Ba \cdot 2H_2O$ complex (I) was investigated using IR and $^1H$ NMR spectroscopy. Additionally, the composition of the complex was determined by microanalysis for carbon and hydrogen. According to the results of the microanalysis, after washing complex (I) with petroleum ether, its composition corresponded to the formula $C_{26}H_{30}Fe_2BaO_2 \cdot 2H_2O$.

According to IR spectroscopy, the $Fc\text{–}C(CH_3)_2\text{–}OH$ (I) complex exhibits a stretching frequency at vOH = 3665 $cm^{-1}$, which disappears after interaction with Ba(OH)2. Based on $^1H$ NMR spectroscopy (spectrum recorded in CDCl3), three signals were observed in the $Fc\text{–}C(CH_3)_2\text{–}OH$ complex in the 4–5 ppm range. Specifically, two signals from the substituted C5H4 ring appeared at 4,85 and 4,33 ppm, while one signal from the unsubstituted C5H5 ring appeared at 4,04

ppm. The signal corresponding to the CH3 group protons was observed at 2,12 ppm. Thus, the investigation of the complex by IR and $^1$H NMR methods provided a reliable basis for determining its structure.

Similar reactions were carried out with simanthrenyl dimethylcarbinol. The bis-simanthrenyl isopropyl barium dihydrate metal complex was obtained in 60–68 % yield via the reaction of isopropyl simanthrene $(OC)_3MnC_5H_4C(CH_3)_2OH$ with Ba(OH)2 in a THF medium.

According to IR spectroscopy, the $C_{22}H_{20}Mn_2BaO_8{\cdot}2H_2O$ (I) complex exhibits a stretching frequency at vOH = 3665 cm-$^1$, which disappears after interaction with Ba(OH)2. Based on $^1$H NMR spectroscopy (spectrum recorded in CDCl3), three signals were observed in the Fc-C(CH3)2–OH complex in the 4–5 ppm region. Specifically, two signals from the substituted C5H4 ring appeared at 4,85 and 4,33 ppm, while one signal from the substituted C5H5 ring appeared at 4,04 ppm. The signal corresponding to the CH3 group protons was observed at 2,12 ppm. Thus, the investigation of the complex by IR and $^1$H NMR methods provided a reliable basis for determining its structure.

The reactions were also carried out with simanthrenyl dimethylcarbinol. The bis-simanthrenyl isopropylcarbinol barium dihydrate metal complex was obtained in 60–68 % yield through the reaction of isopropyl-simanthrenyl $(OC)_3MnC_5H_4C(CH_3)_2OH$ with Ba(OH)2 in THF.

$$2(OC)_3MnC_5H_4C(CH_3)_2OH+Ba(OH)_2\rightarrow[(OC)_3MnC_5H_4C(CH_3)_2\text{-}O\text{-}]_2Ba{\cdot}2H_2O$$

According to the results of the conducted microanalysis, the $(OC)_3MnC_5H_4C(CH_3)_2\text{-}O\text{-}]_2Ba{\cdot}2H_2O$ (II) complex was consistent with the calculated elemental composition. Compared to the (I) complex, this compound decomposes at much lower temperatures, above –105 °C, exhibits a pale yellow color, and is resistant to hydrolysis and oxidation.

The simanthrenylisopropyl barium dihydrate metal complex (II) was also analyzed using IR and H$^1$ NMR methods. The infrared (IR) spectra were recorded in vaseline oil. In the IR spectrum of the (II) complex, signals were observed in the **νC**=O region at 1950–2018 cm$^{-1}$ corresponding to the terminal carbonyl groups, and in the **νO**–H region at 3480–3750 cm$^{-1}$ corresponding to the hydroxyl groups. Regarding the H$^1$ NMR results (spectrum recorded in CDCl3), the signals corresponding to the α and ß protons of the cyclopentadienyl ring (C5H4) appeared in the 4,56–5,08 ppm region, indicating substitution on the cyclopentadienyl ring. In the unsubstituted C5H5 ring, only a single signal at 4,57 ppm was observed, due to the equivalence of the α and ß protons.[15,16,17,18]

As mentioned above, simanthrene is less stable to sunlight compared to ferrocene and undergoes decomposition upon exposure. Although it is ecologically harmless, its light sensitivity limits its practical applications. Unlike ferrocene derivatives, simanthrene derivatives decompose quickly under ordinary light. For example, the (II) complex also undergoes decomposition when exposed to daylight. Therefore, it is recommended to store such compounds in the dark.

The obtained (I) and (II) complexes are poorly soluble in water and alcohols, but are highly soluble in certain polar solvents, while in acidic or basic media they undergo decomposition upon dissolution. On the other hand, both complexes exhibit the ability to dehydrate. The (I) metal complex underwent dehydration in the temperature range of 160–195 °C, whereas the (II) metal complex dehydrated between 80–112 °C. The overall course of the process is as follows:

$[LMC_5H_4C(CH_3R)\text{-}O\text{-}]_2Ba\cdot 2H_2O \rightarrow [LMC_5H_4C(CH_3R)\text{-}O\text{-}]_2Ba + H_2O$

Here, L= CO groups.

Upon dehydration of barium dihydrate of simanthrenyldimethylcarbinol, its dimethylcarbinolate (Complex III) was obtained. The process was reversible. $[(OC)_3MnC_5H_4C(CH_3)_2\text{-}O\text{-}]_2Ba\cdot 2H_2O$ ▫ $[LMC_5H_4C(CH_3)_2\text{-}O\text{-}]_2Ba+2H_2O$

Similarly, upon dehydration of the barium dihydrate of ferrocenyldimethylcarbinol, its dimethylcarbinolate (Complex IV) was obtained. The process was reversible, and unlike Complex III, Complex IV was obtained in high yield.[19]

$[C_5H_5FeC_5H_4C(CH_3R)\text{-}O\text{-}]_2Ba\cdot 2H_2O \rightleftarrows [C_5H_5FeC_5H_4C(CH_3R)\text{-}O\text{-}]_2Ba+H_2O$

R- alkyl groups.

The metal complex derivatives (III) and (IV), obtained after the thermal dehydration process, exhibit good solubility in non-polar solvents, including motor fuels (gasoline and other petroleum fractions) and diesel fuels (kerosene). Specifically, their solubility ranges from 10–14 g/L in motor fuels and 32–38 g/L in diesel fuels. This property significantly broadens their potential applications. It was determined that the addition of 0,02 wt.% of the (III) organometallic compound to gasoline increased the flame height from 8,4 mm to 16,9 mm, and in diesel fuels from 16,1 mm to 26,4 mm. When a 0,001–0,2 % mixture was added to the fuel (this mixture contained 10–15 % of the barium-based ferrocene derivative), engine power increased by up to 15 %, and fuel smoke emission was effectively reduced.

The derivatives obtained from the studied metal complexes—newly synthesized compounds of ferrocene and simanthrene—are used not only as anti-knock agents but also as smoke suppressants. Therefore, the application of these substances in chemical and petrochemical industries is of significant importance.[20]

The primary objects of study in this dissertation were the air and water ecosystems. Investigating the factors contributing to the pollution of both environments constituted the main direction of the research. Currently, the pollution of air and water ecosystems represents one of the most critical global environmental challenges. Against the background of atmospheric pollution, the greenhouse effect is intensified. With the increase in the greenhouse effect, the melting of glaciers leads to a reduction in freshwater resources, and the runoff of clean water mixes with polluted waters. Concurrently, against the background of water ecosystem contamination, the demand for freshwater is increasing daily. For this purpose, the research conducted within this dissertation aimed at taking serious steps toward resolving the problems occurring in the air and water environments.

As is known, the ecosystems of the biosphere are closely interconnected, and pollution in one ecosystem leads to the contamination of another. Furthermore, the oil industry, which is critical in Azerbaijan, contributes to the pollution of both air and water ecosystems. While soil ecosystems are also subject to pollution, the soil layer is less dynamic compared to the air and water ecosystems; therefore, pollution manifests more prominently in these two systems. Given that approximately 85 % of crude oil processed at the Oil Refinery is dedicated to obtaining fuel utilized in the automotive industry, the oil sector is very closely linked with the transport

sector. The environmental damage caused by road transport emissions (particularly in Baku city) is currently one of the foremost negative impacts. Consequently, many of the exhaust gases generated during the operation of automobile engines and the combustion of fuel directly contribute to the formation of greenhouse gases, while a portion causes secondary pollution. At this point, ensuring that the fuel additives meet ecological standards and are non-toxic is a separate issue of great environmental importance. Simultaneously, it is ecologically vital that the additives incorporated into the fuel possess a minimum threshold of smoke-suppressant capability. Ultimately, the non-deleterious nature of the exhaust gases emitted by road transport into the atmosphere is of critical environmental significance.

## CONCLUSIONS

The smoke-suppressing effects of the barium-based organometallic compounds (III) and (IV) are superior both to ferrocene and simanthrene themselves and to existing smoke suppressants. Specifically, in distilled gasoline and diesel fuels, these compounds exhibit 1–1,5 times higher smoke suppression compared to conventional additives, and 0,4–0,6 times higher than ferrocene and simanthrene. Overall, it should be noted that, compared to ferrocene and simanthrene, the derivatives obtained from these complexes contain lower mass fractions of iron and manganese, so engines operating on such fuels experience little or delayed wear. On the other hand, compared to ferrocene and simanthrene (except for the CO groups), the newly synthesized organometallic complexes are more prone to chemical transformations due to the presence of active oxygen. In this regard, the newly synthesized derivatives of ferrocene and simanthrene are considered industrially significant compounds. As noted, the smoke-suppressing properties of the studied metal–organic complexes (I) and (II) were tested in 2016 at the Azneftyag Oil Refinery, currently the H. Aliyev Oil Refinery.

## BIBLIOGRAPHIC REFERENCES

1. Nesmyanov AN. Ferrocene and Related Compounds. Moscow: Nauka; 1982.

2. Suleymanov GZ, Litvishkov YuN, Gadirova EM, et al. Features and Antidetonation Efficiency of Compositions Prepared on the Basis of New Mono- and Binuclear Alkyl and Oxyalkyl Derivatives of Ferrocene and Simanthrene. Izvestiya VUZ. Chemistry and Chemical Technology. 2005;48(12):73–77.

3. Aliyev AM, Suleymanov GZ, Gadirova EM, et al. Alkylation of Ferrocene by Pyrolysis Products of Naphtha in the Presence of Catalytic Systems Activated by Some Ethers Al+CCl4. Izvestiya VUZ. Chemistry and Chemical Technology. 2005;48(12):85–88.

4. Gadirova EM, Suleymanov GZ, et al. Synthesis and Study of Mono- and 1,1-Dihydroxy Derivatives of Ferrocene. Problems of Chemistry. 2007;(3):561–563.

5. Nesmyanov AN. Ferrocene and Related Compounds. Moscow: Nauka; 1982.

6. Hajiyeva SR, Suleymanov GZ, Gadirova EM, et al. Investigation of Applications of Ferrocene Products Obtained from Cyclic Ketones for Environmental Protection. III Republican Scientific Conference Dedicated to the 91st Anniversary of National Leader Heydar Aliyev. “Relevant Problems of Ecology and Soil Science in the 21st Century”. Baku, May 7–8, 2014. p. 32–33.

7. Hajiyeva SR, Gadirova EM, et al. Synthesis of Bis-Ferrocene and Bis-Simanthrene Isopropyl Barium Dihydrate Metal Complexes and Study of Their Smoke-Suppressing. Problems of Chemistry. 2010;(2):313–315.

8. Imanov EV, et al. Synthesis and Structure of Smoke-Reducing Properties of Cyclocarbinol Derivatives of Ferrocene and Simanthrene. Natural and Technical Sciences. 2013;(2):102–113.

9. Suleymanov GZ, et al. Anticorrosive Composite Coatings Based on Ferrocene and Its Functional Substituted Derivatives. Progressive Technologies and Mechanical Engineering Systems. International Collection of Scientific Works. 2011;(41):334–340.

10. Gadirova EM, Mamedov GN, Suleymanov GZ, et al. Anticorrosion Efficiency of Compositions Prepared on the Basis of Ferrocene and Some of Its Functional Substituted Derivatives. XIX Mendeleev Congress on General and Applied Chemistry. Abstracts. Volgograd, September 25–30, 2011. p. 595–596.

11. Suleymanov GZ, et al. Cyclic Carbinol Derivatives of Ferrocene and Simanthrene. Relevant Problems of Humanities and Natural Sciences. 2012;(8):22–26.

12. Hajiyeva SR, Gadirova EM, et al. Cyclic Organometallic Derivatives of Ferrocene and Simanthrene. Young Scientist. 2015;9(I):74–79.

13. Imanov EV, Mammadbeyli EH, Suleymanov GZ. Ferrocene (Simanthrene) Cyclopentyl (Hexyl) Carbinols and Some of Their Derivatives: Reactivity, Smoke-Reducing, and Demercaptanization Properties in Diesel Fuels. Problems of Chemistry. 2012;(2):39–47.

14. Gadirova EM, Suleymanov GZ, et al. Kinetic Study of the Oxialkylation Reaction of Ferrocene and Simanthrene with Acetone. Materials of the V Republican Scientific Conference for PhD, Master, and Young Researchers, Dedicated to the 88th Anniversary of National Leader Heydar Aliyev. Baku, 2011. p. 55.

15. Veliev RA, Gadirova EM, et al. Synthesis of Simanthrene Dimethylcarbinol Metal Complex under Interphase Catalysis and Study of Some Kinetic Patterns of the Process. Chemistry and Chemical Technology. 2010;53(1):79–81.

16. Veliev RA, Gadirova EM, Suleymanov GZ. Investigation of the Possibilities of Using Ferrocenyl Carbinols for Demercaptanization of Mercaptan-Containing Petroleum Products. VII Baku International Mamedaliev Scientific Conference Dedicated to the 80th Anniversary of NHP. Baku, 2009. p. 202.

17. Suleymanov GZ, Mamedov ESh, et al. Environmentally Friendly Antidetonation Fuel Compositions Prepared on the Basis of Alkyl and Oxyalkyl Derivatives of Ferrocene and Their Solubility in Various Gasoline Grades and Components. Izvestiya VUZ. Chemistry and Chemical Technology. 2007;50(5):82–85.

18. Suleymanov GZ, et al. Cyclic Carbinol Derivatives of Ferrocene and Simanthrene. Relevant Problems of Humanities and Natural Sciences. 2012;(8):22–26.

19. Gadirova EM. Investigation of the Use of Ferrocenyl Carbinols for Demercaptanization of Mercaptan-Containing Petroleum Products. Materials of the VI Republican Scientific Conference "Actual Problems of Chemistry" for PhD, Master, and Young Researchers, Dedicated to the 89th Anniversary of National Leader Heydar Aliyev. Baku, 2012. p. 58–59.

20. Gadirova EM. Synthesis of Thioether Derivatives of Ferrocenyl Carbinols. Bulletin of Baku University. 2013;(3):45–48.

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**CONFLICT OF INTEREST**

None.

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