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FURAN DERIVATIVES OF GROUP VIII ELEMENTS (REVIEW)

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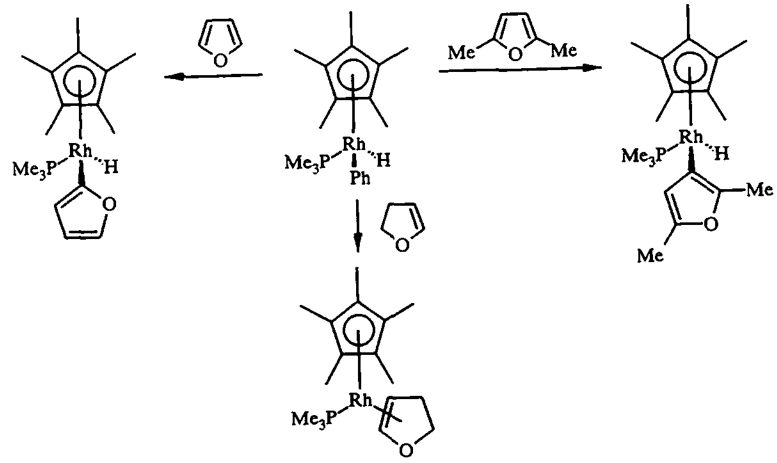
Methods for the synthesis of the furan derivatives of iron, cobalt, nickel, rhodium, palladium, osmium, iridium, and platinum and their physicochemical and chemical properties are reviewed.

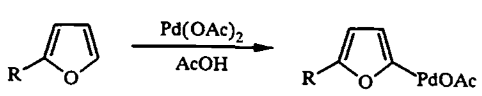
1. METHODS OF SYNTHESIS

Compounds with a C_{furyl}—M bond (where M is a metal of group VIII) are known for iron [1-3], nickel [4], rhodium [5], palladium [6-12], osmium [13-16], iridium [17-19], and platinum [6]. Various methods have been used for their synthesis: Direct metallation of the furan ring [5-7, 9-11, 13, 19]; lithium [4, 17] and mercury [1, 12] synthesis; decarbonylation of the furoyl compounds of the metals [2, 14]; cyclization [8]; and various others.

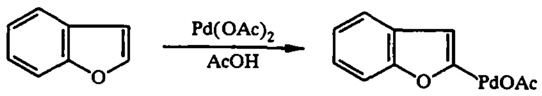
Derivatives of rhodium [5], palladium [6, 7, 9, 11], osmium [13], iridium [19], and platinum [6] were obtained by the direct metallation of the furan ring in a series of furyl-containing compounds. Thus, the thermolysis of the rhodium complex $(Cs_5Me_5)Rh(PMe_3)Ph(H)$ in the presence of furan at 60°C in hexane gave an 84% yield of a 2-furyl-substituted rhodium complex as the only product. The analogous reaction with 2,5-dimethylfuran takes place at position 3 of the furan ring, and in the case of 2,3-dihydrofuran a π complex with the η^2 coordination is formed [5].



Furyl-containing palladium acetates are obtained during the treatment of furan, 2-methylfuran, furfural, 2-acetylfuran, and benzofuran [9-11] with palladium acetate in acetic acid; they were then used without isolation in reactions with aromatic and vinyl compounds.



R = H, Me, CHO, MeCO



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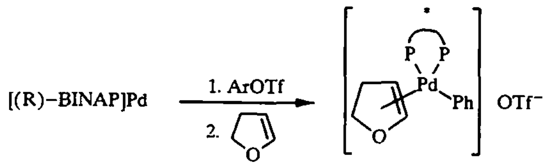
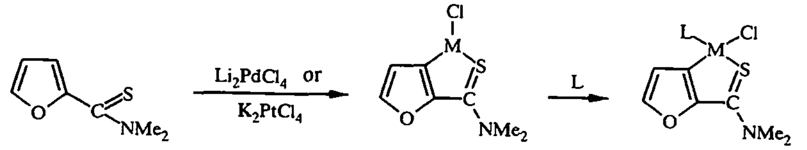
It was possible to arylate 2,3-dihydrofuran with a high degree of stereo- and regioselectivity by the action of aryl triflates in the presence of amines and the complexes of palladium with (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [(*R*)-BINAP]. The main reaction product was (*R*)-2-aryl-2,3-dihydrofuran with high optical purity (96%); a low yield of (*S*)-2-aryl-2,5-dihydrofuran was obtained. The authors [20] consider that asymmetric arylation takes place as a result of the formation of a dihydrofuran arylpalladium intermediate product.



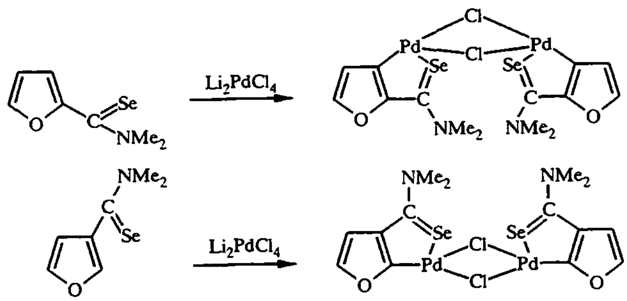
The cyclopalladization and cycloplatinization of the furan ring in N,N-dimethyl-2-furancarbothioamide were realized with lithium tetrachloropalladate and potassium tetrachloroplatinate respectively. This reaction resulted in the formation of chelate complexes in which the metal atom was attached to the sulfur atom and the carbon atom at position 2 of the furan ring. These complexes in turn react readily and with high yields with donating ligands: Bu_2S, Bu_3P, $(o\text{-}MeC_6H_4)_3P$, Ph_3As. In addition to the compounds with a chlorine atom at the palladium, their bromine and iodine analogs were also synthesized [6].



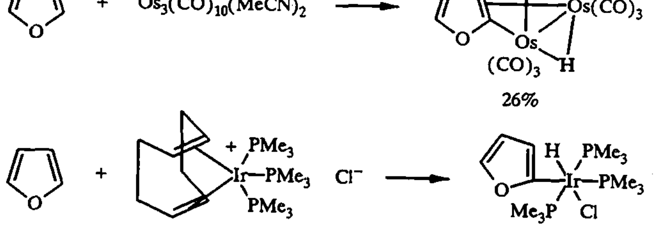
M = Pd; L = Bu_2S, Bu_3P, Ph_3As, $(o\text{-}MeC_6H_4)_3P$

M = Pt; L = Bu_2S, Bu_3P

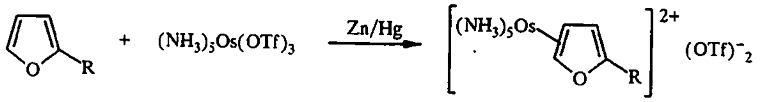
Lithium tetrachloropalladate also reacts with N,N-dimethyl-2(3)-furancarboselenoamide [7]. Cyclopalladization takes place at the free position 3 or 2 of the furan ring.



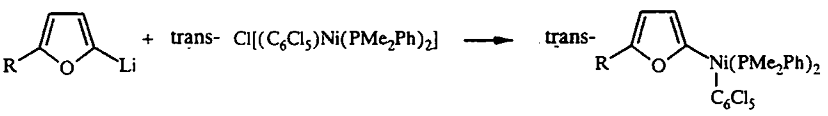
The reaction of furan with the triosmium complex $[Os_3(CO)_{10}(MeCN)_2]$ [13] and the iridium complex $[Ir(COD)(PMe_3)_3]Cl$ [19] takes place through activation of the C—H bond and oxidative addition of the heterocycle to the organometallic fragment. According to the results of x-ray crystallographic analysis, in the obtained triosmium cluster two osmium atoms are linked through a hydrogen bridge and the furan ring, while the furan ring forms a σ bond with one osmium atom and a π bond with the second as a result of the C═C double bond [13]. In the iridium complex the hydrogen is in the *trans* position in relation to the PMe_3 [19].



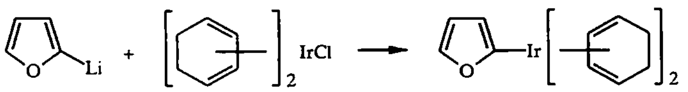
Compounds in which the osmium atom is η^2-bonded with one of the C=C double bonds of the heterocycle were obtained by reduction of the osmium complex $(NH_3)_5Os(OTf)_3$ by the action of Mg or Zn/Hg in the presence of an excess of furan or sylvane [15, 16].



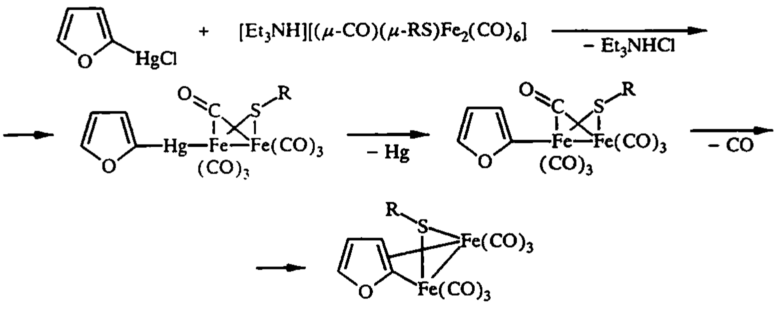
The chlorine atoms in *trans*-chloro[bis(dimethylphenylphosphine)]pentachlorophenylnickel [4] and chloro[bis(η^4-1,3-cyclohexadiene)]iridium [17] were substituted by furyl and 5-methyl-2-furyl by treating the complexes with the lithium derivatives of furan while cooling to 0°C.



R = H(58%), Me(81%)

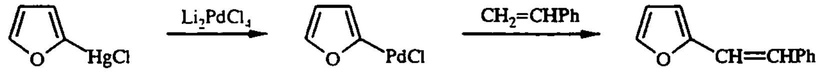


The furan derivatives of mercury were used for the production of compounds of iron [1] and palladium [12]. Di(2-furyl)mercury and 2-furylmercuric chloride react with the iron complex $[Et_3NH]^+[\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^-$ with the formation of a binuclear complex, in which according to x-ray crystallographic analysis one iron atom is σ-bonded to the carbon atom of the furan ring at position 2 while the other is π-bonded to the C=C double bond [1]. The proposed mechanism is shown in the scheme:

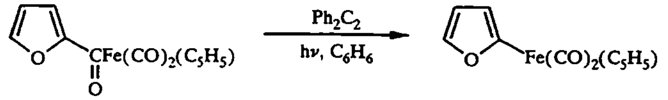


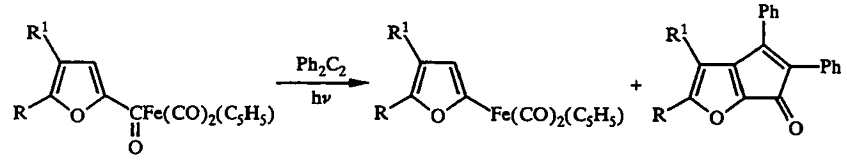
R = Et, *t*-Bu, Ph, $Me_3C_6H_2$

2-Furylpalladium chloride [12], produced *in situ* from 2-furylmercury chloride and lithium tetrachloropalladate, then reacts with olefins to form furylalkenes and 2,2'bifuryl as impurity.



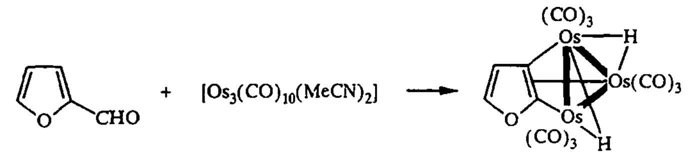
During investigation of the reactivity of the acyl σ complexes of cyclopentadienyldicarbonyliron with diphenylacetylene it was established that the 2-furoyl derivative was fully decarbonylated when irradiated in benzene [2]. Under analogous conditions the sylvane and benzofuran derivatives gave the heterocyclic analogs of 2,3-diphenylindenone as well as the decarbonylation products.



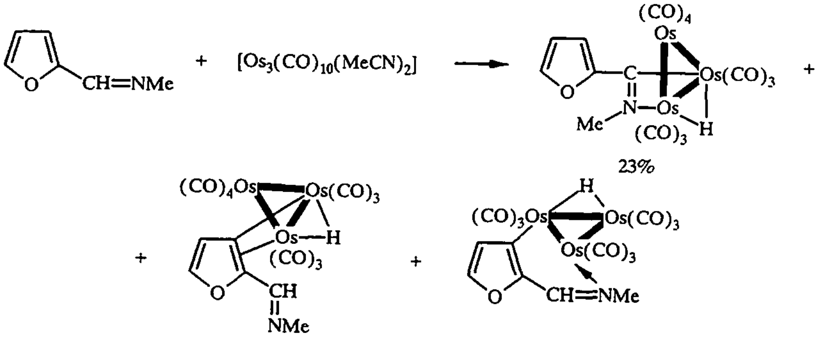


R = Me; R^1 = H; R^1R = –CH=CH–CH=CH–

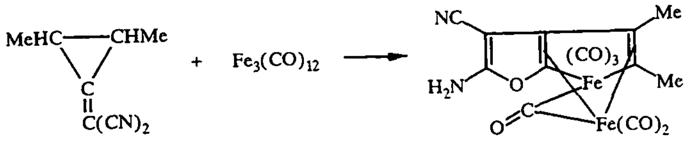
The product from the oxidative addition of the triosmium complex $[Os_3(CO)_{10}(CH_3CN)_2]$ to furfural readily undergoes thermal decarbonylation with the formation of a μ_3-heterocyclic system [14].



N-Furfurylidenemethylamine also reacts with the complex $Os_3(CO)_{10}(CH_3CN)_2$ at room temperature in dichloromethane. However, in addition to the product from oxidative addition (23%), produced during cleavage of the C—H bond of the aldimine group, products with C_{furyl}—Os bonds (17 and 35%) were obtained. Conclusions about the structure of these complexes were based solely on the data from the PMR spectra [14].

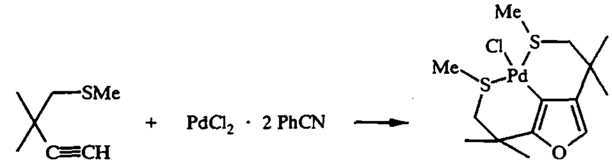


In reaction with the iron complex $Fe_3(CO)_{12}$ in toluene 1,2-dimethyl-3-dicyanomethylenecyclopropane forms the product from the insertion of the $Fe(CO)_4$ group into the three-membered ring. At the same time one cyano group is reduced [3].

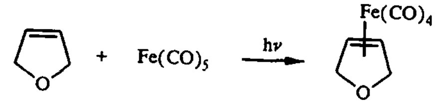


The structure of the obtained product was proved by x-ray crystallographic analysis.

The reaction of 3,3-dimethyl-4-methylthio-1-butyne with $PdCl_2 \cdot 2PhCN$ in dry methylene chloride takes place in a complicated manner with the formation of a mixture of five products (total yield 60%). According to x-ray crystallographic analysis, one of them contains a furan ring attached to a palladium atom (yield 10%) [8].

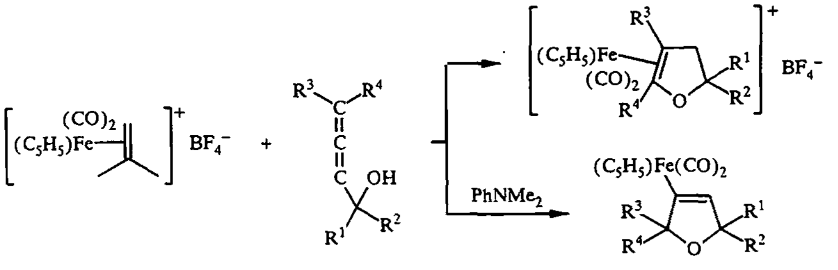


Compounds in which the metal of group VIII is attached to the dihydro- or tetrahydrofuran ring are few and are as a rule produced by cyclization [21-24]. Thermal and photochemical condensation of 2,5-dihydrofuran with the carbonyl complexes of iron $Fe(CO)_5$ and $Fe_2(CO)_9$ was used for the synthesis of tetracarbonyl(η^2-2,5-dihydrofuran)iron [25].



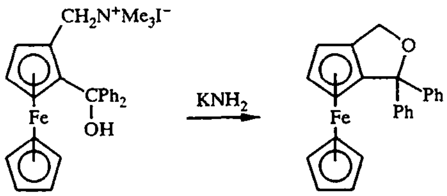
The condensation of hydroxymethylallenes with the dicarbonyl(η^5-cyclopentadienyl)(η^2-isobutylene)iron cation in 1,2-dichloroethane with gentle heating was studied [21]. From the allenes with $R^1 = R^2 = R^3 = R^4 =$ H and with $R^1 = R^3 =$ H and $R^2 = R^4 =$ Me the cationic complexes in which the iron atom is η^2-coordinated with the double bond of the 2,3-dihydrofuran were obtained after 15 min with yields of 84 and 44% respectively. Under analogous conditions the allenes with

$R^1 = R^2 = Me$ and $R^3 = R^4 = H$ and with $R^1 = R^2 = H$ and $R^3 = R^4 = Me$ a mixture of cations is formed on account of rearrangement, while the addition of one equivalent of N,N-dimethylaniline leads to neutral 2,5-dihydrofuran complexes of iron:

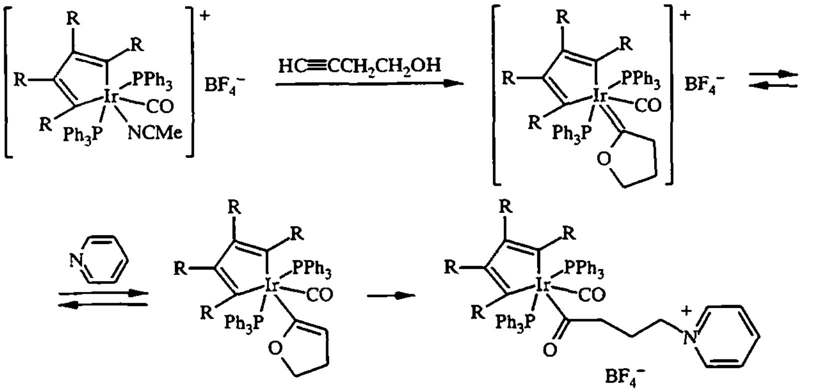


$R^1 = R^2 = R^3 = R^4 = H$; $R^1 = R^3 = H$; $R^2 = R^4 = Me$

The synthesis of a ferrocene derivative in which one of the cyclopentadienyl groups was condensed with a tetrahydrofuran ring was realized by intramolecular condensation of 1-dimethylaminomethyl-2-diphenylhydroxymethylferrocene methiodide in monoglyme under the influence of potassium amide. The degree of reaction after six days was 79% [22].

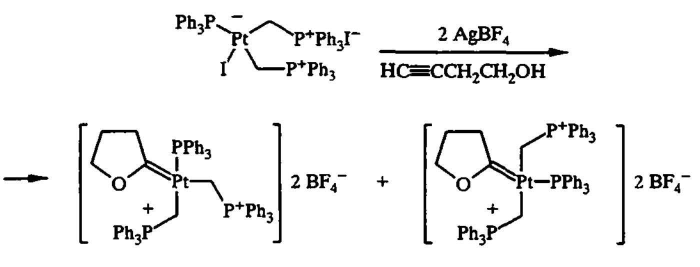


2-Oxacyclopentylidene complexes of iridium [23] and platinum [24] were obtained by the classical method by cyclization of 3-butyn-1-ol. During ^1H NMR spectroscopic investigation of the reaction of the 2-oxacyclopentylidene complex of iridium with pyridine the initial formation of an intermediate 2-(4,5-dihydrofuryl)iridium compound was observed. Opening of the dihydrofuran ring gave an acyl complex [23].



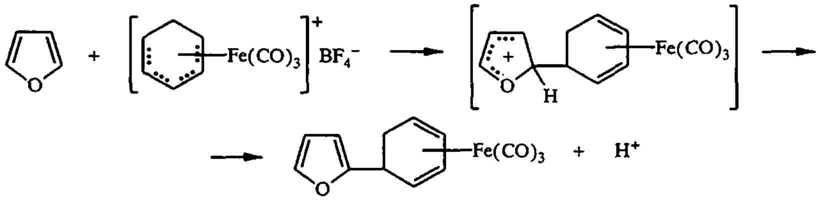
R = COOMe

During the synthesis of the platinum compound cyclization takes place, leading to the formation of two isomeric (*cis* and *trans*) oxacyclopentylidene complexes in equal proportions [24].

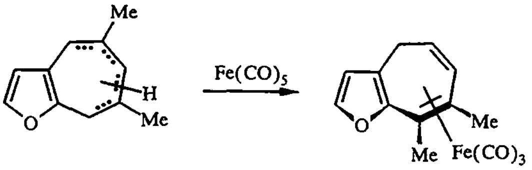


Of the compounds in which the metal atom is not directly attached to the furan ring but is separated from it by some carbon fragment only the derivatives of iron (usually compounds of the ferrocene series) and cobalt have in fact been investigated.

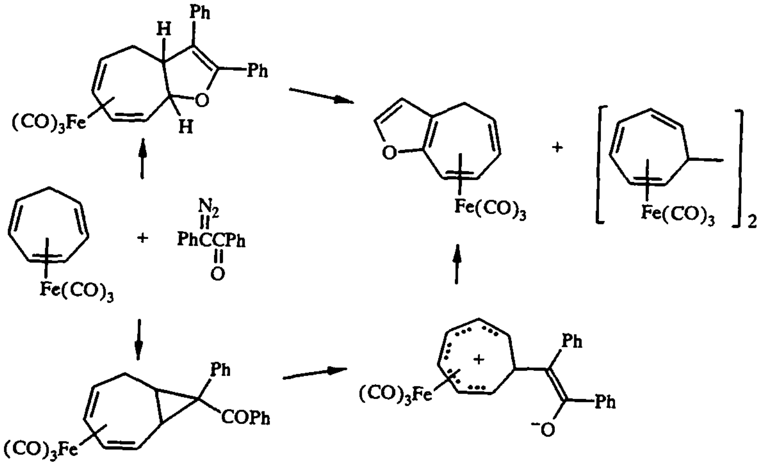
Cyclodienyl complexes of iron, containing a furan ring, have been synthesized by various methods [26-28]. Thus, tricarbonyl[5-(2-furyl)-1,3-cyclohexadienyl]iron was obtained by nucleophilic substitution of the hydrogen atom at position 2 of the furan ring by the cation of the η^5-cyclohexadienyl complex of iron. The reaction takes place through the formation of an intermediate σ complex. 2-Methylfuran also enters into the reaction, but in this case it was not possible to determine the position of the iron-containing substituent in the furan ring [26].



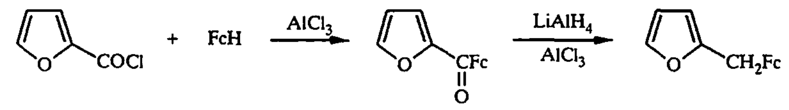
The complexation of the furyltropylium system with pentacarbonyliron was studied. At room temperature after 12 h in a stream of nitrogen a low yield (11%) of a dienyl complex of iron was obtained. Its structure was established by x-ray crystallographic analysis [27].



The second compound of the series was obtained by the condensation of phenyldiazoacetophenone and tricarbonyl(cycloheptatriene)iron in the presence of copper at 45°C. In this case, however, the yield was low (9%), since the dimeric complex di[tricarbonyl(cycloheptatriene)iron] is mainly formed [28]. The authors of [28] suggest two possible methods of synthesis of tricarbonyl[(η-5,6,7,8)-2,3-diphenyl-4H-cyclohepta[*b*]furan]iron, i.e., dipolar 1,3-addition to a double bond of cycloheptatriene followed by dehydrogenation or cyclopropanation and rearrangement of the obtained ketone through a zwitterionic structure.

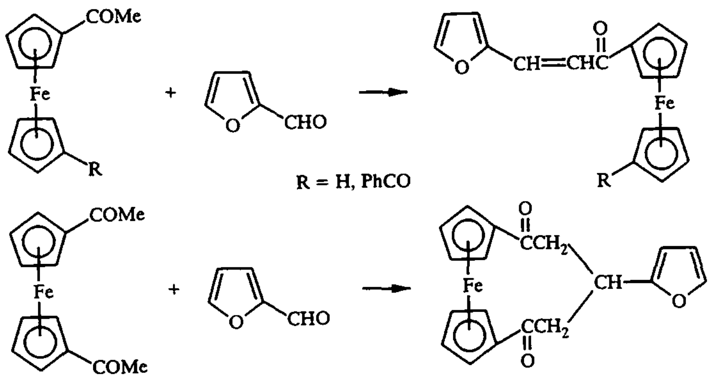


The ferrocene derivatives of furan are the most widely studied type of compound in which the metal atom is not attached to the furan ring. Classical methods were used for their synthesis [29-41]. Ferrocene is easily acylated by 2-furoyl chloride in the Friedel—Crafts reaction in the presence of anhydrous aluminum chloride [29, 30]. In turn the obtained 2-furoylferrocene can be reduced to furfurylferrocene with $LiAlH_4/AlCl_3$ [31].

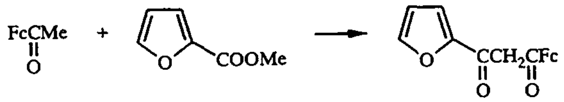


Fc = ferrocenyl

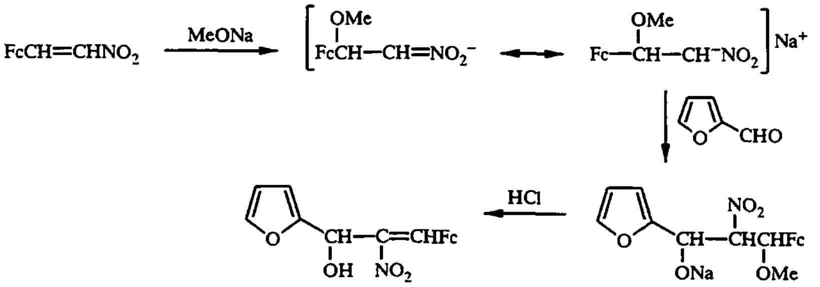
Acetylferrocene enters into condensation with furfural under the conditions of alkaline catalysis (sodium hydroxide) [32-35]. The yield of 1-ferrocenyl-3-(2-furyl)-2-propen-1-one amounted to 58%. The introduction of a benzoyl group into the second cyclopentadienyl ring somewhat reduced the yield of the product [33]. From 1,1′-diacetylferrocene a compound in which the two cyclopentadienyl rings are linked by a C_5-carbon chain was obtained [34].



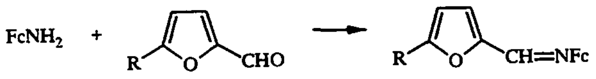
Acetylferrocene also reacts with methyl 2-furancarboxylate with the formation of a diketone, which undergoes cyclization to a derivative of pyrazole under the influence of hydrazine [37].



1-Ferrocenyl-2-nitroethylene enters into condensation with furfural in the presence of sodium methoxide. The latter generates a carbanion from the nitroethylene compound, and the carbanion attacks the carbonyl group of the furfural. A nitroalkenol was then produced with a 35% yield by treatment of the intermediate with hydrochloric acid [38].

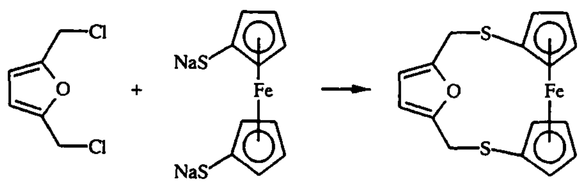


Azomethine bases were synthesized with yields of 82 and 85% respectively by heating aminoferrocene with furfural or 5-nitrofurfural for 1 h [39].



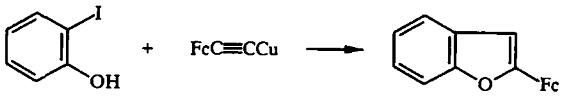
R = H, NO_2

The synthesis of ferrocene containing a furan ring in a bridging chain was realized by the reaction of 2,5-di(chloromethyl)furan with sodium 1,1-ferrocenedithiolate under conditions with strong dilution. However, even under these conditions the yield of the product amounted to only 4% [40].



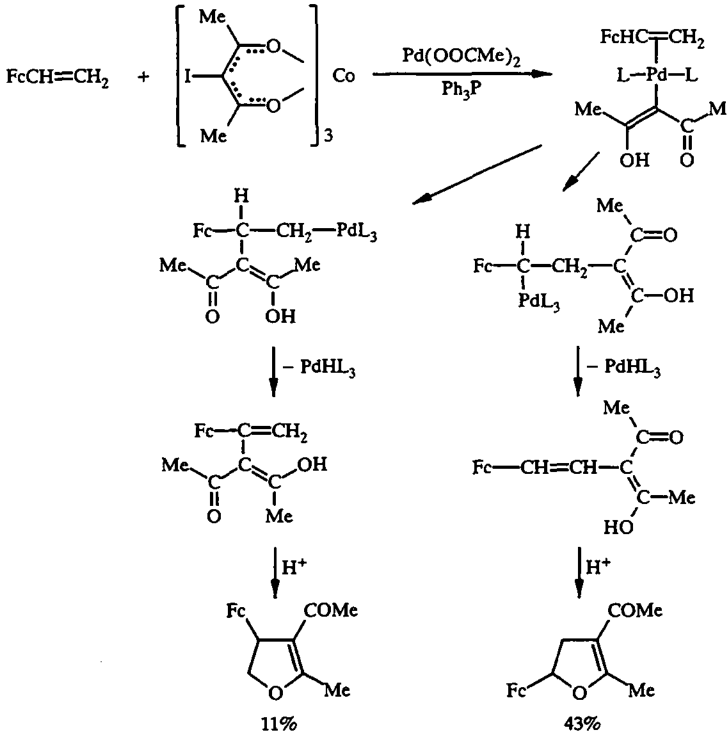
Cyclization was used for the synthesis of 2,5-diferrocenylfuran [41] and 2-ferrocenylbenzofuran [42]. In the first case 1,4-diferrocenylbutane-1,4-dione was converted into a cyclic compound during treatment with freshly prepared polyphosphoric acid (yield 24%) [39].

2-Ferrocenylbenzofuran was obtained with an 85% yield by heating *o*-iodophenol with ferrocenylethynylcopper in pyridine for 8 h [42].

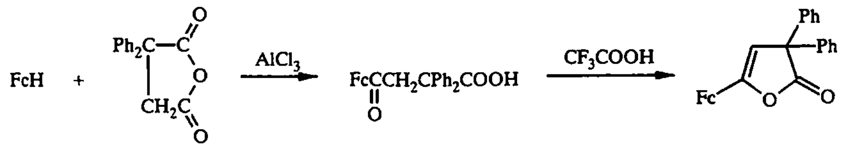


Cyclization has found particularly wide use in the synthesis of derivatives of dihydro- and tetrahydrofuran containing a ferrocenyl substituent in the heterocycle [41, 43-53].

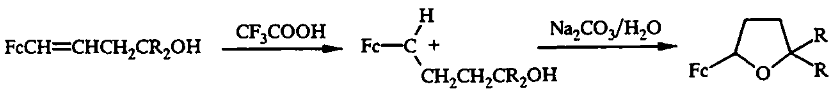
The reaction of vinylferrocene with tris(3-iodopentane-2,3-dionato)cobalt in the presence of triphenylphosphine and a catalytic amount of divalent palladium acetate gave two structural isomers of ferrocenyldihydrofuran. Their formation can be explained by the following processes [43]:



Ferrocene is acylated by α,α-diphenylsuccinic anhydride in the presence of aluminum chloride. Under the action of trifluoroacetic acid in methylene chloride the α,α-diphenyl-γ-ferrocenyl-γ-oxobutyric acid formed as a result of the reaction undergoes cyclization to 3,3-diphenyl-5-ferrocenyl-2(3H)-furanone [44].

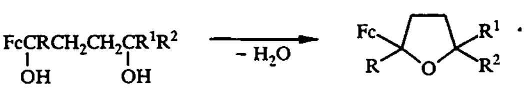


In trifluoroacetic acid 4-ferrocenyl-3-buten-1-ols are converted into carbocations, stabilized by the ferrocenyl substituent. If they are treated with an excess of a saturated aqueous solution of sodium carbonate, 2-ferrocenyltetrahydrofurans are formed with yields of 84-88% [45].



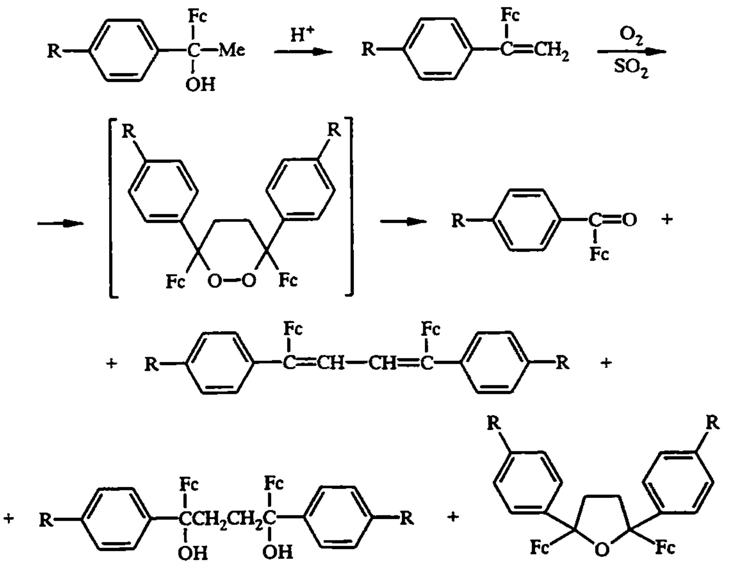
R = H, Me

The most convenient and best studied method for the synthesis of 2-ferrocenyl- and 2,5-diferrocenyltetrahydrofurans is the cyclization of γ-glycols of the ferrocene series [41, 46-49]. The reaction takes place both in the presence of a dehydrating agent (10% sulfuric acid) [41, 49] and during vacuum distillation of the glycol [42-48] and gives a high and almost quantitative yield.



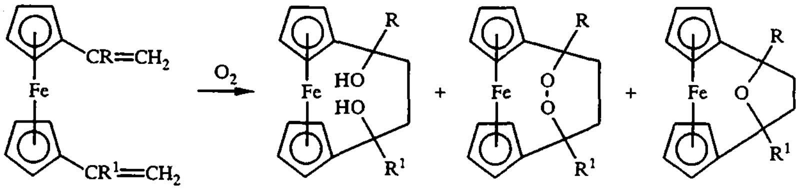
R = Me; R^1 = H; R^2 = Me, Pr, Ph;
R^1 = Me; R^2 = Me, Et, Pr;
R^1R^2 = $(CH_2)_4$, $(CH_2)_5$;
R = Ph; R^1 = R^2 = Me, Pr;
R^1 = Me; R^2 = Et;
R^1R^2 = $(CH_2)_4$, $(CH_2)_5$;
R = R^1 = H; R^2 = Fc

The treatment of 1-hydroxy-1-phenylethylferrocene with molecular oxygen in hexane or acidic aluminum oxide gave a series of products from oxidative dimerization, among which the *cis* and *trans* isomers of 2,5-diphenyl-2,5-diferrocenyltetrahydrofuran were detected. Their yield is low and amounted to 5.5 and 6.8% for the *cis* and *trans* isomers. The introduction of a methyl group at the *p* position of the phenyl ring reduced the yield to 2.3 and 1.1% respectively [50, 51].

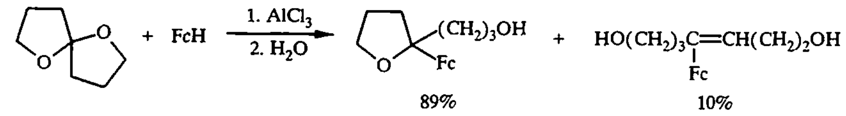


R = H, Me

The oxidation of 1,1'-divinylferrocene in the presence of sodium Cu-chlorophyllin with irradiation took place in an almost identical manner [52].

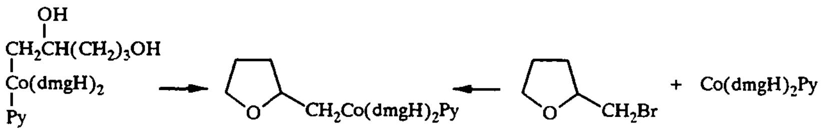


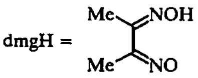
The reaction of 1,6-dioxaspiro[4.4]nonane with ferrocene, catalyzed by Lewis acids (aluminum chloride, boron trifluoride etherate), takes place mainly with opening of one tetrahydrofuran ring [54]. The main reaction product is 2-ferrocenyl-2-(3-hydroxypropyl)tetrahydrofuran (89%).



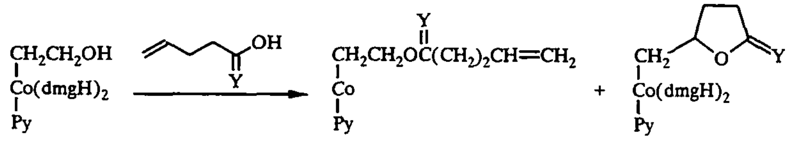
The tetrahydrofuryl derivatives of cobaloximes have been obtained by various methods: Cyclization of the 2,5-dihydroxypentyl substituent σ-bonded with the cobalt atom [55]; substitution of the hydroxyethyl group by tetrahydrofuryl [56]; alkylation of the inorganic bisdimethylglyoximate chelates of cobalt with certain olefins [57].

When its chloroform solution is passed through a column of silica gel, 2,5-dihydroxypentyl(pyridine)cobaloxime readily undergoes cyclization to the tetrahydrofuryl derivative of cobaloxime. The formation of the latter was also confirmed by an alternative synthesis [55].



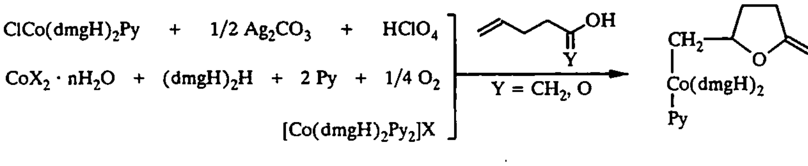


In the presence of acidic catalysts (perchloric acid, boron trifluoride etherate) the tetrahydrofuryl cobaloximes are formed with very low yields in the reaction of 2-hydroxyethyl(pyridine)cobaloxime with 4-penten-1-ol or 4-pentenoic acid. The main products of this process are linear ethers [56].



$Y = CH_2, O$

The alkylation of the complexes and salts of cobalt has been carried by various methods [57]. Thus, when treated with 4-penten-1-ol or 4-pentenoic acid in methylene chloride and alcohol in the presence of a stoichiometric amount of silver carbonate and perchloric acid chloro(pyridine)cobaloxime forms tetrahydrofurfuryl(pyridine)cobaloxime (25-30%) or the corresponding lactone. It was possible to isolate the same products with a yield of more than 16% after the oxidation of a mixture of a divalent cobalt salt, dimethylglyoxime, pyridine, and an excess of an olefin with atmospheric oxygen in alcohol. Cationic dipyridine cobaloximes did not react with olefins in neutral and acidic media. In the presence of potassium hexacyanoferrate, however, they gave small yields of the alkylation products.

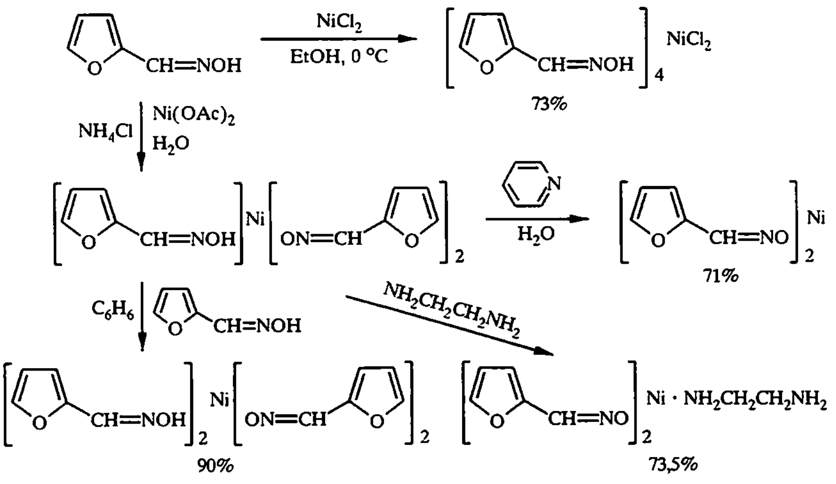


X = AcO, ClO_4, BF_4

Of the compounds with a C_{furyl}—$(C)_nXM$ fragment in which the metal atom is attached to different heteroatoms (O, S, N, P) the 2,2′-furyldioxime complexes of cobalt [58], nickel [59-63], ruthenium [64], palladium [59, 65-68], and osmium [69] have been investigated most. This is due to the fact that 2,2′-furyldioxime is a reagent more sensitive to the ions of the given metals than the usually employed dimethylglyoxime. For example, under optimum conditions 1 mg of nickel can be easily detected in 6 liters of aqueous solution while 1 mg of palladium in 20 liters can be detected if 2,2′-furyldioxime is used [59]. This reagent is particularly useful during analysis for palladium, since complete precipitation is achieved even from solutions of strong mineral acids. The ions of cobalt [58] and nickel [59] are more sensitive to the pK value of the medium, and they are only precipitated quantitatively in an alkaline medium. The quantitative determination of the metals in complexes with 2,2′-furyldioxime was carried out by a gravimetric method [60, 64] by ignition of the precipitated complexes to the metal oxides and by spectrophotometry [60, 61, 69]. In addition, 2,2′-furyldioxime was used as titrant during the conductometric titration of nickel [63] and palladium [65] salts.

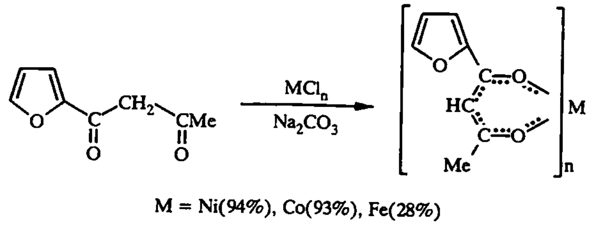
2,2′-Furylmonooxime also forms chelate complexes with the salts of trivalent ruthenium [64] and divalent palladium [70].

The complexation of divalent nickel with the *anti* isomer of furfural oxime was studied [71].

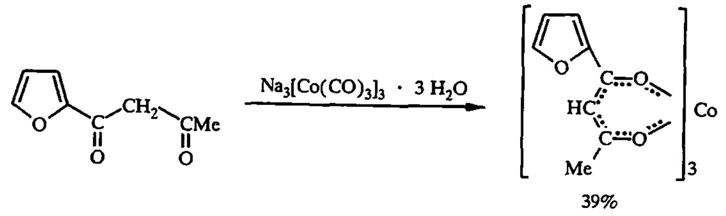


In the opinion of the authors [71] the ligands in these complexes are mono- and/or bidentate and are coordinated with the metal through the oxygen atoms of the oxime and the furan ring. In all the compounds except (2-furyl—CH═NO)$_2$Ni the nickel atom is octahedral.

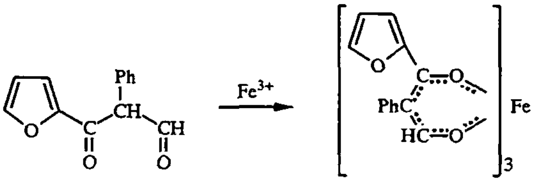
The treatment of furoylacetone with cobalt(II), nickel(II), and iron(III) chlorides in dimethylformamide in the presence of sodium carbonate gives the corresponding furoylacetonates. The furoylacetonate of trivalent cobalt was obtained by the reaction of furoylacetone with the carbonyl complex $Na_3[Co(CO)_3]_3 \cdot 3H_3O$ [72].



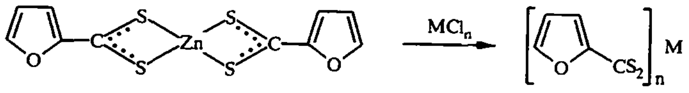
M = Ni(94%), Co(93%), Fe(28%)



2-Phenyl-2-(2-furoyl)acetaldehyde reacts similarly with Fe^{3+} ions [73].

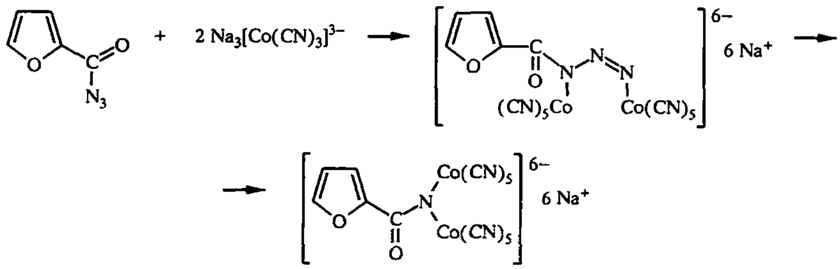


The 2-furancarbodithioate complexes of nickel(II), cobalt(III), and iron(III) were obtained by the substitution of zinc in zinc bis(2-furancarbodithioate) the action of $NiCl_2$, $CoCl_3$, and $FeCl_3$ respectively [74].

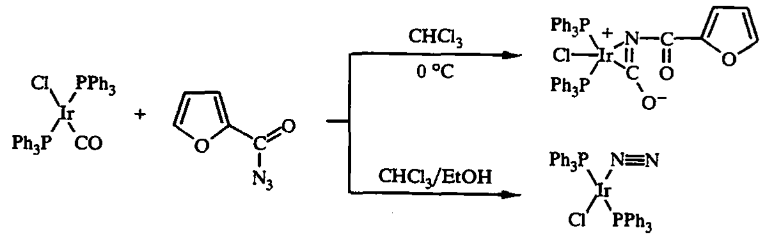


M = Ni, n = 2; M = Co, n = 3; M = Fe, n = 3

2-Furoyl azide reacts with the pentacyanocobaltate ion at 0°C in water—ethanol solution. The reaction takes place with the release of nitrogen through an intermediate triazide complex [75].

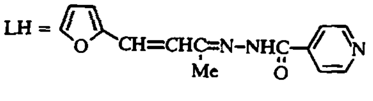


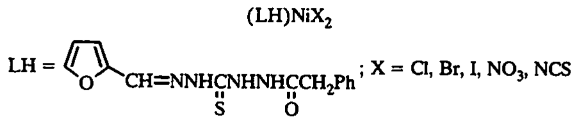
With chlordi(triphenylphosphine)carbonyliridium 2-furoyl azide forms various products, depending on the purity of the chloroform. An iridium complex of molecular nitrogen was obtained in chloroform containing alcohol impurity, while an iridium isocyanate complex was obtained in chloroform free from ethanol [76].

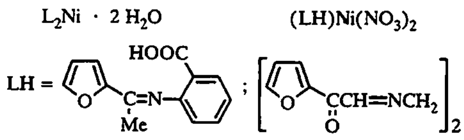


The following types of complexes are formed when cobalt [77] and nickel [78, 79] salts are heated with furyl-containing hydrazones, thiocarbohydrazides, and azomethine bases:

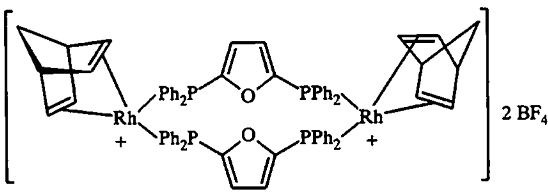
$(LH) \cdot CoCl_2$ $\quad L_2Co \cdot 2\,H_2O \quad L_3Co \cdot 3\,H_2O$

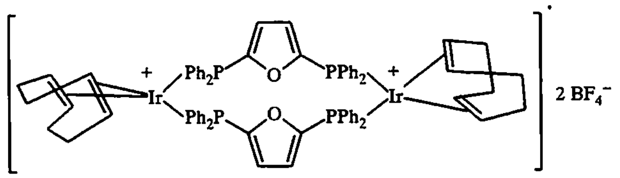






2,5-Bisdiphenylphosphinofuran reacts with bisbicyclo[2.2.1]heptadienerhodium tetrafluoroborate in chloroform. This reaction results in the formation of a binuclear complex [80]. An iridium compound was obtained similarly [81].

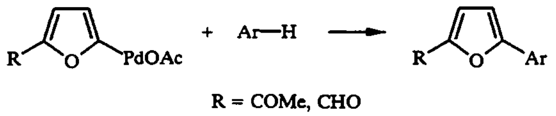


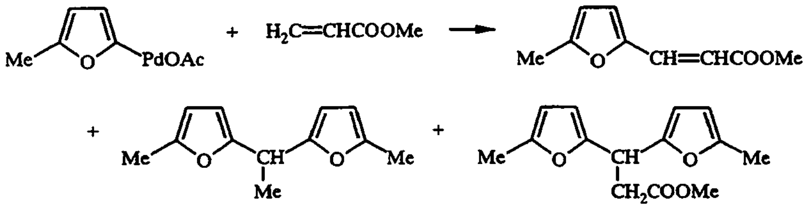


2. CHEMICAL PROPERTIES

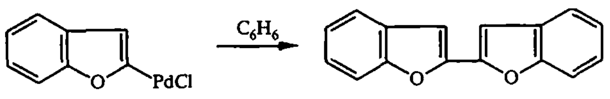
The reactions of the furan derivatives of group VIII elements can be subdivided into several types: Transformations taking place with cleavage of the C—M bond; transformations affecting the furan ring; reactions of the groups attached to the metal.

Among reactions of the first type the arylation and vinylation of furan have often been used in organic synthesis. They take place *in situ* through the formation of intermediate furylpalladium chlorides and acetates [9-12]. Thus, furylpalladium acetates containing aldehyde and acetyl groups in the furan ring react with aromatic compounds with the formation of aryl-substituted furans [10]. The vinylation of 5-methyl-2-furylpalladium acetate with methyl acrylate does not take place so selectively. 1,1-Bis(5-methyl-2-furyl)ethane (22%) and methyl 3,3-bis(5-methyl-2-furyl)propionate (10%) were obtained with fairly high yields in addition to the vinyl derivative of furan (yield 27%) [11].

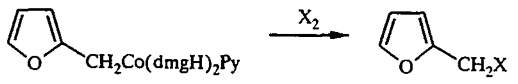


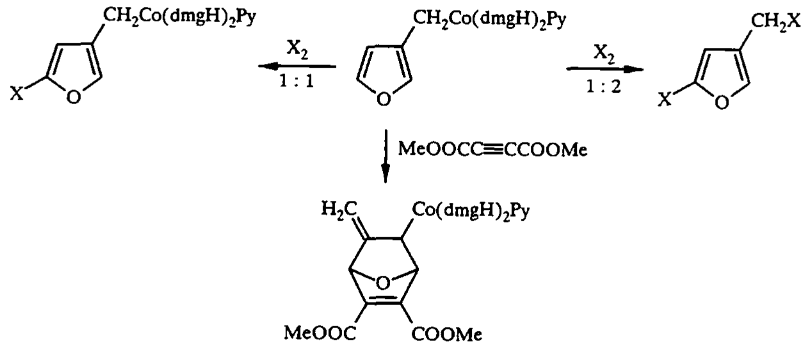


2-Furylpalladium chloride also reacts with olefins with the formation of furylalkenes. This process is accompanied by the formation of a small amount of 2,2'-bifuryl [12]. It was not possible to arylate the palladium derivative of benzofuran with benzene, since the only reaction product was 2,2'-bibenzofuryl [9].

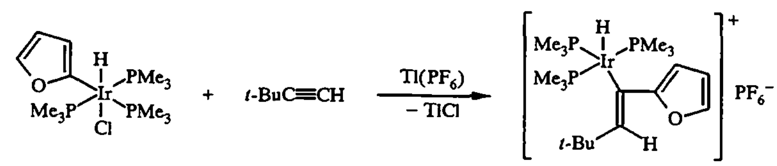


The reactivities of 2- and 3-furylmethylcobaloximes during halogenation were compared [82, 83]. The reaction of furfurylcobaloxime with chlorine, bromine, iodine, and bromine iodide in a molar ratio of 1:1 in chloroform or acetic acid in an atmosphere of nitrogen takes place quickly and with cleavage of the Co—C bond. Under analogous conditions the 3-substituted isomer gives the products from halogenation of the furan ring at position 5 of the furan. The Co—C bond was only cleaved when twice the amount of the halogenating agent was used. In reaction with dimethyl acetylenedicarboxylate 3-furylmethylcobaloxime acts as diene [84]. Im methylene chloride the cyclocondensation takes place at room temperature and gives a quantitative yield.

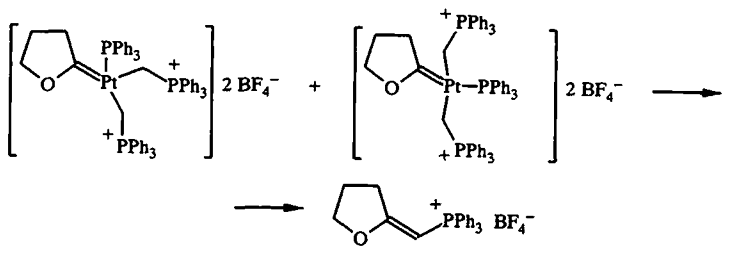




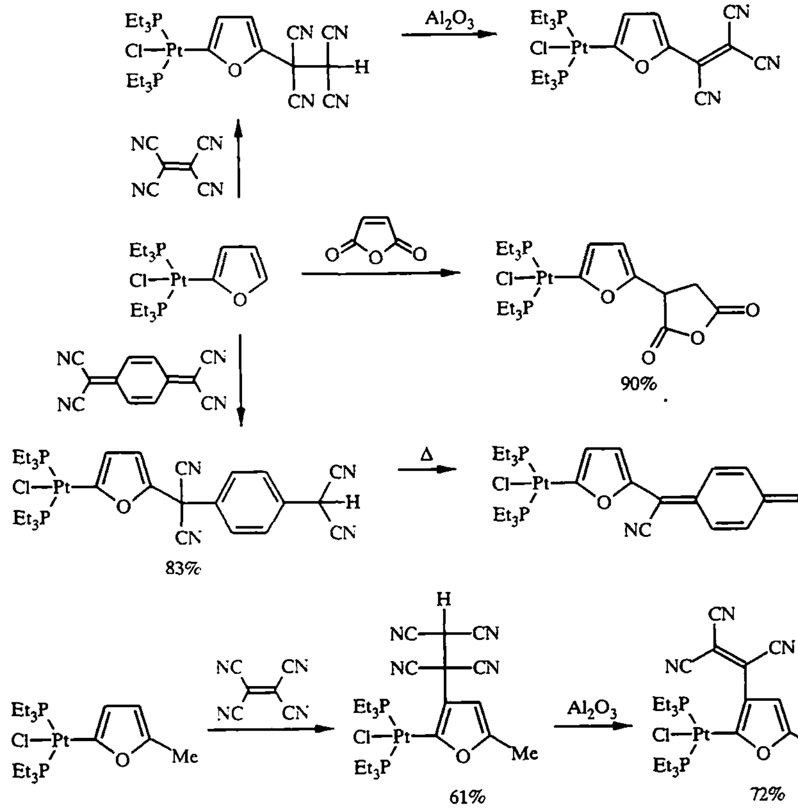
During the reaction of the furyliridium complex (2-furyl)(Ir)(PMe$_3$)$_3$(Cl) with *tert*-butylacetylene and Tl(PF$_6$) in methylene chloride a vinyliridium complex, which can be regarded formally as the product from insertion of the *tert*-butylacetylene at the Ir—C$_{\text{furyl}}$ bond, is formed with a yield of 58%. It should be noted that the furyl group attacks the α- and not the β-carbon atom [85].



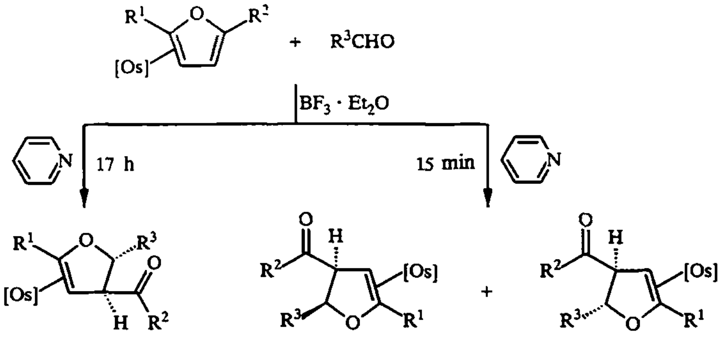
The *cis* and *trans* isomers of the 2-oxacyclopentylidene complex of platinum in the individual state and also in the form of a mixture are transformed quantitatively when heated into a phosphonium salt by insertion of the carbenium ligand at the Pt—C bond [24].



The diene synthesis reaction does not occur when the phosphine complexes of 2-furylplatinum are treated with maleic anhydride (in methylene chloride, boiling), tetracyanoethylene, or 7,7,8,8-tetracyanoquinodimethane (in methylene chloride, room temperature), but high yields of the products from the insertion of the olefins at the C—H bond at position 5 of the furan ring are formed. The product from the insertion of tetracyanoethylene was unstable and was gradually decomposed with the release of HCN. It was possible to eliminate the HCN completely during chromatography on aluminum oxide. The complex of 7,7,8,8-tetracyanoquinodimethane undergoes a similar transformation when heated. If a methyl group is introduced at position 5 of the heterocycle, the tetracyanoethylene molecule is inserted at the C—H bond at position 3 [86].

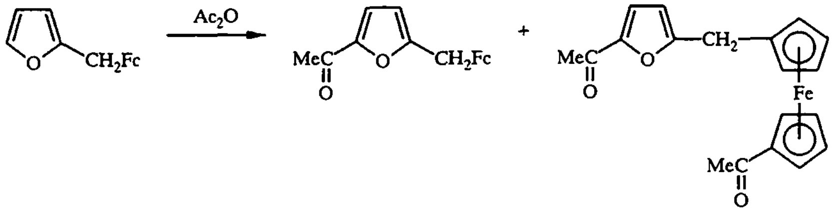


The 2,3-η^2-furan complexes of osmium react with various aldehydes in the presence of Lewis acids [$Sn(OTf)_2$, $BF_3 \cdot OEt_2$] with the formation of 4-acyl-substituted 4,5-dihydrofuran complexes, in which the oxygen atom of the aldehyde group has been inserted into the furan ring. Detailed analysis of the reaction products showed that aldol condensation initially takes place at position 4 of the furan, and the oxygen of the heterocycle is then displaced by the oxygen of the alkoxide group. If the reaction mixture of the osmium complex with the aldehydes and the acid is kept at −40°C for 17 h and the Lewis acid is then neutralized with pyridine, the reaction takes place stereoselectively. Reduction of the time to 15 min leads to a mixture of stereoisomers [16].

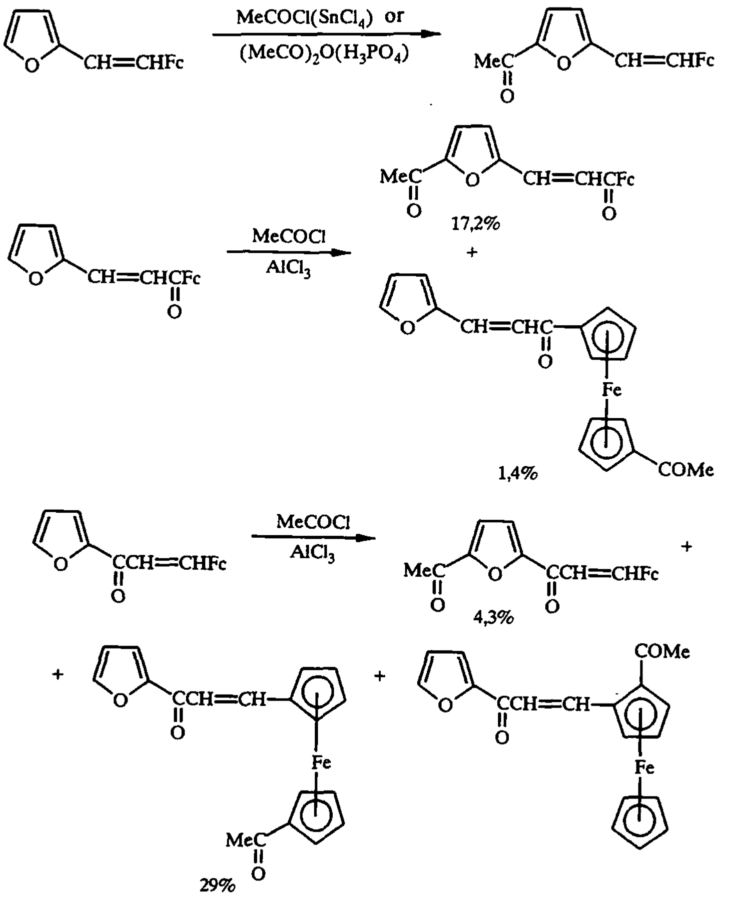


$[Os] = [Os(NH_3)_5]^{2+}(OTf)_2^-$

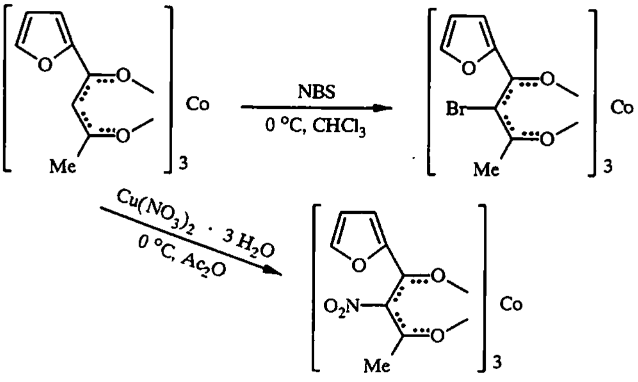
Of the reactions taking place in the furan ring the acylation of various furan derivatives of ferrocene was also investigated [31, 87]. The main product from the reaction of furfurylferrocene with acetic anhydride in benzene under the influence of phosphoric acid at room temperature was 5-acetylfurfurylferrocene (yield 40%). In addition, a small yield (4%) of the product from its acylation in the unsubstituted cyclopentadienyl ring was obtained [31].



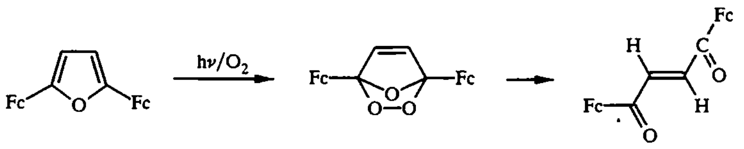
The acylation of 2-furylvinylferrocene both with acetic anhydride (H_3PO_4) and with acetyl chloride ($SnCl_4$) takes place with a small yield only in the furan ring [31]. 2-Furylvinyl ferrocenyl ketones and 2-furylvinylferrocene react with acetyl chloride in the presence of aluminum chloride in a more complicated manner [87].



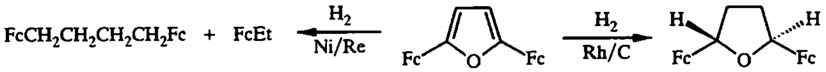
The nitration of the furoylacetate complex of cobalt with copper(II) nitrate and its bromination with N-bromosuccinimide were undertaken in order to compare the aromaticity of the furan and chelate rings [72]. It was found that the hydrogen atom of the chelate ring was easily substituted by bromine and the nitro group with the formation of the tribromo derivative (yield 60%) and trinitro derivative (yield 55%). Substitution of the hydrogen in the furan ring was not observed at all.



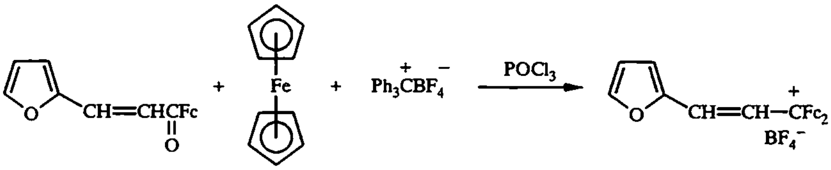
The photooxidation of 2,5-diferrocenylfuran was conducted in acetone with cooling to −60 to −80°C. Initially the formation of an intermediate ozonide was observed. It was converted at room temperature into *trans*-1,2-diferrocenoylethylene (yield 18.5%) [88].



The hydrogenation of 2,5-diferrocenylfuran at rhodium deposited on carbon and at Raney nickel takes place in a different way. In the first case in ethanol at room temperature the furan ring is hydrogenated to a tetrahydrofuran ring, and *trans*-2,5-diferrocenyltetrahydrofuran is formed with a yield of 9%. Hydrogenation at Raney nickel at 110°C in ethanol leads to the products from opening of the furan ring [41].

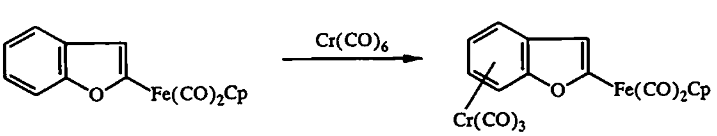


Certain chemical transformations of 2-furylacryloylferrocene were studied. Thus, its reaction with ferrocene under the influence of triphenylmethyl tetrafluoroborate gave a 28% yield of the (2-furylvinyl)methyl cation [89].



It was not possible to homopolymerize 2-furylacroylferrocene, but it entered into copolymerization with styrene and methyl methacrylate [90].

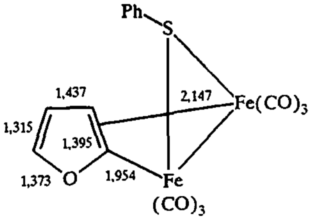
The condensation of 2-benzofurylcyclopentadienyldicarbonyliron with chromium hexacarbonyl takes place readily. A high yield of a compound in which the chlorine atom is π-coordinated with the benzene ring of benzofuran is obtained [91].



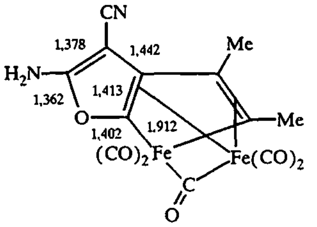
3. PHYSICOCHEMICAL PROPERTIES

X-ray crystallographic analysis has most often been used to study the furan derivatives of the elements of group VIII [1, 3, 8, 13, 19, 24, 27, 28, 86, 92-95]. In a number of cases this method was the only method by means of which it was possible to prove the structure of the complexes unambiguously. In addition, various furan derivatives of ferrocene were investigated by IR spectroscopy [96, 97]. However, these investigations were mostly concerned with features of the absorption bands of the ferrocene fragment. The *E*/*Z* isomerization of the platinum complexes with furylideneamines was studied by NMR spectroscopy [98].

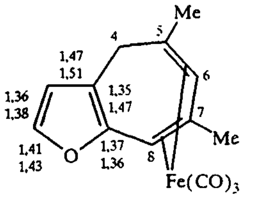
Certain geometric parameters of the complexes of iron (**1-5**), rhodium (**6**), palladium (**7**), osmium (**8**, **9**), iridium (**10-12**), and platinum (**13-15**) are given in the figures.



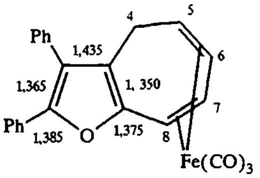
1 [1]



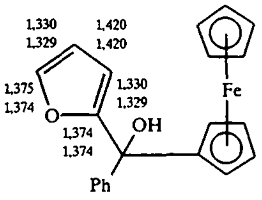
2 [3]



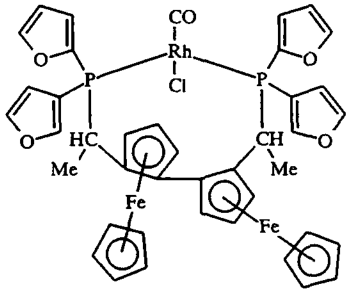
3 [27]



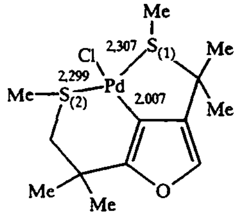
4 [28]



5 [94]



6 [95]



7 [8]

The geometry of the furyl ligand in complexes **1**, **2**, **8**, and **9** is greatly affected by the π interaction of the $C_{(2)}{=}C_{(3)}$ double bond with the metal atom. The coordinated $C_{(2)}{=}C_{(3)}$ bond in the complexes is considerably longer than the uncoordinated $C_{(4)}{=}C_{(5)}$ bond. Elongation is also characteristic of the $C_{(2)}$—O bond compared with the $C_{(5)}$—O bond. the length of the $C_{(2)}$—M σ bonds amounts to 1.954 and 1.912 Å for the iron derivatives **1** and **2** and 2.11 Å for the osmium complex **8**. The $C_{(2)}$—M and $C_{(3)}$—M distances for the π-bonded metal are nonequivalent.

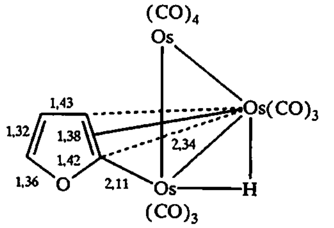
In complex **2** the furan ring is condensed with the ferracyclopentadiene system, which in turn is coordinated with the $Fe(CO)_3$ group. The heterocycles are almost coplanar, and the dihedral angle amounts to 178.9°C

Compounds **3** and **4** have largely similar structural characteristics. The iron atom is coordinated with four carbon atoms of the seven-membered ring, and the $C_{(5)}$—Fe and $C_{(8)}$—Fe distances are longer than $C_{(6)}$—Fe and $C_{(7)}$—Fe. In complex **4** the $C_{(2)}$—C_{Ph} bond is significantly shorter (1.459 Å) than the $C_{(3)}$—C_{Ph} bond (1.480 Å). The phenyl group at position 2, which lies in the same plane as the furan ring, is probably more conjugated with the heterocycle than the rotated phenyl group at position 3.

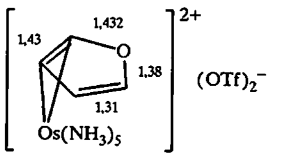
The molecules of racemic ferrocenyl(2-furyl)phenylmethanol **5** form a centrosymmetric dimer through hydrogen bonds with the hydroxyl groups. In the rhodium complex **6** the chiral phosphine ligand — (*R*,*R*)-(*S*,*S*)-2,2″-bis[di(2-furyl)phosphinoethyl]-1,1″-biferrocene — is in the *trans* position.

The palladium atom in complex **7** has square planar geometry. The deflections of the atoms from the PdS_1S_2ClC plane amount to 0.023, 0.113, 0.115, and 0.114 Å for Pd, S_1, S_2, and the carbon atom of the furan ring respectively. The geometric parameters for the furyl group were not given in [8].

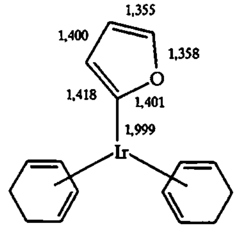
The lengths of the C_{furyl}—Ir bonds in the iridium complexes **10** and **11** are 1.999 and 2.065 Å respectively. As in compounds **1**, **2**, **8**, and **9**, the lengths of the $C_{(2)}{=}C_{(3)}$ and $C_{(4)}{=}C_{(5)}$ bonds and also the $C_{(3)}$—O and $C_{(5)}$—O bonds of the furan ring in the complex **10** are nonequivalent.



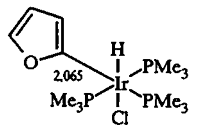
8 [13]



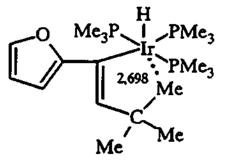
9 [93]



10 [18]

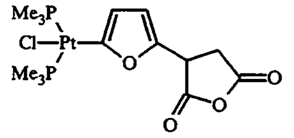


11 [19]

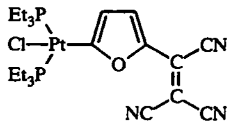


12 [85]

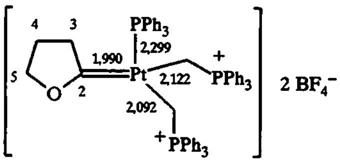
According to x-ray crystallographic analysis, the plane of the furan ring in the furylplatinate **13** is perpendicular to the coordination plane at the platinum atom and the average plane of the 2-oxacyclopentane-1,3-dion-4-yl substituent. In the complex **14** the $C(CN){=}C(CN)_2$ olefinic part is almost coplanar with the 2-furyl group. The substituents at the platinum atom in the 2-oxacyclopentylidene derivative **15** form a square, while the plane passing through the $C_{(2)}$, $C_{(3)}$, O, and Pt atoms intersect the $PtPC_{(CH_2)}C_{(CH_2)}$ plane at an angle of 61.75°C.



13 [86]



14 [86]



15 [24]

The presented reviews complete a series of publications [99-104], in which published data and the results of our own investigations into the synthesis, chemical transformations, physicochemical properties, and biological activity of furan derivatives covering the period from the end of the 1940s to the present have been reviewed.

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