Synthesis of ruthenium(III) and rhodium(III) tris-acetylacetonates and palladium(II) bis-ketoiminate using microwave heating

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Preparation of ruthenium(III) and rhodium(III) tris-acetylacetonates and palladium(II) bis-ketoiminate (Pd(i-acac)$_2$) under microwave irradiation using different synthetic conditions, both in the solid-phase and in solution, was studied with precise control of parameters. In the solid-phase systems, the preparation of the target product was hindered. The efficiency of the microwave heating increased when liquid phases of the reagent mixtures were used. For Pd(i-acac)$_2$, the highest yield was achieved under elevated temperature of the process, with the reaction time decreasing to several minutes. A laboratory procedure for the microwave synthesis of ruthenium(III) and rhodium(III) tris-acetylacetonates and palladium(II) bis-ketoiminate in aqueous solutions was developed, which allowed us to obtain them in 85, 55, and 80% yields, respectively. These yields are higher than those reported in the literature, with the process becoming considerably less time consuming and laborious.

Key words: ruthenium(III) and rhodium(III) acetylacetonates, palladium(II) ketoiminate, synthesis, microwave irradiation.

A constant interest to the chemistry of volatile coordination and organometallic compounds is due to a possibility of their use in analytics, microelectronics, catalysis, extraction, gas chromatography, and other fields. β-Diketonate complexes possess high vapor pressure at relatively low temperatures, thermal stability in condensed (at vaporization temperatures) and gas phases, resistance to exposure, stability on storage, and low toxicity. A combination of these properties determines prospects of their practical application as precursors in the processes of metal-organic chemical vapor deposition (MOCVD) of films and coatings of different functional purposes.

For the MOCVD processes to be successfully effected, it is important that the target compound during the synthesis could have been isolated in high yield, which is even more important for the platinum group metal complexes because of their high cost. Analysis of the literature data showed that there is no versatile procedure for the synthesis of the platinum group metal β-diketonates. Such complexes, in particular, acetylacetonates of the general formula M(acac)$_n$ and their derivatives, as a rule,[1—5] are synthesized by the reaction of aqueous metal chlorides with β-diketones in water-alcohol solutions under different reaction conditions or by the reactions of β-diketones with the corresponding freshly precipitated metal hydroxides upon heating the reagents in the range of pH = 5—6 with subsequent recrystallization of the target products from solutions in chloroform, benzene or by chromatographic purification on alumina.

The processes were carried out by prolonged heating, sometimes under inert atmosphere, at the constant pH of the medium. In this case, an excess of the chelating agent was required as a rule. For example, according to the data published earlier[6,7] a necessary condition for the reaction of rhodium(III) chlorides with acetylacetone was the use of a large excess of the ligand and the presence of a high-capacity buffer medium. The yields of final products in such processes varied from 20 to 70%, whereas no complexes were formed in a number of cases. This can result from the competition of the acidoligands and β-diketone for the coordination site, which leads to the formation of polymeric forms in solution, where, besides β-diketone also capable of serving as a bridging ligand, coordinated Cl$^-$ and OH$^-$ ions are present, as well.

We have developed an original method for the synthesis of the platinum group metal β-diketonates from the corresponding metal hexafluoro complexes, which allowed us to considerably increase yields of the final products.[8,9]

However, this procedure required the use of elementary fluorine, hydrofluoric acid, and the corresponding equipment.

Platinum metal ketoiminates of the general formula $M(i\text{-}acac)_n$ (i-acac = 2-imino-4-pentanonato($-$), [MeC-NH—CH—COMe]$^-$) are much less studied than β-diketonate complexes, the information in the literature is very limited and before our studies were reported only in separate works. This is because of the poorer availability of the ligand and different requirements to the conditions for the existence in solutions of the starting metal complexes (acidic medium) and the ketoiminate ligand (alkaline medium). In acidic solutions, at low pH values, where, as a rule, exist the starting metal aqua-ions, β-ketoimine easily undergoes acid hydrolysis.[10—13] The procedure developed by us allows one to obtain $Pd(i\text{-}acac)_2$ in 60—75% yields, but is a multi-step process and laborious enough.

Upon analysis of the approaches described, the following major disadvantages of the methods listed can be found: the requirement to preliminary obtain purified reagents (hydroxides, aqua forms in solutions, *etc*.), impossibility to achieve high yields of the target products, which in the case of rhodium(III) and ruthenium(III) β-diketonates and palladium(II) ketoiminates did not exceed 60—70%, the long time of the process, necessity to maintain an inert atmosphere and a constant pH value of the medium, involvement of a considerable excess of the ligand into the synthesis. The low yield of the products is explained by the weak coordination ability of the oxygen atoms of acetylacetone as compared to the chloride ligands and/or high degree of polymerization of noble metal chlorides.

The high cost of the starting reagents and the wide use of the final products make it actual to develop rapid and efficient methods for the synthesis of noble metal β-diketonates. The use of nontraditional methods of preparation involving microwave (MW) activation of the processes would allow one to develop environmentally friendly method of the synthesis with recycling the unreacted agent into the starting mixture, *i.e.*, virtually a waste-free pro-

duction. Comparatively recent paper[14] in the open literature demonstrated prospects in the use of MW-irradiation for the synthesis of Rh^I and Ir^I heteroligand compounds with another type of coordination ([Rh(cod)Cl]$_2$, [Ir(cod)Cl]$_2$, *etc*., cod = 1,4-cyclooctadiene), which can be used for further preparation of noble metal β-diketonate derivatives in the yields from 60 to 90%.

The purpose of the present work is development and optimization of the procedure for the synthesis of ruthenium(III) ($Ru(acac)_3$) and rhodium(III) ($Rh(acac)_3$) tris-acetylacetonates and palladium(II) bis-ketoiminate ($Pd(i\text{-}acac)_2$) with involvement of MW-heating, as well as studies of the dynamics of parameters of the MW-irradiation and effect of the nature and concentration of the starting reagents on the reaction systems studied in the work.

Results and Discussion

Two versions of the starting compositions were considered in the studies of a possibility of MW-synthesis of ruthenium and rhodium tris-acetylacetonates: the solid-phase systems and reaction systems with organic solvents and water. In the case of the synthesis of palladium bis-ketoiminate, we used the reaction systems with aqueous solutions. Parameter of the MW-action, nature of the starting components and their molar ratio, as well as characteristics of the products for each of the experiment performed are given in Tables 1 and 2.

Solid-phase synthesis of rhodium and ruthenium tris-acetylacetonates. Initially, we attempted to obtain $M(acac)_3$ from solid reagents (Scheme 1) without use of solvents in order to avoid a possibility of emergence of unreactive forms of complexes.
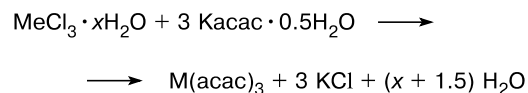
Scheme 1

$$MeCl_3 \cdot xH_2O + 3\ Kacac \cdot 0.5H_2O \longrightarrow$$

$$\longrightarrow M(acac)_3 + 3\ KCl + (x + 1.5)\ H_2O$$

Table 1. Conditions for solid-phase synthesis of $Rh(acac)_3$ and $Ru(acac)_3$

Entry	Reagents		Power/W	t^a/min	T/°C	Product weight^b/mg
	Components	Molar ratio				
	$Rh(acac)_3$ (a weighed amount of $RhCl_3 \cdot xH_2O$ — 0.14 g)					
1	$RhCl_3 \cdot xH_2O$ + Kacac $\cdot$ 0.5H$_2$O	1 : 6	100	10	140	16
2	$RhCl_3 \cdot xH_2O$ + Kacac $\cdot$ 0.5H$_2$O	1 : 6	200	10	150	30
	$Ru(acac)_3$ (a weighed amount of $RuCl_3 \cdot xH_2O$ — 0.12 g)					
3	$RuCl_3 \cdot xH_2O$ + Kacac $\cdot$ 0.5H$_2$O	1 : 6	100	10	140	18

^{a} Here and in Table 2: the time of MW-irradiation is designated as t.
^{b} In all the cases, mixtures of products were obtained, and the isolation of the target product was impossible.

Table 2. Conditions for the synthesis of Rh(acac)$_3$, Ru(acac)$_3$, and Pd(i-acac)$_2$ in the liquid-phase systems (the solvent in entries *1*, *2* was Hacac, *3*, *4* MeCN, *5—17* H$_2$O, the power of MW-irradiation in entries *1—4* was 200 W, *5—16* 100 W, *17* 150 W)

Entry	Reagents		t^a/min	T/°C	Product characteristics		
	Components^a	Molar ratio			Purity^b	Weight /mg	Yield (%)
		Rh(acac)$_3$ (a weighed amount of RhCl$_3 \cdot x$H$_2$O in entry *1* and *2* — 0.13 g, *3—6* — 0.06—0.07 g, *8* and *9* — 0.2—0.3 g)					
1	RhCl$_3 \cdot x$H$_2$O KOH	1 : 1 10	5	90	m	42	–
2	RhCl$_3 \cdot x$H$_2$O KOH in EtOH	1 : 3 10	10	100	m	46	–
3	RhCl$_3 \cdot x$H$_2$O + Kacac $\cdot$ 0.5H$_2$O	1 : 6	10	100	m	24	+
4	RhCl$_3 \cdot x$H$_2$O + Kacac $\cdot$ 0.5H$_2$O	1 : 6	20	100	m	59	+
5	RhCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 13 : 3 10 5	15	100	p	38	45
6	RhCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 18 : 3 10 5	30	100	p	44	50
7	RhCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 15 : 3 10 5	20	100	p	100	25
8	RhCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 15 : 3 10 5	20	120	p	170	40
9	RhCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 15 : 3 10 10	30	110	p	154	55
	Ru(acac)$_3$ (a weighed amount of RhCl$_3 \cdot x$H$_2$O in entry *10* — 0.06 g, *11* and *12* — 0.25 g)						
10	RuCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 13 : 3 5 5	15	100	p	55	70
11	RuCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 15 : 3 5 5	10	100	p	311	75
12	RuCl$_3 \cdot x$H$_2$O Hacac NaOH in H$_2$O	1 : 15 : 3 15 10	10	100	p	349	85
	Pd(i-acac)$_2$ (a weighed amount of PdCl$_2$ — 0.2 g)						
13	PdCl$_2$ + NH$_3$ + H(i-acac) in H$_2$O	1 : 25 : 2	20	80	p	252	40
14	PdCl$_2$ + NH$_3$ + H(i-acac) in H$_2$O	1 : 25 : 2.5	20	90	p	194	60
15	PdCl$_2$ + NH$_3$ + H(i-acac) in H$_2$O	1 : 25 : 3	30	90	p	217	65
16	PdCl$_2$ + NH$_3$ + H(i-acac) in H$_2$O	1 : 25 : 3	6	100	p	250	75
17	PdCl$_2$ + NH$_3$ + H(i-acac) in H$_2$O	1 : 25 : 3	2	110	p	270	80

^{a} In some cases the reagents were added to the reaction system sequentially after a certain period of time (*t*).
^{b} In some entries the product was obtained as an individual phase ("p"), in others the reaction gave a mixture of products ("m"), and the target product was not isolated (the weight of the final products was too low).
^{c} The signs "+" or "–" indicate the presence or the absence of the product in the mixture, respectively.

However, the identification by TLC and elemental analysis showed that the isolated products are mixtures of metal-containing forms, among which the target M(acac)$_3$ were present.

It was interesting to follow the dynamics of parameters of the MW-irradiation. The starting reagents, the corresponding metal chlorides, and potassium acetylacetonate used for the solid-phase MW-synthesis are solid polar di-

electrics. The major polarization processes of the indicated compounds are electron, ion, and ion-relaxation polarization. In the SHF-range, these processes are extremely negligible, that results in the low speed of heating of such dielectric compounds and materials. In this case, it is logical to expect low rates of heating of the reaction systems used. However, we detected high rates of the MW-heating (from 3 to 5 °C s^{-1}) in the course of the reaction, which was not characteristic of the salt systems. The results obtained can be possibly explained by the use of platinum metal chlorides and potassium acetylacetonate in the form of hydrates. The crystal water possesses considerable lability and undergoes polarization in the SHF-field relatively easily.[15] The further increase in the temperature (>100 °C) causes liberation of the crystal water and formation of solutions of the starting reagents, which can be considered as ionic liquids. Mechanism of ionic polarization is typical of ionic liquids, which leads to the active absorption of the MW-irradiation.

Additional specific feature of the reaction systems used for the solid-phase synthesis of platinum metal tris-acetylacetonates consists in the formation of high-frequency surface and bulk discharges, which leads to considerable local overheatings. As a result, both the starting reagents

and the target products undergo active decomposition. This results in the low yields of M(acac)$_3$ and impossibility of the reaction to reach completion in the solid-phase synthesis.

The dynamics of the change of experimental parameters (power of MW-irradiation, pressure in the reaction ampule, and temperature of the process) were registered by the specialized Synergy program. The experimental results of the solid-phase MW-synthesis of Rh(acac)$_3$ are shown in Fig. 1. If temperature was chosen as a controlled parameter, the program decreased the MW-power to the level of 10—20% from the initial value when the appropriate temperature was reached. Excessive pressure in the capped ampule was recorded simultaneously (~17 atm, see Fig. 1, *b*), its high values indicated considerable decomposition of Kacac · 0.5H$_2$O and Rh(acac)$_3$ formed.

Synthesis of rhodium and ruthenium tris-acetylacetonates in liquid media. Rhodium(III) trichloride hydrate is known to have a chain motif of crystal structure consisting of the polymeric chains, which are difficult enough to destroy.[6,7] The synthesis of rhodium coordination compounds, as a rule, resulted in the mixtures of products with the incomplete substitution for the chlorine atoms with the corresponding ligands. The activation of rhodium
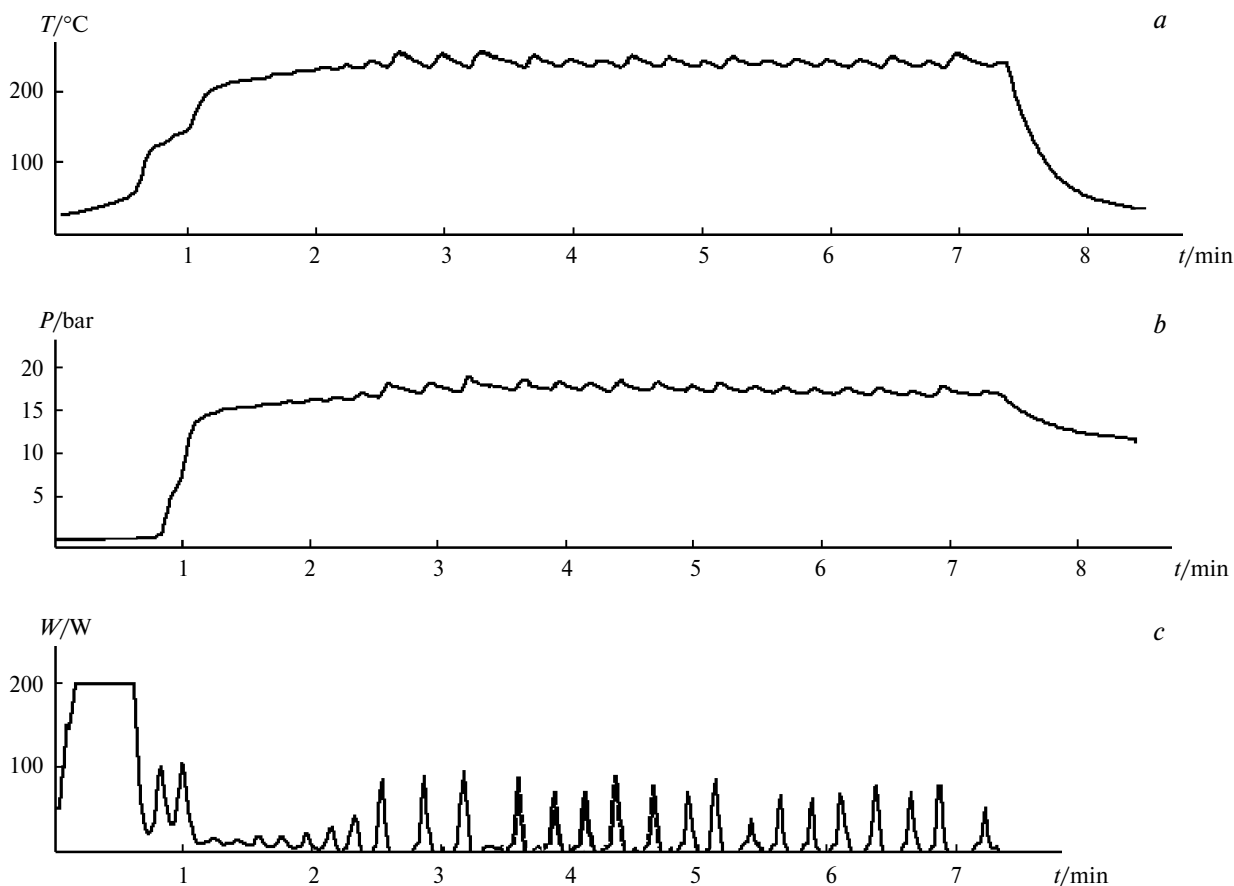

Fig. 1. Dynamics of the changes in temperature (*a*), excessive pressure (*b*), and power of microwave irradiation (*c*) in the solid-phase synthesis of rhodium(III) tris-acetylacetonate from rhodium(III) chloride and potassium acetylacetonate.

trichloride leads to its partial or complete depolymerisation, which increases the yield and the selectivity of the reaction leading to the formation of a desired product. A traditional method for the activation of such metal chlorides of polymeric structure consists in their preliminary reflux in water over a long period of time (up to 40 h).[6,7] The MW-activation can considerably shorten the time for depolymerisation. In our case, the synthesis was carried out in both organic solvent (Schemes 1 and 2) and aqueous medium (see Scheme 2).

Scheme 2

$$MCl_3 \cdot xH_2O + 3\ Hacac + 3\ NaOH \longrightarrow$$

$$\longrightarrow M(acac)_3 + 3\ NaCl + (3 + x)\ H_2O$$
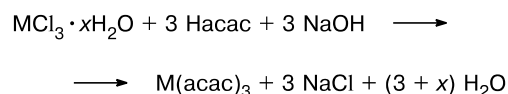
Experiments in the liquid-phase systems with organic solvents were carried out only in order to obtain $Rh(acac)_3$. Acetylacetone and acetonitrile have been chosen as the solvents. Analysis by TLC showed that the use of the ligand as the organic phase did not lead to the formation of the target product, *i.e.*, $Rh(acac)_3$. Found (%): C, 48.7; H, 5.4. $C_{15}H_{21}O_6Rh$. Calculated (%): C, 45.0; H, 5.3. When MeCN was used as the liquid reagent, a mixture of products was obtained, one of which was the target product $Rh(acac)_3$. The system supposedly contained the intermediate forms, in which the incomplete substitution for the chlorine atom with the acetylacetonate ion took place with possible incorporation of the acetonitrile molecule into the internal coordination sphere of the metal, which was indicated by the elemental analysis data. Found (%): C, 44.1; H, 5.5; N, 1.7.

The synthesis in aqueous solutions resulted in the formation of only single product, *viz.*, $Rh(acac)_3$. In the first step, the aqueous solution of $RhCl_3 \cdot xH_2O$ was subjected to MW-heating to 100—120 °C for depolymerisation of rhodium trichloride (see Table 2). Then, excess of acetylacetone was added to the activated solution and the mixture was subjected to further MW-irradiation over 5—10 min. To shift the equilibrium toward formation of the product, a solution of sodium hydroxide in water was added to pH = 6—7. According to the TLC and elemental analysis data, the product isolated by filtration and without any further purification completely corresponded to $Rh(acac)_3$. Found (%): C, 45.8; H, 5.7. The highest yield after sublimation ($T = 170$—190 °C, $P = 5 \cdot 10^{-5}$ Torr) was 55%.

When ruthenium tris-acetylacetonate was synthesized in aqueous solutions, the higher yields of the final product were achieved. Ruthenium trichloride hydrate in water was preliminary activated at the temperature of 100 °C, followed by addition of excess of acetylacetone. The mixture was activated for 10—15 min, then, after addition of an alkaline solution, the mixture was further activated. The alkaline solution was added until complete neutral-

ization of acidity. According to the TLC and elemental analysis data, the product isolated by filtration and without any further purification completely corresponded to $Ru(acac)_3$. Found (%): C, 46.0; H, 5.7. $C_{15}H_{21}O_6Ru$. Calculated (%): C, 45.2; H, 5.3. The yield after sublimation ($T = 170$—190 °C, $P = 5 \cdot 10^{-5}$ Torr) was 85%.

It should be noted that the highest yields reported in the literature for $Ru(acac)_3$ (see Ref. 3) and $Rh(acac)_3$ (see Ref. 4) were 60 and 70%, respectively, whereas the shortest time for their synthesis was 8 and 30 h. Our studies showed that the process of preliminary MW-activation of the corresponding metal chlorides took 15—30 min and led to simplification of the isolation of platinum metal tris-acetylacetonates. The solid precipitates of chelates can be isolated by filtration, which do not require additional purification of the target product.

Synthesis of palladium bis-ketoiminate in liquid media. The methods developed by us for the synthesis of palladium(II) β-diketonates from preliminary obtained metal aqua ions in acid solutions in high yield[10−13] did not lead to the formation of the final products when the synthesis of ketoiminate derivative was attempted, since, as it was mentioned above, β-ketoimine underwent acid hydrolysis to be converted to β-diketone at pH 2—3. Therefore, a new procedure was developed for the synthesis of compounds of this class, which was based on the reaction of $PdCl_2$ and the ligand in ammonia (Scheme 3).

Scheme 3

$$PdCl_2 \xrightarrow{\ i\ } [Pd(NH_3)_4]Cl_2 \xrightarrow{+3\ HL,\ pH\ =\ 8—9}$$

$$\longrightarrow Pd(i\text{-}acac)_2$$
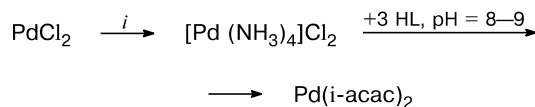
i. Excess of NH_3 (solution).

The reaction proceeded through the step of the formation of the intermediate colorless complex $[Pd(NH_3)_4]Cl_2$ in the solution, which further reacted with the ligand. In this case, the isolation of the precipitate of $Pd(i\text{-}acac)_2$ began at pH 8—9, the chelate complex was formed slowly, the reaction lasted no less than 5 h. The intermediate tetraminepalladium chloride is stable only in alkaline medium and at a decreased pH of the solution is easily converted to the low-soluble *trans*-$[Pd(NH_3)_2Cl_2]$. Therefore, to obtain high yield of chelate palladium complex, the reaction was necessary to carry out under conditions excluding the formation of the side product *trans*-$[Pd(NH_3)_2Cl_2]$, which, forming a precipitate, removes palladium from the reaction mixture thus causing a decrease in the yield of $Pd(i\text{-}acac)_2$. The yields of palladium ketoiminate derivatives vary in the range of 60—75%. In the case of MW-irradiation, the reaction reached completion within several minutes, in this case, with the concentration of the starting palladium chloride being the same,

the increase in the activation temperature resulted in the increase in the yield of the target product and the decrease in the experimental time to several minutes (see Table 2).

A typical dynamics of the changes in the experimental parameters of the MW-synthesis of palladium bis-ketoiminate in solution recorded by the Synergy program is shown in Fig. 2. When the appropriate temperature was reached, the MW-power was automatically decreased to the level of 10—20% from the initial value. The excessive pressure recorded was a result of overheating the aqueous solution of reagents (higher than water boiling point).

According to the TLC and elemental analysis data, the product isolated by filtration and without any further purification completely corresponded to Pd(i-acac)$_2$. Found (%): C, 39.7; H, 5.2; N, 9.2. $C_{10}H_{16}N_2O_2Pd$. Calculated (%): C, 39.6; H, 5.3; N, 9.3. The highest yield after sublimation ($T = 170$—190 °C, $P = 5 \cdot 10^{-3}$ Torr) was 80%.

In conclusion, we developed laboratory environmentally friendly procedure for the MW-synthesis of ruthenium(III) and rhodium(III) tris-acetylacetonates and palladium(II) bis-ketoiminate in aqueous solutions, which allowed us to obtain them in good yields by a considerably simplified synthetic procedure and decrease the experimental time down to several minutes. The solid precipitates of chelates can be isolated by filtration without additional purification of the target products. The processes for the synthesis of compounds under MW-heating were studied with a precise monitoring of parameters and with the use of different versions of the synthesis: both the solid-phase and in solutions. It was found that in the solid-phase systems, the preparation of the target product was hindered: the processes of decomposition of both the starting reagents and the products of the synthesis took place in the system; one of the reasons of which was the formation of the surface and bulk high-frequency discharges. Thus, it was shown that the efficiency of MW-synthesis increased when the liquid-phase mixture of reagents was used.

Experimental

The following solvents and reagents of reagent, high purity, and analytical grade were used: distilled water, potassium and sodium hydroxides, diethyl ether, chloroform, toluene, and 25% aqueous ammonia. The chlorides $RhCl_3 \cdot xH_2O$ (the content of Rh was 36%), $RuCl_3 \cdot xH_2O$ (the content of Ru was 42%), $PdCl_2$ (the content of Pd was 60%) purchased from Krastsvetmet were
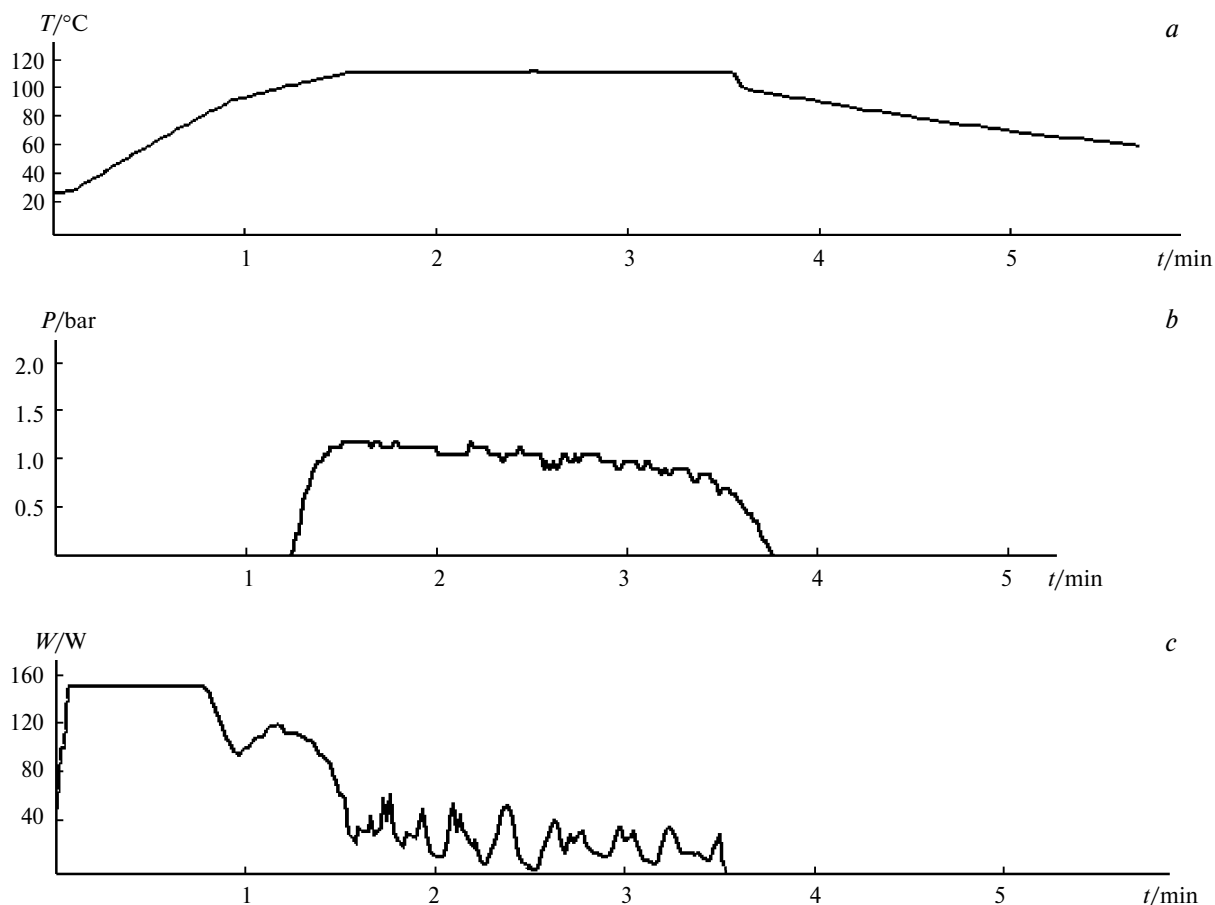

Fig. 2. Dynamics of the changes in temperatures (*a*), excessive pressure (*b*) and power of microwave irradiation (*c*) in the synthesis of palladium bis-ketoiminate in solution.

used as the starting compounds. Potassium acetylacetonate was synthesized according to the procedure described earlier:[16] stoichiometric amount of acetylacetone was added dropwise to a solution of potassium hydroxide in ethanol with heating and constant stirring; after the reaction reached completion, a pearl precipitate formed was filtered off using paper filter and dried in air. According to the IR spectroscopic data and elemental analysis, the product under these conditions is semi hydrated potassium acetylacetonate (Kacac·0.5H$_2$O). Found (%): C, 40.5; H, 5.6. C$_5$H$_8$O$_{2.5}$K. Calculated (%): C, 40.8; H, 5.4. Ketoimine was synthesized according to the known procedure[12] by the reaction of acetylacetone with aqueous solution of ammonia, the ketoimine formed was extracted with toluene.

The reaction systems were activated on a CEM Explorer 48 MW-installation (USA), which was a combination of a Discover S-class reaction module and automatic sample loading-unloading module.

The installation was additionally equipped with a digital video camera for the visual monitoring and video recording reaction systems in the process of the MW-irradiation. The operating system also contained 10- and 35-mL vials (mini-reactors) to function at an increased (up to 20 atm) pressure.

The maximal power of the MW-irradiation was 300 W, the power was regulated with the discreteness of 1 W. An IR sensor of temperature with the range of measured temperatures up to 300 °C was incorporated into the system, the compositions under study could be magnetically stirred with different intensity, that increased homogeneity of the MW-heating of reaction mixtures.

The system had convenient for users interface, was connected through a network cable to computer with the Synergy licensed software to control the experiment and record the experimental data. The simultaneous control of MW-power, temperature, and pressure enabled one to accurately reproduce conditions of the MW-reaction in subsequent experiments.

In the case of solid-phase systems (see Table 1), a mixture of solid MCl$_3$·xH$_2$O and Kacac·0.5H$_2$O was placed into an ampule with a heat-proof stopper and subjected to MW-activation. After that, the product of the synthesis was extracted with chloroform.

In the case of liquid-phase systems with organic solvents (see Table 2, entries *1—4*), we used MCl$_3$·xH$_2$O, Kacac·0.5H$_2$O or Hacac, alkali. Acetylacetone and acetonintrile were chosen as organic solvents.

Synthesis of M(acac)$_3$ in aqueous solutions (see Table 2, entries *5—12*). Water was added to a weighed amount of metal trichloride hydrate MCl$_3$·xH$_2$O in an ampule until the concentration of the solution reached 0.15 mol L^{-1}. The ampule was placed into the reactor of a MW-oven for preliminary depolymerisation of the starting salt. Then, a 5-fold excess of acetylacetone was poured into the ampule and the mixture was subjected to MW-irradiation once more. After an appropriate time (see Table 2), the experiment was stopped and a concentrated solution of stoichiometric amount of potassium/sodium hydroxide was added (to pH = 6—7). The product was isolated either by filtration, or by extraction with chloroform with subsequent evaporation of the solvent. A precipitate formed was filtered off and dried in air.

Synthesis of Pd(i-acac)$_2$ in aqueous solutions (see Table 2, entries *13—17*). Palladium dichloride PdCl$_2$ (0.2 g, 1.13 mmol) was added to an aqueous solution of concentrated ammonia (25 : 25 mL), the mixture was heated in a water bath until the salt was completely dissolved and a colorless solution obtained. Further, the solution of [Pd(NH$_3$)$_4$]Cl$_2$ was transferred into an am-

pule, which was placed into the reactor of a MW-oven, followed by the addition of excess of ketoimine dissolved in water, and the mixture was subjected to MW-irradiation. After an appropriate time (see Table 2), the experiment was stopped and the product was isolated either by filtration, or by extraction with toluene with subsequent evaporation of the solvent.

Identification of products. Analysis by TLC was carried out on Silufol plates precoated with SiO$_2$, eluent chloroform—diethyl ether (19 : 1). The comparison compounds were M(acac)$_3$ (M = Rh, Ru) or Pd(i-acac)$_2$ obtained by us according to the procedures developed in the A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences[8—11] and subjected to purification by sublimation in vacuum gradient oven at P = 10^{-2} Torr and T = 150—180 °C. Elemental analysis was carried out on a Euro EA 3000 CHN-analyzer.

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