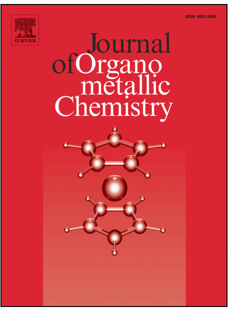

Polymorphism and thermodynamic properties of chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex

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Graphical abstract: pictogram

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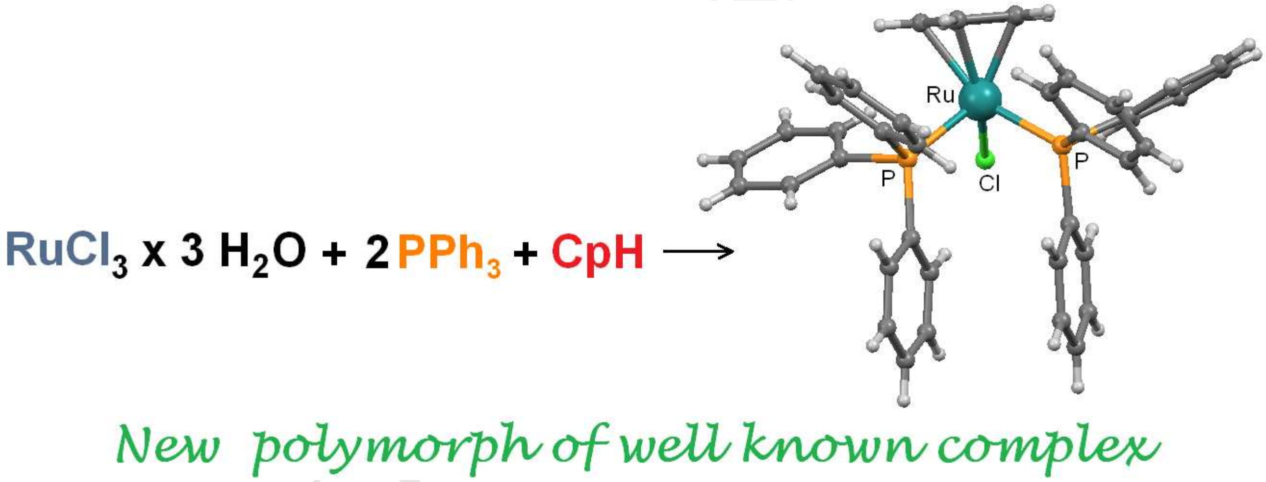
Elena V. Gorbachuk[a,b,] Elena K. Badeeva[a], Ruzal G. Zinnatullin[a,b], Pavel O. Pavlov[a,b], Alexey B. Dobrynin[a], Aidar T. Gubaidullin[a], Marat A. Ziganshin[b], Alexander V. Gerasimov[b], Oleg G. Sinyashin[a], Dmitry G. Yakhvarov[a,b,*]

The graphical abstract pictogram.



New polymorph of well known complex

Polymorphism and thermodynamic properties of chloro(cyclopentadienyl)bis(triphenylphosphine)-ruthenium(II) complex

Elena V. Gorbachuk[a,b], Elena K. Badeeva[a], Ruzal G. Zinnatullin[a,b], Pavel O. Pavlov[a,b], Alexey B. Dobrynin[a], Aidar T. Gubaidullin[a], Marat A. Ziganshin[b], Alexander V. Gerasimov[b], Oleg G. Sinyashin[a], Dmitry G. Yakhvarov[a,b,*]

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Keywords: cyclopentadienide-anion, polymorphism, ruthenium complexes, thermodynamic properties, triphenylphosphine

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ABSTRACT

A new crystalline polymorph of known chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex $[RuCl(PPh_3)_2(\eta^5-C_5H_5)]$ was obtained and characterized by various analytical methods including single-crystal and powder X-ray diffraction (XRPD) and differential scanning calorimetry (DSC) in combination with thermo-gravimetric analysis (TG-DSC). The obtained crystals of new polymorph are monoclinic, space group $P2_1/n$, with a = 11.125(4), b = 19.184(6), c = 15.946(5) Å, α = 90, β = 100.174(5), γ = 90, and Z = 4. It has been found that real melting point of the complex (M.p. = 252-253°C) can be determined only in inert atmosphere while an apparent melting is observed in the range 142-150°C due oxygen promoted oxidative dissociation of triphenylphosphine ligand.

1. Introduction

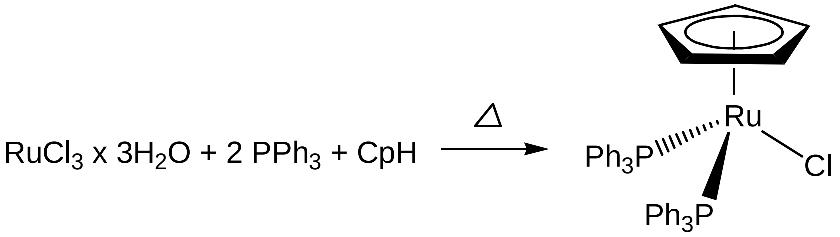
The ruthenium complexes based on cyclopentadienyl ligand are widely used in organic chemistry and have different applications as homo- and heterogeneous catalysts and useful materials [1-3]. The chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex $[RuCl(PPh_3)_2(\eta^5-C_5H_5)]$ (**1**) firstly prepared by Gilbert and Wilkinson [4] is one of the most investigated and useful for synthetic chemistry ruthenium compound [5-10]. However its solid state properties are an object of several contradictions [11-15]. According to the published literature data, the experimentally observed melting temperature of **1** has been found to be different. Thus, Bruce reported the melting point determined for this compound as 131-135°C [11] that is also supported by some textbooks [16]. Meanwhile, Wilczewski claimed that the melting at this temperature is occurring only in open capillary when the complex starts melting at 135-138°C and completely melted at 180-200°C, while the use of a sealed capillary results in melting point 236-248°C [14]. Unfortunately, up to present the driving forces of these incompatibilities have not been properly understood as yet. In order to clarify this long scientific discussion, we decided to synthesize and investigate the properties of this very well known organometallic specie in solid state.

In the present work we have found that complex **1** can be crystallized in different polymorphic states: previously reported polymorph **1a** [13] and synthesized by us new polymorph **1b** reported in this communication. The properties of each polymorph in solid state have been studied by single-crystal and powder X-Ray diffraction (XRPD) and differential scanning calorimetry (DSC) involving thermogravimetric and mass-spectrometry (TG/DSC/MS) analysis.

2. Results and Discussion

2.1. Syntheses

The known polymorph of the ruthenium complex $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ **1a** was obtained by previously described procedure [11] by heating of a mixture of aqueous ruthenium(III) chloride ($RuCl_3$ x $3H_2O$), triphenylphosphine, and freshly obtained cyclopentadiene by thermal cracking of its dimer in ethanol solution. The polymorph **1b** was obtained by fractional addition of the mentioned above aqueous ruthenium salt to a boiling ethanol solution containing cyclopentadiene and triphenylphosphine (Scheme 1). The crystals of both polymorphs **1a** and **1b** suitable for X-ray crystal structure analysis were obtained directly in the reaction medium without special recrystallization procedure.



1

Scheme 1. Synthesis of complex **1.**

2.2. Description of crystal structure

Both obtained polymorphs **1a** and **1b** were characterized by various methods, including X-ray crystallography (Fig.1). The X-ray crystal structure parameters obtained for **1a** were found identical to the previously described [13,15].

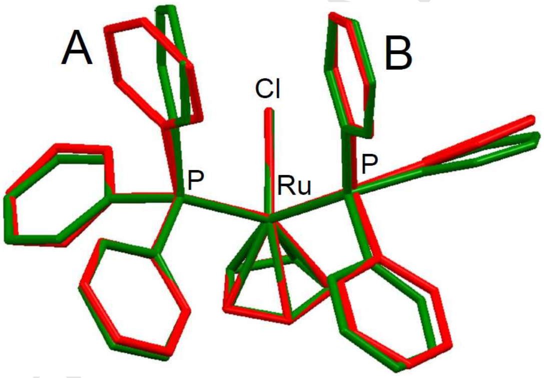


Fig.1. Overlay of the molecular structures of the complex units in **1a** (red) and **1b** (green). Hydrogen atoms have been omitted for clarity.

The comparison of the X-ray data parameters obtained for polymorphs **1a** and **1b** (Table 1) allowed us to find some differences in the structure of the complex **1** in solid state. According to the single-crystal X-ray structure analysis, main difference observed for the molecules **1a** and **1b** is the orientation of the phenyl groups of triphenylphosphine ligands (Fig.1). Thus, the longest distances between the carbon atoms of phenyl groups **A** and **B** in **1a** is 4.19 Å in comparison with the value 3.825(3)Å in **1b**. The angle of rotation of the benzene rings in **1a** is 28.76°, while it is significantly less in **1b** (8.55°). It means that the phenyl rings **A** and **B** of two triphenylphosphine ligands are almost parallel in **1b**. Moreover, in **1b** the formed complex structure angels P(1)RuP(2) 100.05°, P(1)RuCl 91.32° and P(2)RuCl 91.48° are different from the corresponding values reported for **1a** by Bruce et al (103.99°, 90.41° and 89.05°, respectively) [13] and Wilczewski et al (103.88°, 90.52° and 88.90° respectively) [15] due to presence of intramolecular π-π-interaction between the benzene rings of two PPh_3 ligands in the molecule of new polymorph **1b**.

The analysis of the intermolecular interactions in both crystals of **1a** and **1b** shows the presence of complex 3D-structure that arises from C-H…π-interactions and additionally from C-H…Cl^- in **1a** (Fig.2).

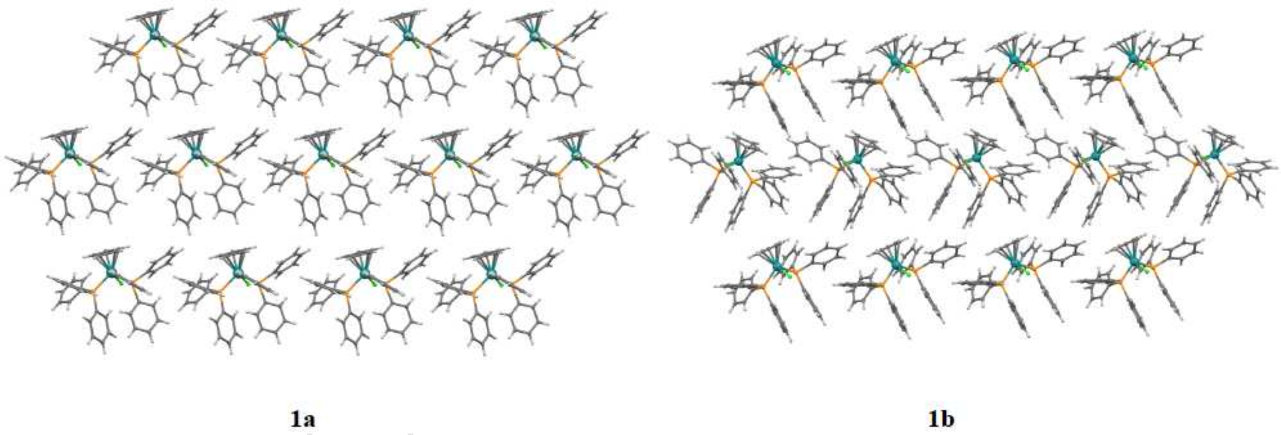

1a **1b**

Fig.2. Packing of the previously reported **1a** and new **1b** polymorphs.

Table 1. Parameters of the crystal cell and selected bond lengths (Å) and angles (°) for **1a** and **1b.**

	1a	**1b**
Crystal cell parameters		
Space group	P-1	$P2_1/n$
a	14.493(8)	11.125(4)
b	11.315(4)	19.184(6)
c	11.745(4)	15.946(5)
α	69.99(3)	90
β	84.67	100.174(5)
γ	67.27(3)	90
Z	2	4
Bond lengths		
Ru(1)-P(1)	2.3366	2.3202(14)
Ru(1)-P(2)	2.3353	2.3143(15)
P(1)-C(12)	1.8393	1.842(4)
P(2)-C(36)	1.8536	1.826(4)
Ru(1)-Cl(1)	2.4534	2.4622(14)
Bond angels		
P(1)-Ru(1)-P(2)	103.99	100.05(4)
Ru(1)-P(1)-C(12)	125.70	126.55(15)
Ru(1)-P(2)-C(36)	118.58	119.89(15)
Cl(1)-Ru(1)-P(1)	89.05	91.32(4)
Cl(1)-Ru(1)-P(2)	90.41	91.48(4)

2.3. X-ray powder diffraction (XRPD)

A thermal stability of both polymorphs was studied by XRPD at variable temperature up to 170°C. According to the obtained data for **1b** (Fig.3), the heating of the sample up to 150°C and subsequent cooling don't cause a substantial change in the total diffraction pattern which is clearly identified by the interference peaks corresponding to both polymorphs, though acquiring somewhat diffuse view as a result of the change in the crystallite size and the deformation of some long-range order therein. Further increasing of the temperature up to 170°C leads to amorphization of the sample and disappearance of all reflexes in the diffraction pattern of the crystal. This allows concluding that increasing of the temperature higher than 150°C leads to the destruction of this compound.

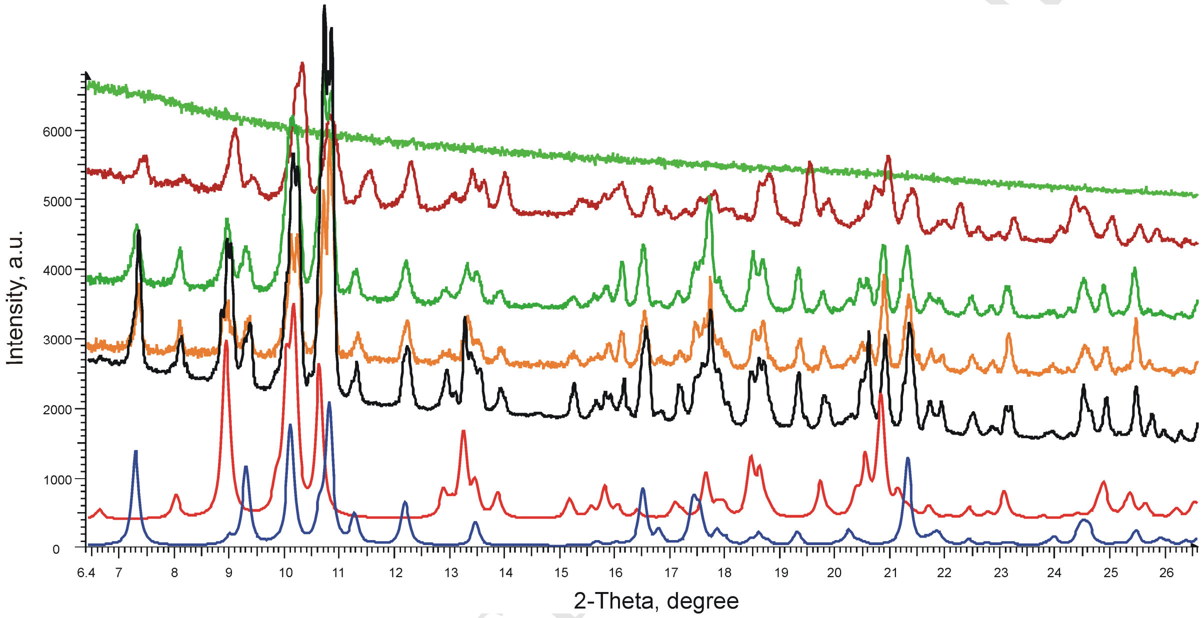


Fig.3. Experimental X-ray powder patterns for **1b** at room temperature (black curve) and after heating up to 100°C (orange curve), 130°C (green curve), 150°C (brown curve) and 170°C (pale green curve). At the bottom – theoretical XRD curve for polymorph **1b** (blue curve) and polymorph **1a** (red curve) calculated on the basis of the X-Ray data [13].

It is interesting to note that for the sample representing polymorph **1a**, the diffraction pattern remains unchanged up to temperature 150°C (Fig.4), but at this temperature additional interference peaks at the angles of 11.5, 12.3 and 19.4° 2θ have been observed. One would assume that at this temperature occurs partial transition to a polymorph **1b**, but in this case reflections in the scattering angles 7.3 and 9.4° 2θ on the diffraction pattern would be clearly observed.

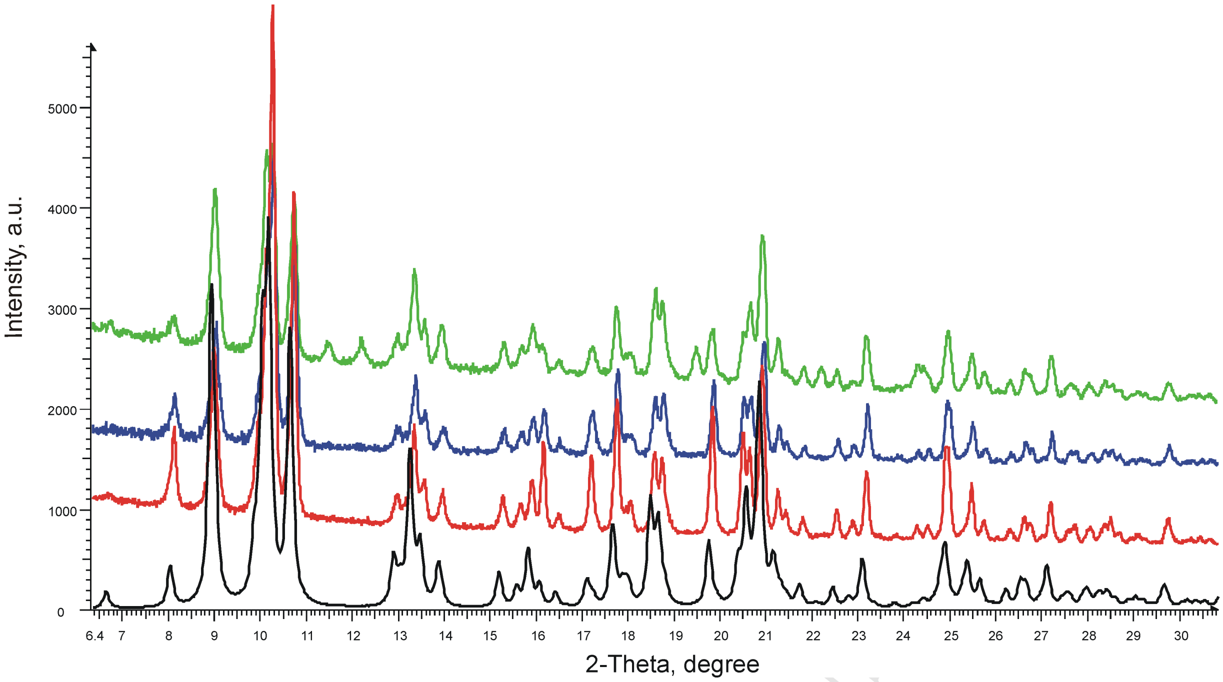


Fig.4. Experimental X-ray powder patterns for the sample **1a** at room temperature (red curve) and after heating up to 130° (blue curve) and 150° C (green curve). At the bottom - theoretical XRD curve for polymorph **1a** (black curve) and polymorph **1b** (brown curve) calculated on the basis of the X-Ray data [13].

The performed experiments allow concluding that oxygen has a crucial influence on the temperature of the observed phase transition. Thus, the solid-liquid transition observed in the presence of air in the range 140-145°C for both polymorphs is not real melting process. Indeed, the careful study of the solid-liquid transition at this temperature allows to determine the formation of colourless crystals formed by sublimation. Applying of the single crystal X-ray diffraction towards the analysis of the nature of the formed new crystals allows to conclude that these crystals are one of the crystalline form of triphenylphosphine oxide Ph_3PO (a = 29.120(2), b = 9.143(1), c = 11.252(1), Space group Pbca) [17], formed by oxygen promoted oxidative decoordination of triphenylphosphine ligand from the coordination sphere of ruthenium in complex **1** during experiment. Note, the literature melting point data obtained for Ph_3PO 155-158.8°C [18] is slightly higher than the temperature range of the destruction of the complex. Thus, the published by Bruce et al melting point for complex **1** 131-135°C [9, 10] is an apparent one and arises from the melting of triphenylphosphine oxide formed by oxidative decoordination of triphenylphosphine ligand from the ruthenium center initiated by heating in the presence of oxygen. And the real melting point can be determined only in inert (oxygen free) atmosphere (argon, dry nitrogen etc.).

2.4. Differential scanning calorimetry

Additional proof of the melting temperature range was obtained from DSC analysis. Thus, it was found that **1b** sample melts at 252°C. The experimentally found enthalpy of melting is ΔH = 46.5 kJ mol^{-1}. Moreover, the cooling of the molten complex results in formation of glass due glass transition at 93°C (cooling rate 10° min^{-1}). Second heating gives glass transition at T_g = 95°C, the cold crystallization of amorphous component with an onset at 161°C and M.p. = 241°C (ΔH = 41.9 kJ mol^{-1}). The second cooling gives crystallization in the range of 208-168°C (Fig.5).

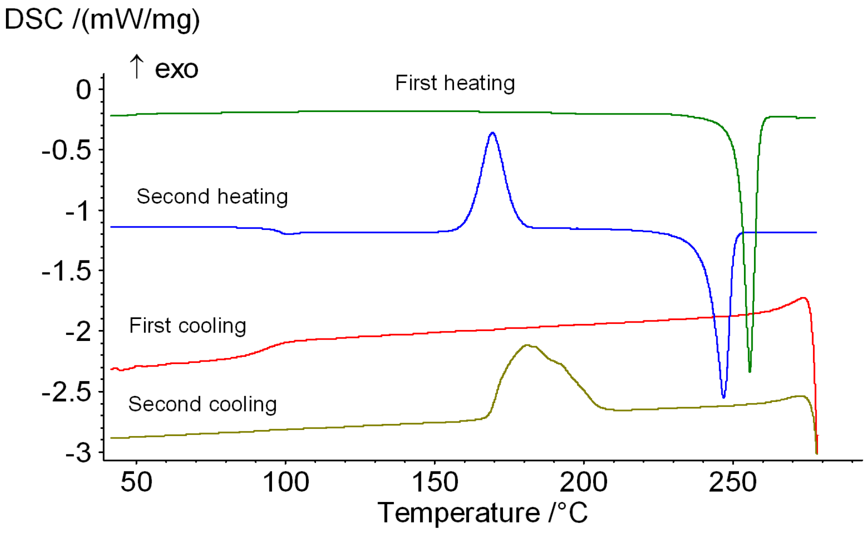


Fig.5. DSC curves of two consecutive heating and cooling runs for polymorph **1b**.

First heating of **1a** gives a slightly higher melting point 253°C and enthalpy of melting (ΔH = 47.8 kJ mol^{-1}). First cooling leads to partial crystallization in the range of from 180°C to 147°C (crystallization of about 50% molecules occurs) with less glass transition at 95°C at a cooling rate of 10° min^{-1}. Second heating gives glass transition at T_g = 95°C, the cold crystallization of amorphous component with an onset at 134°C followed by the melting beginning at 245°C (ΔH = 42.1 kJ mol^{-1}) (Fig.6).

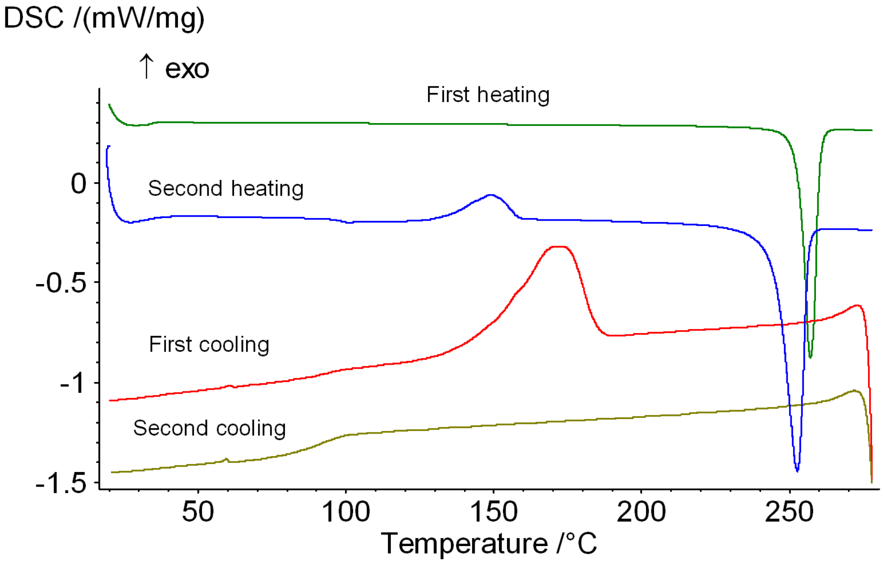


Fig.6. DSC curves of two consecutive heating and cooling runs for polymorph **1a**.

It should be noted that no polymorphic transition and no weight loss of the investigated samples have been observed in TG/DSC/MS experiments even by heating up to 250°C (see electronic supplementary material, Figs. S2 and S3).

2.5. Conclusions

Chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ forms two polymorphs displaying different crystal packing and physico-chemical properties. The observed polymorphism provides an opportunity to examine the thermodynamic properties depending on the complex structure and its thermal stability. The real melting point of the investigated complex can be determined only in inert atmosphere due possibility of oxygen promoted oxidative dissociation of triphenylphosphine ligand. These results nicely complement previously described thermal properties of the investigated $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ complex [11-15].

3. Experimental

3.1. General Procedures

Main manipulations and chemical reactions were carried out under an atmosphere of dry nitrogen. All solvents were purified and dried prior to use. Ethanol, petroleum ether and diethyl ether were dried with sodium followed by distillation under dry nitrogen. Ruthenium trichloride trihydrate ($RuCl_3 \cdot x\ 3H_2O$, Alfa Aesar), triphenylphosphine (Sigma-Aldrich) and dicyclopentadiene (Acros Organics) were commercial products.

NMR spectra were measured at ambient temperature on a Bruker MSL-500 (500.13 MHz, ^1H; 125.7 MHz, ^{13}C) and Bruker MSL-400 (161.97 MHz, ^{31}P) spectrometers in deuterated chloroform. IR spectra were recorded on a FTIR spectrometer Tensor 27 (Bruker) in the 4000-400 cm^{-1} middle IR range at an optical resolution of 4 cm^{-1}. Solid samples were prepared as KBr pellets. Far-IR spectra were recorded on a FTIR spectrometer IFS-66v/s (Bruker) in the 600-100 cm^{-1} range at an optical resolution of 4 cm^{-1}. Solid sample, mixed with nujol, was placed between polyethylene plates. ESI-MS measurements were performed using an AmazonX (Bruker Daltonics, Germany) ion trap mass spectrometer in positive mode in the mass range of 250–2000 Da. The optimized ESI-MS conditions were as follows: capillary voltage, –4.5 kV; nitrogen drying gas, 10 L min^{-1}, 300°C. Melting points were measured with Stanford Research System MPA-100 OptiMelt.

X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using Cu radiation (40 kV, 40 mA) monochromated by the curved Johansson monochromator (λCu $K_{\alpha 1}$ 1.5406 Å). Room-temperature data were collected in the reflection mode with a flat-plate sample. The samples were loaded on a standard zero diffraction silicon plate, which was kept spinning (15 rpm) throughout the data collection. Patterns were recorded in the 2θ range between 3^o and 90^o, in 0.008^o steps, with a step time of 0.3–5.0 s. Several diffraction patterns in various experimental modes were collected and summed for the sample. Processing of the obtained data performed using EVA software packages [19].

Differential scanning calorimetry (DCS) studies were performed with DSC 204 F1 Phoenix (Netzsch). Sample of ruthenium complex was placed in a standard aluminium crucible (40 μL) with lid having a hole with diameter of 0.5 mm. All experiments were made in argon flow (150 mL min^{-1}) with heating and cooling rates of 10°C min^{-1} [20]. Simultaneous method of thermogravimetry and differential scanning calorimetry (TG/DSC/MS) was used in combination with mass spectrometry of the evolved vapours. For this, a STA 449 C Jupiter thermoanalyzer (Netzsch) with a QMS 403 C Aëolos quadrupolarmass-spectrometer (Netzsch) were used. Experiments were conducted at a heating rate of 10°C min^{-1} in an argon flow of 75 mL min^{-1}.

*3.2. Synthesis of **1a** and **1b***

Polymorph **1a** was prepared according to the previously described method [11] using 1.31 g (5.0 mmol) of $RuCl_3$ x $3H_2O$, 4.00 g (15.2 mmol) of triphenylphosphine and 2.6 mL (30.9 mmol) of freshly distilled cyclopentadiene. This slightly modified procedure has been also used for the synthesis of polymorph **1b**. For preparation of **1b** a solution containing 1.31 g (5.0 mmol) of $RuCl_3$ x $3H_2O$ in 17.4 mL of ethanol was added in two steps (with interval 6 hours) to a boiling ethanol solution (180 mL) containing 4.00 g (15.2 mmol) of triphenylphosphine and 2.6 mL (30.9 mmol) of cyclopentadiene. After that the resulting mixture was additionally refluxing for 10 hour and slowly cooled to room temperature. After one night the orange crystals suitable for single-crystal X-ray analysis were collected and successively washed with ethanol (2 x 10 mL), petroleum ether (2 x 10 mL) and diethyl ether (2 x 10 mL). The obtained solid was dried in vacuum prior to NMR and IR studies (1.71 g, 47%). M.p. 245-252°C (capillary, argon). NMR (δ, chloroform-*d*): ^{1}H (500.13 MHz) 7.38 m, 7.25 m, 7.15 m (30H, $P(C_6H_5)_3$), 4.11 (s, 5H, C_5H_5); $^{13}C\{^1H\}$ (125.7 MHz) 138 (t, $^1J_{CP}$ = 19.1 Hz, ipso-C_6H_5), 133.8 (t, $^2J_{CP}$ = 5.0 Hz, o-C_6H_5), 128.6 (s, p-C_6H_5), 127.5 (t, $^3J_{CP}$ = 4.7 Hz, m-C_6H_5), 81.4 (t, $^2J_{CP}$ = 2.3 Hz, C_5H_5); $^{31}P\{^1H\}$ (161.9 MHz) 39.9 (s). IR (cm^{-1}, KBr): 1586 (w), 1571 (w), 1480 (m), 1433 (s), 1182 (w), 1158 (w), 1089 (m), 998 (w), 834 (m), 804 (w), 749 (m), 695 (s), 519 (s). IR (cm^{-1}, nujol): 277 (m) (Ru-Cl); ESI-MS, m/z: $[Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)]^+$ 691.2. $C_{41}H_{35}ClP_2Ru$ (M = 726.19 g mol^{-1}): calcd: C, 67.81; H, 4.86; Cl, 4.88; P, 8.53; Ru, 13.92; found: C, 67.94; H, 5.09; Cl, 4.99; P, 8.11; Ru, 13.87.

Acknowledgments

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Appendix A. Supplementary material

For detailed procedure of the X-ray crystal structure determination of **1b**, see Online Supplementary Materials. CCDC 1438379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Highlights

Polymorphism and thermodynamic properties of chloro(cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) complex

Elena V. Gorbachuk[a,b], Elena K. Badeeva[a], Ruzal G. Zinnatullin[a,b], Pavel O. Pavlov[a,b], Alexey B. Dobrynin[a], Aidar T. Gubaidullin[a], Marat A. Ziganshin[b], Alexander V. Gerasimov[b], Oleg G. Sinyashin[a], Dmitry G. Yakhvarov[a,b,*]

Highlights.

► New polymorph of known chloro(cyclopentadienyl)-bis(triphenylphosphine)ruthenium(II) complex $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ has been synthesised and fully characterized. ► The real melting point of $[RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ complex has been determined. ► An oxygen promoted oxidative dissociation of triphenylphosphine ligand was observed.