



**M.V. Lomonosov Moscow State Academy
of Fine Chemical Technology**

(Department of chemistry and technology of rare
elements and materials for electronic technique)



**A.N. Nesmeyanov Institute of Organoelement
Compounds Russian Academy of Sciences**

(Laboratory of Organofluorine Compounds)

**Complexes of Rhenium with
 β -diketones (synthesis and properties).**

A.I. Irtegov, M.A. Kurykin, V.N. Khrustalev,

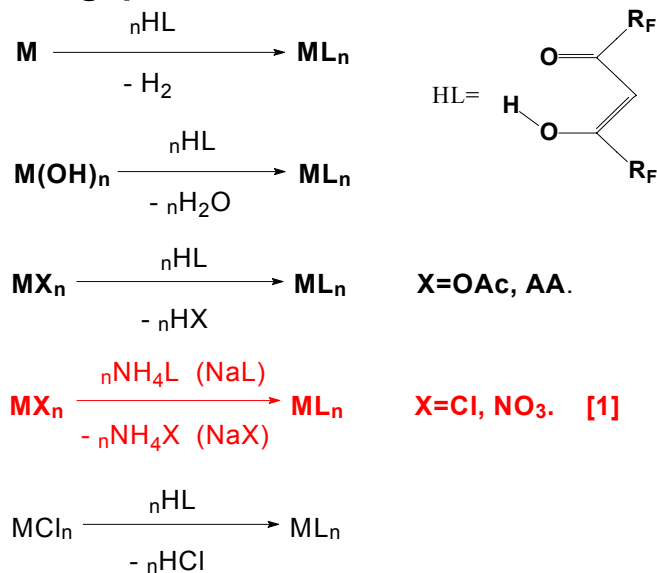
E.E. Nikishina and D.V. Drobot

ISTR - 2011 Moscow, Russia

Compound	Propertys		
	Lattice parameter	Colour	Solubility
$\text{ReCl}_2(\text{CF}_3\text{COCHCOCH}_3)(\text{PPh}_3)_2$		purple red (needles) [1]	•soluble in C_6H_6 •dissoluble in light petroleum 30-400C [1]
$\text{ReCl}_2(\text{CF}_3\text{COCHCOCF}_3)(\text{PPh}_3)_2$		deep blue (needles) [1]	•soluble in C_6H_6 •dissoluble in light petroleum 30-400C [1]
$\text{Re}(\text{CF}_3\text{COCHCOCF}_3)_3$	syngony hexagonal $a = 18.44(1) \text{ \AA}$, $c = 12.13(1) \text{ \AA}$, $Z = 6$	Dark purple [2] Black needles [3]	•soluble in the most organical solvents •dissoluble in water. [2]

1. Grove D. E and others // J.Chem. Soc., 1965, **77**, 490-494
2. Courier W. D. and others // Canad. J. Chem., 1972, **50**, 8-17
3. Anderson H.J., Brenner A. //J. Electrochem. Soc., 1969, **116**, 513.

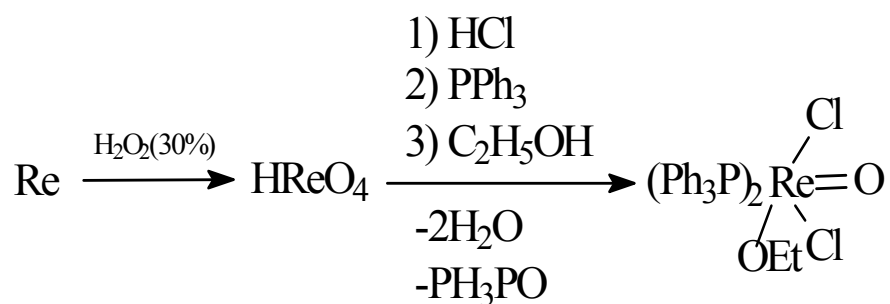
The methods of syntheses of fluorine-containing β -diketonates of transition metals.



1. Anderson H.J., Brener A. //J. Electrochem. Soc., 1969, **116**, 513.

3

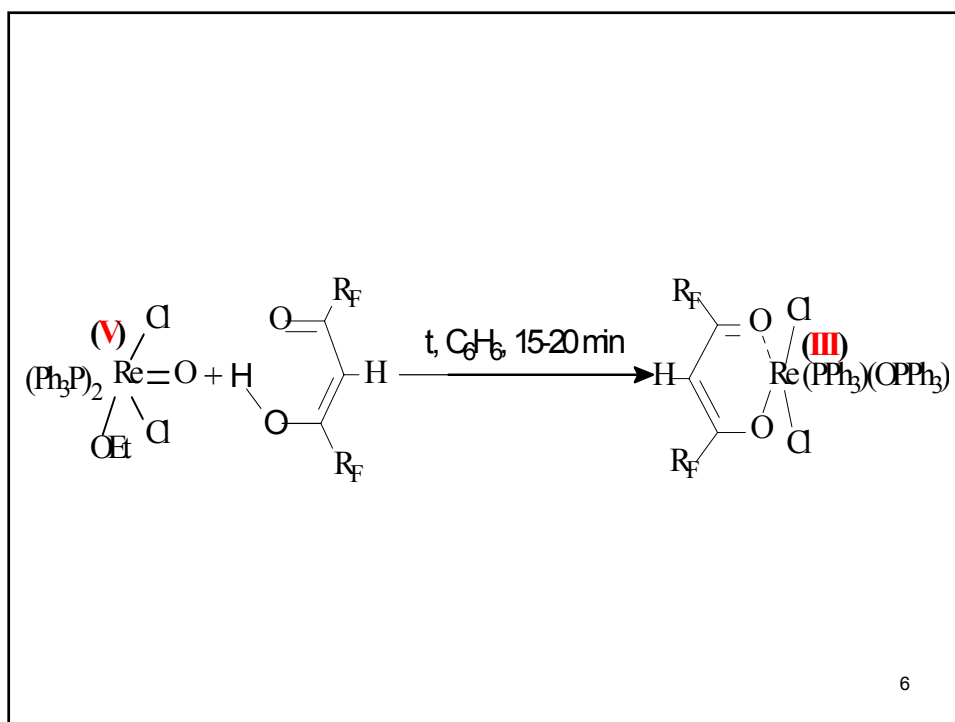
Synthesis oxodichloroethoxybis (triphenylphosphine) rhenium (V)



4

General formula	R _F	Name	Identification code
	CF ₃	Dichloro-(1,1,1,5,5,5-hexafluoro-2,4-pentanedione)-(triphenylphosphine oxide)(triphenylphosphine) rhenium (III)	IIa
	C ₂ F ₅	Dichloro-(1,1,1,2,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione)-(triphenylphosphine oxide)(triphenylphosphine) rhenium (III)	IIb
	C ₃ F ₇	Dichloro-(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedione)-(triphenylphosphine oxide)(triphenylphosphine) rhenium (III)	IIc
	C ₄ F ₉	Dichloro-(1,1,1,2,2,3,3,4,4,8,8,9,9,10,10,11,11,11-octadecafluoro-5,7-decanedione)-(triphenylphosphine oxide)(triphenylphosphine) rhenium (III)	IId
	CF ₃ CF- C ₃ F ₇ O-	Dichloro-(1,3-bis(3-oxoperfluoro-2-hexil)-1,3-propanedione)-(triphenylphosphine oxide)(triphenylphosphine) rhenium (III)	IIe

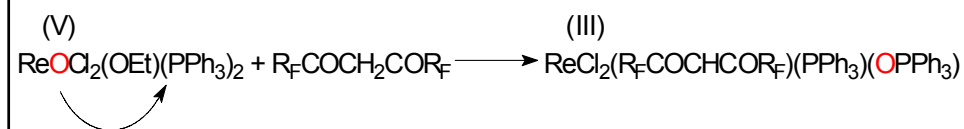
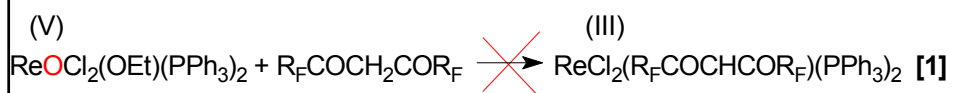
5



The data of elemental analysis of all obtained complexes

Compound	Calculated					Found					T _m ^a °C	Yield, %
	C%	H%	Cl%	F%	P%	C%	H%	Cl%	F%	P%		
ReOCl ₂ (OEt)(PPh ₃) ₂ C ₃₈ H ₃₅ Cl ₂ O ₂ P ₂ Re	54.16	4.19	8.41	---	7.35	54.14	4.21	8.48	---	7.38	190	85
IIa C ₄₁ H ₃₁ Cl ₂ F ₆ O ₃ P ₂ Re	49.01	3.11	7.06	11.34	6.16	48.89	3.03	6.82	11.19	6.08	200	90
IIb C ₄₃ H ₃₁ Cl ₂ F ₁₀ O ₃ P ₂ Re	46.75	2.82	6.42	17.20	5.61	46.97	2.63	6.30	16.90	5.58	194	93
IIc C ₄₅ H ₃₁ Cl ₂ F ₁₄ O ₃ P ₂ Re	44.86	2.59	5.88	22.08	5.14	44.92	2.47			5.10	160	91
IId C ₄₇ H ₃₁ Cl ₂ F ₁₈ O ₃ P ₂ Re	43.26	2.39	5.43	26.20	4.74	43.11	2.33	5.22	25.96	4.77	171	88
IIe C ₄₉ H ₃₁ Cl ₂ F ₂₂ O ₃ P ₂ Re	40.96	2.17	4.93	29.09	4.31	40.74	2.11	4.89	28.51		155	88

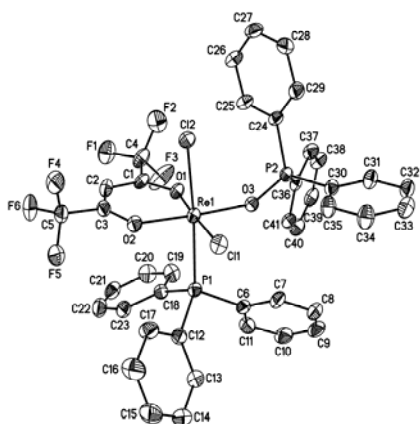
7



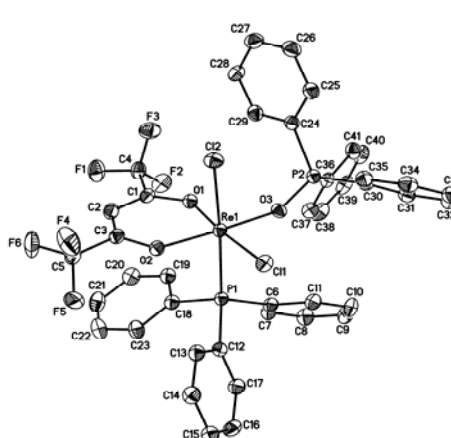
1. Grove D. E and others // J.Chem. Soc., 1965, 77, 490-494

8

Molecular structures of IIa (CF₃).



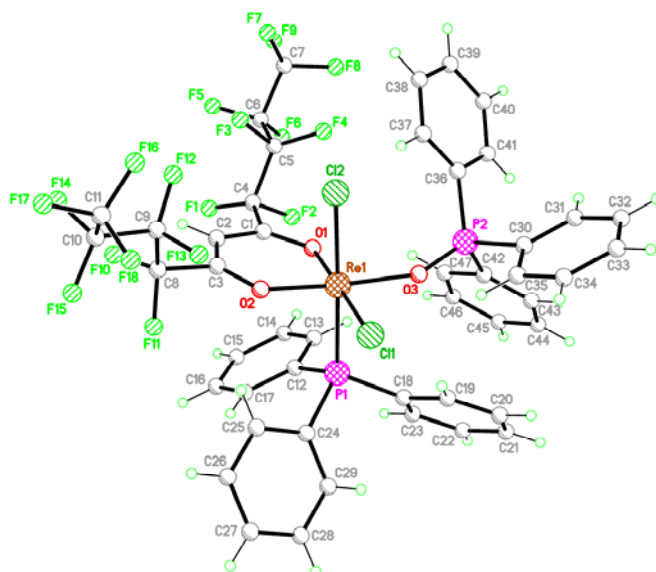
Monoclinic syngony.
 Spatial group: C2/c
 $a = 42.357(2) \text{ \AA}$ $a = 90^\circ$
 $b = 10.4898(6) \text{ \AA}$ $\beta = 106.851(1)^\circ$
 $c = 18.4349(10) \text{ \AA}$ $\gamma = 90^\circ$
 $V = 7839.3(8) \text{ \AA}^3$, $Z = 8$
 The crystals are grown from acetone



Monoclinic syngony.
 Spatial group: P2₁/n
 $a = 12.6176(9) \text{ \AA}$ $a = 90^\circ$
 $b = 23.9022(17) \text{ \AA}$ $b = 107.490(1)^\circ$
 $c = 13.4285(10) \text{ \AA}$ $\gamma = 90^\circ$
 $V = 3862.7(5) \text{ \AA}^3$, $Z = 4$
 The crystals are grown from ethanol

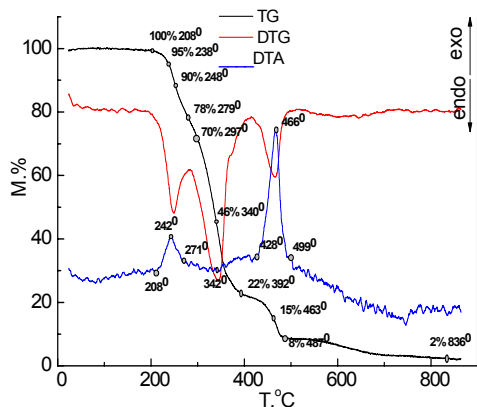
9

Molecular structure of IIc (C₄F₉).



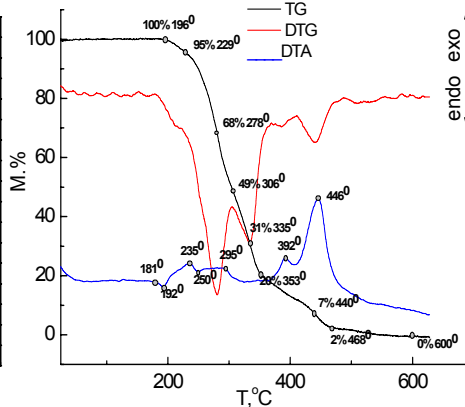
10

Thermogravimetric analysis of complex IIa (CF₃) in the air



$T_{\text{initial}} = 24^{\circ}\text{C}$, $T_{\text{final}} = 864^{\circ}\text{C}$, $\Delta M = 98\%$

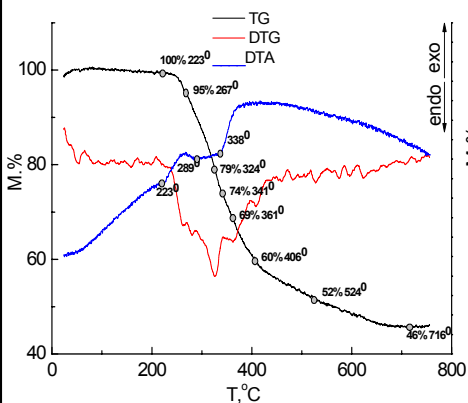
Thermogravimetric analysis of complex IIb (C₄F₉) in the air



$T_{\text{initial}} = 24^{\circ}\text{C}$, $T_{\text{final}} = 628^{\circ}\text{C}$, $\Delta M = 100\%$

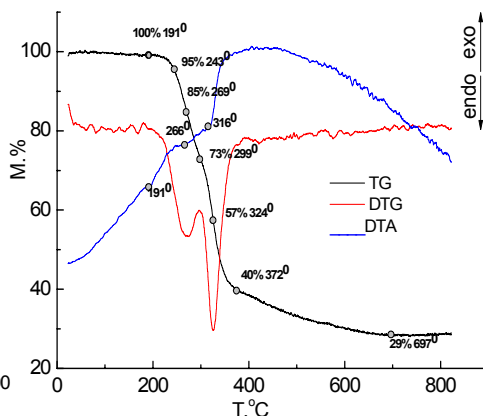
11

Thermogravimetric analysis of complex IIa (CF₃) in the argon



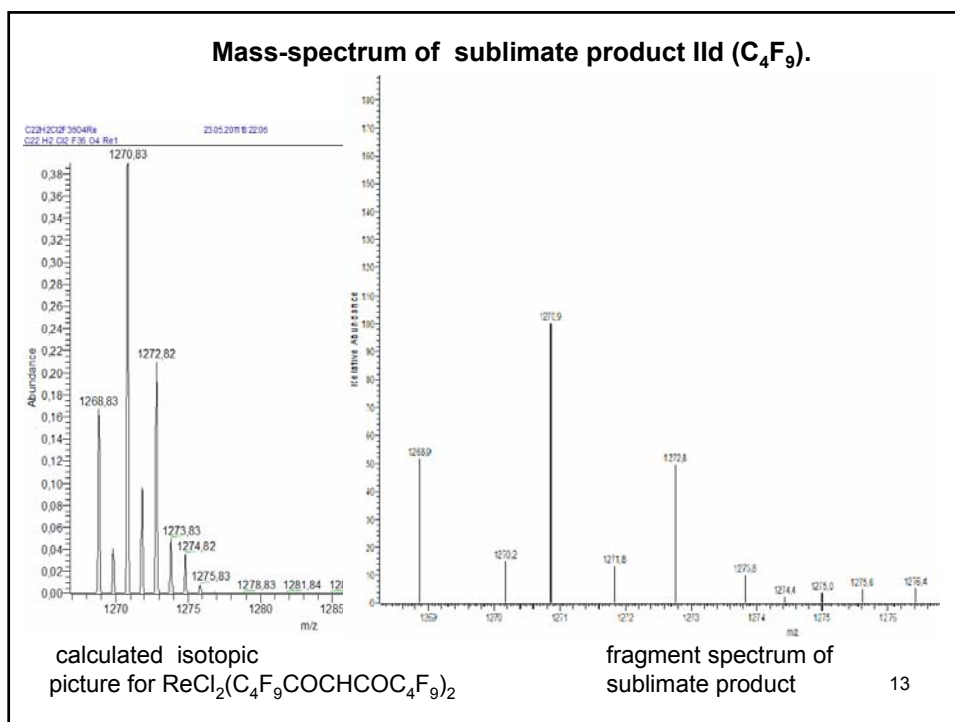
$T_{\text{initial}} = 23^{\circ}\text{C}$, $T_{\text{final}} = 756^{\circ}\text{C}$, $\Delta M = 54\%$

Thermogravimetric analysis of complex IIb (C₄F₉) in the argon



$T_{\text{initial}} = 23^{\circ}\text{C}$, $T_{\text{final}} = 822^{\circ}\text{C}$, $\Delta M = 71\%$

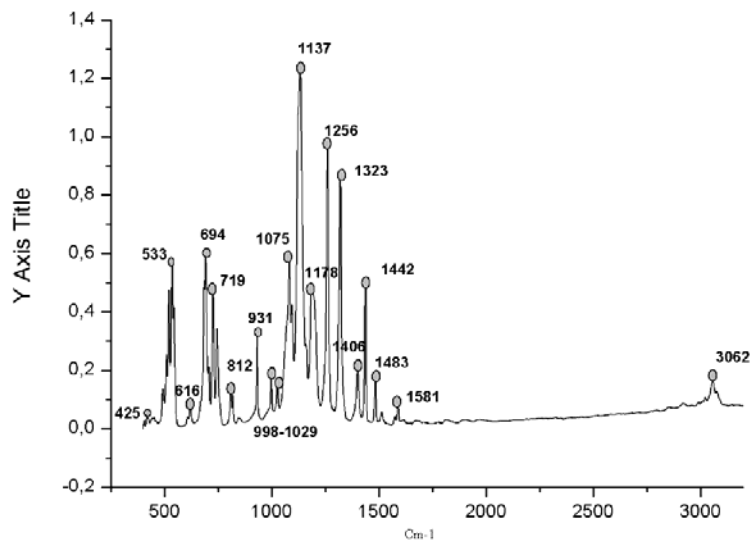
12



Conclusion:

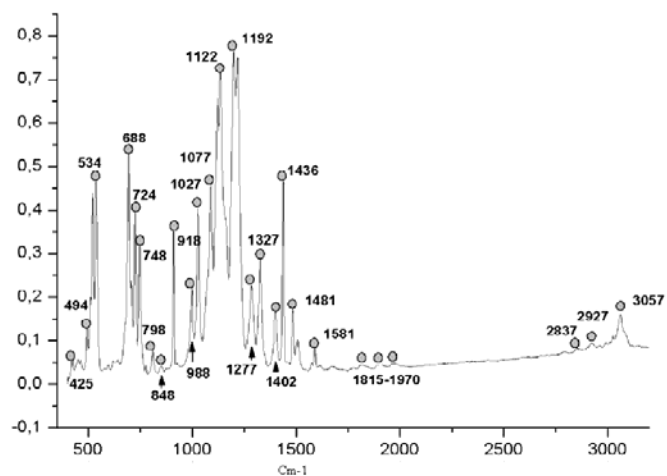
1. Were obtained five new fluorine-containing complexes of rhenium. Composition and structure of these compounds was confirmed by the data of elemental analysis, X-Ray crystal structure analysis and mass-spectrometry method; thermal properties were examined.
2. It is stated that the fluorinated complexes can pass the vapour phase and can be used for the obtaining of rhenium film by methods of CVD.

ИК-спектр соединения IIa.



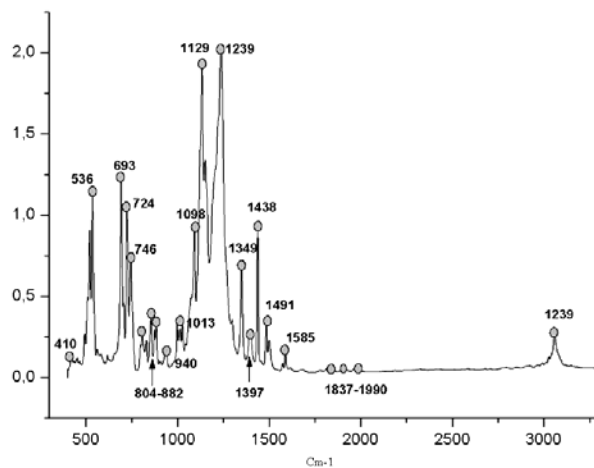
15

ИК-спектр соединения IIb.



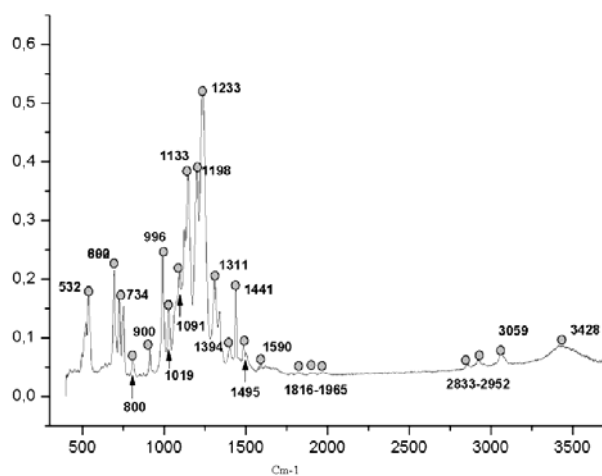
16

ИК-спектр соединения **II d.**



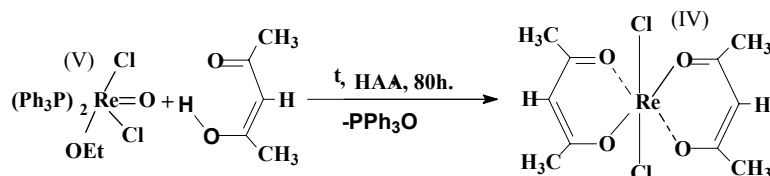
17

ИК-спектр соединения **II e.**



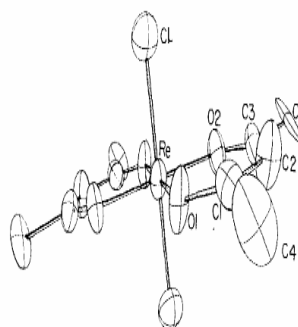
18

Synthesis of dichlorobis(pentane-2,4-dionato) rhenium (IV)



Parameters of cell:

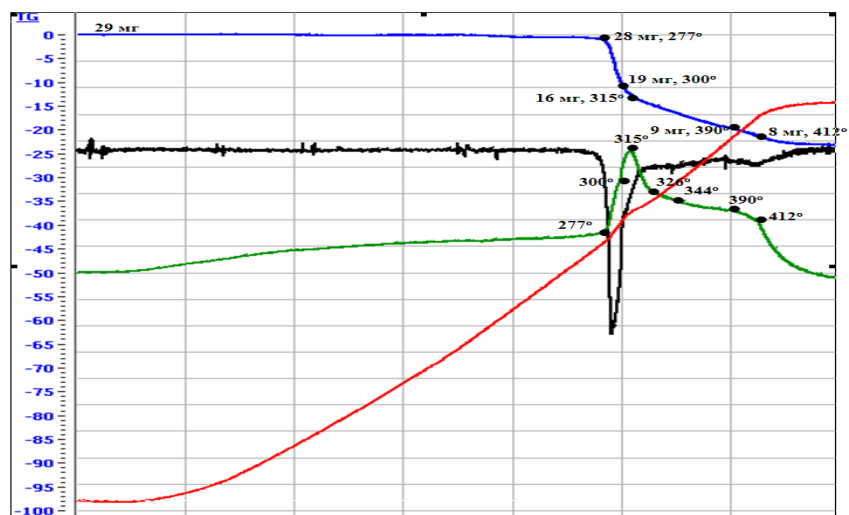
- syngony triclinic
- (deformed octahedron, pulled in the line of Re-Cl)
- $a = 8.032(4) \text{ \AA}$
- $b = 8.344(6) \text{ \AA}$
- $c = 7.429(6) \text{ \AA}$
- $\alpha = 118.1(2)^\circ$
- $\beta = 92.3(2)^\circ$
- $\gamma = 55.5(2)^\circ$
- $V = 334.0 \text{ \AA}^3$
- $Z=1$
- P-1 spatial group



19

Brown I.D and others // Canad. J. Chem., 1973, 51, 2073-2076

Thermogravimetric analysis of **complexes** $\text{ReCl}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ in the air.



$M_{\text{initial}} = 29,0 \text{ mg}$, $M_{\text{final}} = 6,5 \text{ mg}$ (22,4%), loss in weight- 22,5 mg (77,6%).
 $T_{\text{initial}} = 22^\circ\text{C}$, $T_{\text{final}} = 420^\circ\text{C}$

20