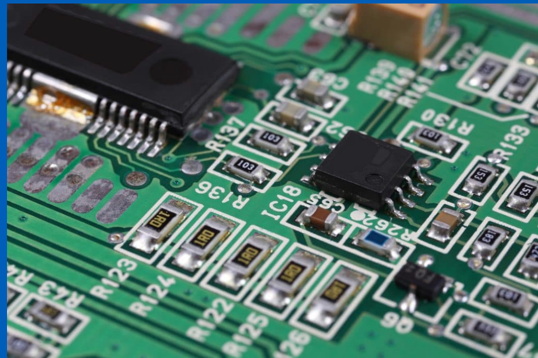


Chip resistor

Pen nib

Jewelry

anode of electrochemical cells

A?
Aalto University

Ruthenium

Miklós Nemesszeghy & Timo de Jonge

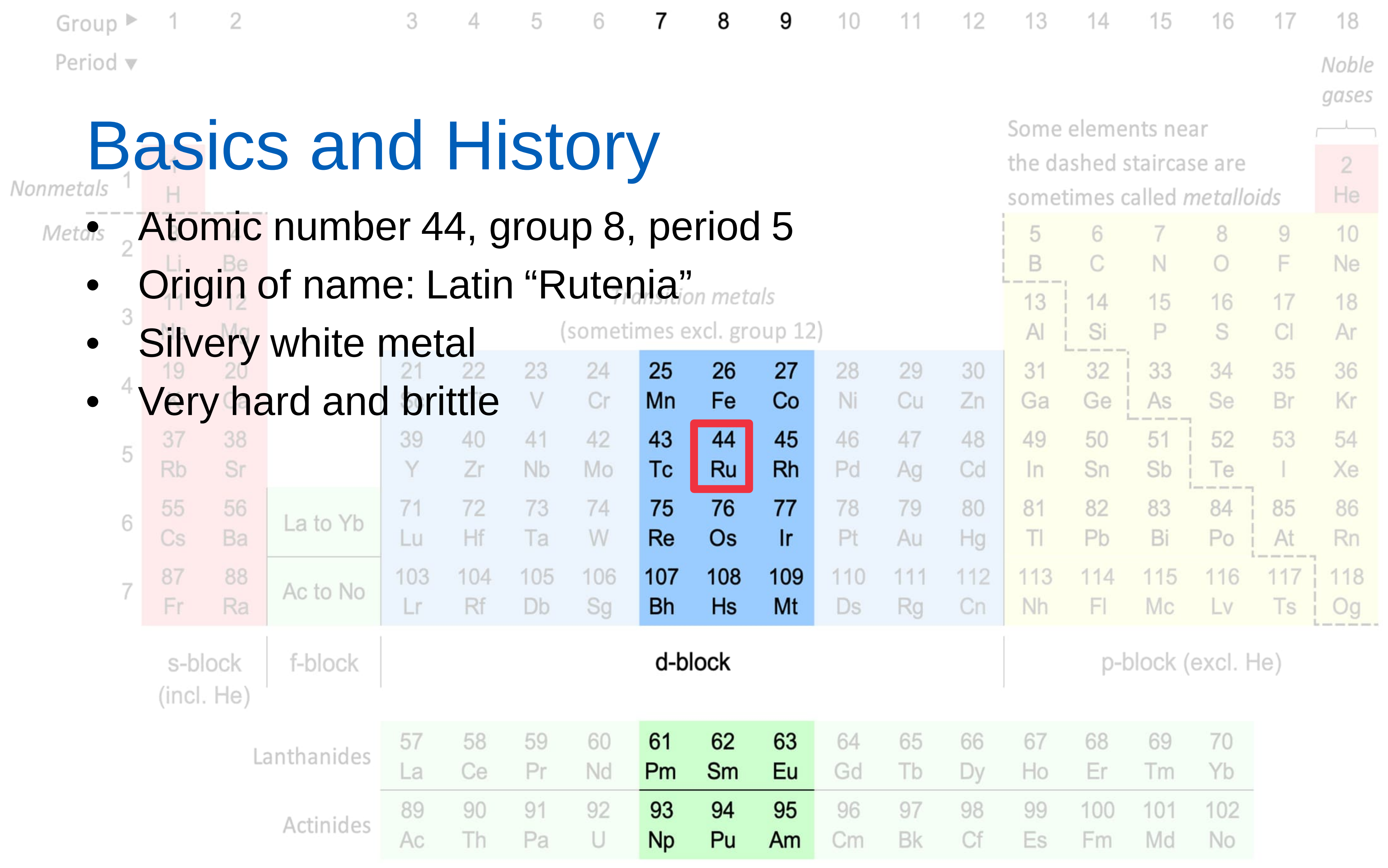
CHEM-4130 Chemistry of the elements
27.9.2023

Luciteria.com, R.Suarez

Contents

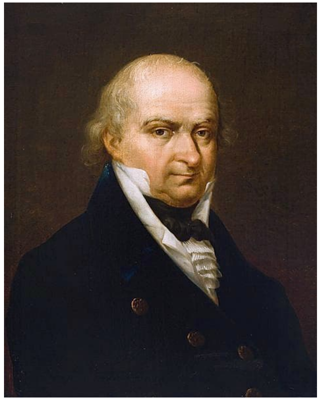
Basics and History

- Atomic number 44, group 8, period 5
- Origin of name: Latin “Rutenia”
- Silvery white metal
- Very hard and brittle



Discoveries

Native south Americans



Jędrzej Andrei Śniadecki
1807-1808

Vesta -> vestium

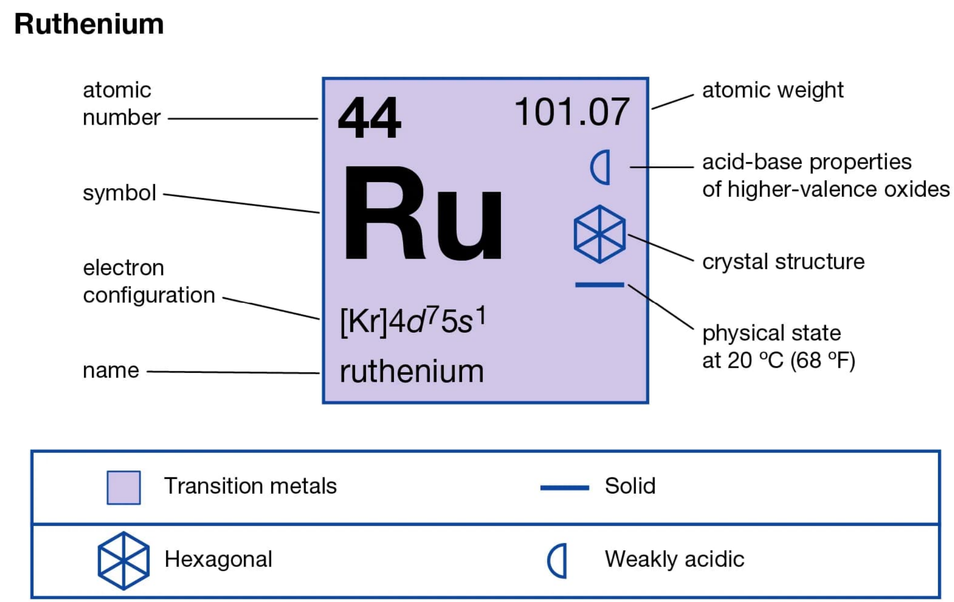
Gottfried Wilhelm Osann
1825

Ruthenium

Karl Karlovich Klaus
1844

The Bogota Post, 2023

Chemistry of Ru



encyclopædia britannica, inc

Chemical properties

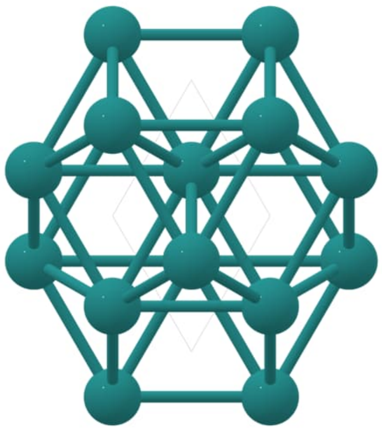
- Electron configuration: [Kr] $4d^7\ 5s^1$
  - Anomaly in its group
- Stable oxidation states: +III and +IV
- Can also be found in –II, +I, +II, +III, +IV, +V, +VI, +VII and +VIII
- Electronegativity: 2.2
- Reactivity:
  - Platinum group metal
  - Not oxidized by acids
  - “Attacked” by halogens and hydroxides:
    $Ru(s) + 3F_2(g) \rightarrow RuF_6(s)$

Chemical properties

- Hexagonal crystal structure: $P6_3/mmc$
- Melting point: 2333 °C
- Atomic mass: 101.07 ± 0.02 u
- Atomic radius (in metallic form): 1.34 Å

Species	atomic/ionic radii (Å)
Ru(s)	1,34
Ru^{3+}	0,68
Ru^{4+}	0,62
Ru^{5+}	0,565
Ru^{7+}	0,38
Ru^{8+}	0,36

R. D. Shannon., 1976



From the Materials Project for Ru (mp-33) 2022

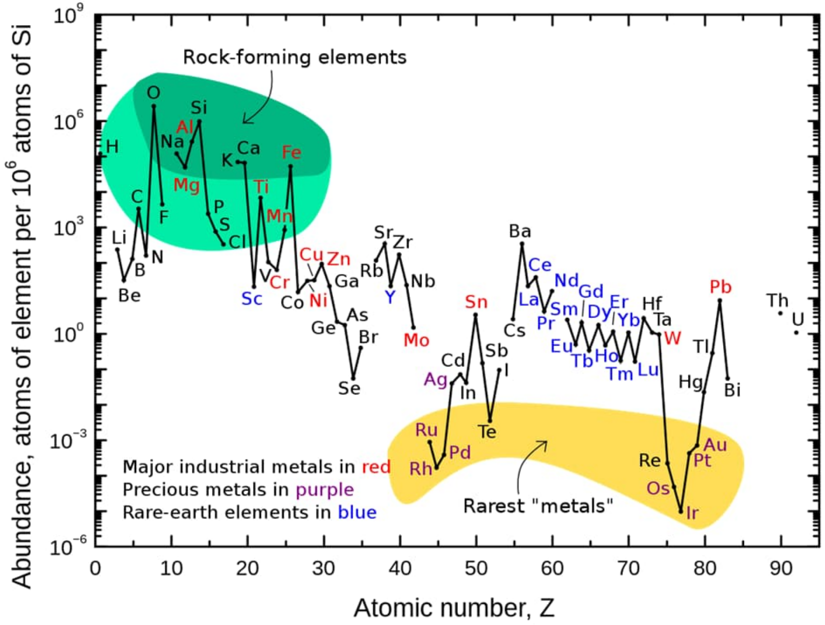
Isotopes

- ‘7’ stable isotopes
- 27 radioactive isotopes

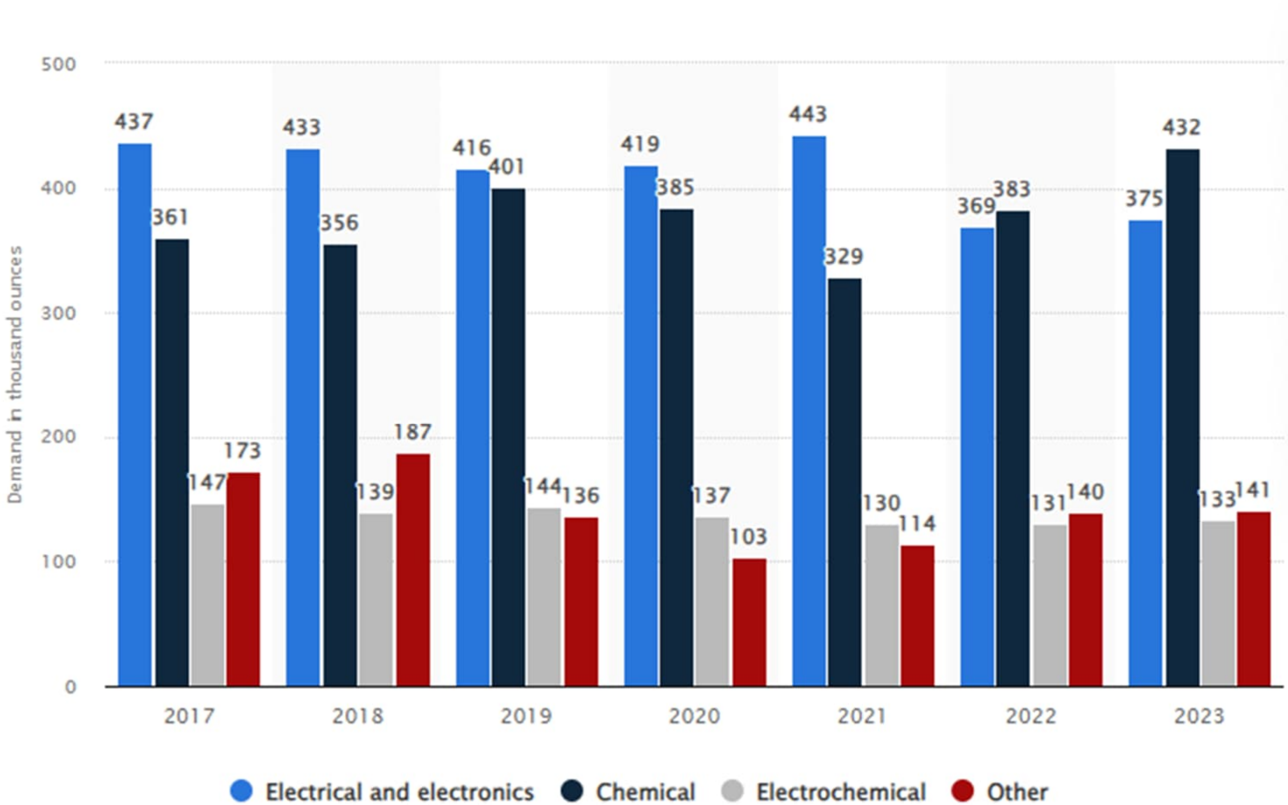
Isotope	Atomic mass	Natural abundance (%)	Half life	Mode of decay
^{96}Ru	95,908	5,54	> 3.1 x 10^{16} y	β+β+
^{98}Ru	97,905	1,87	-	-
^{99}Ru	98,906	12,76	-	-
^{100}Ru	99,904	12,6	-	-
^{101}Ru	100,906	17,06	-	-
^{102}Ru	101,904	31,55	-	-
^{104}Ru	103,905	18,62	-	-

Abundancy and production

- Roughly 30 tons / year
- Found with other platinum metals
- Trace metal in pentlandite and pyroxenite; nickel minerals
- Obtained from nickel refinement waste



Haxel et al. 2005



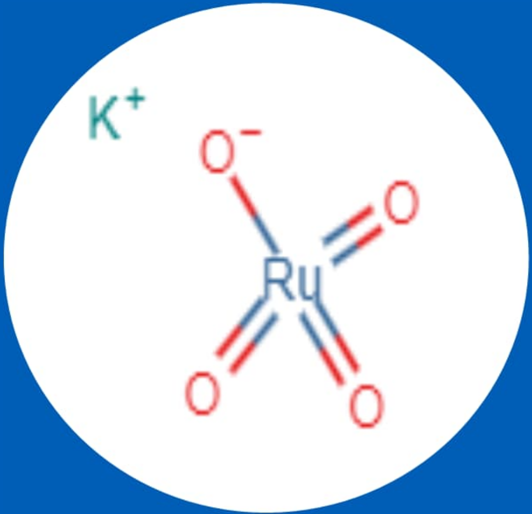
1000 OUNCES
=
0.02835 TONS

Statista, 2023

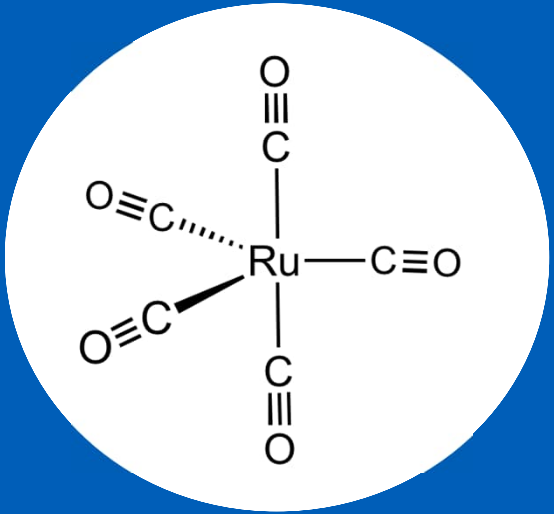
Uses

- Hardener for platinum and palladium
- Catalyst in hydrogenation reactions
  - Hydrogen dissociation
- Many of its compounds and complexes function as catalysts in several different reactions:
  - Dehydrogenation, oxidation, hydrogenation, amination of alcohols, *N*-alkylation of amines, olefin metathesis reaction, synthesis of *N*-heterocycles, and most importantly formation of α-alkylated ketones (intermediate organic synthesis)

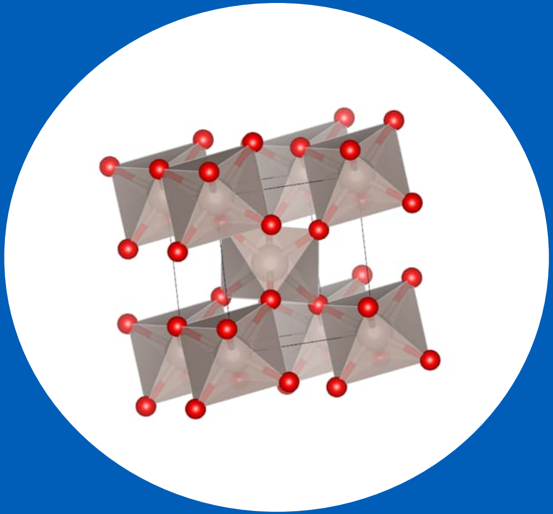
Compounds



$KRuO_4$



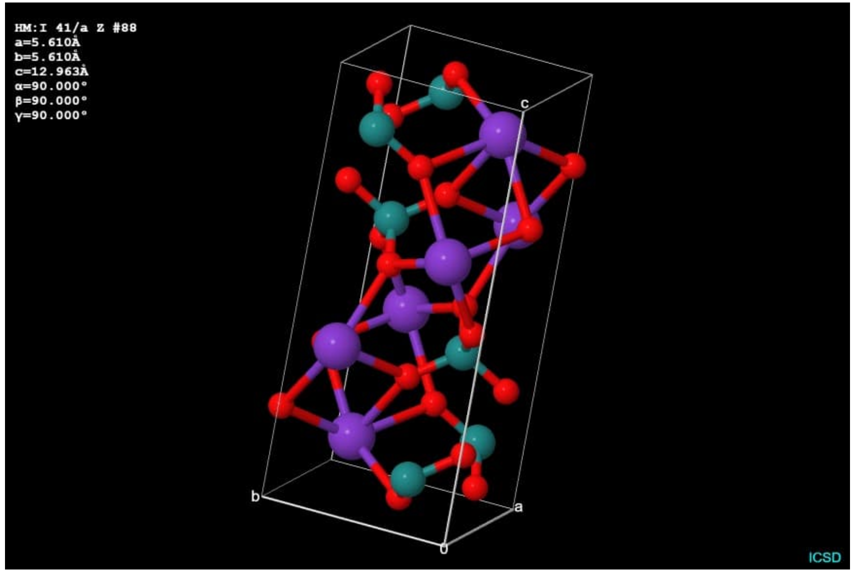
$Ru(CO)_5$



RuO_2

$KRuO_4$

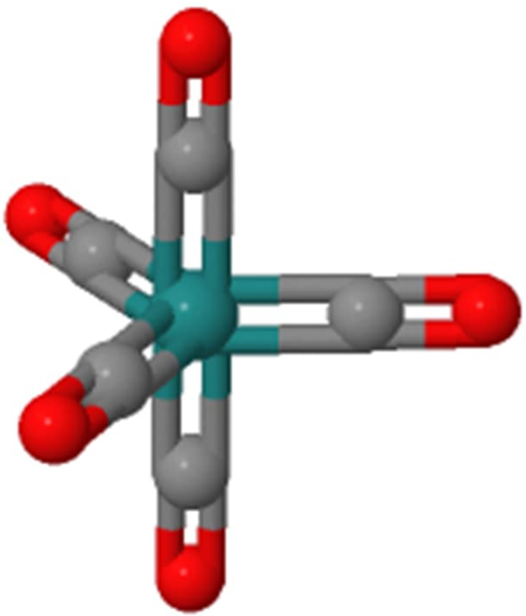
- Oxidation state +VII
- Antiferromagnetic
- Reagent in oxidizing primary alcohols to carbonyls



C. A. Marjerrison et al., "Structure and Magnetic Properties of KRuO4," 2016

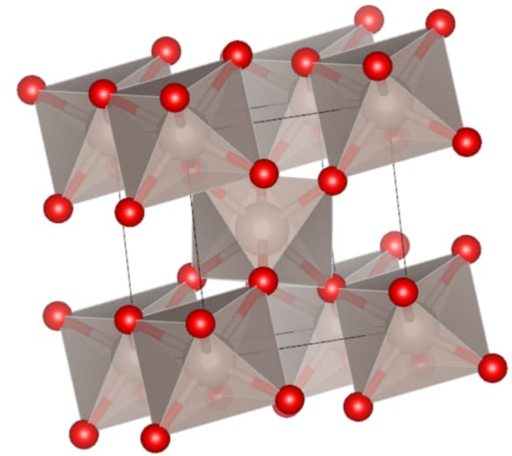
$Ru(CO)_5$

- Intermediate for the synthesis of metal carbonyl complexes.
- Colorless and light-sensitive liquid that readily decarbonylates upon standing at room temperature
- Relatively unstable Ru compounds



Paul Rushman, et al. Properties of the pentacarbonyls of ruthenium and osmium, 1983

RuO_2



- Electrically conductive
- Used as supercapacitor cathode
  - Pseudo-capacitor
  - $Ru(IV)O^{2-} + H^{+} + e^{-} \rightarrow Ru(III)OH^{-}$
- Used as catalyst in Cl_2 recovery reaction
  - $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$
  - Adsorbs oxygen
- Used as catalyst in oxygen evolution reaction
  - Binds and deprotonates H_2O

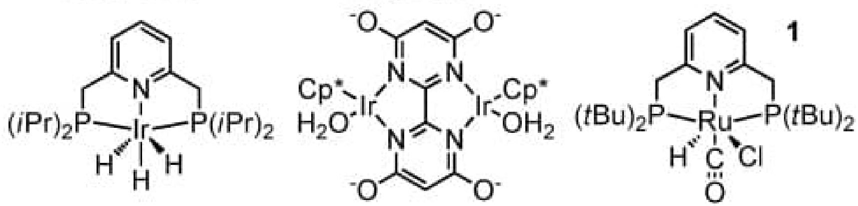
D. Majumdar et al., "Recent Progress in Ruthenium Oxide-Based Composites for Supercapacitor Applications," 2019

Aalto University

Promising research

Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis

Nozaki et al[6] | Fujita et al[7] | This work



1

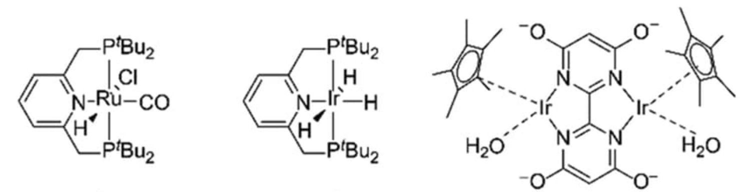
Hydrogenation:

	Nozaki et al[6]	Fujita et al[7]	This work
T / *P*	200 °C / 80 bar	80 °C / 50 bar	120 °C / 40 bar
solvent / base	H_2O,THF / KOH	H_2O / $KHCO_3$	DMF / DBU
TOF, h^{-1}	**150 000**[6a,b]	**54 000**[7]	**1 100 000**

Dehydrogenation:

	Nozaki et al[6]	Fujita et al[7]	This work
T	80 °C	90 °C	90 °C
solvent / base	*t*BuOH / NEt_3	H_2O / HCO_2Na	DMF / NEt_3
TOF, h^{-1}	**120 000**[6b]	**228 000**[7]	**257 000**

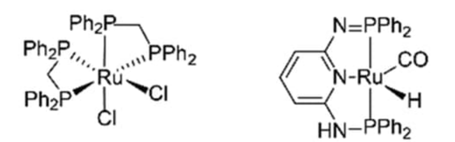
Pidko (2014) | Nozaki (2009) | Fujita (2012)



1 | 2 | 3

	1	2	3
T / P	120 °C / 40 bar	200 °C / 80 bar	RT, 1 bar
solvent/base	DMF/ DBU	H_2O, THF / KOH	H_2O / $KHCO_3$
TON	206 000	3,5 x 10^6	2230

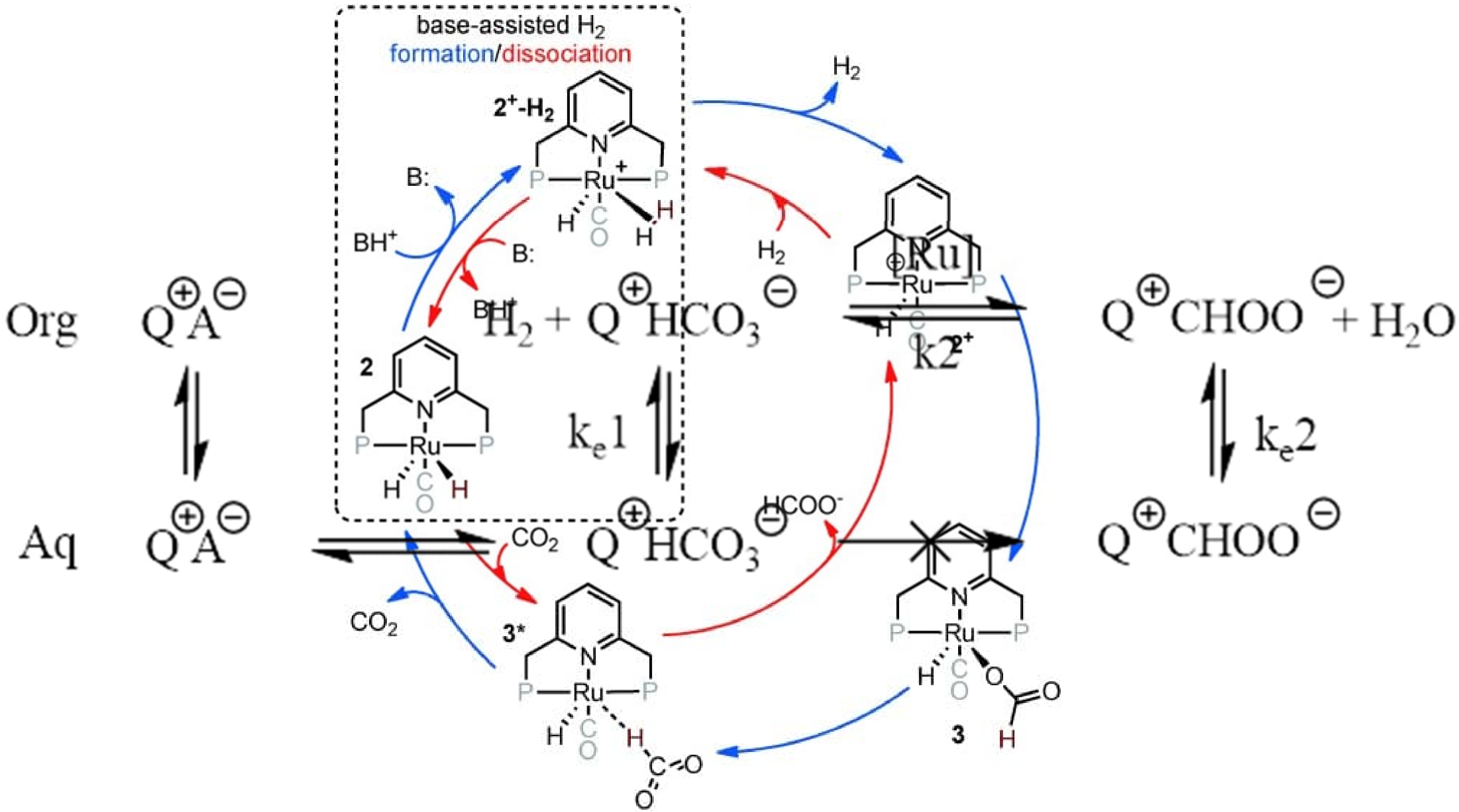
Leitner (2017) | Huang (2018)



4 | 5

	4	5
T / P	70 °C / 90 bar	130 °C / 110 bar
solvent/base	H_2O, MIBC / MEA	H_2O, THF / $NaHCO_3$
TON	150 000	33 000

G. A. Filonenko, et al. "Highly efficient reversible hydrogenation of carbon dioxide to formates using a ruthenium PNP-pincer catalyst," 2014
E. A. Pidko, et al. Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis, 2021



G. A. Filonenko, et al. “Highly efficient reversible hydrogenation of carbon dioxide to formates using a ruthenium PNP-pincer catalyst,” 2014

Flexible supercapacitor cathode with thin film RuN

- Carbon nanotubes coated with RuN
  - High surface area and flexibility
- RuN instead of RuO_2
  - Not studied because difficult to synthesize
- Probably $Ru(III)N_xO_y + OH^- \rightarrow Ru(IV)N_xO_yOH + e^-$
  - Where did the oxygen come from?
  - What is the actual oxidation state
- The role of Ru…

H. Kazari et al. "Dry Synthesis of Binder-Free Ruthenium Nitride-Coated Carbon Nanotubes as a Flexible Supercapacitor Electrode," *2022*

Aalto University

Kiitos paljon

Thank you

Aalto University

Ruthenium

Miklós Nemesszeghy & Timo de Jonge

CHEM-4130 Chemistry of the elements
27.9.2023

Luciteria.com, R.Suarez

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2. C. Rebreyend, E. A. Pidko, and G. A. Filonenko, “Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis,” Green Chemistry, vol. 23, no. 22, pp. 8848–8852, Nov. 2021, doi: 10.1039/d1gc02246f.

3. C. A. Marjerrison et al., "Structure and Magnetic Properties of KRuO4," Inorganic Chemistry, vol. 55, no. 24, pp. 12897-12903, 2016/12/19 2016, doi: 10.1021/acs.inorgchem.6b02284

4. D. Majumdar, T. Maiyalagan, and Z. Jiang, "Recent Progress in Ruthenium Oxide-Based Composites for Supercapacitor Applications," *ChemElectroChem, vol. 6, no. 17, pp. 4343-4372, 2019, doi: https://doi.org/10.1002/celc.201900668.*

5.

6. H. Kazari, E. Pajootan, P. Hubert, and S. Coulombe, "Dry Synthesis of Binder-Free Ruthenium Nitride-Coated Carbon Nanotubes as a Flexible Supercapacitor Electrode," *ACS Applied Materials & Interfaces, vol. 14, no. 13, pp. 15112-15121, 2022/04/06 2022, doi: 10.1021/acsami.1c22276.*

7.

8.

9.

10.

Chlorine evolution

Replacing the less performing graphite anodes

low chlorine evolution overvoltage

high selectivity and a remarkable effectiveness in energy saving

Isotopes

- ‘7’ stable isotopes
- 27 radioactive isotopes

Isotope	Atomic mass	Natural abundance (%)	Half life	Mode of decay
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