Development of a Heterogeneous Photocatalyst for Carbon Dioxide Sequestering

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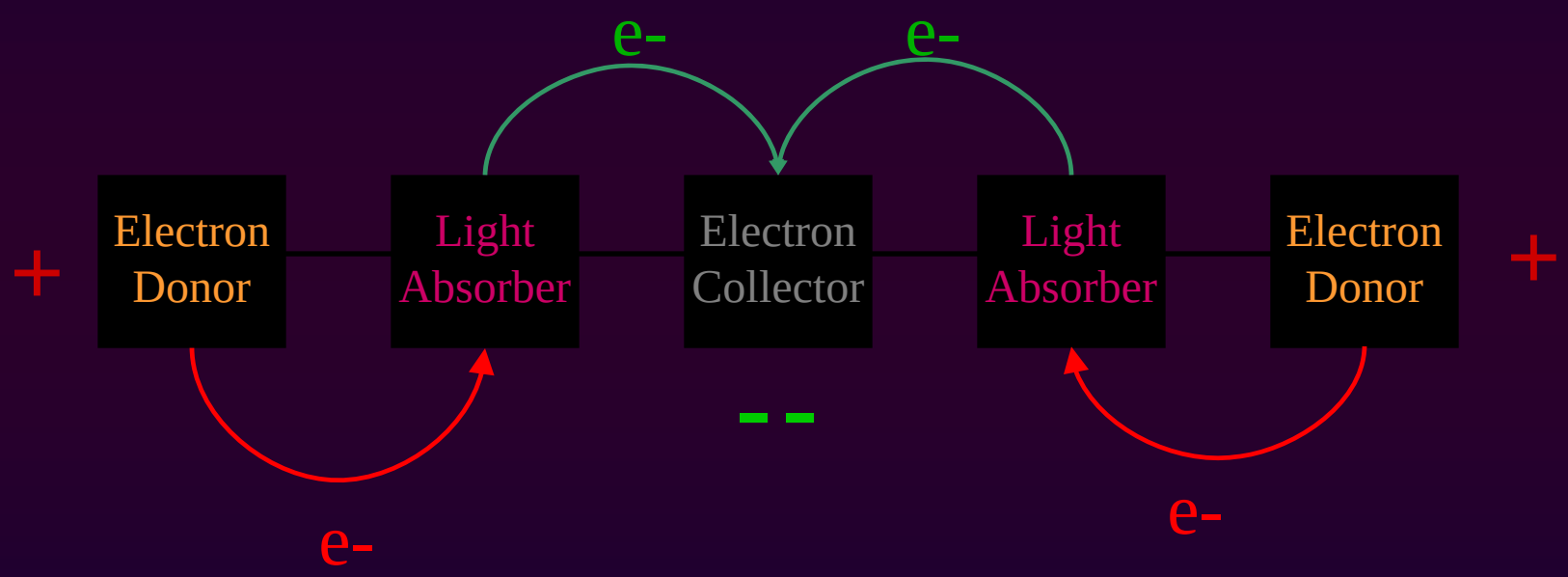
Introduction

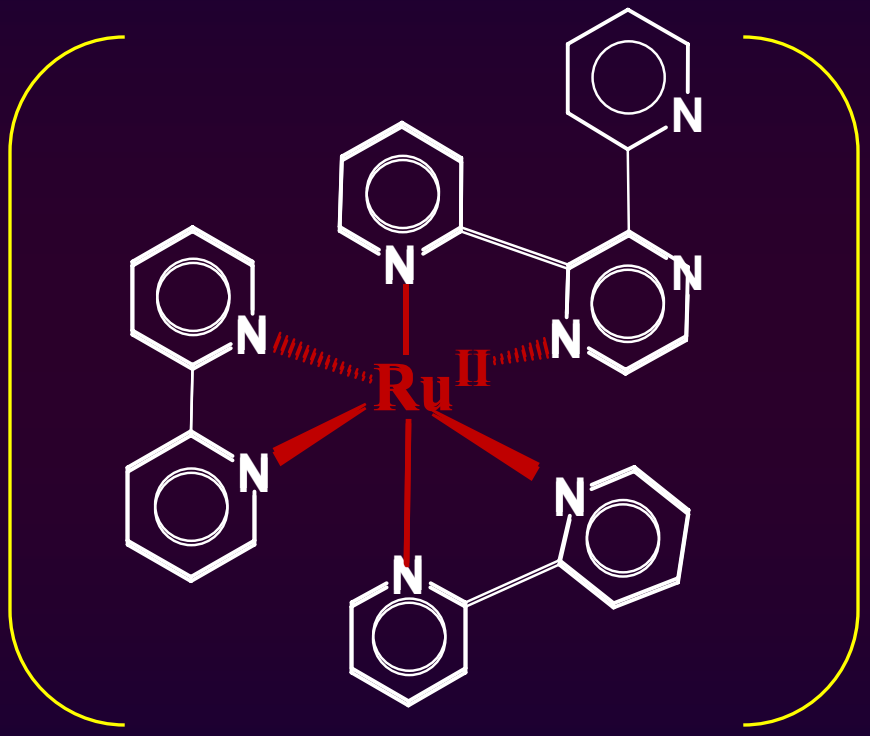
- Due to the high over-potential needed, carbon dioxide reduction via electrochemical methods is not cost effective.
- Modeled after nature's efficient photosynthetic pathways, new methods involving photoinitiated supramolecular catalysts have been devised to circumvent this problem.
- These devices provide the opportunity to transfer more than one electron to a substrate

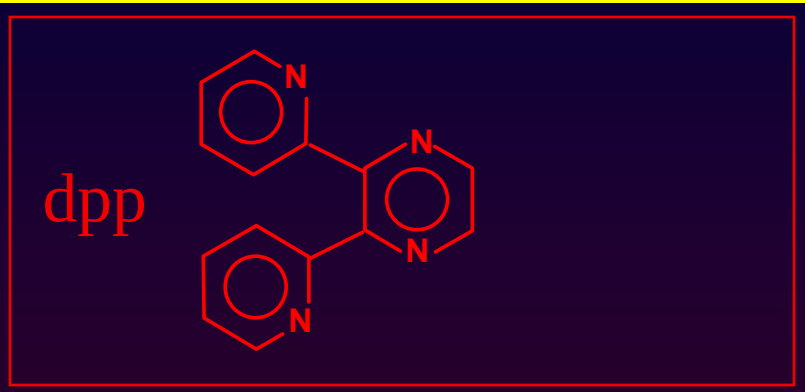
Photoinitiated Electron Collector : Conceptual Design

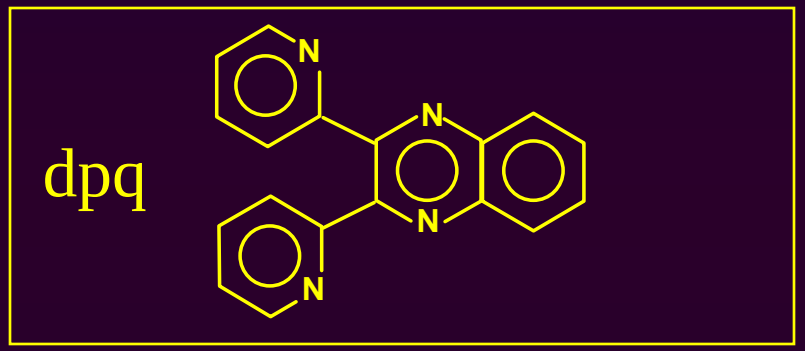


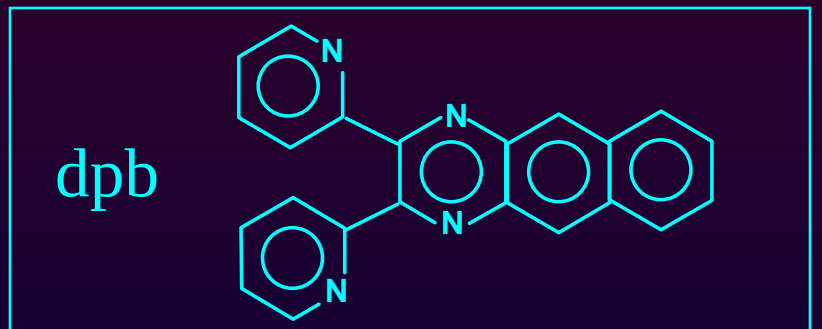
Balzani,V. *Supramolecular Photochemistry*, NATO ASI Series **1987**, 214, 135

The Light Absorber





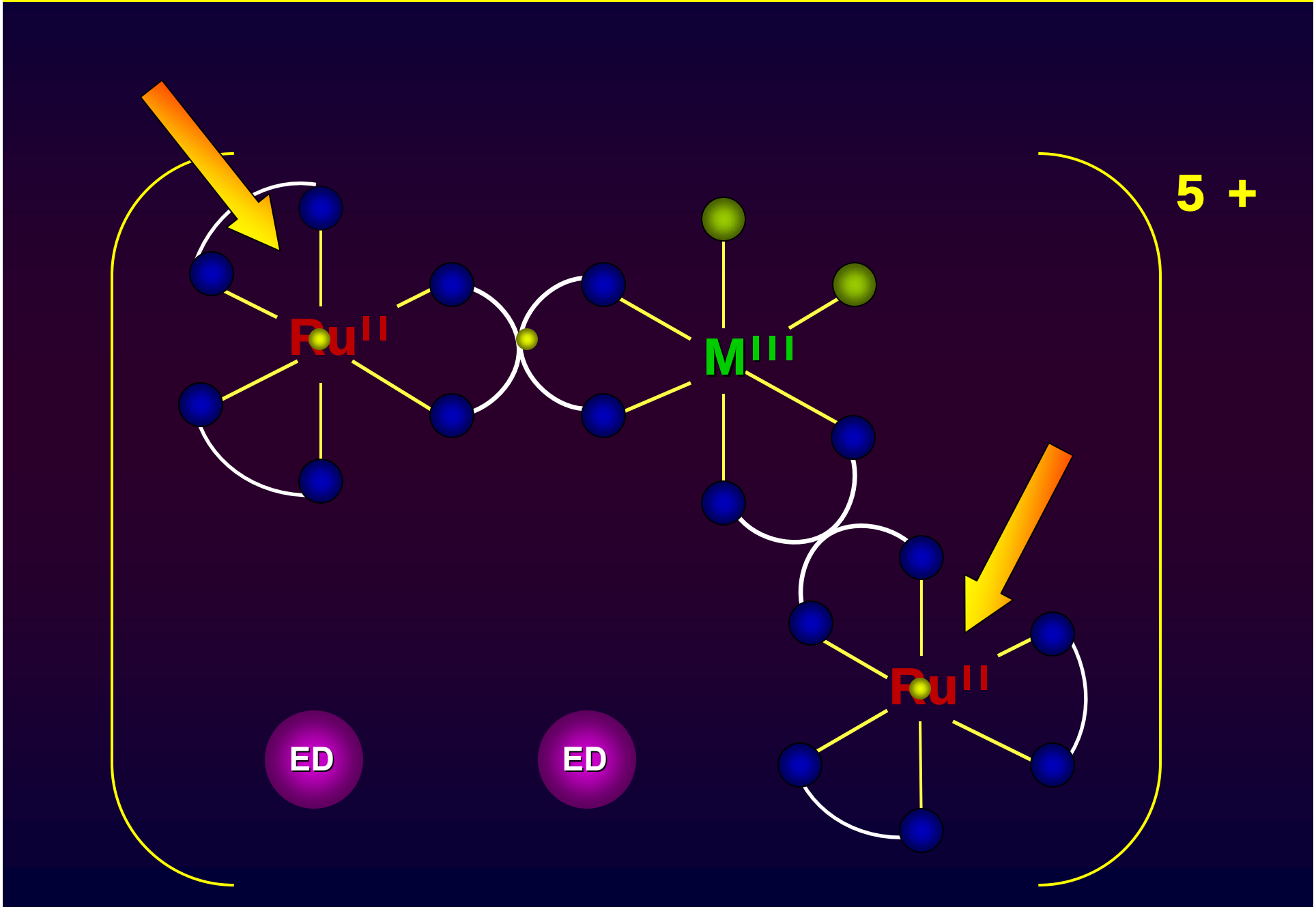




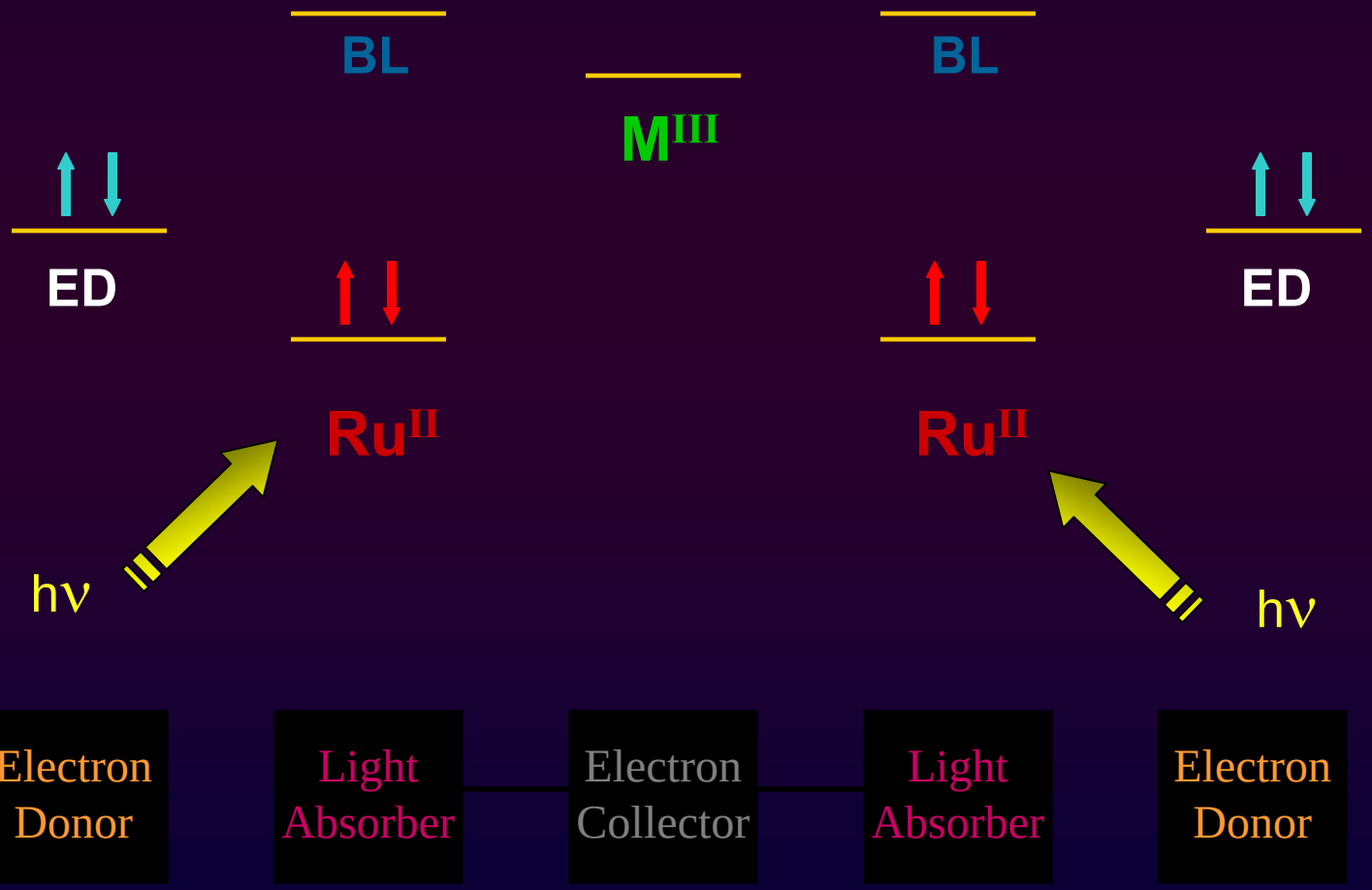
(a) Braunstein,C.H. *et al*, *Inorg.Chem.* **1984**, 23, 857

(b) Rillema, D.P. *et al* , *Inorg. Chem.* **1982**, 21, 3849

The Homogeneous Ru^{II}/M^{III} Trimetallic Catalyst



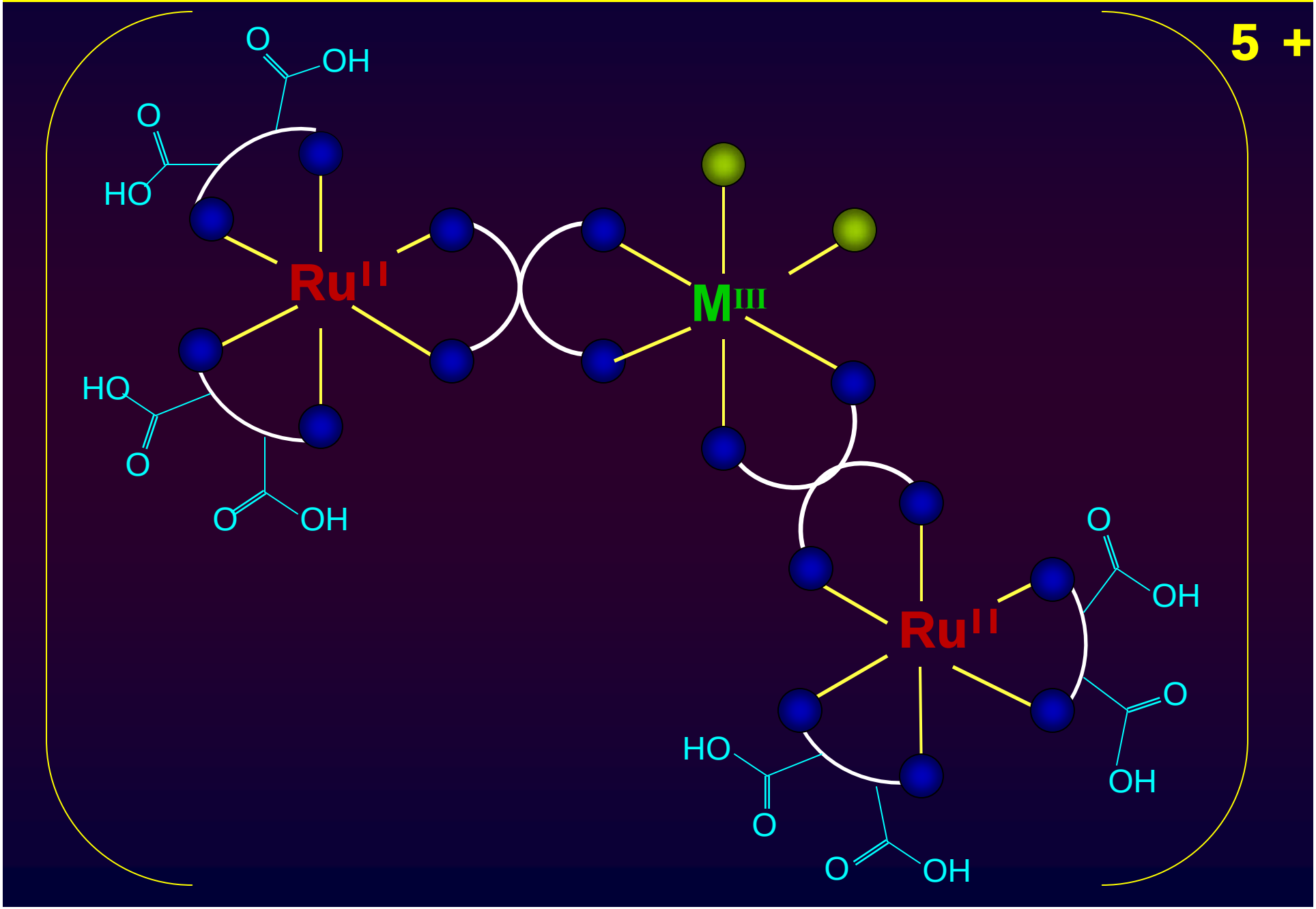
MO Diagram of the Ru^{II}/M^{III} Homogeneous Trimetallic Catalyst

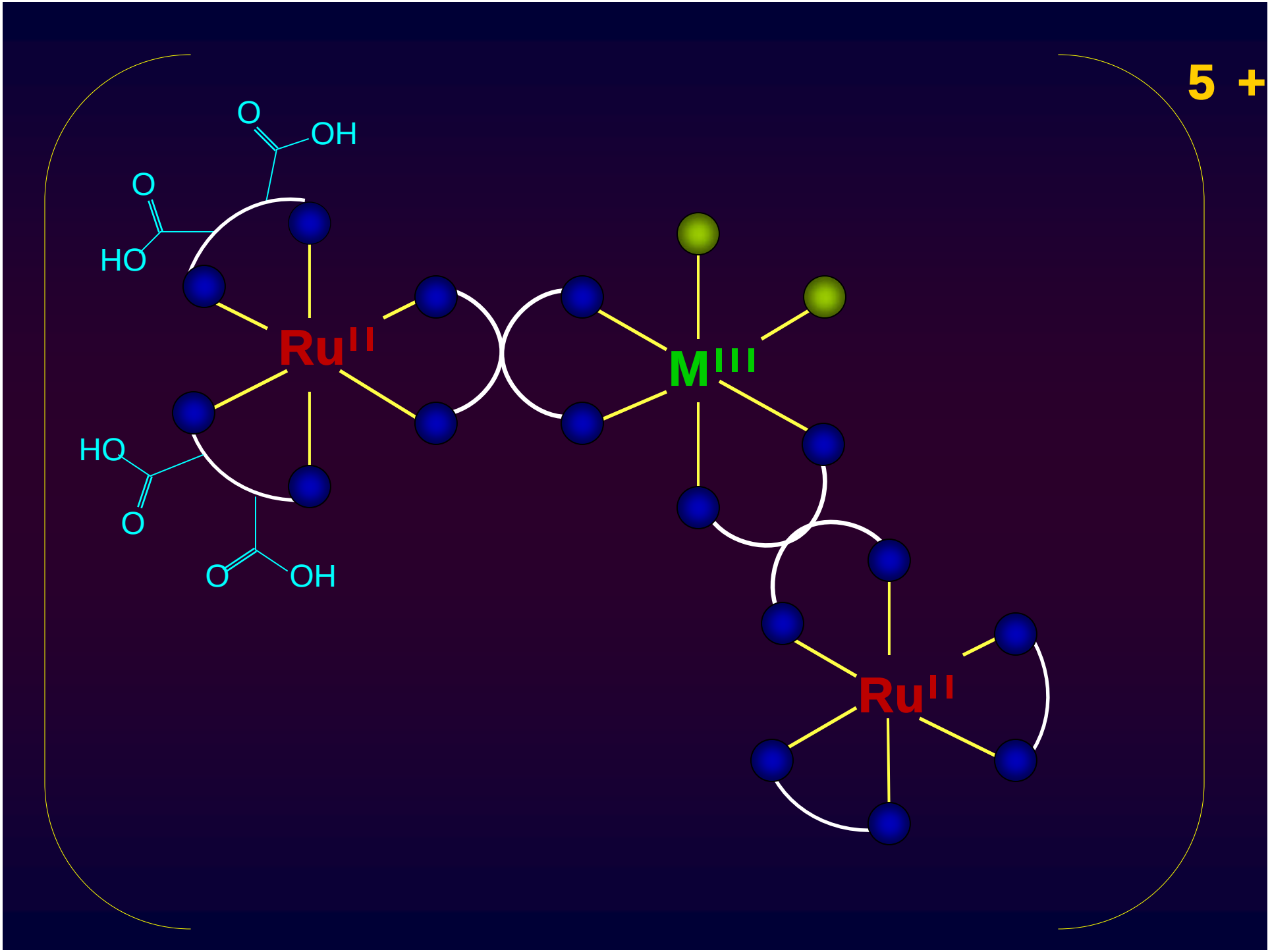


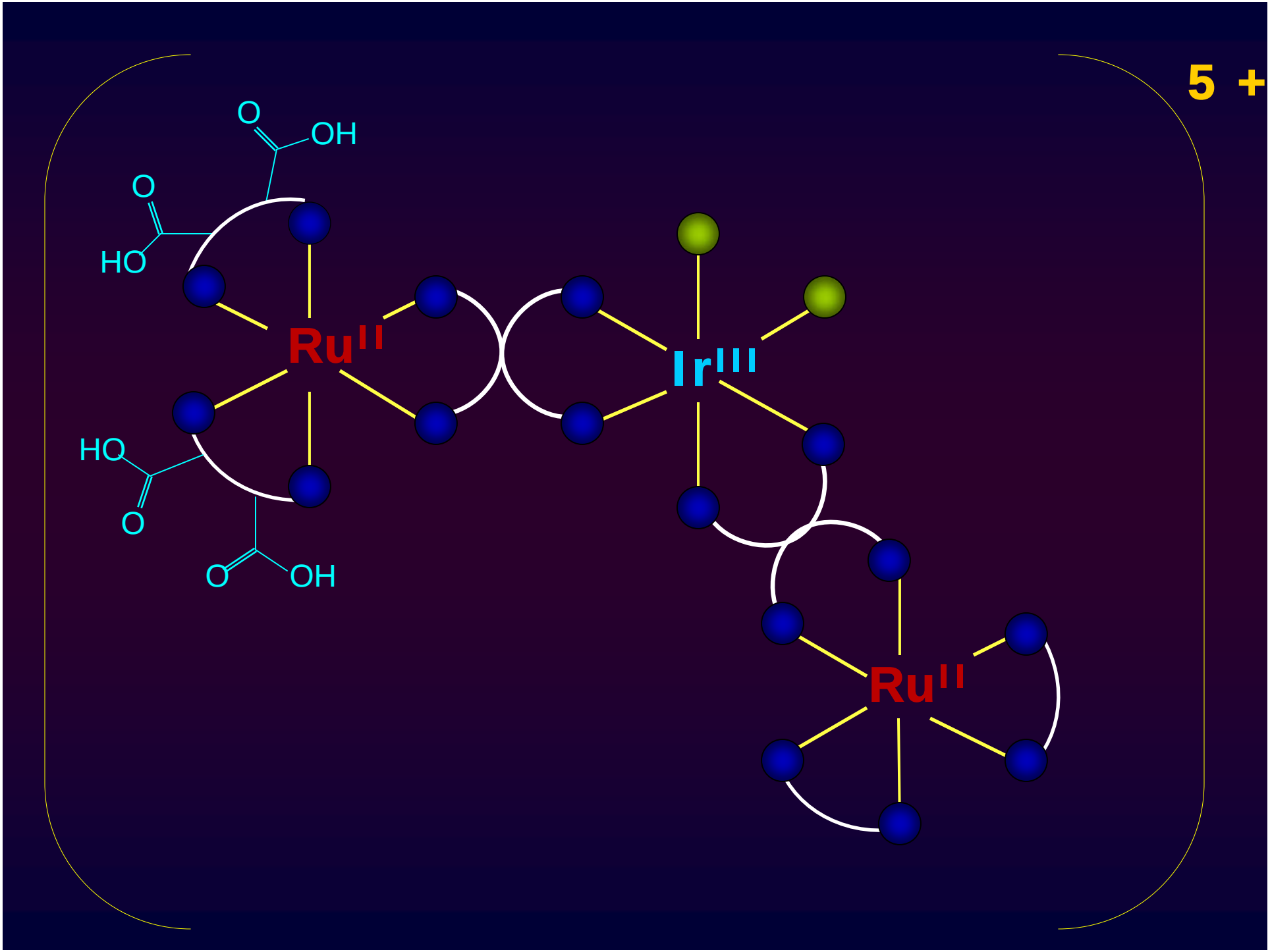
Characterization Techniques

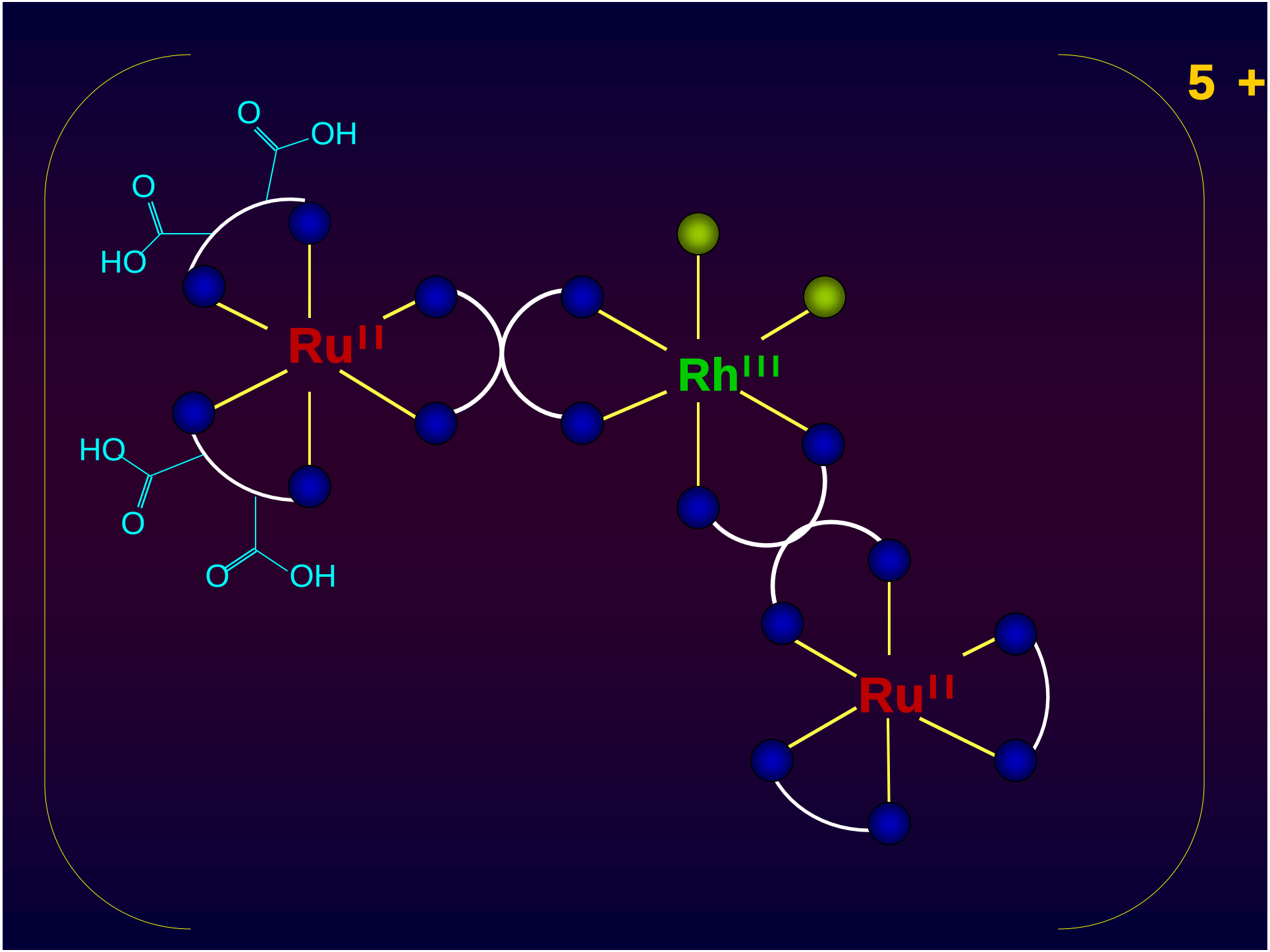
- Infrared Spectroscopy
- NMR
- UV-vis Spectroscopy
- Photostability
- Fluorimetry
- Excited State Lifetimes
- Cyclic Voltammetry
- Bulk Electrolysis
- Bulk Electrolysis with Cyclic Voltammetry
- Spectroelectrochemistry
- Coulometry

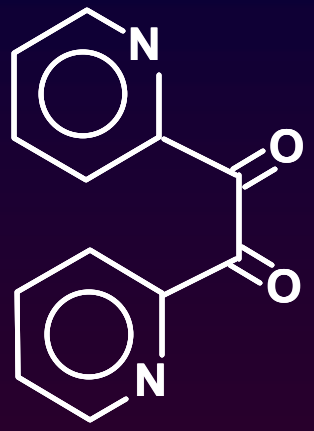
The Heterogeneous Ru^{II}/M^{III} Trimetallic Catalyst Precursor




5 +
O
OH
O
HO
Ru II
M III
HO
O
O
OH
Ru II


5 +
O
OH
O
HO
Ru II
Ir III
HO
O
O
OH
Ru II

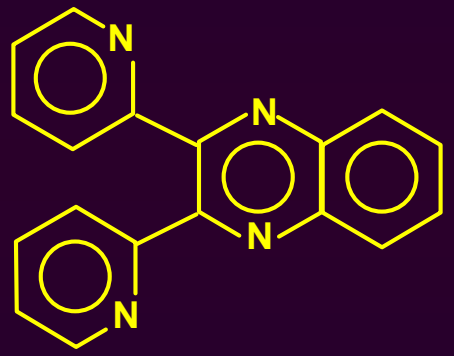

5 +
O
OH
O
HO
Ru II
Rh III
HO
O
O
OH
Ru II

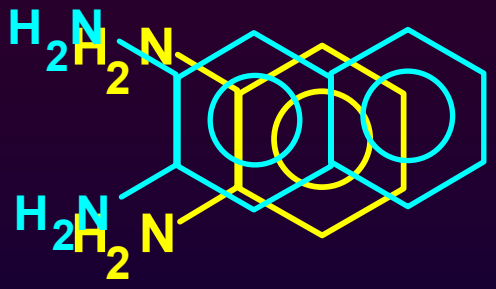


2,2’-pyridyl

dpp

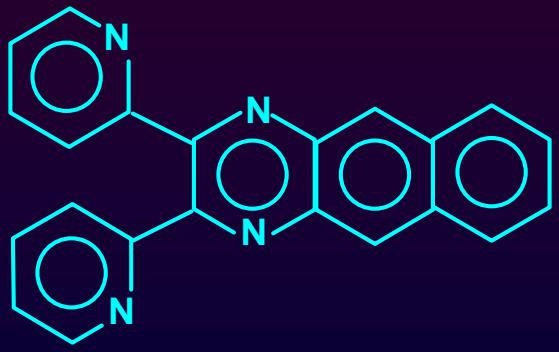
dpq





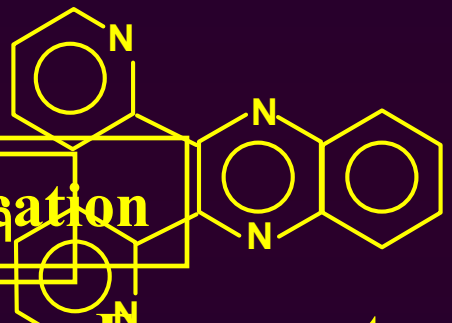
2,3-diamino naphthalene

dpb

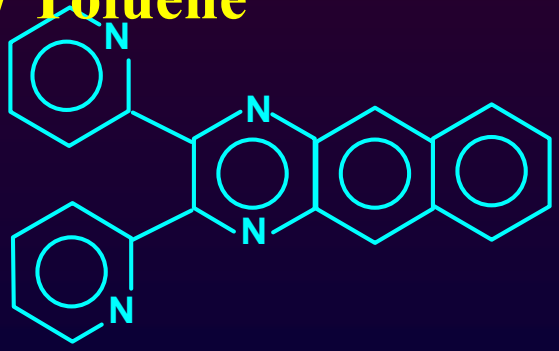


dpp

dpq



dpb



Starting Material Purification

SM1

✧ Acetone → Filter → Rotary Evaoporate

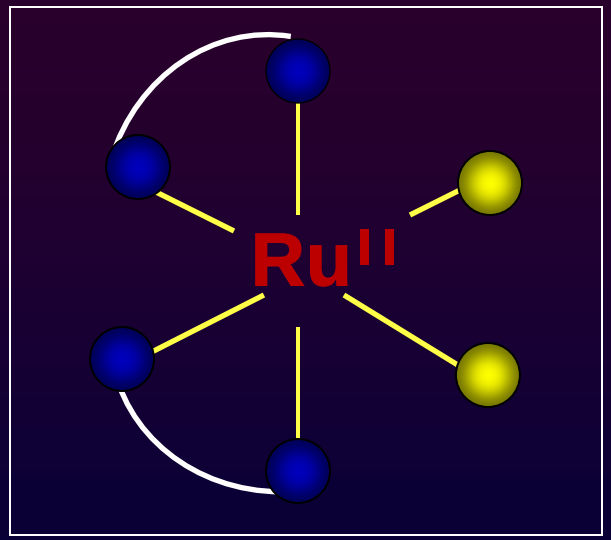
✧ Wash with Ethanol

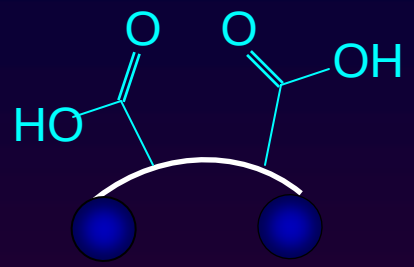
Previous Ligand Purification

✧ Methylene Chloride / Toluene

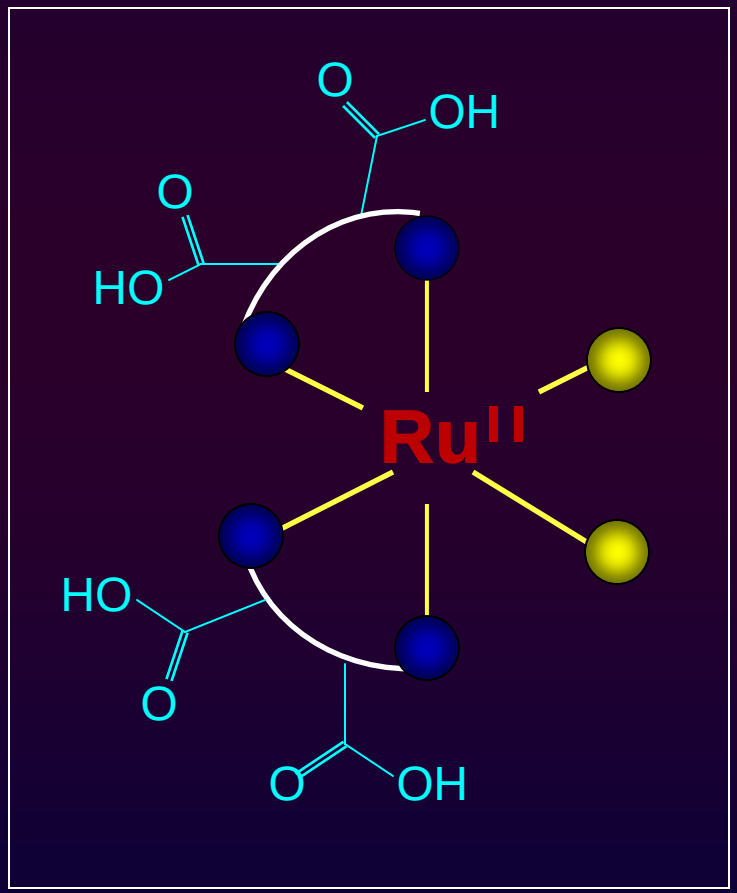
SM1 Sharon Molnar, 4/20/2006

- Reflux in DMF
- Precipitate in acetone
- Wash with water (0° C)
- Wash with ether



$RuCl_3 \bullet H_2O$ + 2.1  + LiCl

- ✧ Reflux in DMF
- ✧ Precipitate in acetonitrile
- ~~✧ Wash with water (0° C)~~
- ✧ Wash with ether

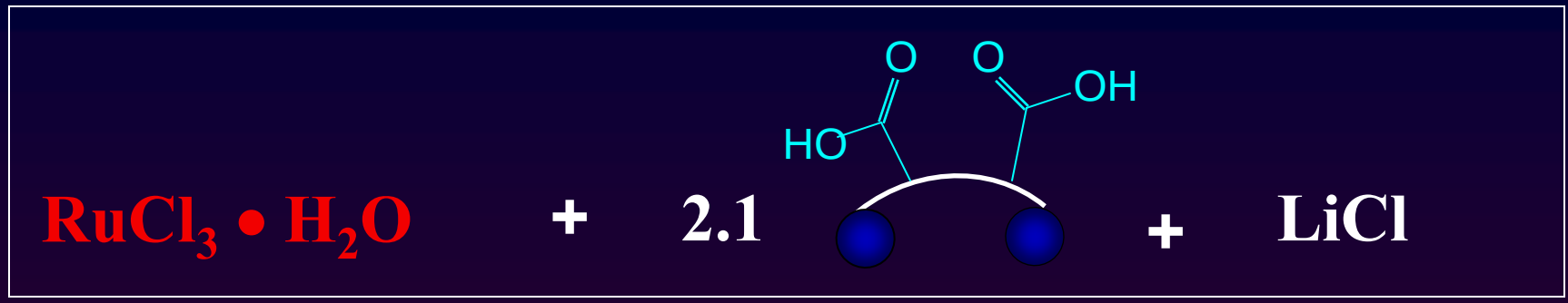


Alumina

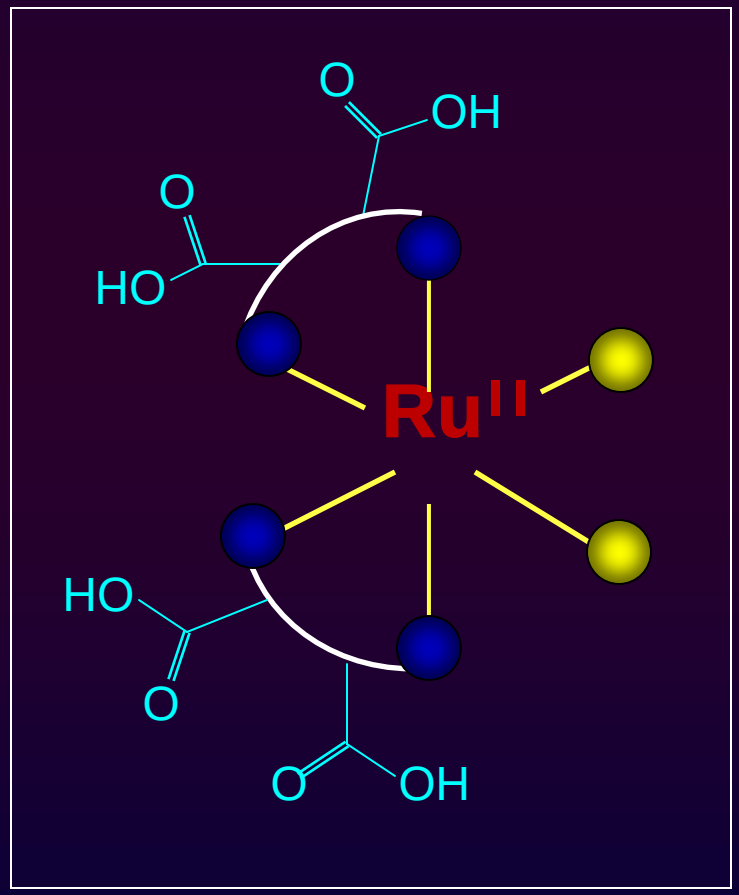
Silica gel

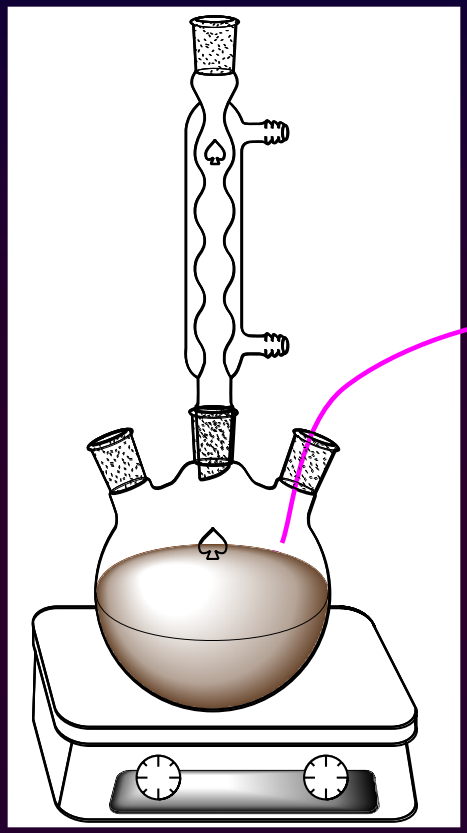
Sephadex G-10

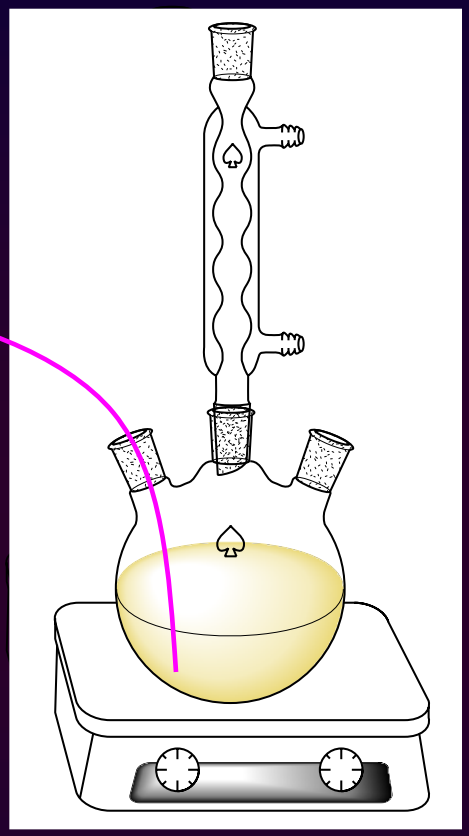
Sephadex G-15



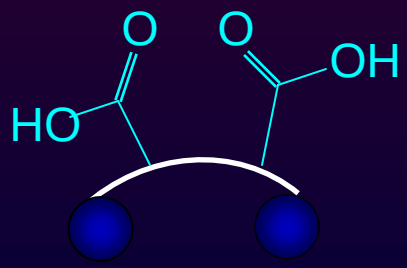
- Reflux in DMF
- Precipitate in acetone
- Wash with ether

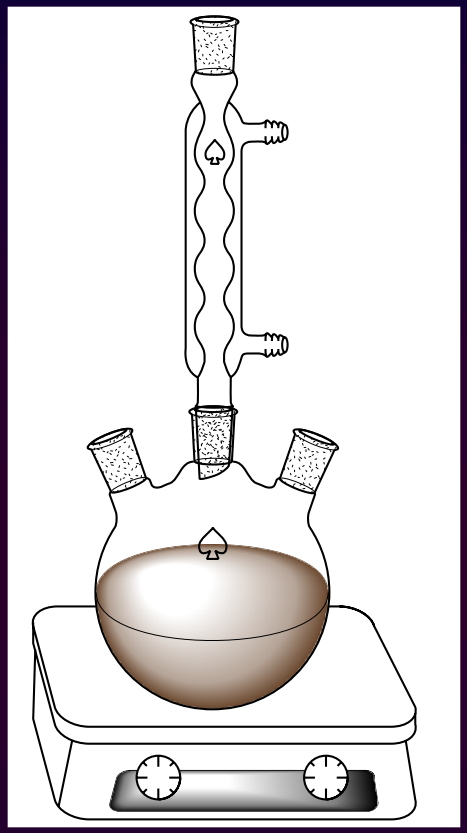


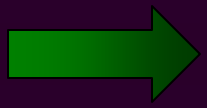


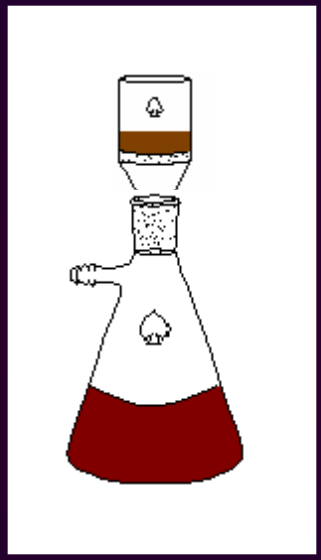


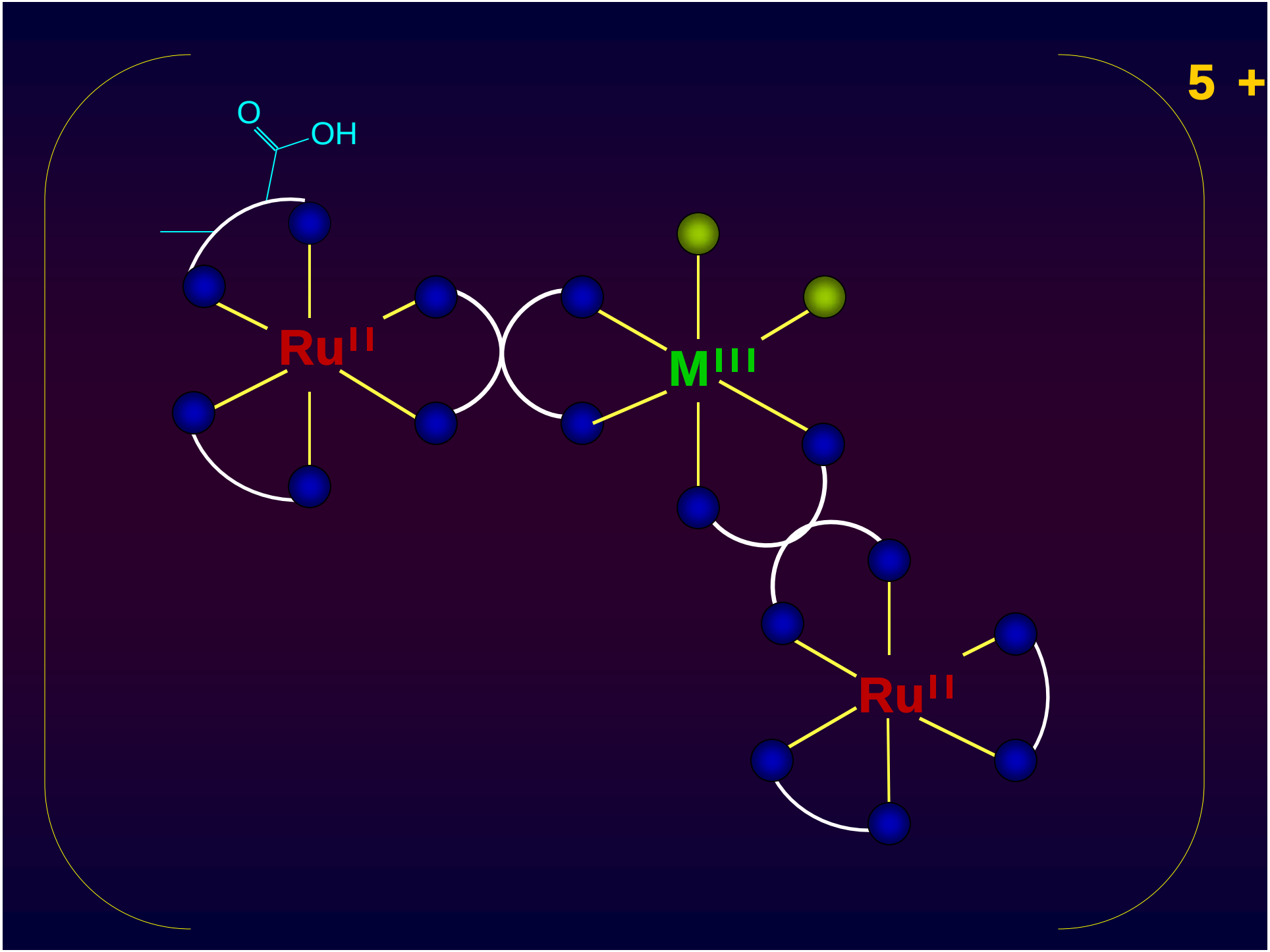
$RuCl_3 \bullet H_2O$

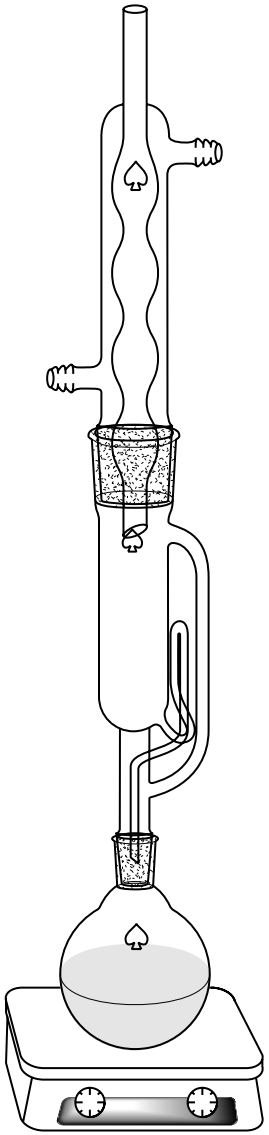


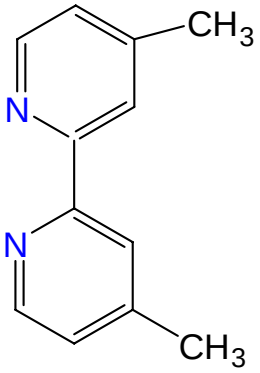






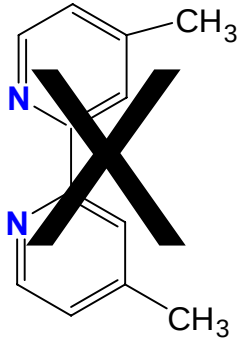

5 +
O
OH
Ru II
M III
Ru II



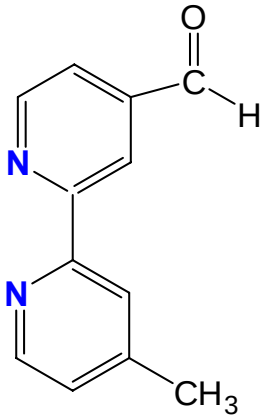


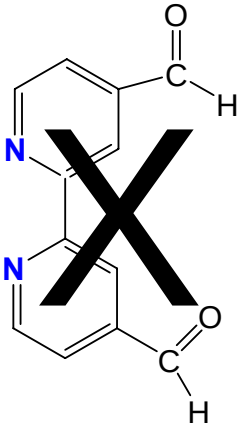
(1) SeO_2

(2) Ag_2O



chloroform extraction

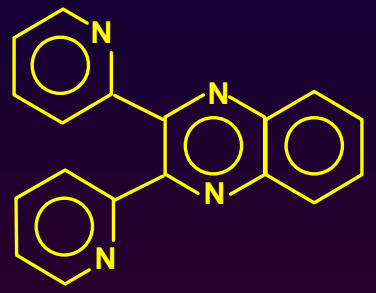




Soxhlet extraction

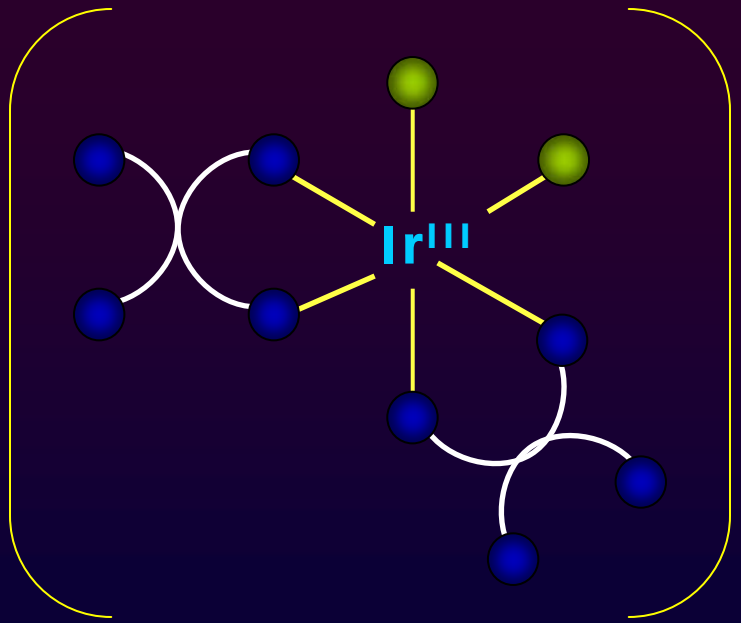
McCafferty, D.G. *et al*, *Tetrahedron*, **1995,** 51,vol. 4,1093-1106

Synthesis of $[Ir^{III} (dpq)_2 Cl_2](PF_6)$



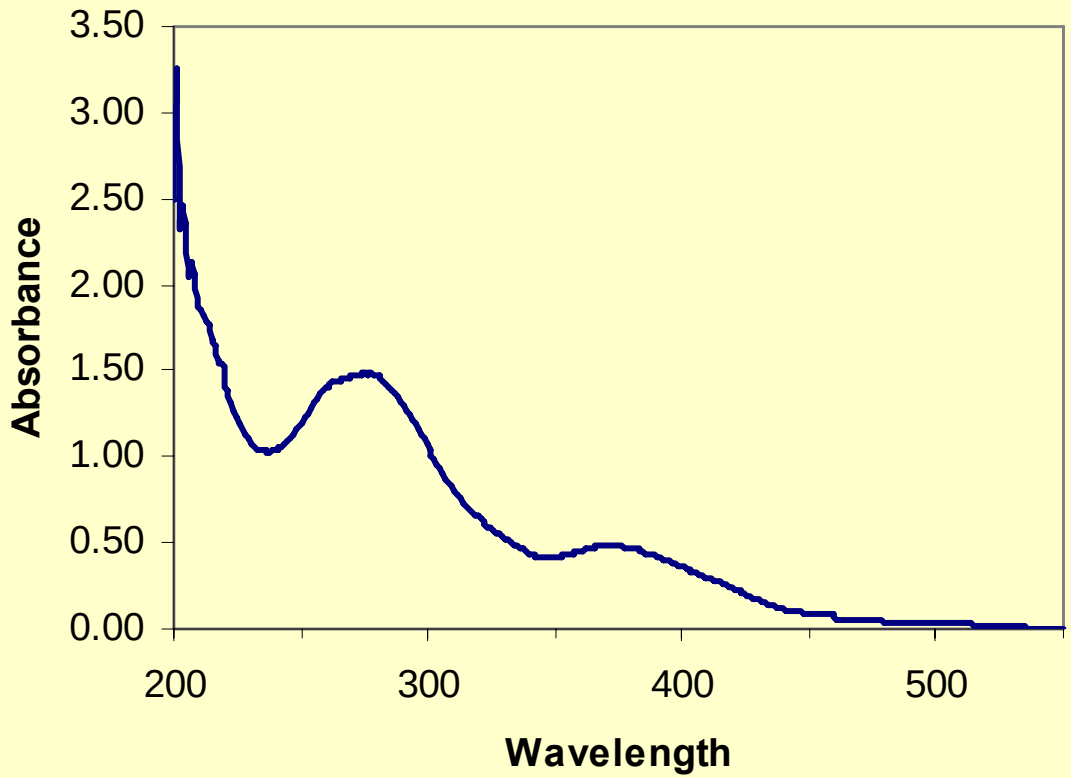
+ $IrCl_3 \bullet H_2O$ + LiCl

- Reflux in ethylene glycol
- Precipitate in KPF_6
- Wash with ether



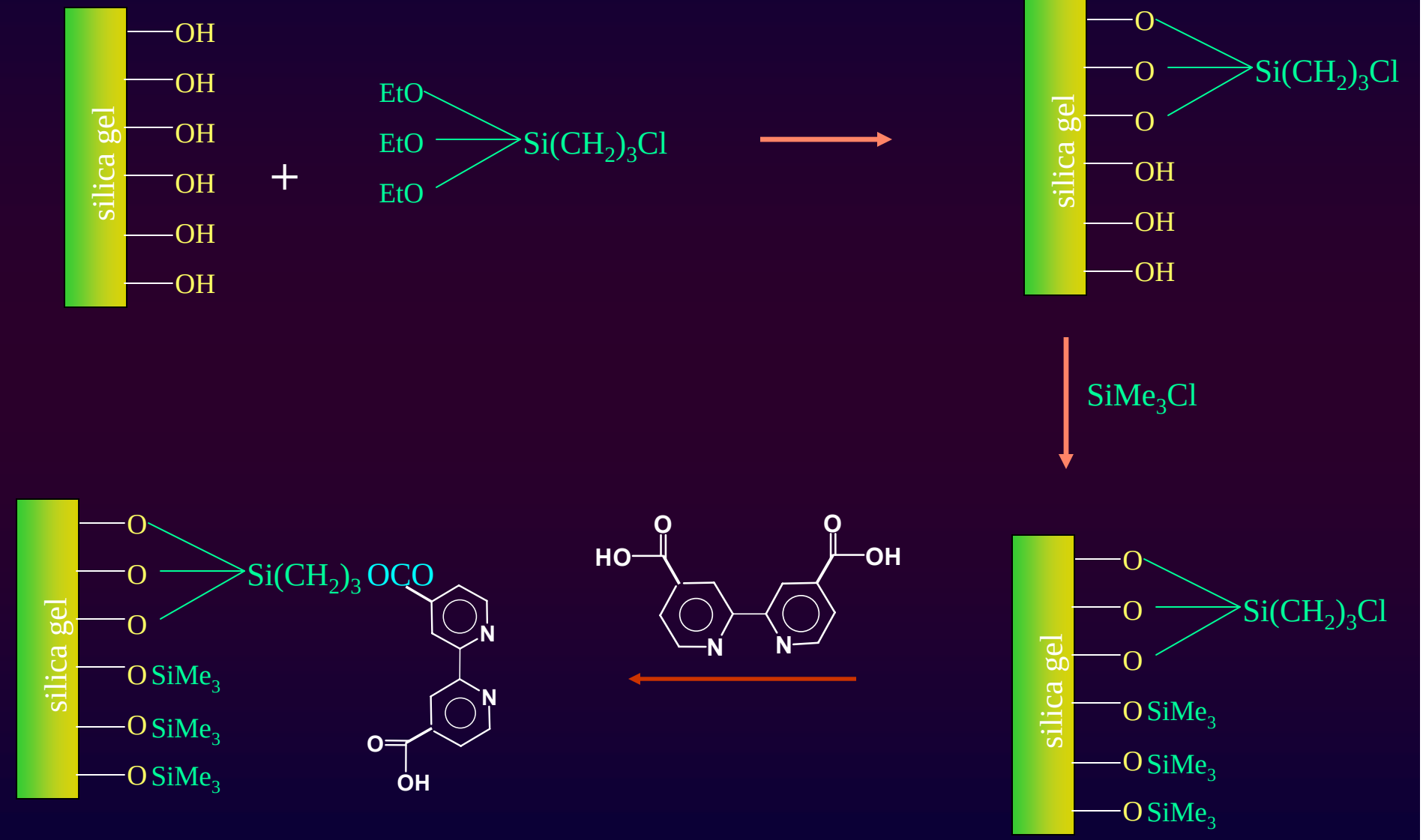
Electronic Absorption Spectrum

[Ir $(dpq)_2Cl_2$] (PF_6)



λ_{max} (nm)	
Literature	**Experimental**
218	215.0
276	274.9
372	373. 8
460	459.3

Attachment to the Solid Support



Acknowledgements

Department of Energy

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West Virginia State University

Gus R. Douglas Institute

Melissa D. Wolfe