

I U P A C

**INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY**

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Chemical/Digital Standards and Their Implications for Your Chemistry and Mine

Richard Hartshorn, IUPAC Secretary General,
University of Canterbury
Christchurch, New Zealand

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IUPAC Vision

IUPAC is an indispensable resource for chemistry.



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Mission and Membership



Mission:

The International Union of Pure and Applied Chemistry is the global organization that provides objective scientific expertise and develops the essential tools for the application and communication of chemical knowledge for the benefit of humankind and the world.

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Mission and Membership

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Membership:

About 2300 Volunteers, 800 Affiliate Members,
53 Member Organizations),
31 Associated Organizations, about 32 Company Associates.

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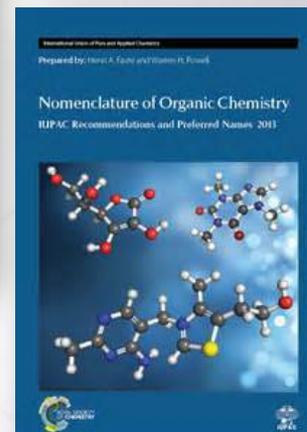
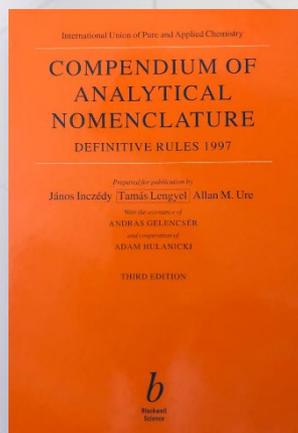
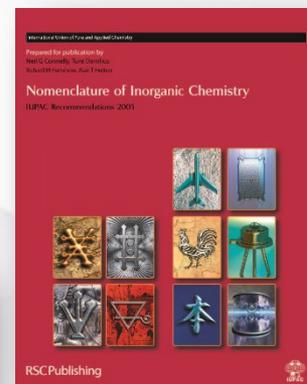
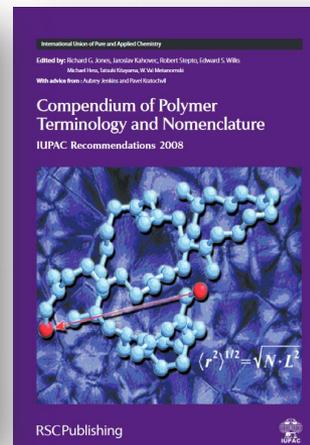
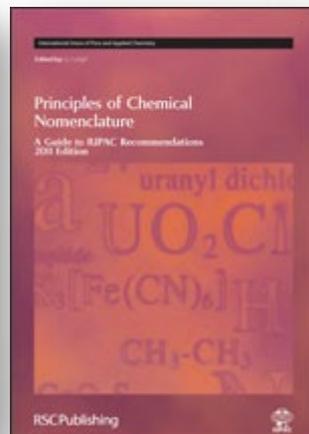
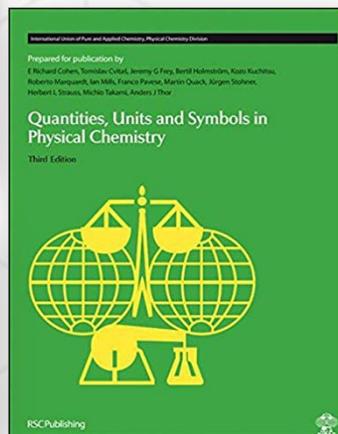
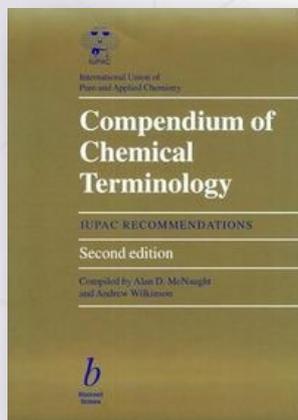
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Principal IUPAC Activities

- Curation of the Periodic Table
- Colour books, Recommendations, and Technical Reports



IUPAC Colour Books



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Principal IUPAC Activities

- Curation of the Periodic Table
- Color books, Recommendations, and Technical Reports
- Cheminformatics (e.g. InChI)
- Green Chemistry and Sustainable Development
- Education and Training; Diversity and Younger Chemists



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Principal IUPAC Activities



- Curation of the Periodic Table
- Color books, Recommendations, and Technical Reports
- Cheminformatics (e.g. InChI)
- Green Chemistry and Sustainable Development
- Education and Training; Diversity and Younger Chemists
- Collaborations: UNESCO, ISC, BIPM, OPCW, CODATA, IUPAP, etc.

IUPAC's Scientific Work Divisions and Standing Committees–

Physical & Biophysical Chemistry

Inorganic Chemistry

Organic & Biomolecular Chemistry

Polymer Chemistry

Analytical Chemistry

Chemistry & the Environment

Chemistry & Human Health

Chemical Nomenclature & Structure Representation

Committee on Chemistry and Industry (COCI)

Committee on Chemistry Education (CCE)

CHEMRAWN Committee

Committee on Publications and Cheminformatics Data Standards (CPCDS)

Interdivisional Committee on Terminology, Nomenclature and Standards (ICTNS)

Interdivisional Committee on Green Chemistry for Sustainable Development (ICGCSD)

IUPAC Issues for Today and the Future: FAIR Data and Cheminformatics

Data Should Be:

- Findable
- Accessible
- Interoperable
- Reusable

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CODATA and WorldFAIR

Tools (File/Data Standards) & Repositories (certification/accreditation)

IUPAC Issues for Today and the Future: FAIR Data and Cheminformatics

- Data Management Plans – coming to organisations near you
- Electronic Lab Notebooks – will be used routinely
- Fully linked spectra and characterisation data
- Extended through into publication – being FAIR, digital standards and validation suites

IUPAC Issues for Today: International Chemical Identifier (InChI) Standards

- Taking InChI Beyond Publications/Databases
- Inorganic/Coordination/Organometallic Compounds
- Mixtures
- Reactions
- QR Code Standard

IUPAC Issues for Today: IUPAC Standards

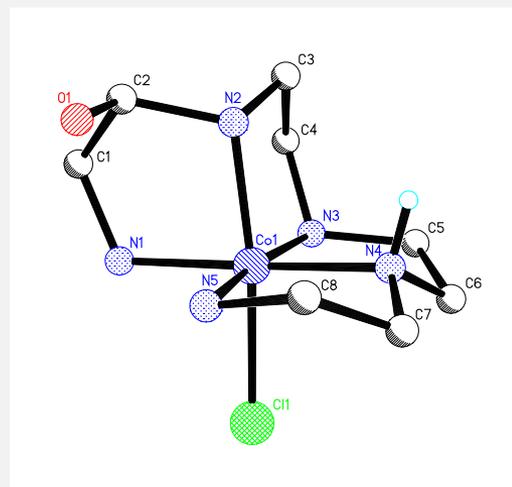
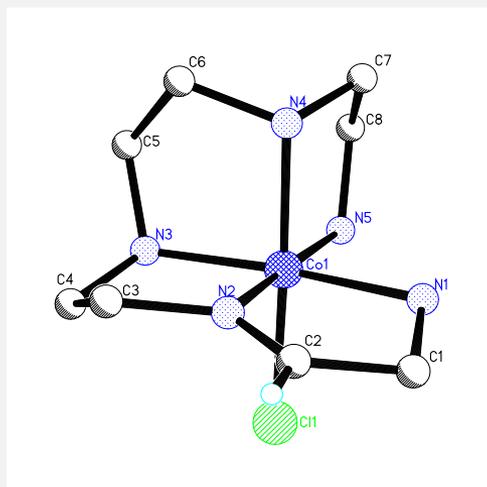
Heading to FAIR...	In some electronic form...	Analog equivalent...
<ul style="list-style-type: none">• InChI (and family)• HELM• ThermoML• SMILES+• Adsorption Information File (AIF)• FAIRSpec	<ul style="list-style-type: none">• Gold Book (+Orange +Silver +White)• Periodic Table (CIAAW tables)• Atmospheric kinetics• Polymerization kinetics• NPU: properties & units for clinical chemistry• Dissociation constants• Stability constants• JCAMP-DX	<ul style="list-style-type: none">• Solubility Data Series*• Green Book*• Blue Book• Red Book• Purple Book• Graphical representation

Secretary General Responsibilities?

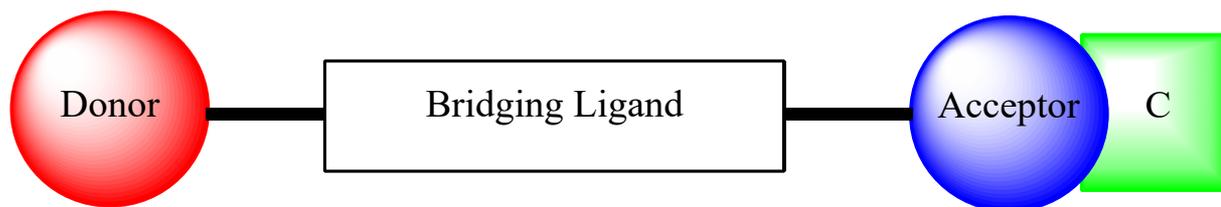
- Secretariat Oversight
- Science Oversight (projects and conferences)
- Strategic Directions
- Wrangling Volunteers
- Statutes and By-laws and their Application
- Business of the Union

And How Did I Get There?

- Leadership in Division of Chemical Nomenclature and Structure Representation
- Red Book and Other Projects
- Nomenclature Development
- From Research (a need for structure representation)

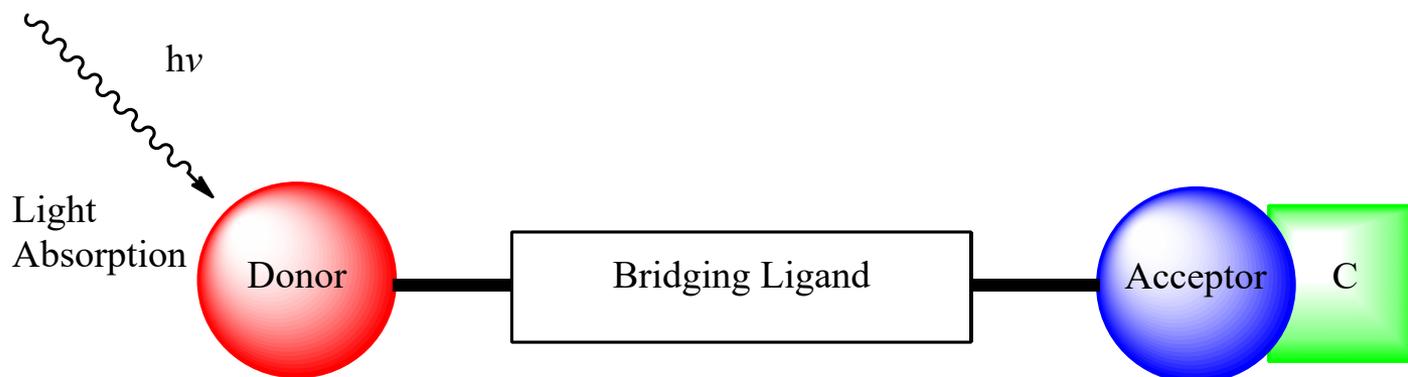


Photoactivated Cytotoxins



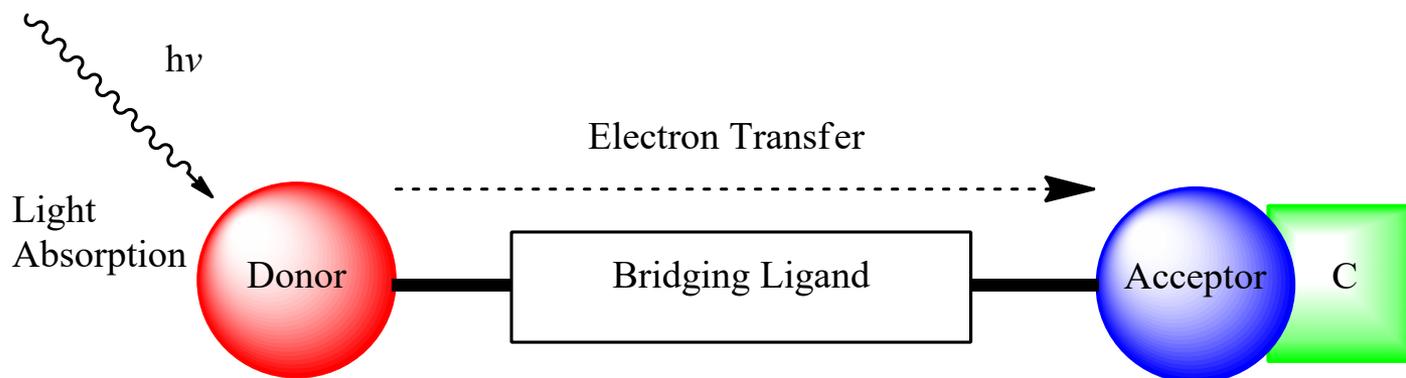
Using light to trigger release of an anti-cancer drug

Photoactivated Cytotoxins



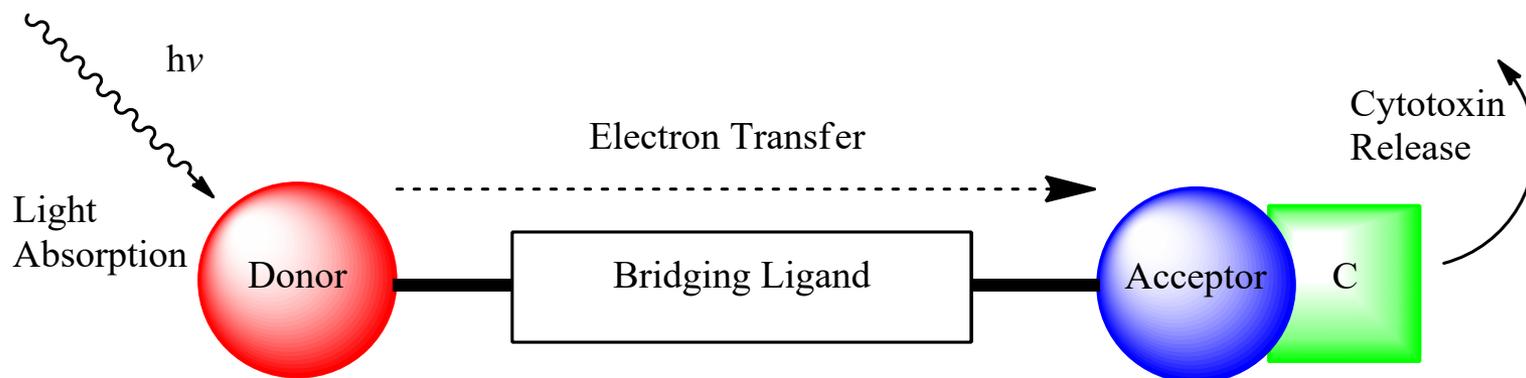
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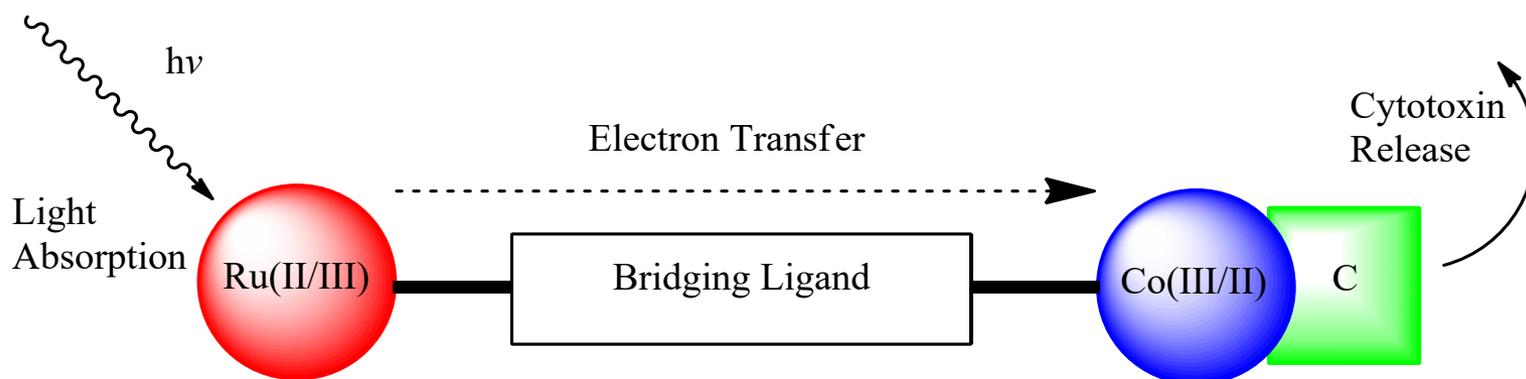
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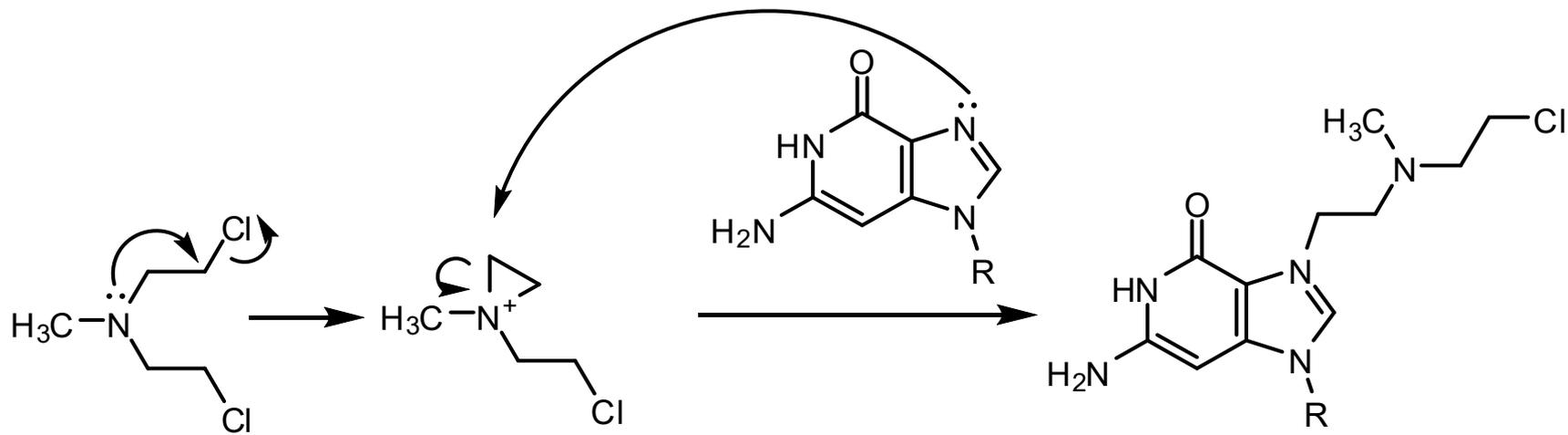
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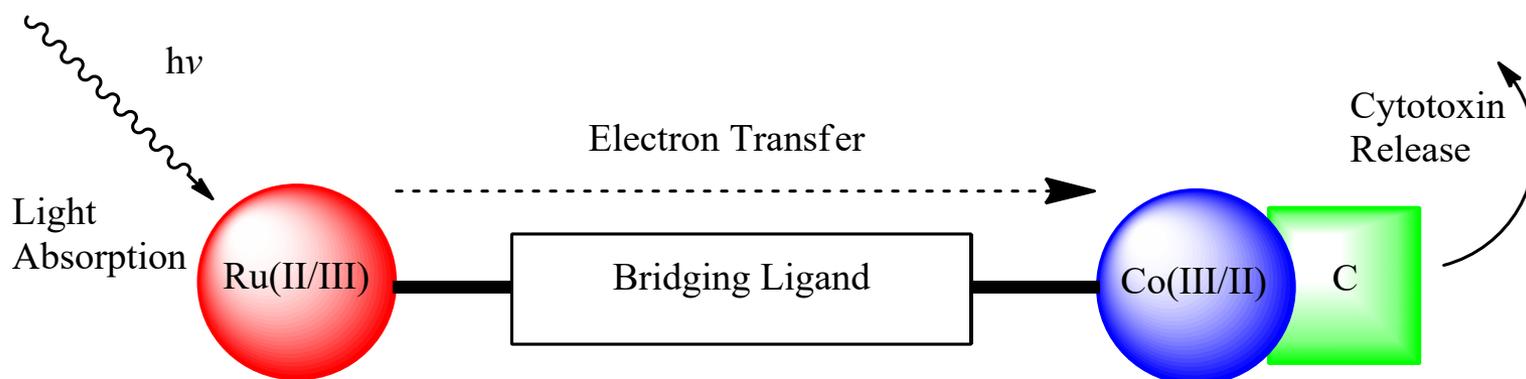


Using light to trigger release of an anti-cancer drug

Nitrogen Mustards



Photoactivated Cytotoxins

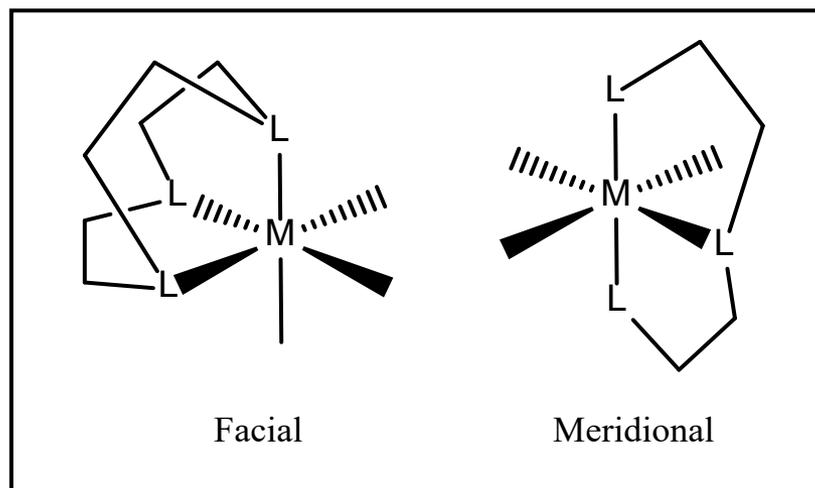
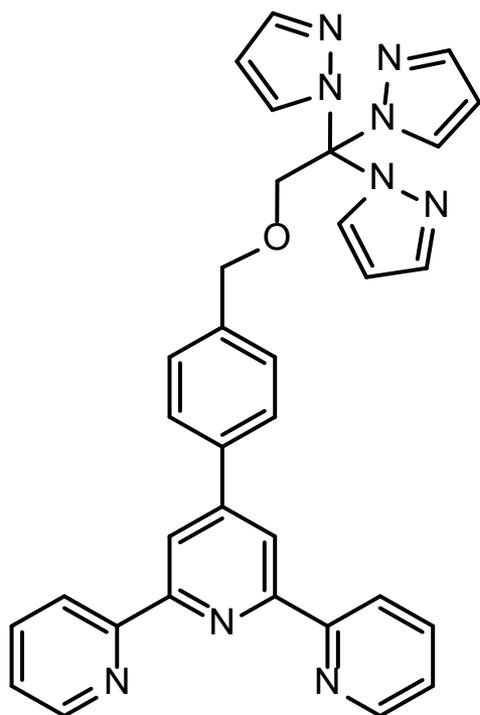


Using light to trigger release of an anti-cancer drug

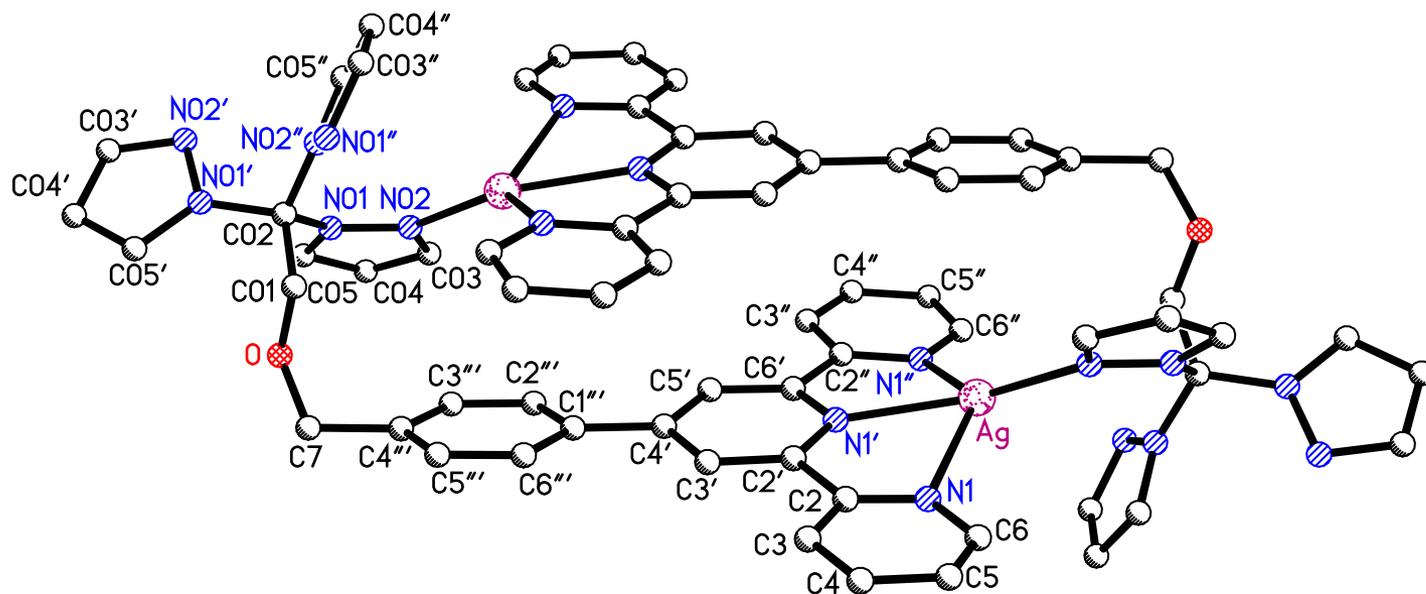
Strategies

- Binding site geometries
- Numbers of donors
- Construct a ligand on one of the metal ions

Binding Site Geometry

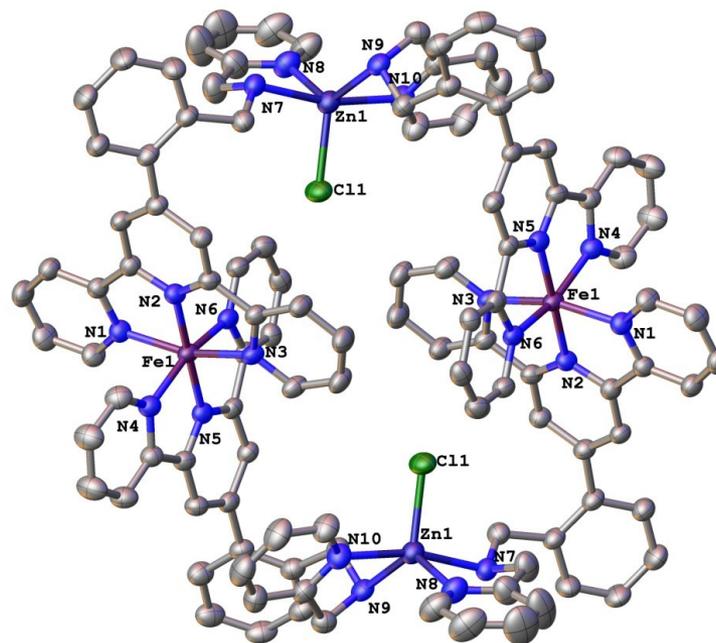
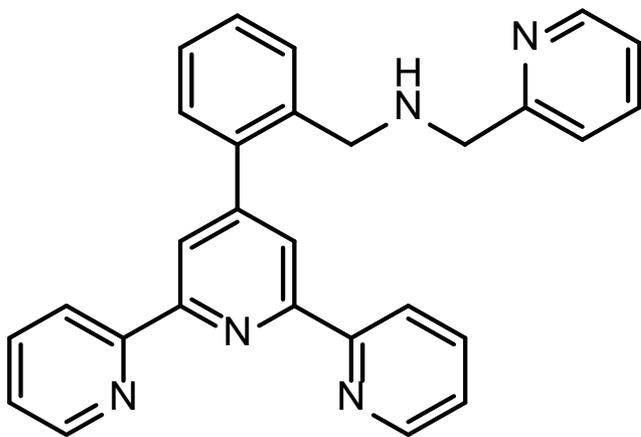


Binding Site Geometry



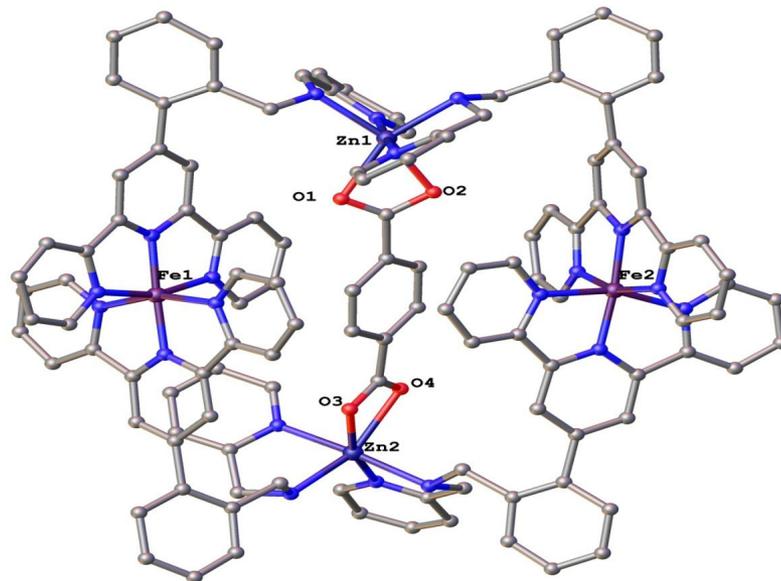
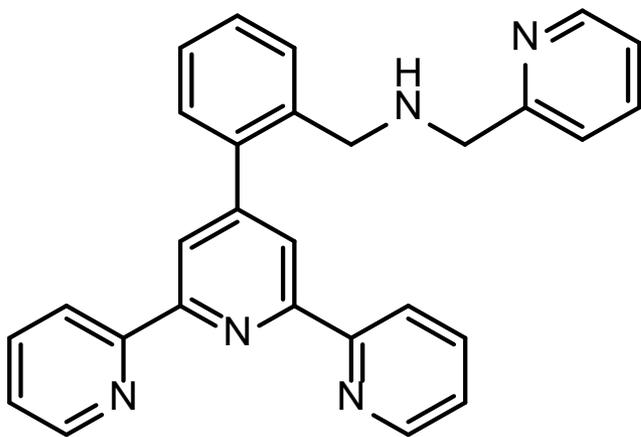
[μ -4'-4-{[2,2-di(1*H*-pyrazol-1-yl)-2-(1*H*-pyrazol-1-yl-1 κ ^{N2})ethoxy]methyl}phenyl)-2,2':6',2''-terpyridine-2 κ^3 N][μ -4'-4-{[2,2-di(1*H*-pyrazol-1-yl)-2-(1*H*-pyrazol-1-yl-2 κ ^{N2})ethoxy]methyl}phenyl)-2,2':6',2''-terpyridine-1 κ^3 N]disilver(I)

Number of Donors



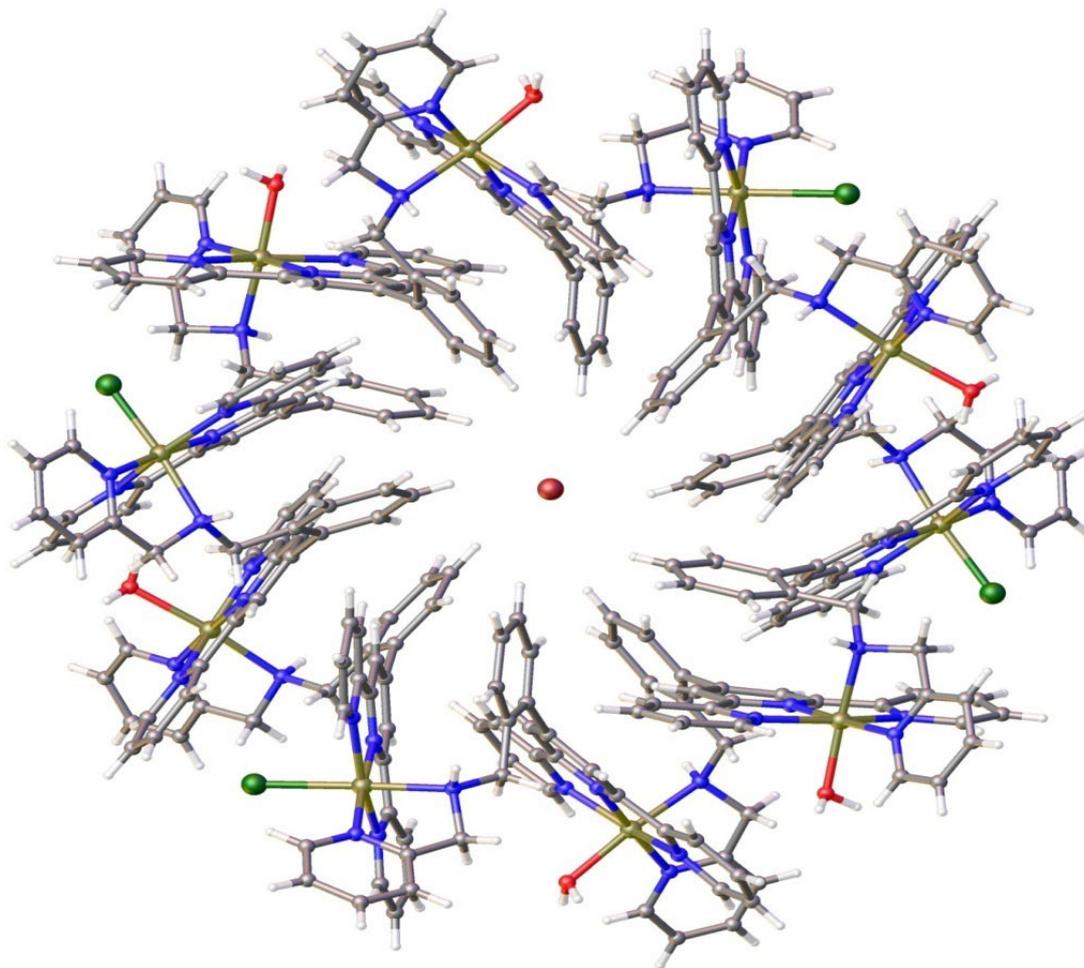
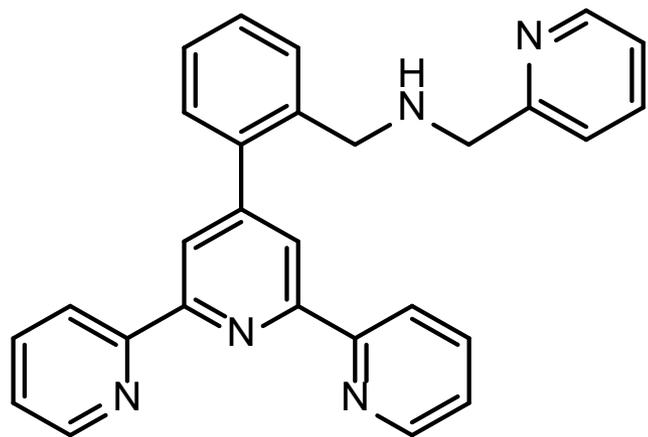
Dichlorido-3κCl,4κCl- $\{\mu$ -4'-[2-(2-pyridyl-3κN-methylamino-3κN-methyl)phenyl]-2,2':6',2''-terpyridine-1κ³N} $\{\mu$ -4'-[2-(2-pyridyl-3κN-methylamino-3κN-methyl)phenyl]-2,2':6',2''-terpyridine-2κ³N} $\{\mu$ -4'-[2-(2-pyridyl-4κN-methylamino-4κN-methyl)phenyl]-2,2':6',2''-terpyridine-1κ³N} $\{\mu$ -4'-[2-(2-pyridyl-4κN-methylamino-4κN-methyl)phenyl]-2,2':6',2''-terpyridine-2κ³N}diiron(II)dizinc(II)

Number of Donors



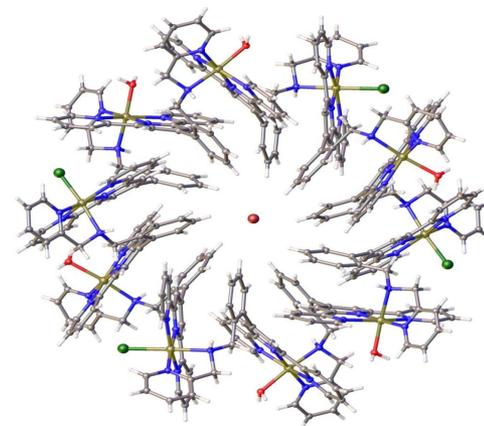
(μ -benzene-1,4-dicarboxylato- $3\kappa^2O^1:4\kappa^2O^4$){ μ -4'-[2-(2-pyridyl- $3\kappa N$ -methylamino- $3\kappa N$ -methyl)phenyl]-2,2':6',2''-terpyridine- $1\kappa^3N$]{ μ -4'-[2-(2-pyridyl- $3\kappa N$ -methylamino- $3\kappa N$ -methyl)phenyl]-2,2':6',2''-terpyridine- $2\kappa^3N$ }{ μ -4'-[2-(2-pyridyl- $4\kappa N$ -methylamino- $4\kappa N$ -methyl)phenyl]-2,2':6',2''-terpyridine- $1\kappa^3N$ }{ μ -4'-[2-(2-pyridyl- $4\kappa N$ -methylamino- $4\kappa N$ -methyl)phenyl]-2,2':6',2''-terpyridine- $2\kappa^3N$ }diiron(II)dizinc(II)

Number of Donors

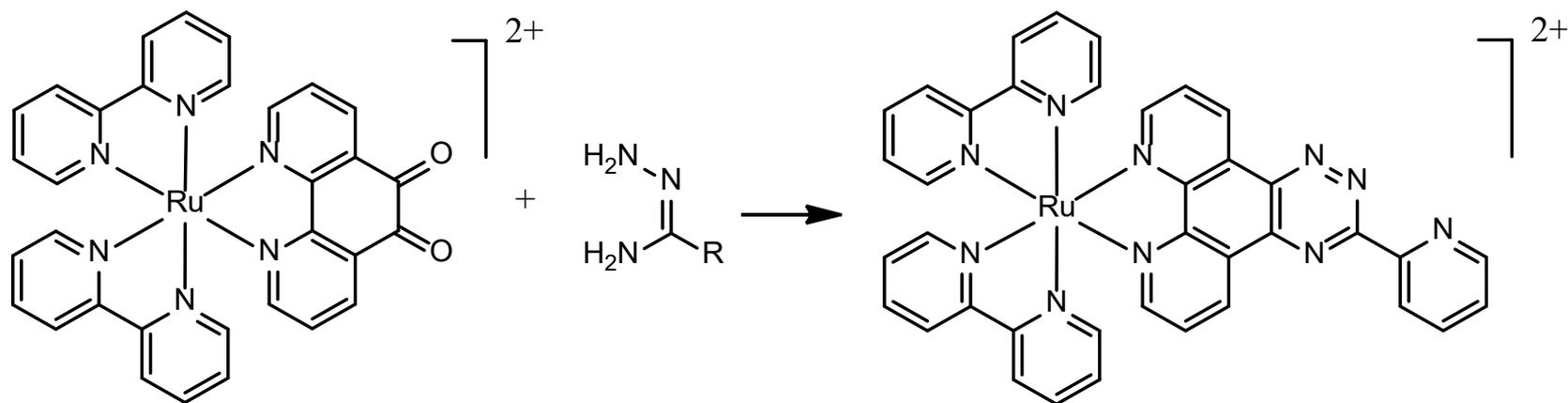


Number of Donors

Hexaaqua-1κO,2κO,3κO,4κO,5κO,6κO-tetrachlorido-7κCl,8κCl,9κCl,10κCl- $\{\mu$ -4'-[2-(2-pyridyl-1κN-methylamino-1κN-methyl)phenyl]-2,2':6',2''-terpyridine-7κ³N} $\{\mu$ -4'-[2-(2-pyridyl-2κN-methylamino-2κN-methyl)phenyl]-2,2':6',2''-terpyridine-5κ³N} $\{\mu$ -4'-[2-(2-pyridyl-3κN-methylamino-3κN-methyl)phenyl]-2,2':6',2''-terpyridine-9κ³N} $\{\mu$ -4'-[2-(2-pyridyl-4κN-methylamino-4κN-methyl)phenyl]-2,2':6',2''-terpyridine-6κ³N} $\{\mu$ -4'-[2-(2-pyridyl-5κN-methylamino-5κN-methyl)phenyl]-2,2':6',2''-terpyridine-1κ³N} $\{\mu$ -4'-[2-(2-pyridyl-6κN-methylamino-6κN-methyl)phenyl]-2,2':6',2''-terpyridine-3κ³N} $\{\mu$ -4'-[2-(2-pyridyl-7κN-methylamino-7κN-methyl)phenyl]-2,2':6',2''-terpyridine-10κ³N} $\{\mu$ -4'-[2-(2-pyridyl-8κN-methylamino-8κN-methyl)phenyl]-2,2':6',2''-terpyridine-2κ³N} $\{\mu$ -4'-[2-(2-pyridyl-9κN-methylamino-9κN-methyl)phenyl]-2,2':6',2''-terpyridine-8κ³N} $\{\mu$ -4'-[2-(2-pyridyl-10κN-methylamino-10κN-methyl)phenyl]-2,2':6',2''-terpyridine-4κ³N}decanickel(16+)

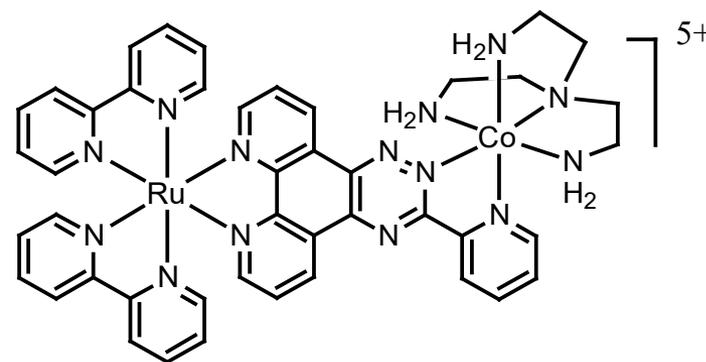
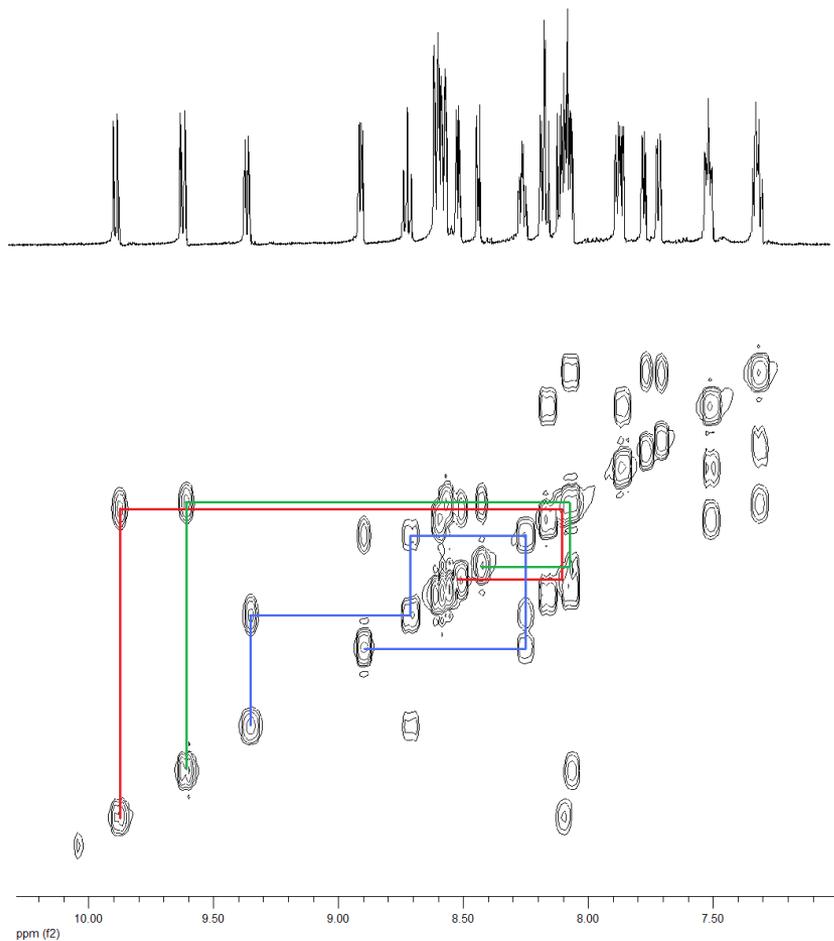


Constructing Bridging Ligands

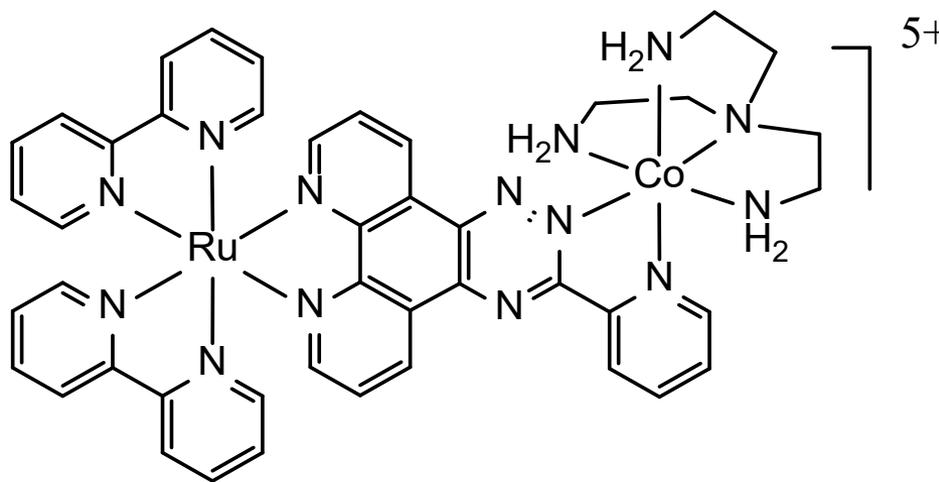


(OC-6)-bis(2,2'-bipyridine- κ^2N){3-(pyridin-2-yl)
 [1,2,4]triazino[6,5-*f*][1,10]phenanthroline-
 κ^2N }ruthenium(II)

Formation of $[(bpy)_2Ru(pytp)Co(tren)]^{5+}$

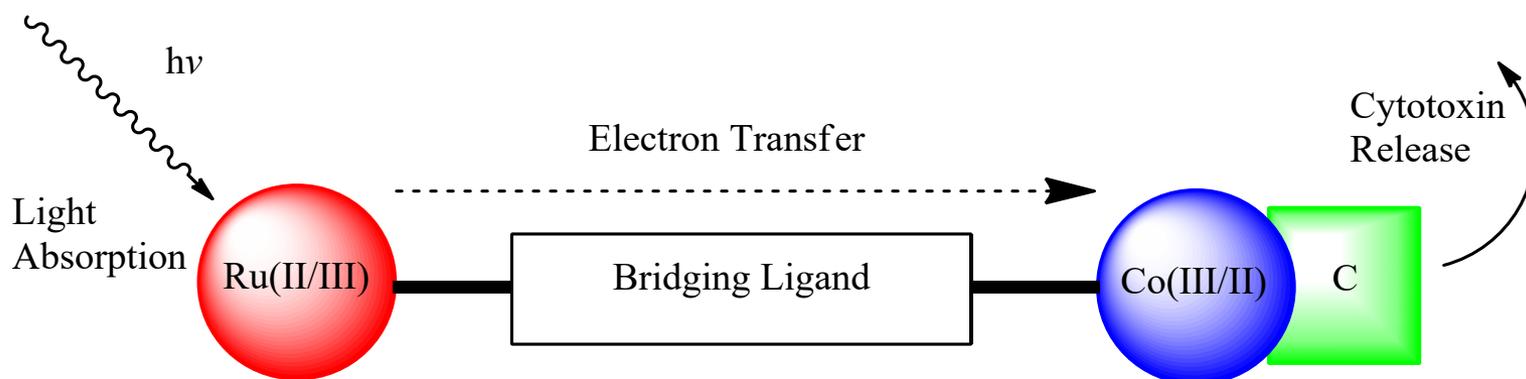


Formation of [(bpy)₂Ru(pytp)Co(tren)]⁵⁺



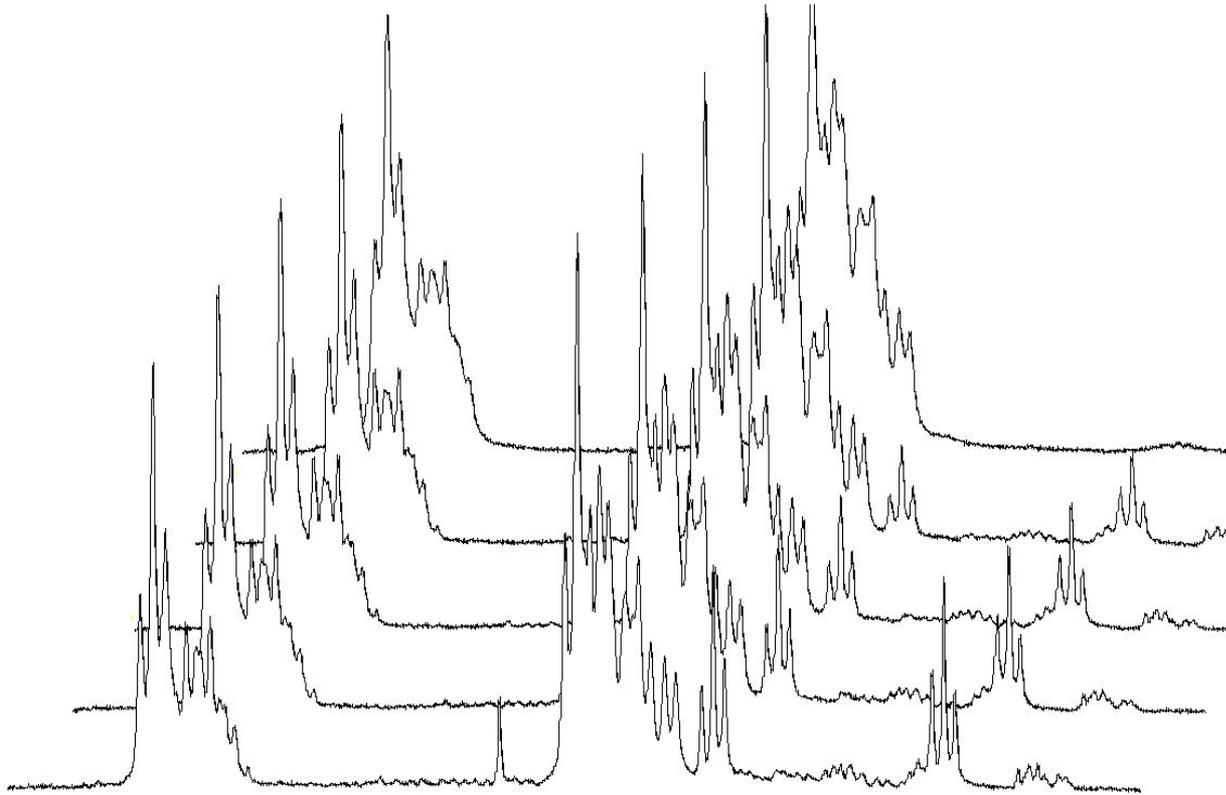
(OC-6)-(OC-6-34)-bis(2,2'-bipyridine-1κ²N)[N,N-bis(2-amino-2κN-ethyl)ethane-1,2-diamine-2κ²N]{μ-3-(pyridin-2-yl-2κN)[1,2,4]triazino-2κN²-[6,5-f][1,10]phenanthroline-1κ²N}rutheniumcobalt(5+)

Photoactivated Cytotoxins

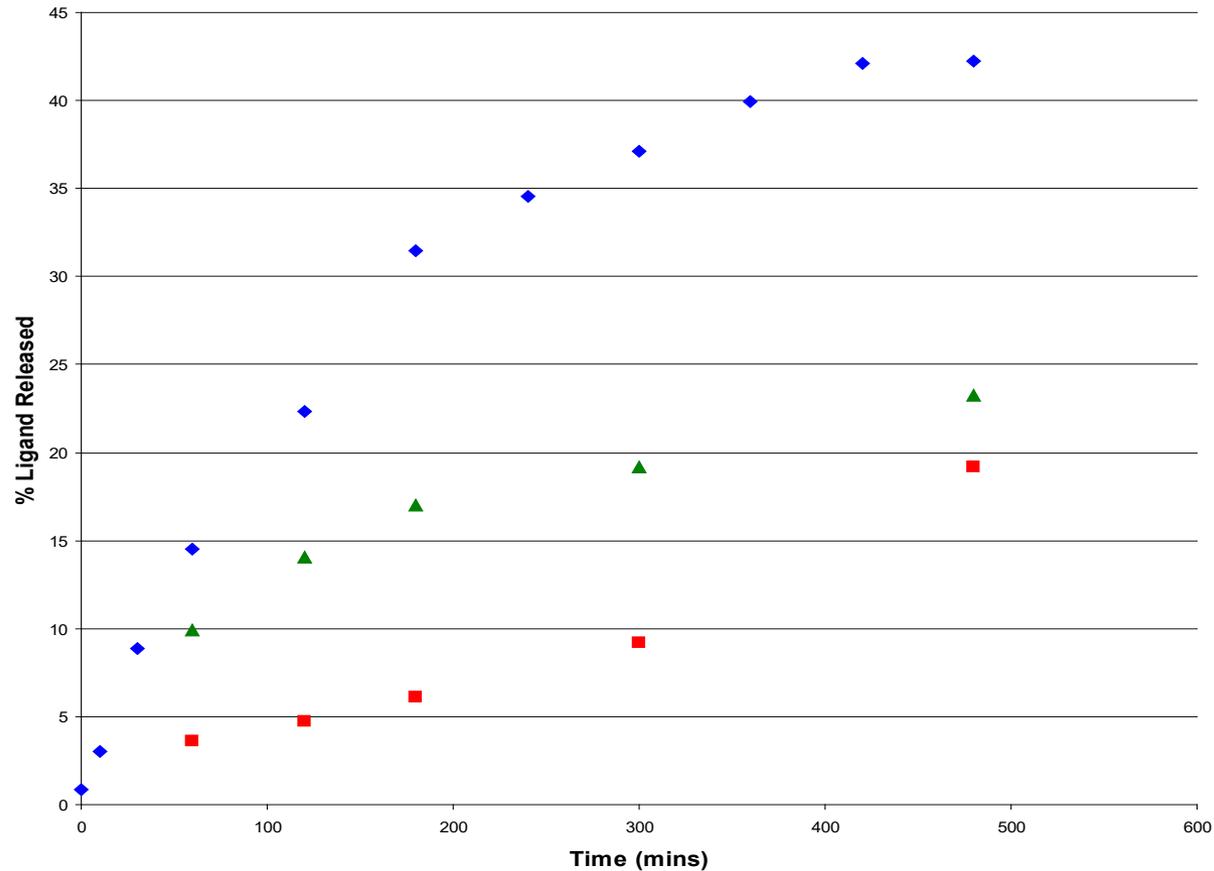


Using light to trigger release of an anti-cancer drug

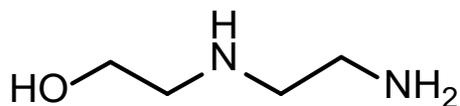
Ligand Release on Irradiation



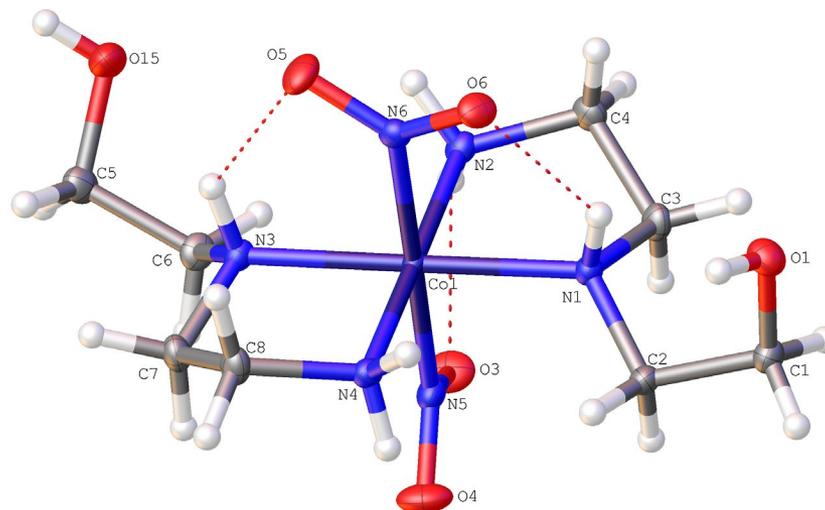
O₂ Dependence of Ligand Release



Hydroxyethylamines

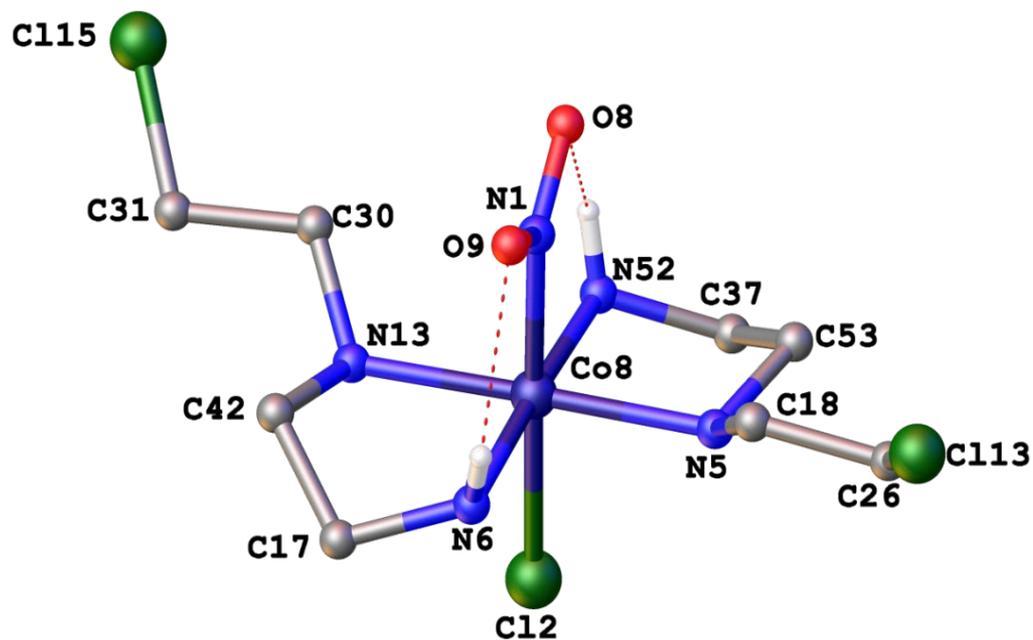


- Single diastereoisomer
- HCl or HOTf treatment leads to alcohol coordination and deprotonation (ms evidence)

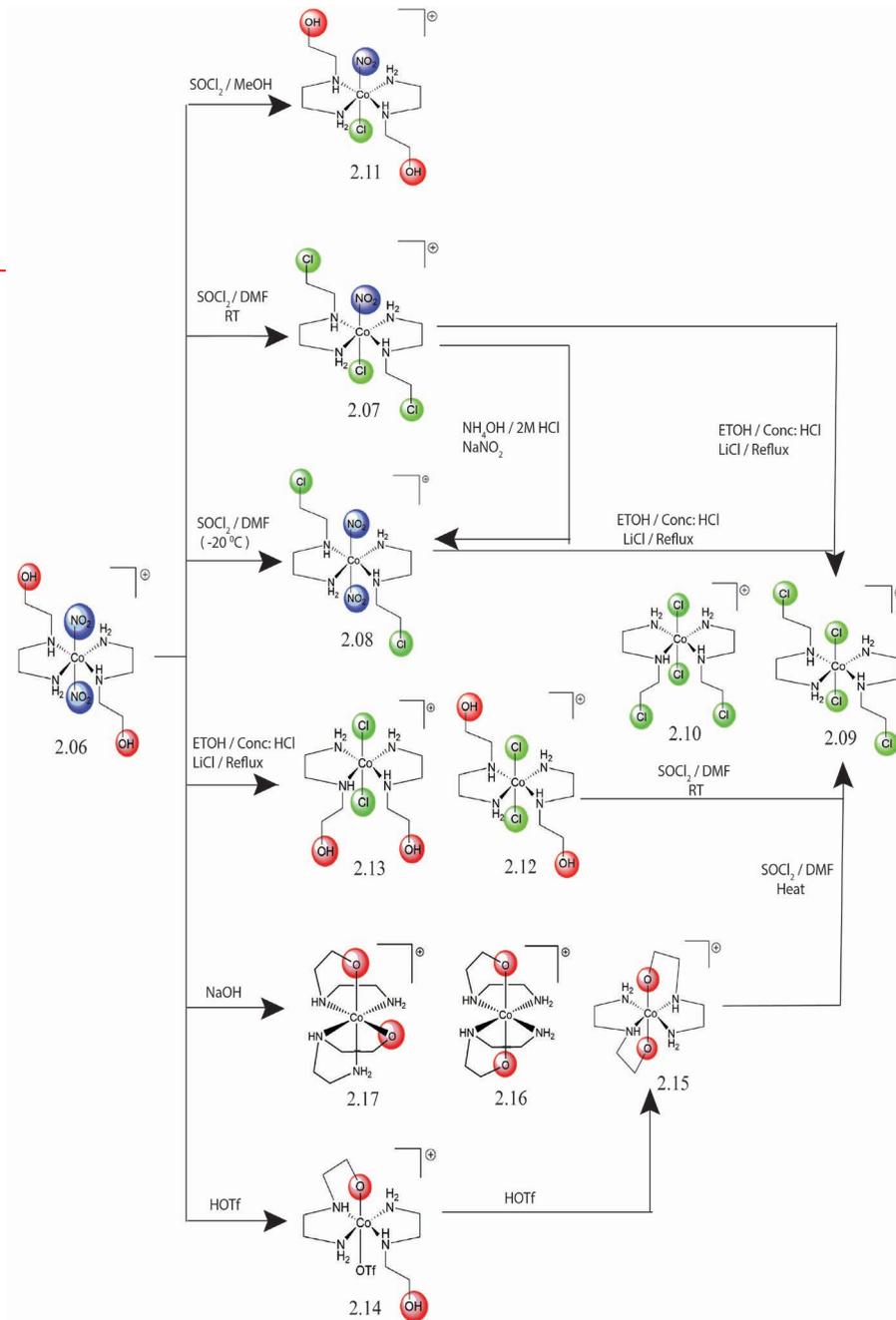


(OC-6-12)-Bis[*N*-(2-hydroxyethyl)ethane-1,2-diamine- κ^2N]dinitrito- κ^2N -cobalt(+)

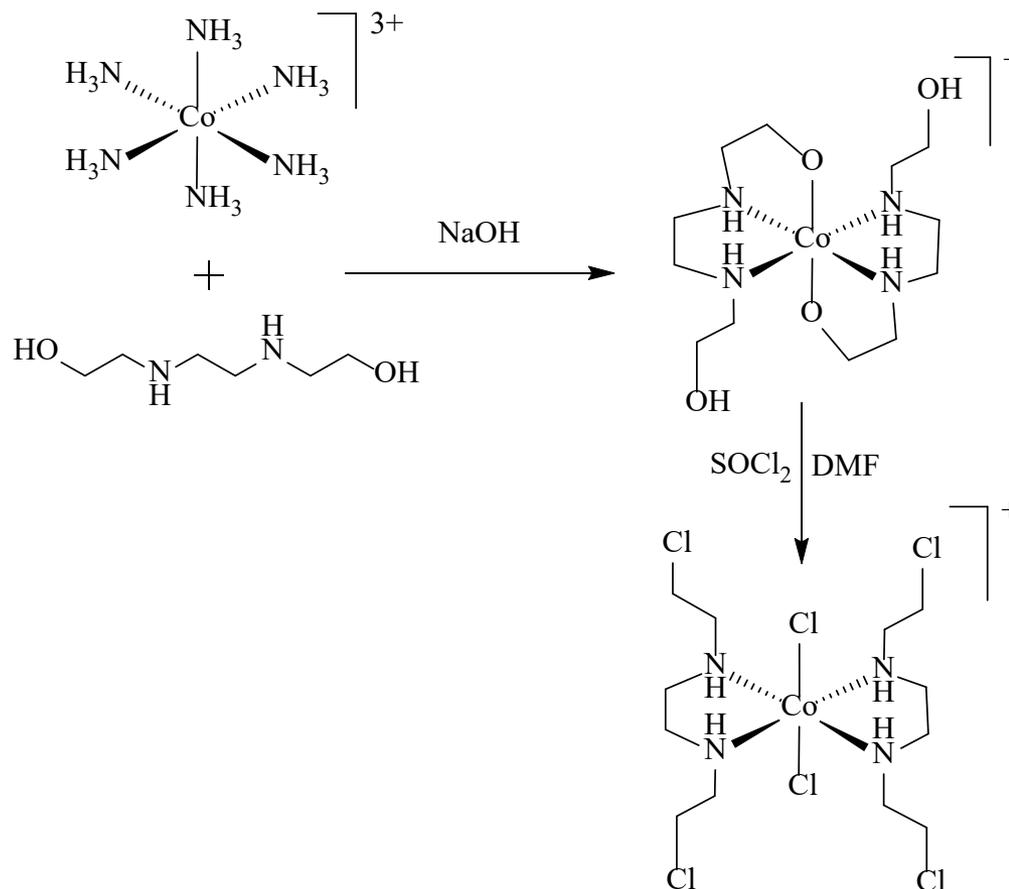
Hydroxyethylamines



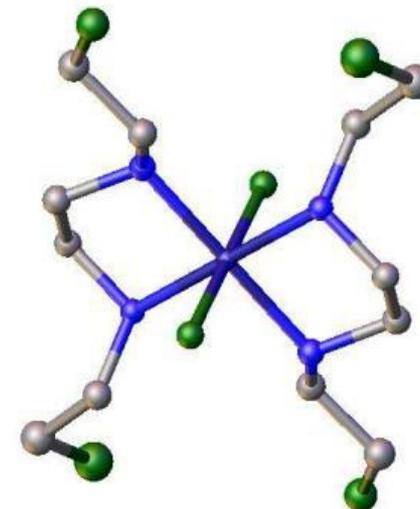
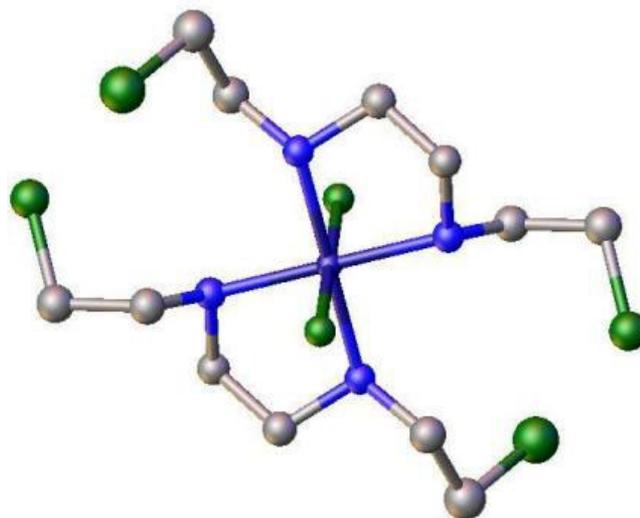
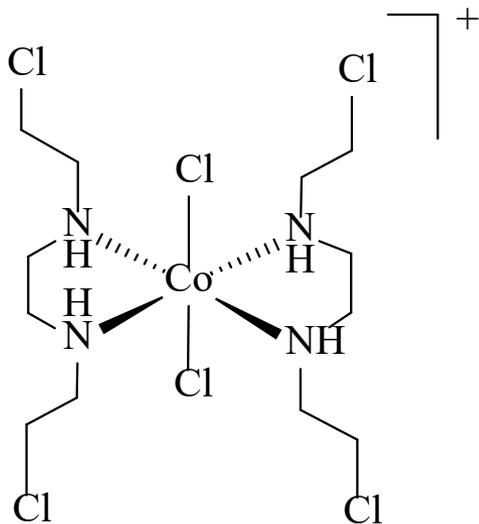
(OC-6-23)-Chloridobis[*N*-(2-chloroethyl)ethane-1,2-diamine- κ^2N]nitrito- κN -cobalt(+)



Making a Cobalt-Mustard Complex

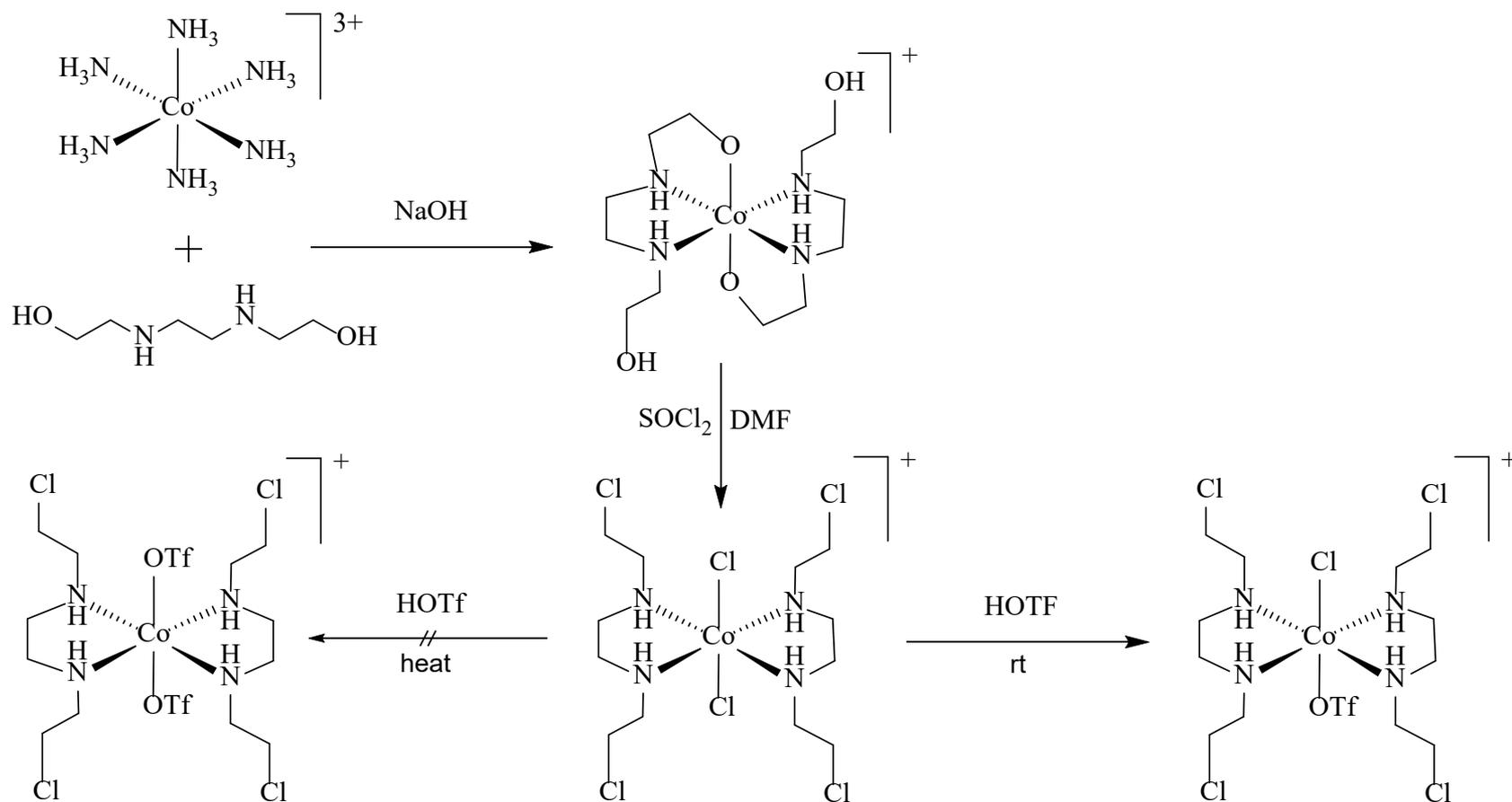


Making a Cobalt-Mustard Complex

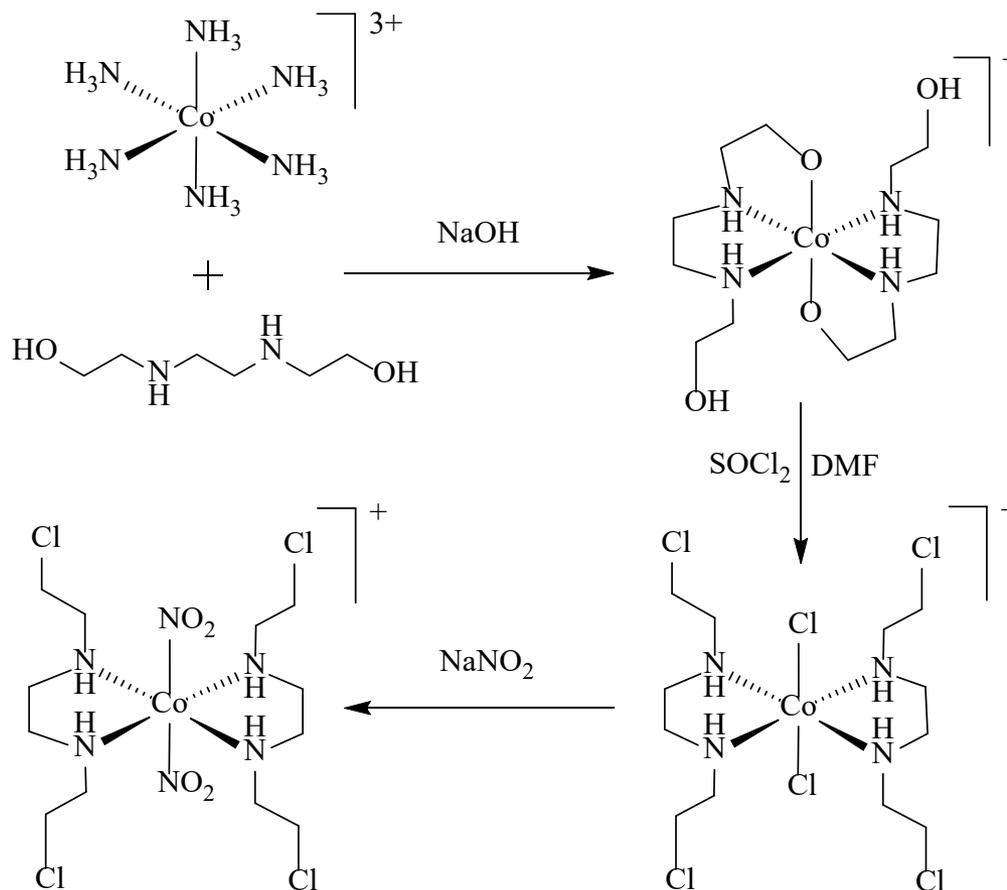


(OC-6-12)-Bis[*N*¹,*N*²-bis(2-chloroethyl)ethane-1,2-diamine]dichloridocobalt(+)

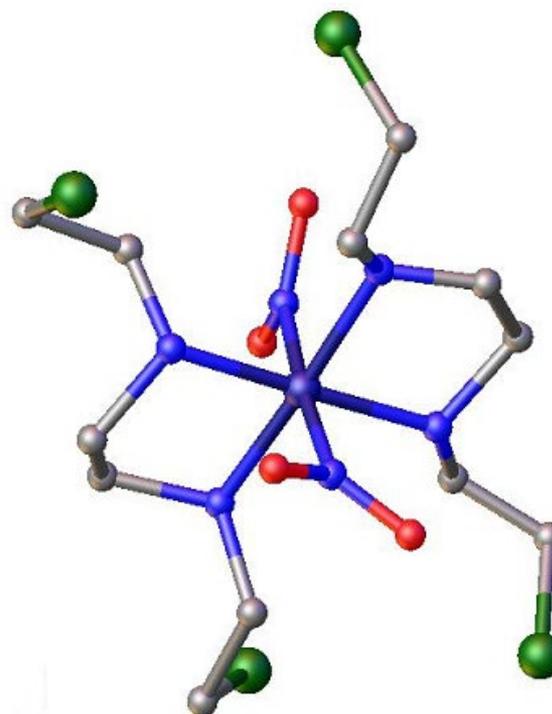
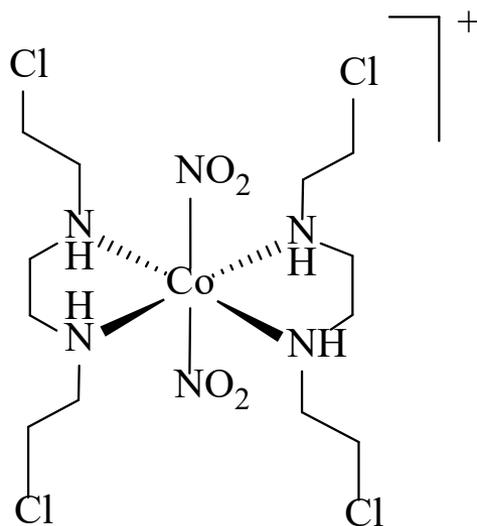
Making a Cobalt-Mustard Complex



Making a Cobalt-Mustard Complex

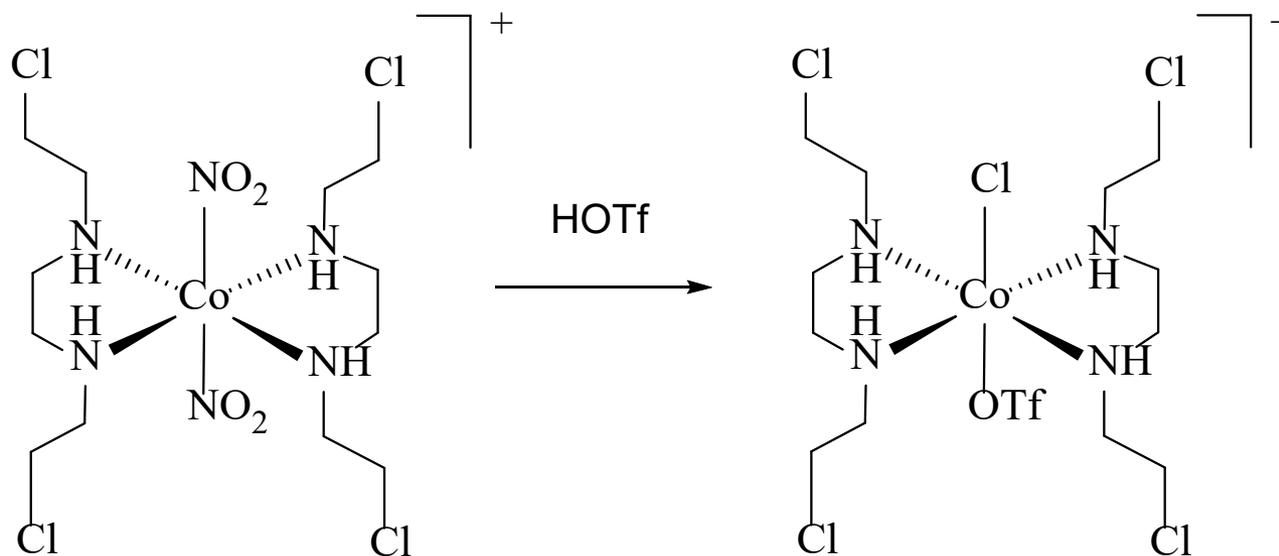


Making a Cobalt-Mustard Complex



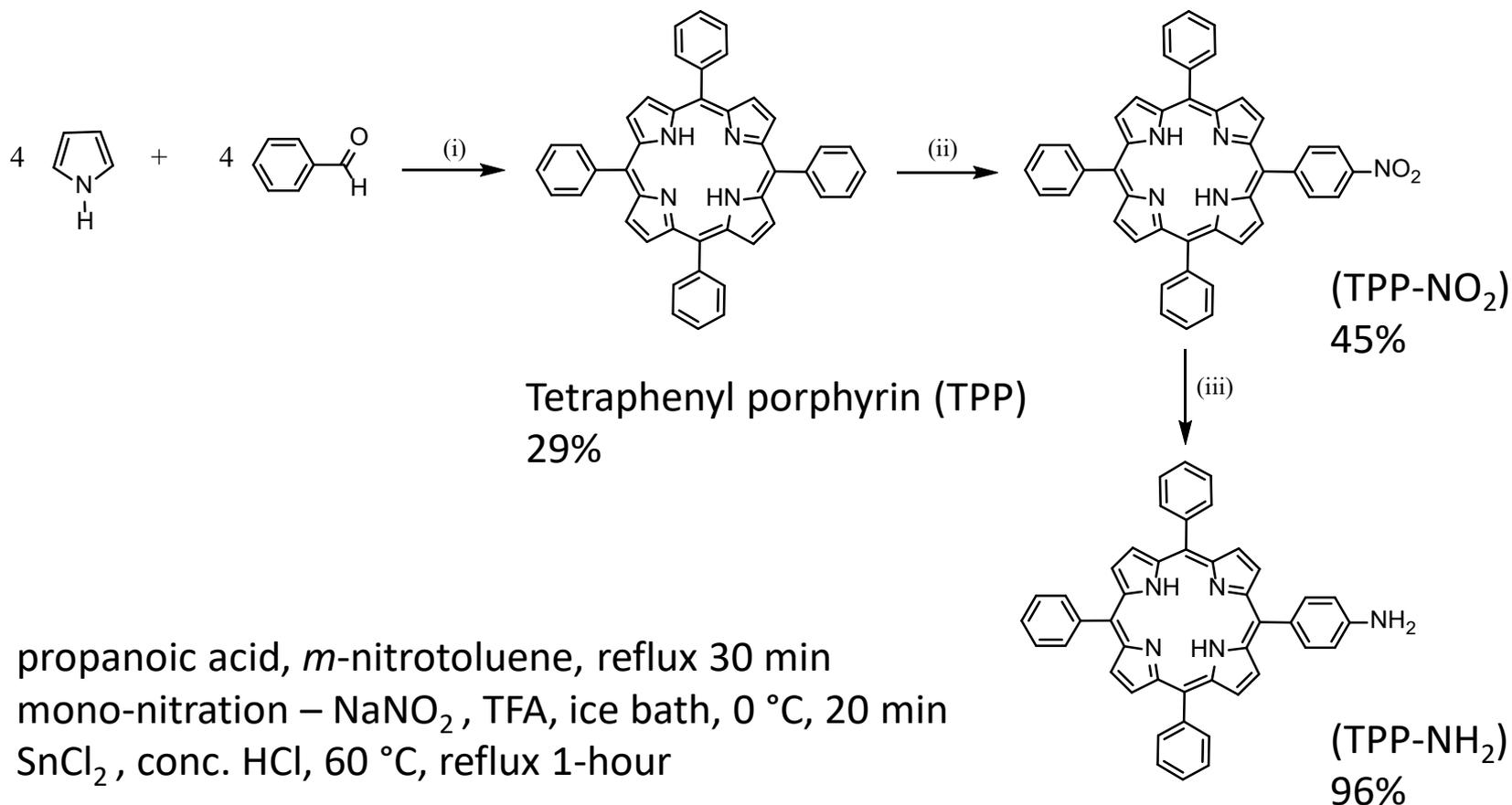
(OC-6-12)-Bis[*N*¹,*N*²-bis(2-chloroethyl)ethane-1,2-diamine- κ^2N]dinitrito- κ^2N -cobalt(+)

Making a Cobalt-Mustard Complex



(OC-6-23')-Chloridobis[*N*¹,*N*²-bis(2-chloroethyl)ethane-1,2-diamine- κ^2N]trifluoromethanesulfonato- κO -cobalt(+)

Synthesis of a Monosubstituted Porphyrin Ligand



(i) propanoic acid, *m*-nitrotoluene, reflux 30 min

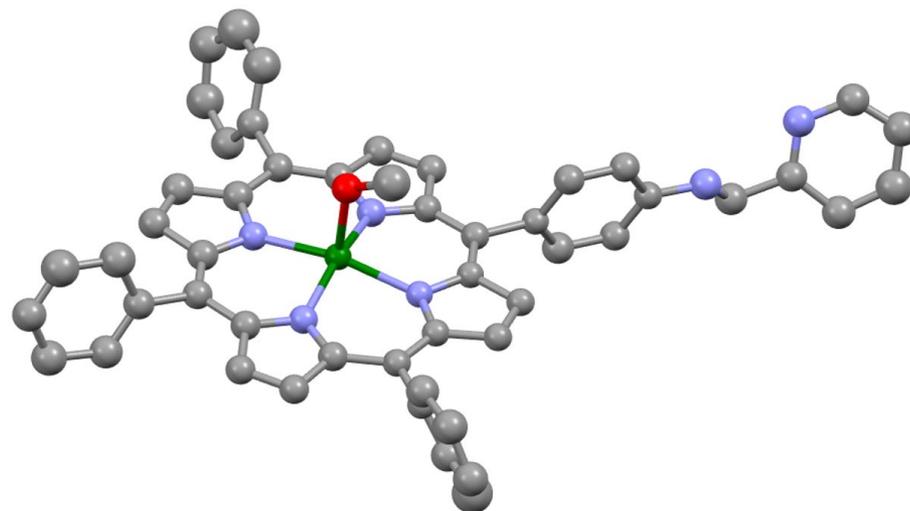
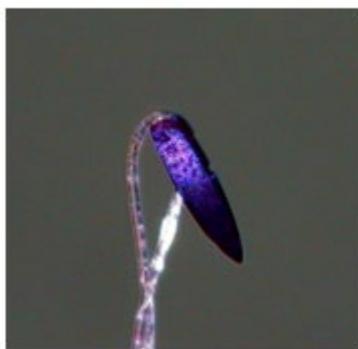
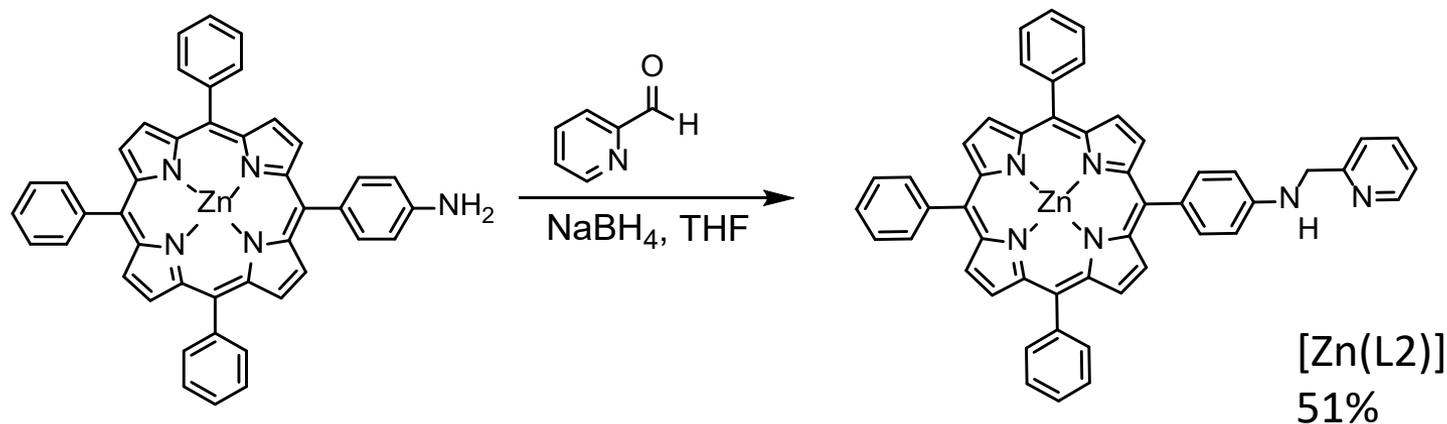
(ii) mono-nitration – NaNO₂, TFA, ice bath, 0 °C, 20 min

(iii) SnCl₂, conc. HCl, 60 °C, reflux 1-hour

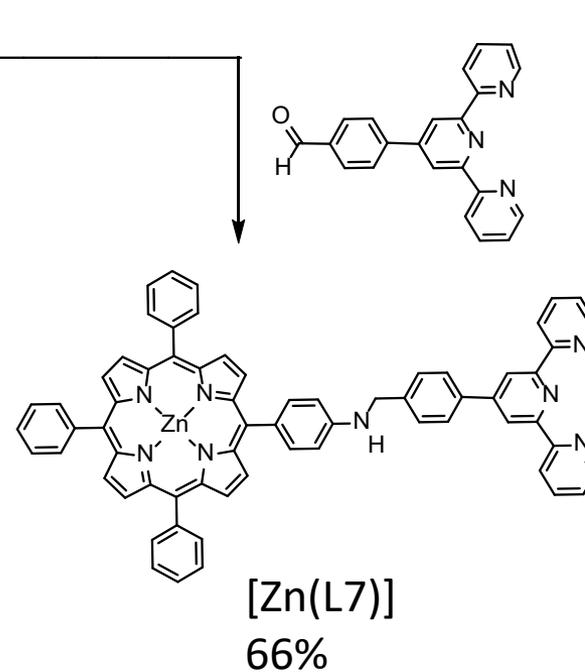
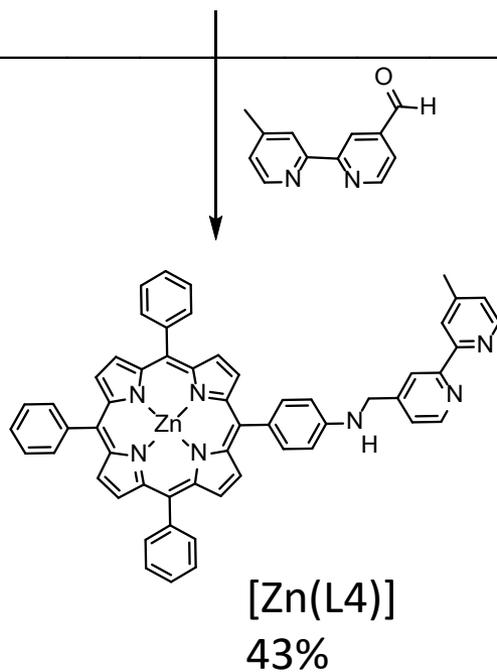
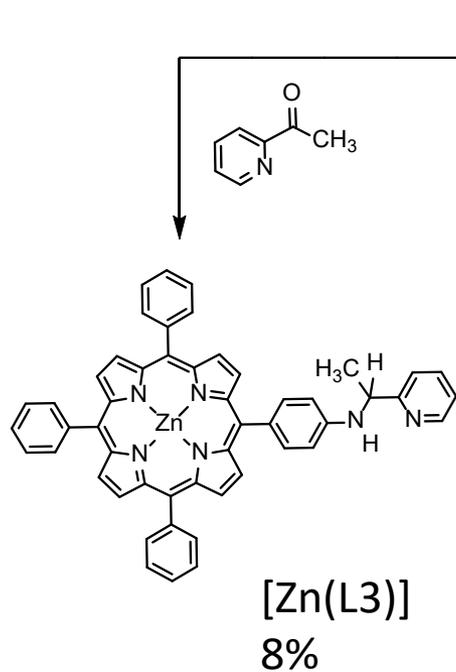
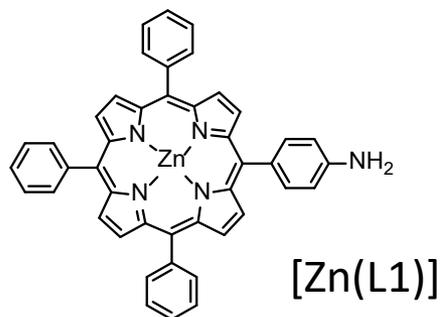
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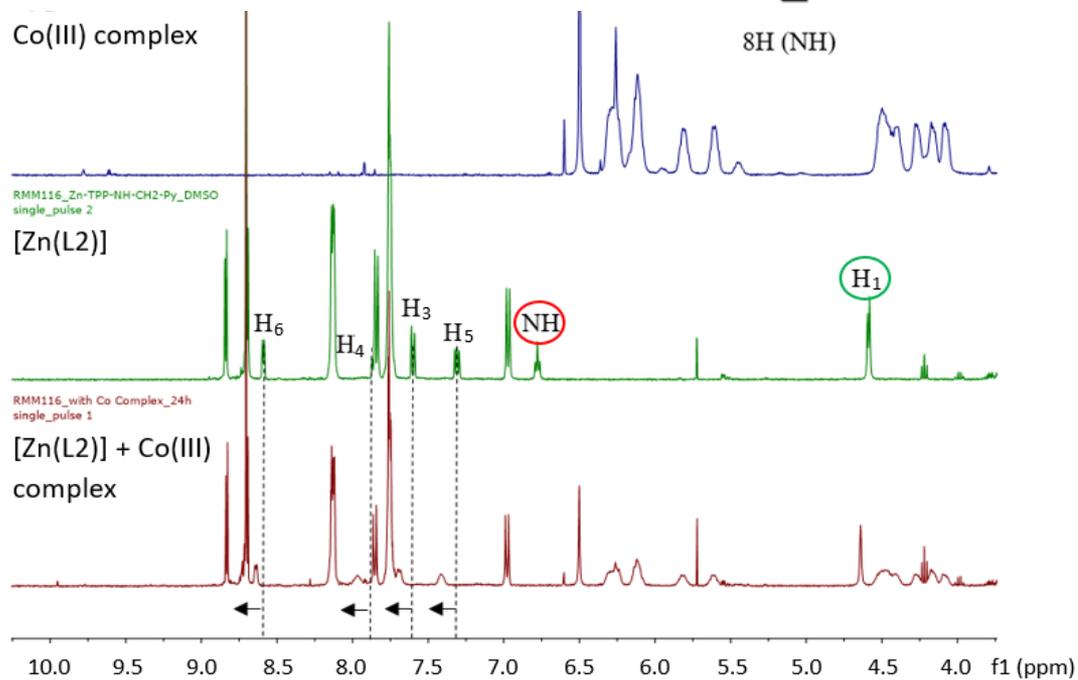
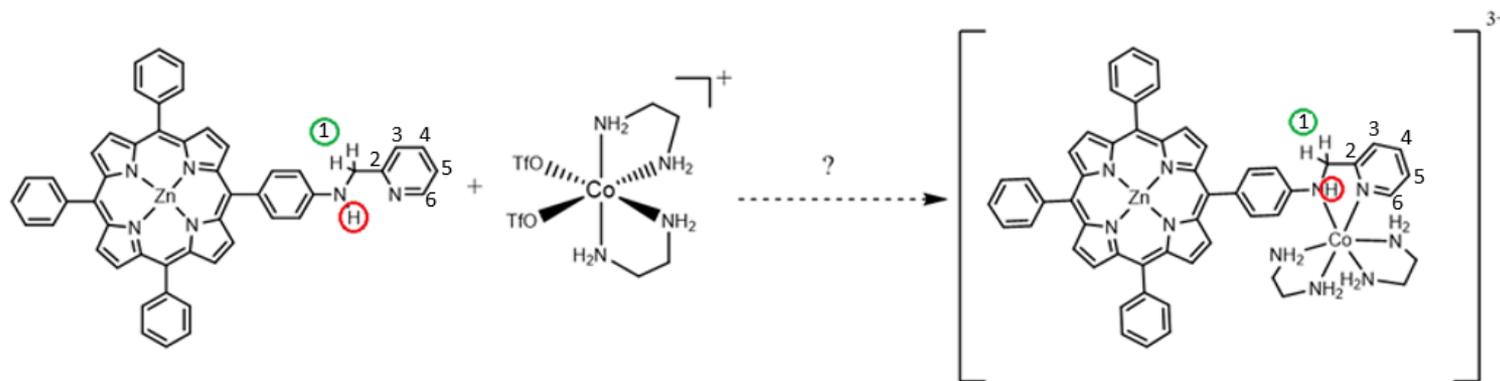
Reductive Amination



Further Reductive Amination Reactions



Complexation of Co(III)



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