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Outer-Sphere Ruthenium Catalysts for the Generation of Value Added Chemicals

Austin College – Sherman, Texas

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and John C. Gordon

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Around Town

Manhattan Project

J. Robert Oppenheimer
1st Director of LANL

Leslie Groves
Army Corps of Engineers

Fat Man

Trinity Test Site

Little Boy

Los Alamos Today

“Roadrunner”
Supercomputer

LANL/P&G
Engineering

Ultrasound-Waveform
Tomography

Pu-Power Source/
Onboard Analyzers

Zika/Dengue
Vaccines

HIV Vaccine
(Theoretical Biology)

Research Portfolio

Nuclear Fuel Development for Commercial Reactors (TerraPower)

Earth's Field NMR

Unnatural Base Pairs for Detecting Gene Expression/DNA Storage

Catalysis Studies at LANL

- DOE: Replace 25% of petroleum-derived chemicals with bio-renewable alternatives by 2025.
- Majority of Platform Chemicals in use today are carboxylic acids (CAs) or esters.

Why Catalysis?

- Organic synthesis of dimethylcarbonate:

- Use of toxic reagents
 - Moderate yields
 - Requires tedious purification
 - Low efficiency and plenty of waste
- Catalytic synthesis of dimethylcarbonate:

- Selective
- High yielding
- Easy workup
- Minimal waste

One More Example

- Hydrocyanation of acetaldehyde:

- Biochemical fermentation of sugars, starch, milk products, etc.

Technical Problems

Largely resolved using
Noyori-type catalysts
under mild conditions

Less electrophilic
carbonyl makes reaction
more challenging

Catalyst Types

Heterogeneous

Nanocatalysis

Enzymatic

Pyrococcus furiosus

Homogeneous

Firmenich

TAKASAGO

Industry Standards

Relatively inexpensive, high reactivity, limited selectivity, highly air sensitive

Relatively inexpensive, lower reactivity, limited selectivity, mildly air sensitive

Very inexpensive, high reactivity, limited selectivity, highly air sensitive

Breaking Symmetry

Givaudan®

- Ligand synthesis (LANL v. Givaudan v. Takasago)
- Catalyst synthesis
- Catalysis (Reaction conditions, substrate scope, etc.)

Ligand Synthesis (Competition)

Ligand Synthesis (LANL)

Ligand Synthesis (LANL)

Ligand Reduction and Complex Synthesis

R = Me, ^tBu, Ph, Bn

Ligand Reduction and Complex Synthesis

R = Me, ^tBu, Ph, Bn

Initial Reactivity Studies

Ru-MACHO

Ru-Gusev

Ru(SNAPOR)

Ru(SNPR)

S/C = 20,000

Pictet-Spengler
Reaction

Initial Reactivity Studies

Catalyst	%Conversion	%Selectivity (Hem)	Catalyst	%Conversion	%Selectivity (Hem)
Ru-MACHO	96	86	Ru-Gusev	43	98
Ru(SNAPO ^{Me})	12	98	Ru(SNP ^{Me})	92	98
Ru(SNAPO ^{tBu})	11	98	Ru(SNP ^{tBu})	79	98
Ru(SNAPO ^{Ph})	9	98	Ru(SNP ^{Ph})	90	98
Ru(SNAPO ^{Bn})	8	98	Ru(SNP ^{Bn})	82	99

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Base Optimization

% conv.⁻¹

Comparative Studies

Catalyst	Substrate	Product	Solvent	T, °C	h	Conv.	Sel.
Ru-MACHO			neat	40	6	33	42
Ru-Gusev			neat	40	6	100	>99
Ru(SNPMe)			neat	40	6	>99	99

Proposed Mechanism

C=O/C=C Bond Selectivity

Eucalyptus olida

Methyl Cinnamate

*Widely used in
perfume industry*

C=O/C=C Bond Selectivity

TON = 2,400

Solvent (5 mL)	Conv.	A	B	C
Neat	0	0	0	0
THF	0	0	0	0
Toluene	100	4	5	82
MeOH	>98	48	17	28

Catalyst	Time (h)	Conv.	Sel.
Ru-MACHO	24	10	0
Ru-Gusev	4	59	33
Ru(SNP^{Me})	4	98	48

Firmenich

2008, Saudan

TON ~200

2015, Pidko

TON = 1800

2017, de Vries

TON ~360

Hydrogenation of Chiral Molecules

Catalyst	Solvent	T, °C	h	Conv.	%ee
 Ru-MACHO	MeOH	40	24	30	~97
 Ru-Gusev	MeOH	40	24	74	~97
 Ru(SNPMe)	MeOH	40	24	69	~97

Higher concentrations of base result in racemization of product.

Determination of ee prior to acquisition of chiral GC column was not possible. Need another substrate bearing chromophore.

Hydrogenation of Chiral Molecules

Catalyst	Solvent	T, °C	h	Conv.	%ee
 Ru-MACHO	MeOH	40	18	99	~1
 Ru-Gusev	MeOH	40	18	82	~3
 Ru(SNPMe)	MeOH	40	18	95	~1

Benzylic proton highly prone to deprotonation and racemization.

A Few Other Examples – Unsaturated Esters

Catalyst	Substrate	Product	Solvent	Time	Conv.	Sel.
Ru-MACHO (S/C=5,000)			neat	6	22	0
Ru-Gusev (S/C=5,000)			neat	6	97	94
Ru(SNP ^{Me}) (S/C=5,000)			neat	6	97	94
Ru-MACHO (S/C=2,500)			MeOH	48	85	4
Ru-Gusev (S/C=2,500)			MeOH	48	54	45
Ru(SNP ^{Me}) (S/C=2,500)			MeOH	48	88	40

A Few Other Examples – Fluorinated Esters

A Few Other Examples – Fluorinated Esters

Catalyst	Substrate	Product	Base	Time	Conv.	Sel.
Ru-MACHO (S/C=100k)			<i>t</i> BuOK (25 mol%)	8	72	74
Ru-Gusev (S/C=100k)			<i>t</i> BuOK (25 mol%)	8	54	96
Ru(SNP ^{Me}) (S/C=100k)			<i>t</i> BuOK (25 mol%)	8	80	86
Ru-MACHO (S/C=5,000)			MeONa (25 mol%)	6	100	57
Ru-Gusev (S/C=5,000)			MeONa (25 mol%)	6	57	75
Ru(SNP ^{Me}) (S/C=5,000)			MeONa (25 mol%)	6	85	88

A Few Other Examples – Fluorinated Esters

Catalyst	Substrate	Product	Base	Time	Conv.	Sel.
Ru-MACHO (S/C=50k)			<i>t</i> BuOK (25 mol%)	8	75	83
Ru-Gusev (S/C=50k)			<i>t</i> BuOK (25 mol%)	8	43	93
Ru(SNP ^{Me}) (S/C=50k)			<i>t</i> BuOK (25 mol%)	8	76	96
Ru-MACHO (S/C=50k)			<i>t</i> BuOK (25 mol%)	6	95	63
Ru-Gusev (S/C=50k)			<i>t</i> BuOK (25 mol%)	6	37	100
Ru(SNP ^{Me}) (S/C=50k)			<i>t</i> BuOK (25 mol%)	6	70	90

As A Result...

Provisional Patent
068177/529350

2nd Provisional Patent
in Preparation

Licensing Agreement
MTA: 16-N03712

Manuscript in Preparation

Future Work with Ru(SNP^R)

- Targeting other DOE specified biorenewables.
- Wastewater remediation (agricultural nitrates).
- Degradation of polyesters.

- Destruction of Chemical Warfare Agents (Emerging Threats Lab).

G-Series

V-Series

GV-Series

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Extra Slides

Fluorinated Ester is Reduced Via H-/H⁺ Outer-Sphere Hydrogenation (X = H, Na, Me)

DFT/ ω B97X-D/ECP60MDF_VTZ(Ir) /6-311+G**(C,H,N,O,P,S,F,Na)/SMD(MeOH) level of theory

N-H group is not involved in H-bonding
i.e. ligand is **non-cooperative**

Decreased Activities Upon Alkylation for the Alternative Mechanism of the Noyori Hydrogenation Reaction

“Chemically innocent” but “cooperative” ligand

- H-bonding is destroyed!
- Steric constraints are increased!