Chemical Fixation of CO_2 to Acrylates Using Low-Valent Molybdenum Sources

DE-FE0004498

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Brown University
In cooperation with Charles Stark Draper Labs

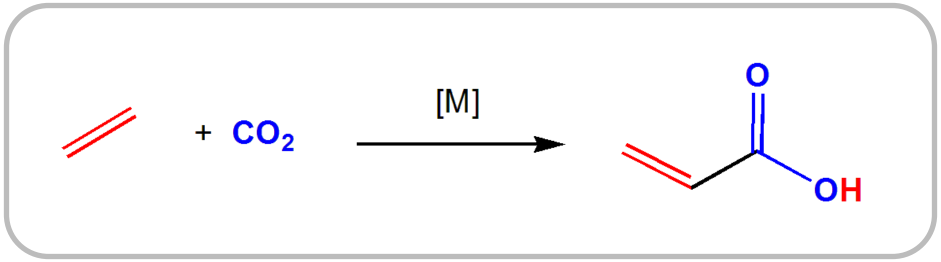
U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage

August 21-23, 2012

Presentation Outline

- Benefits & overview of deriving acrylates from coupling carbon dioxide and ethylene



- Chemical catalysis approach: background and battles left to fight
- Experimental assessment of the viability of thermochemical acrylate production
- Perspectives for the future

Benefit to the Program

- This project identifies the critical catalyst features necessary to promote carbon dioxide coupling with ethylene to acrylate at molybdenum catalysts. This research demonstrates the viability of acrylate production as a target for beneficial CO_2 utilization, and initiates this catalyst technology develop. This methodology will contribute to the goal of fixing CO_2 in stable products for indirect storage.

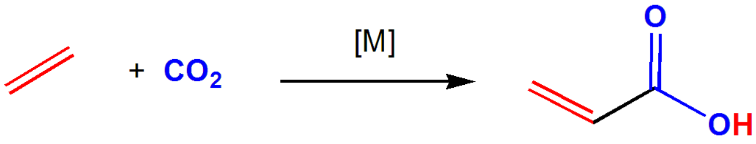
Project Overview:
Goals and Objectives

- Determine the scope and mechanism of CO_2 and ethylene coupling at molybdenum.
  - Test a range of zerovalent molybdenum complexes for activity with a family of ligands and determine the factors that control the reaction.
- Validate reductive elimination of acrylates required for catalysis.
  - Use active species to assay the potential for reductive acrylate extrusion.
- Employ findings regarding critical features for CO_2 and ethylene coupling in optimized catalyst screening methods

Guiding Motivations

Present & Future of Acrylate Synthesis

Proposed:



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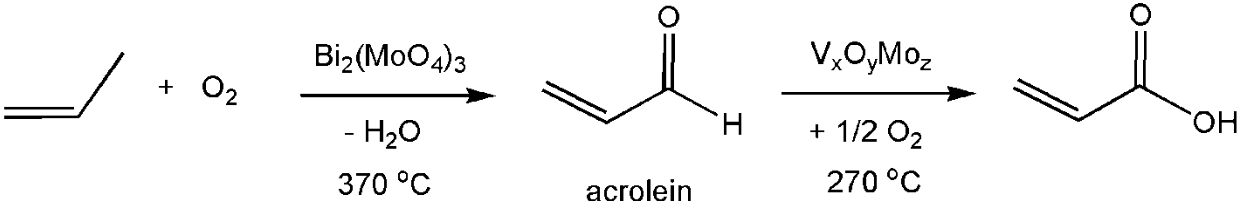

Guiding Motivations

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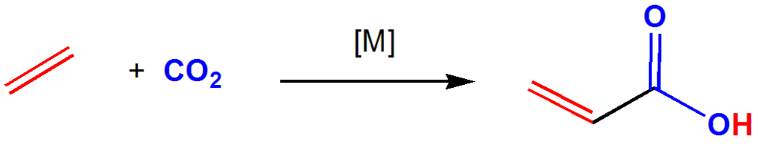

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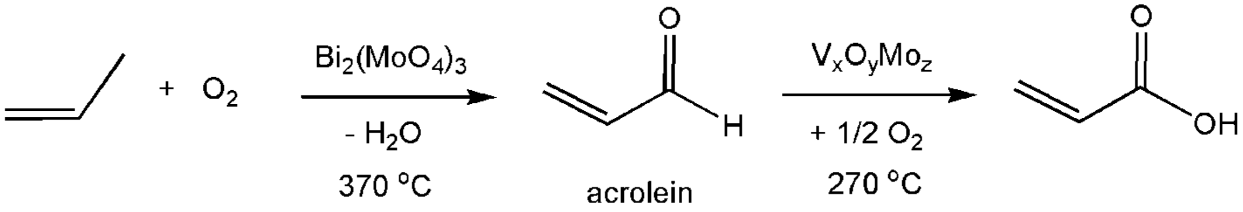
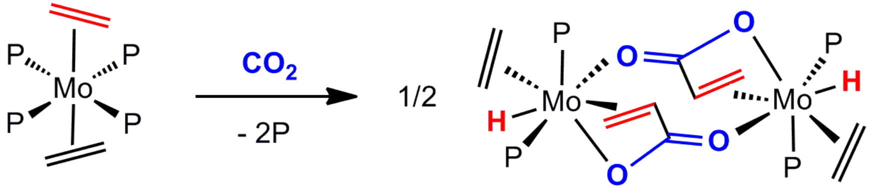


- Currently produce ~5 MMT of acrylic acid/yr (SAP largest single use)
- Using CO_2 as carbon source with same net carbon requirements of the current process would equate to 3-8 MMT tons of CO_2 (up to 1 billion gal of gasoline)
- Economic Value and Industrial Investment: Propylene (~70 ct/lb); Ethylene (~55ct/b)

Reference: The Chemical Economics Handbook & EPA Gas Equivalence Calculator

Why Molybdenum?

Prior Art-Molybdenum



P = PMe$_3$, PMe$_2$Ph,
P(OMe)$_3$, P(OEt)$_3$

Carmona, E.; *et al*. *J. Am. Chem. Soc.* **1985**, *107,* 5529*.*
Galindo, A.; Pastor, A.; Pérez, P.J.; Carmona, E. *Organometallics* **1993**, *12,* 4443*.*
Collazo, C.; Conejo, M.; Pastor, A.; Galindo, G. *Inorg. Chim. Acta* **1998**, *272,* 125.

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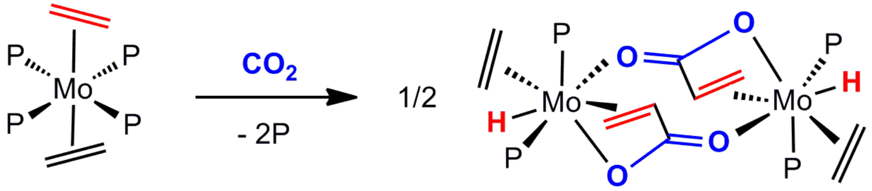

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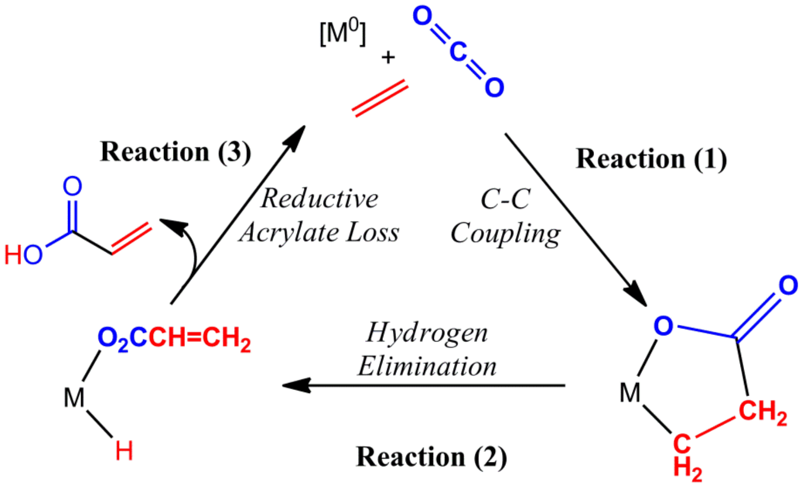
Catalysis Needs

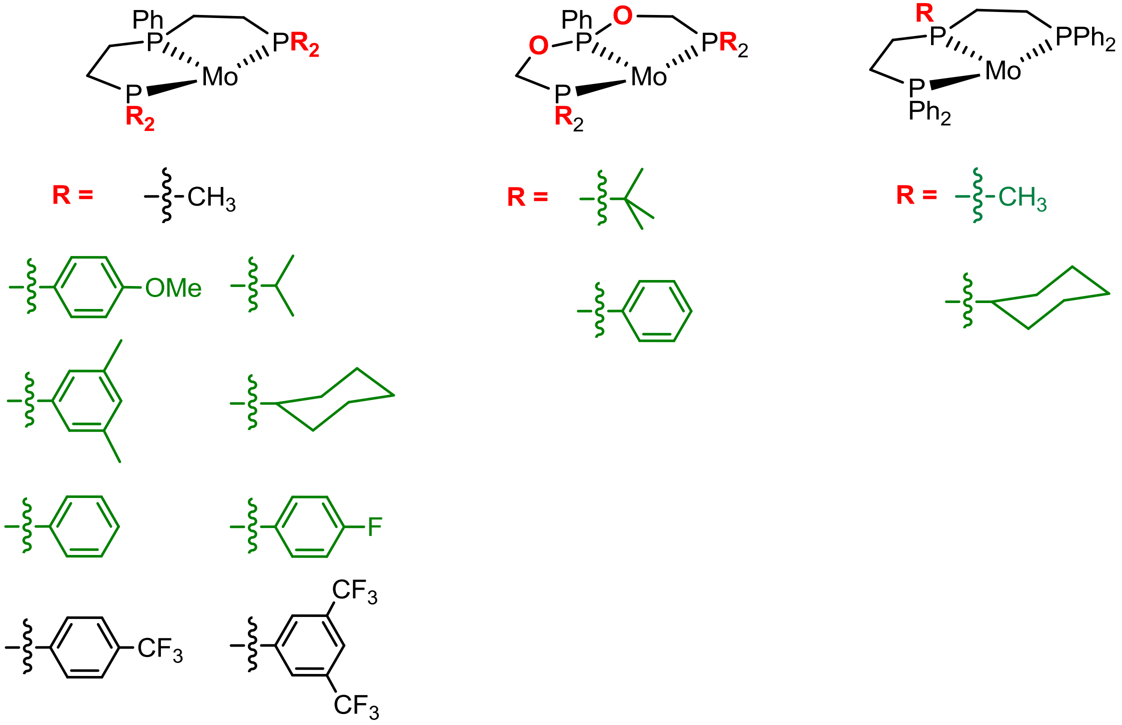


- Molybdenum is quite capable of reactions 1 & 2
- Little is known about what makes molybdenum the “rare” success
- Reductive acrylate loss and catalyst regeneration methods (reaction 3) still require viability test

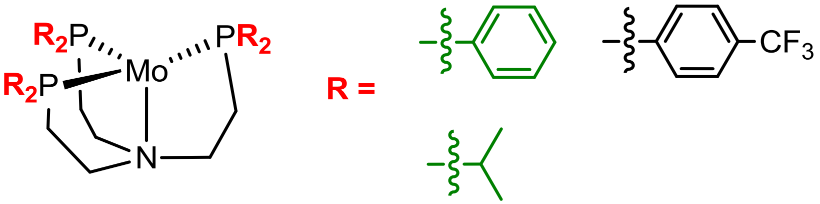
Tridentate and Tetradentate

Targeted Family of Zerovalent Complexes

Tridentate:



Tetradentate:



Tridentate and Tetradentate

Targeted Family of Zerovalent Complexes

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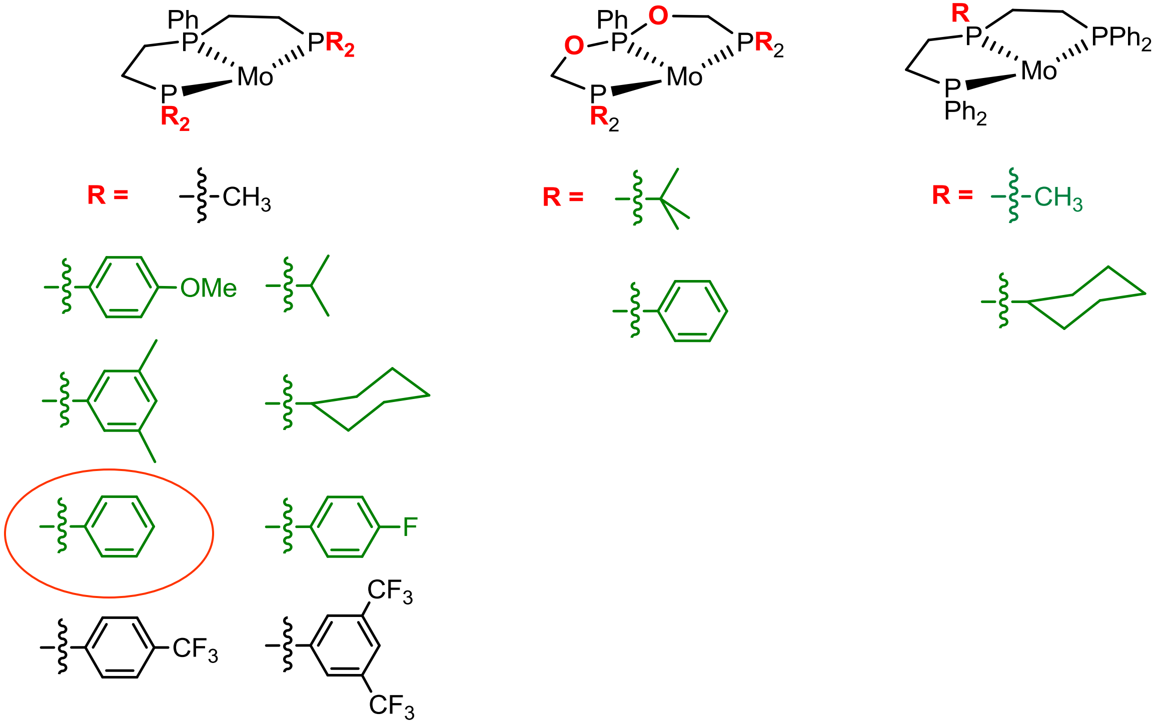
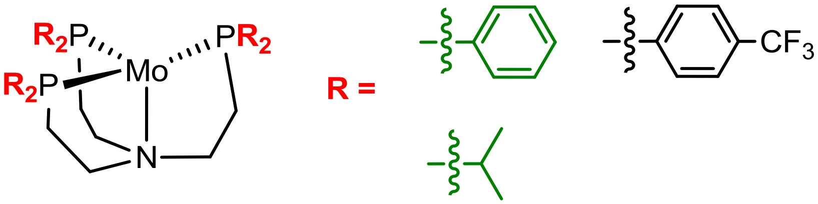
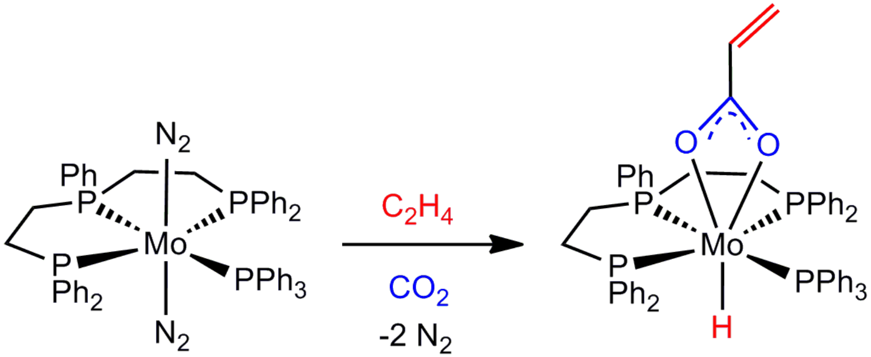


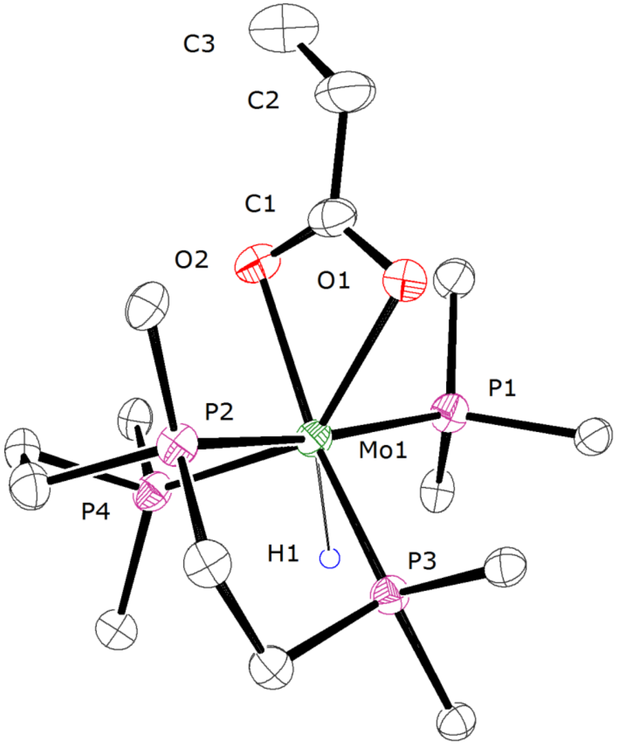
Tetradentate:



Leading Candidate

First New CO_2-Ethylene Acrylate in 15 Years





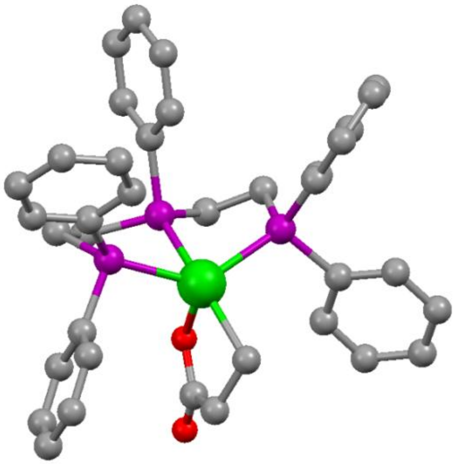
^{1}H NMR: δ -4.71, tdd, Mo-*H*
$^2J_{P\text{-}H}$ = 14, 42, 75Hz
4.68, dd, $CH=CH_2$
5.15, dd, $CH=CH_2$
5.48, dd, $CH=CH_2$

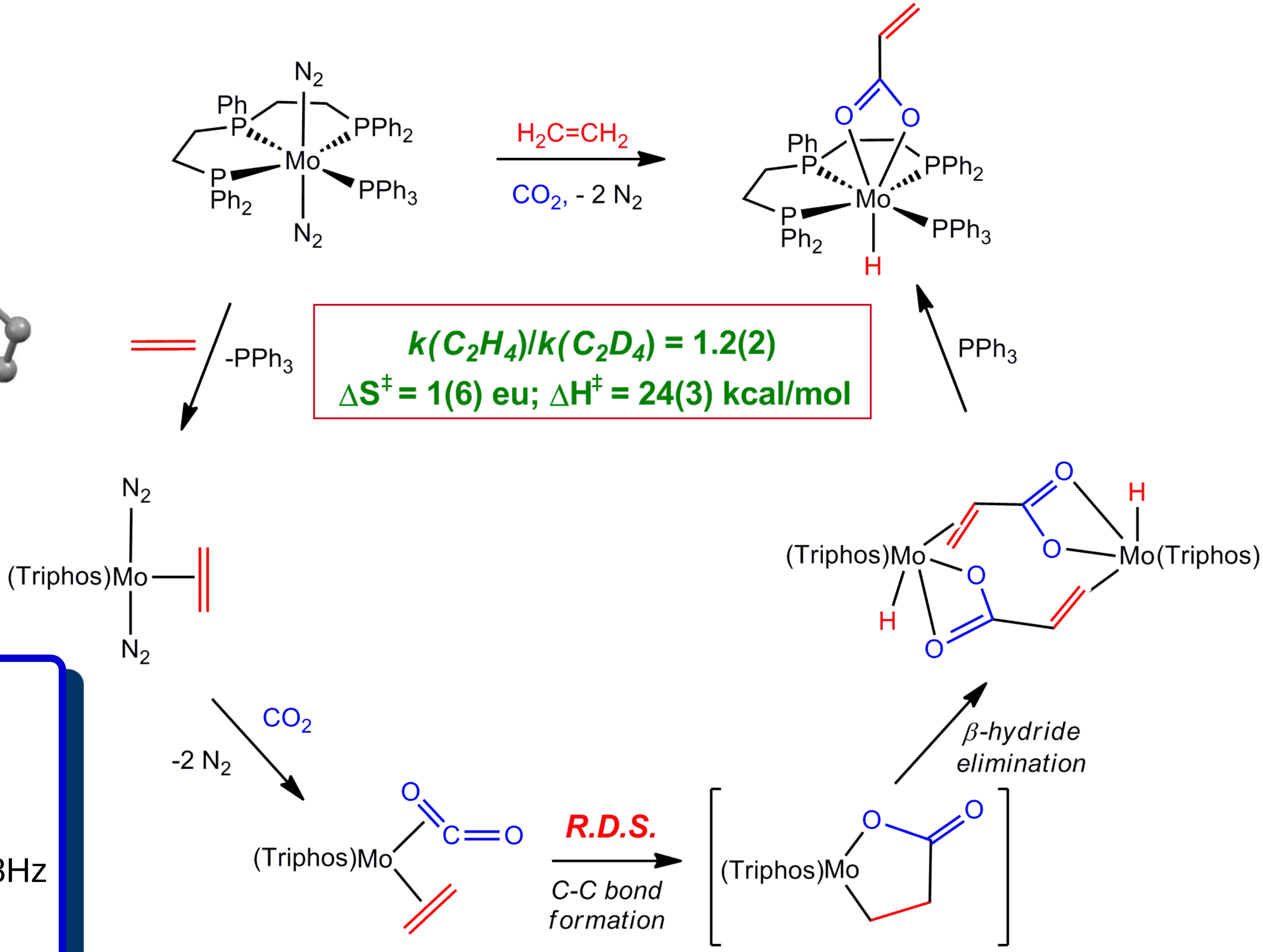
^{31}P NMR: δ 47.7, dt, 12, 155Hz
99.4, dt, 19, 155Hz
109.7, dd, 12, 19Hz

IR(KBR): $\nu_{C=O}$: 1516 cm^{-1}

Bernskoetter, W.H.; Tyler, B. T. *Organometallics* **2011**, *30*, 520.

Mechanism of Action





$k(C_2H_4)/k(C_2D_4)$ = 1.2(2)
$\Delta S^{\ddagger}$ = 1(6) eu; $\Delta H^{\ddagger}$ = 24(3) kcal/mol

^{1}H NMR: δ 0.25, m, C_2H_4

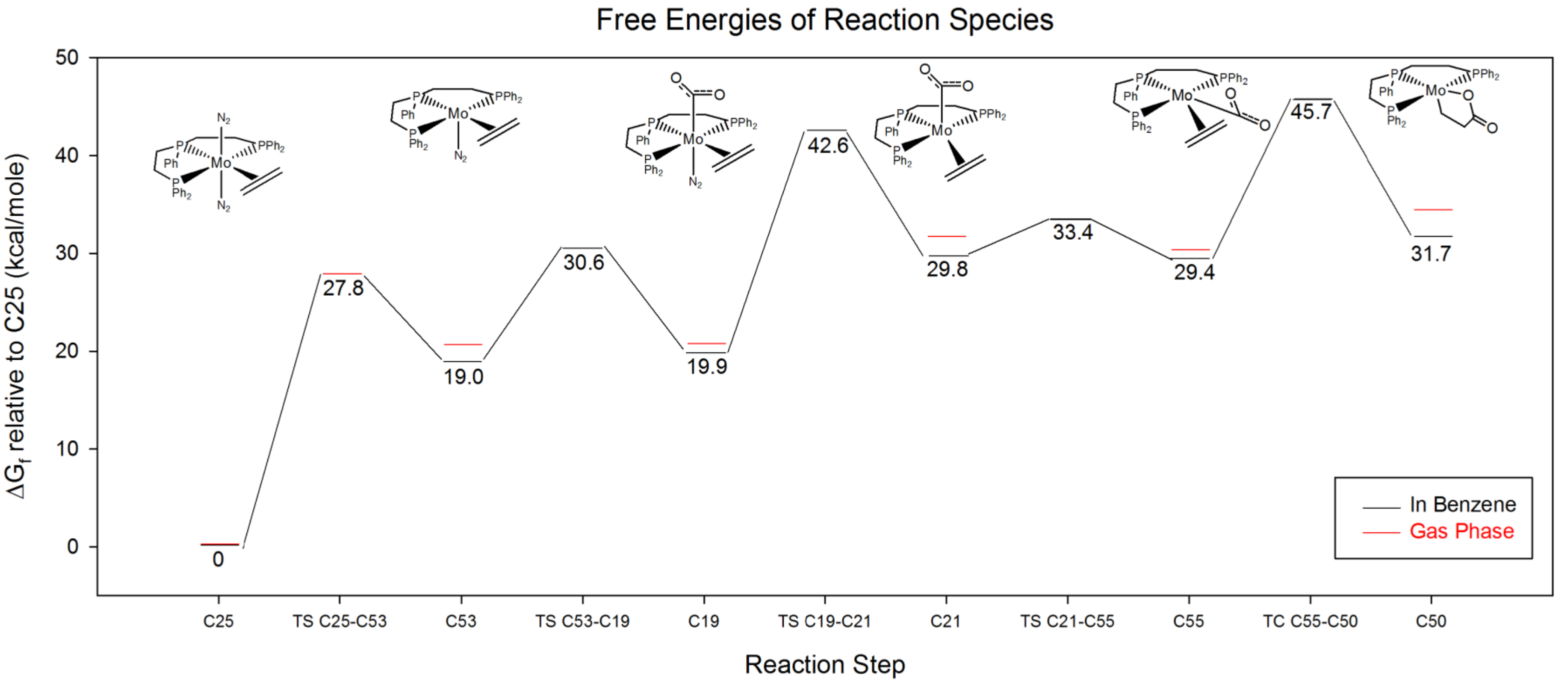
^{31}P NMR: δ 64.7, d, 6.1Hz
95.3, t, 6.1Hz

^{13}C NMR: δ 193.6, dt, 15, 28Hz

IR(KBr) $\nu_{C=O}$ = 1700 cm^{-1}

Mechanism of Action

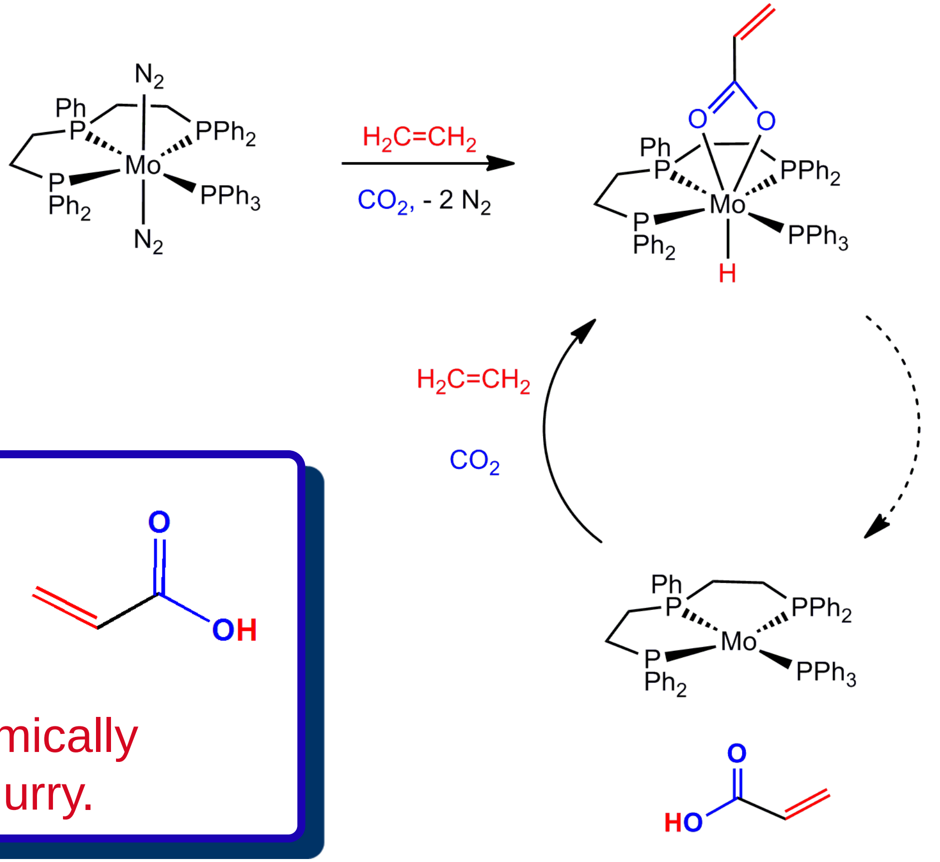
Computational Modeling



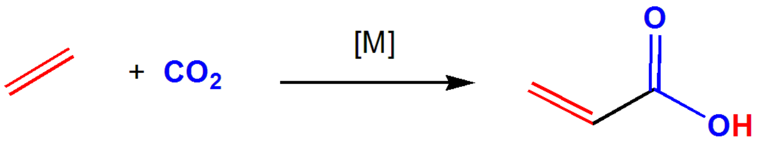
Viability of Elimination

Direct Elimination

Oxidation state = 2



Oxidation state = 0

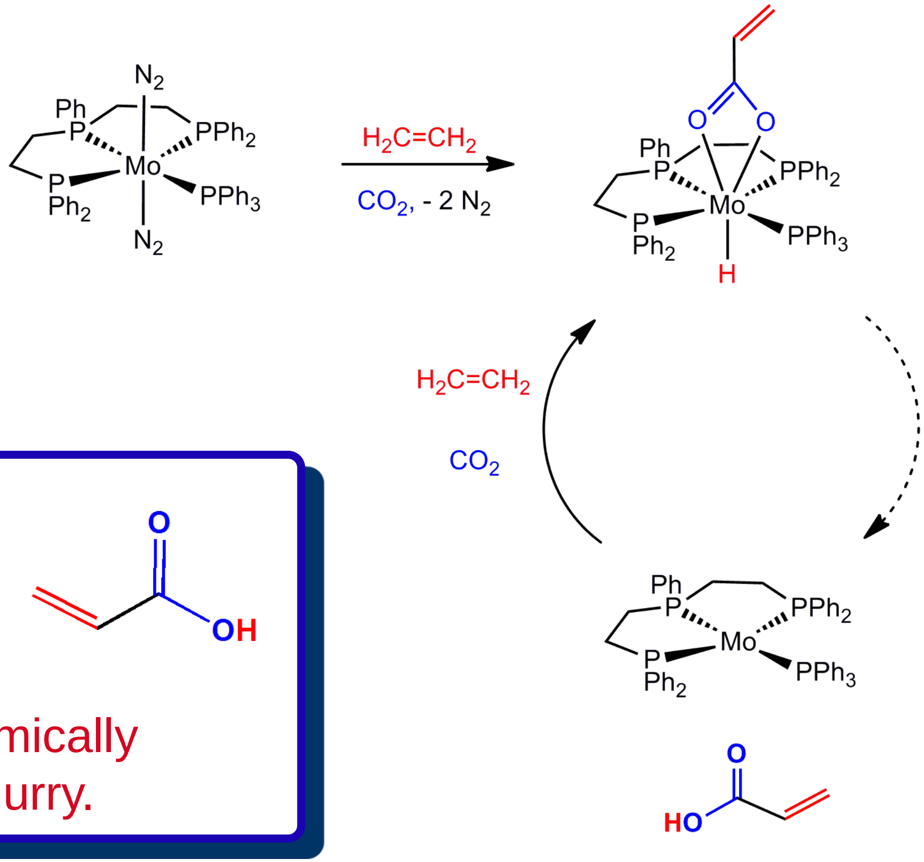


Overall thermodynamically feasible in solvent/slurry.

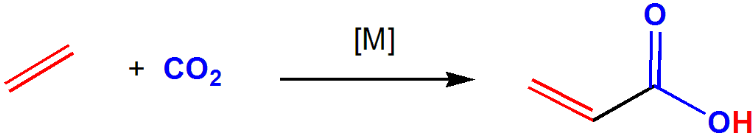
Viability of Elimination

Direct Elimination

…but pKa ~30-35



pKa ~13



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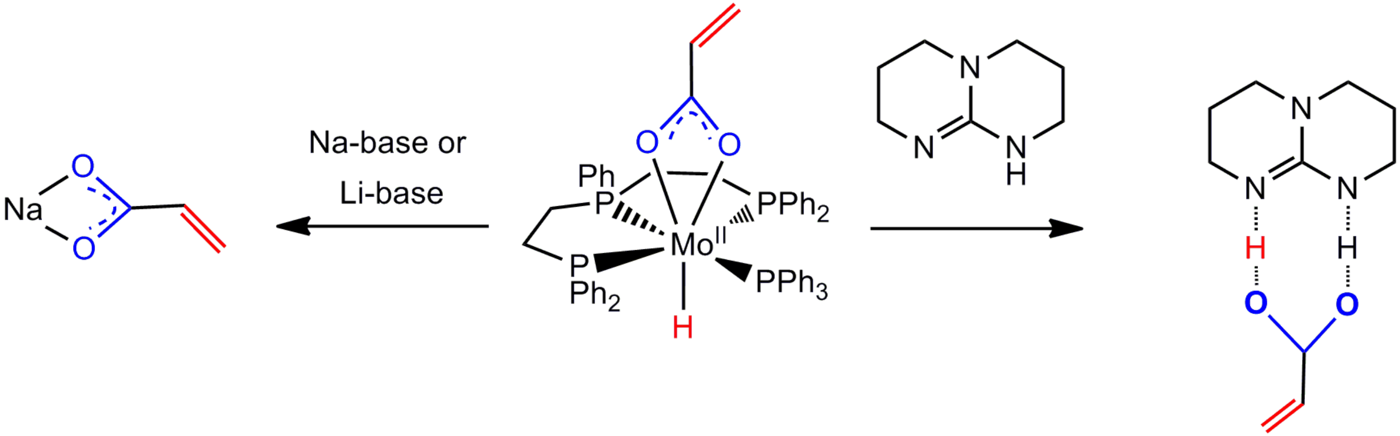
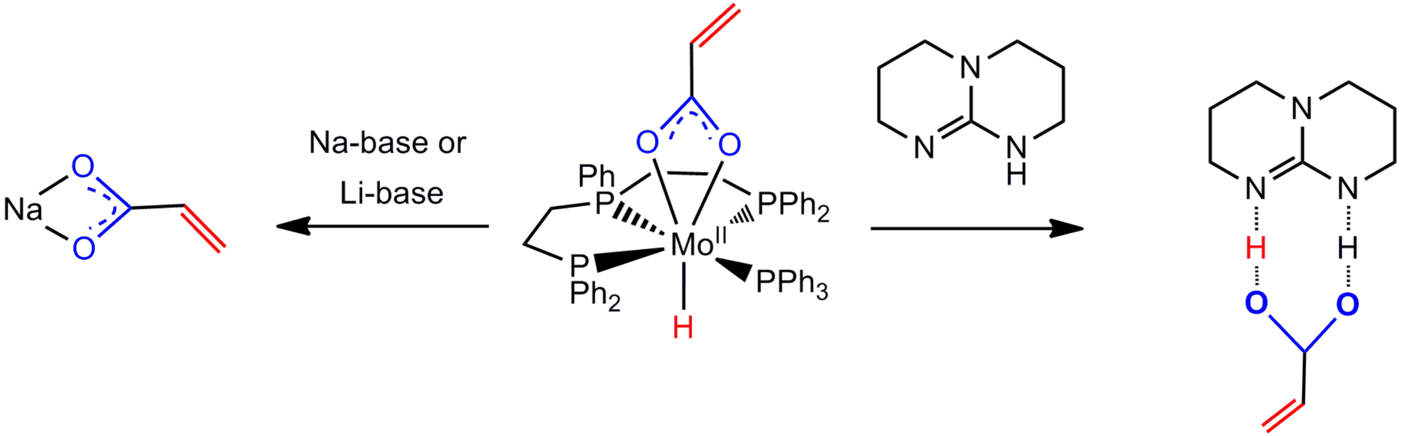
Viability of Elimination

Indirect Elimination-Base

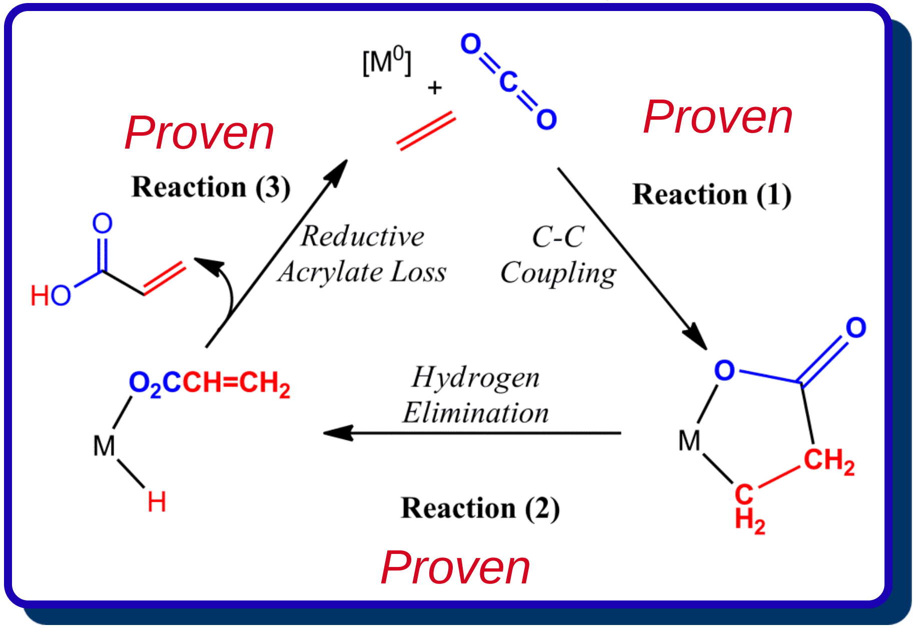


Viability of Elimination

Indirect Elimination-Base



- Base must be hindered enough to avoid acting as a ligand or nucleophilic
- Base cannot have other easily activated groups
- Base must be strong enough to deprotonate Mo-H



Proven

Reaction (3)

Reductive Acrylate Loss

C-C Coupling

Proven

Reaction (1)

Hydrogen Elimination

Reaction (2)

Proven

Accomplishments to Date

- Discovery of rare metal complex for of CO_2 and ethylene coupling to acrylates.
- Identified the tridentate structural features that best enable CO_2 utilization.
- Developed a basic profile for CO_2 reduction pathway.
- Ruled out direct elimination as a viable path acrylate extrusion.
- Found indirect base mediated acrylate elimination is viable for completing the last step of catalytic acrylate formation.

Future Plans

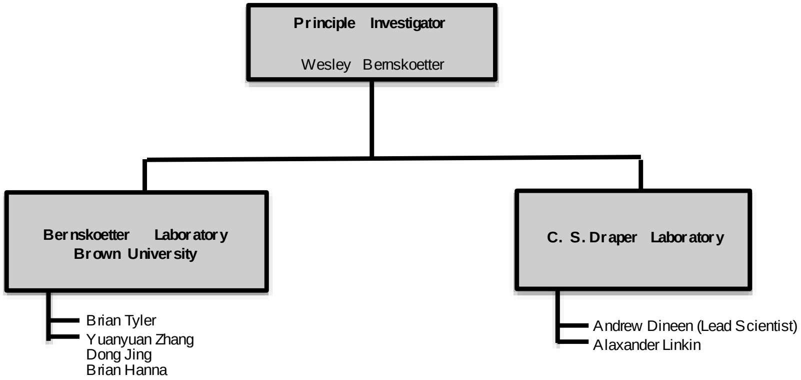
- Identify optimum cheap or recyclable base for indirect acrylate elimination.
- Enable Combinatorial Screening of Metal-Ligand Pairs by Accessing Zerovalent.

(Outside Current NETL Project)

- Use of Nanoparticles as Zerovalent Metal Source
- Alternatives to Base Mediated Acrylate Removal
  - Electrocatalytic Catalyzed Regeneration
  - Palladium Catalyzed

Appendix

Organization Chart



Principle Investigator

Wesley Bernskoetter

Bernskoetter Laboratory
Brown University

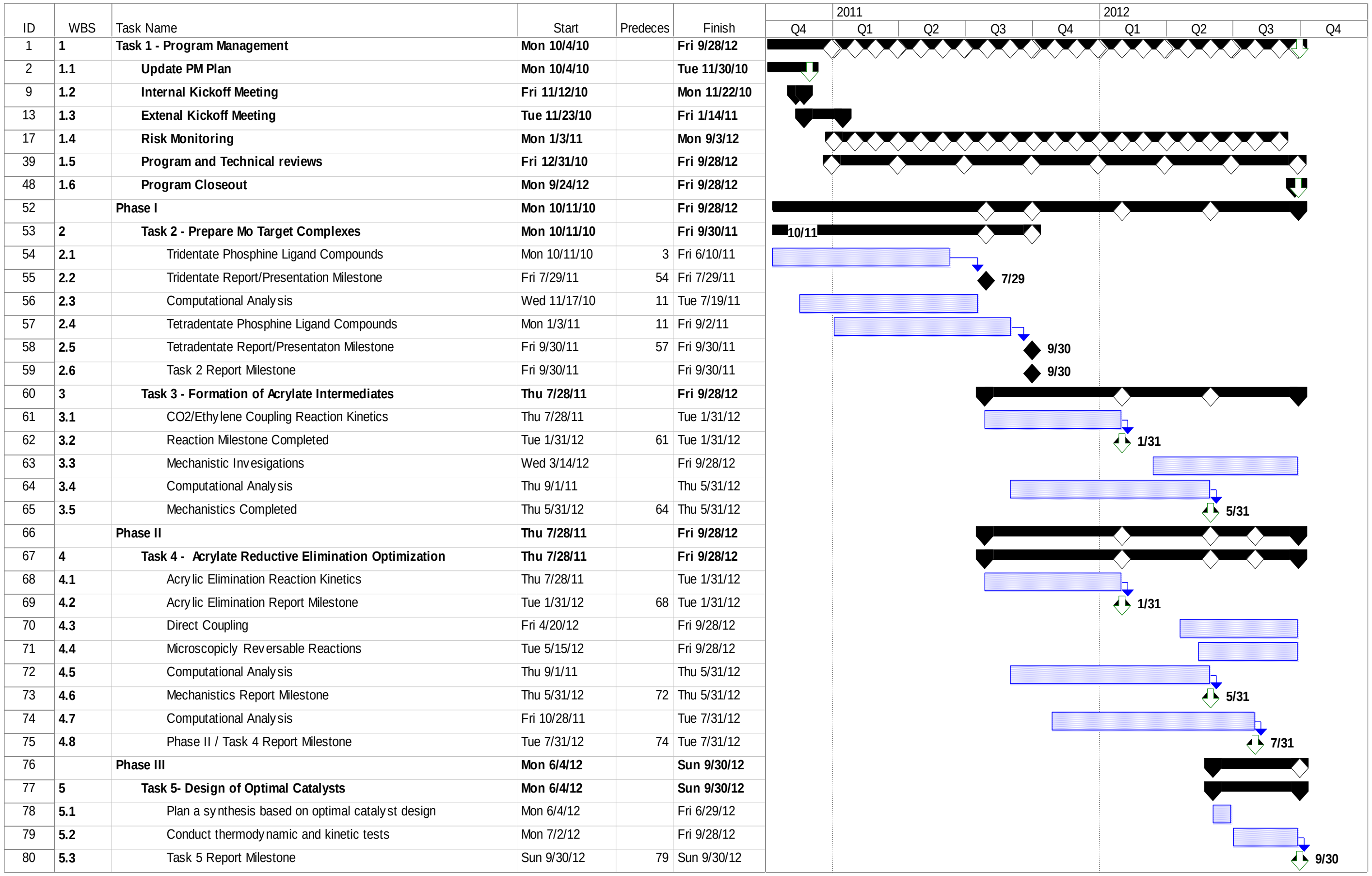
- Brian Tyler
- Yuanyuan Zhang
- Dong Jing
- Brian Hanna

C. S. Draper Laboratory

- Andrew Dineen (Lead Scientist)
- Alaxander Linkin

This program is run under the auspices of Wesley Bernskoetter, Assistant Professor of Chemistry at Brown University as the principle investigator. Dr. Bernskoetter and his graduate students are part of the chemistry department, and as such, have access to the facilities of Brown and its chemistry department. In addition to the Brown, the project team has access to computational chemistry support and additional chemical and engineering support, as required, through its collaboration with Draper Laboratory.

Gantt Chart



ID	WBS	Task Name	Start	Predeces	Finish
1	**1**	**Task 1 - Program Management**	**Mon 10/4/10**		**Fri 9/28/12**
2	**1.1**	**Update PM Plan**	**Mon 10/4/10**		**Tue 11/30/10**
9	**1.2**	**Internal Kickoff Meeting**	**Fri 11/12/10**		**Mon 11/22/10**
13	**1.3**	**Extenal Kickoff Meeting**	**Tue 11/23/10**		**Fri 1/14/11**
17	**1.4**	**Risk Monitoring**	**Mon 1/3/11**		**Mon 9/3/12**
39	**1.5**	**Program and Technical reviews**	**Fri 12/31/10**		**Fri 9/28/12**
48	**1.6**	**Program Closeout**	**Mon 9/24/12**		**Fri 9/28/12**
52		**Phase I**	**Mon 10/11/10**		**Fri 9/28/12**
53	**2**	**Task 2 - Prepare Mo Target Complexes**	**Mon 10/11/10**		**Fri 9/30/11**
54	**2.1**	Tridentate Phosphine Ligand Compounds	Mon 10/11/10	3	Fri 6/10/11
55	**2.2**	Tridentate Report/Presentation Milestone	Fri 7/29/11	54	Fri 7/29/11
56	**2.3**	Computational Analysis	Wed 11/17/10	11	Tue 7/19/11
57	**2.4**	Tetradentate Phosphine Ligand Compounds	Mon 1/3/11	11	Fri 9/2/11
58	**2.5**	Tetradentate Report/Presentaton Milestone	Fri 9/30/11	57	Fri 9/30/11
59	**2.6**	Task 2 Report Milestone	Fri 9/30/11		Fri 9/30/11
60	**3**	**Task 3 - Formation of Acrylate Intermediates**	**Thu 7/28/11**		**Fri 9/28/12**
61	**3.1**	CO2/Ethylene Coupling Reaction Kinetics	Thu 7/28/11		Tue 1/31/12
62	**3.2**	Reaction Milestone Completed	Tue 1/31/12	61	Tue 1/31/12
63	**3.3**	Mechanistic Invesigations	Wed 3/14/12		Fri 9/28/12
64	**3.4**	Computational Analysis	Thu 9/1/11		Thu 5/31/12
65	**3.5**	Mechanistics Completed	Thu 5/31/12	64	Thu 5/31/12
66		**Phase II**	**Thu 7/28/11**		**Fri 9/28/12**
67	**4**	**Task 4 - Acrylate Reductive Elimination Optimization**	**Thu 7/28/11**		**Fri 9/28/12**
68	**4.1**	Acrylic Elimination Reaction Kinetics	Thu 7/28/11		Tue 1/31/12
69	**4.2**	Acrylic Elimination Report Milestone	Tue 1/31/12	68	Tue 1/31/12
70	**4.3**	Direct Coupling	Fri 4/20/12		Fri 9/28/12
71	**4.4**	Microscopicly Reversable Reactions	Tue 5/15/12		Fri 9/28/12
72	**4.5**	Computational Analysis	Thu 9/1/11		Thu 5/31/12
73	**4.6**	Mechanistics Report Milestone	Thu 5/31/12	72	Thu 5/31/12
74	**4.7**	Computational Analysis	Fri 10/28/11		Tue 7/31/12
75	**4.8**	Phase II / Task 4 Report Milestone	Tue 7/31/12	74	Tue 7/31/12
76		**Phase III**	**Mon 6/4/12**		**Sun 9/30/12**
77	**5**	**Task 5- Design of Optimal Catalysts**	**Mon 6/4/12**		**Sun 9/30/12**
78	**5.1**	Plan a synthesis based on optimal catalyst design	Mon 6/4/12		Fri 6/29/12
79	**5.2**	Conduct thermodynamic and kinetic tests	Mon 7/2/12		Fri 9/28/12
80	**5.3**	Task 5 Report Milestone	Sun 9/30/12	79	Sun 9/30/12

Bibliography

Peer Reviewed Publications

- Bernskoetter, W.H.; Tyler, B.T. 2011, Kinetics and Mechanism of Molybdenum Mediated Acrylate Formation from Carbon Dioxide and Ethylene: *Organometallics*, v. 30, p. 520-527 , available at: DOI: 10.1021/om100891m.

- Wolfe, J.M.; Bernskoetter, W.H. 2012, Reductive Functionalization of Carbon Dioxide to Methyl Acrylate at Zerovalent Tungsten: *Dalton Transactions*, v. 41, Advance Articles, available at: DOI:10.1039/C2DT31032E.