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
Infrastructure for CCS

August 20-22, 2013

Presentation Outline

- Deriving acrylates from CO_2: How and why

- Assessing viability of chemical catalysis approach.
- Method for enhanced throughput catalyst screening
- Perspectives for the future.

Benefit to the Program

- This project pinpoints the critical catalyst features necessary to promote carbon dioxide conversion to acrylate, validate the chemical catalysis approach, and develop an enhanced screening method identification of active molybdenum catalysts targets. This methodology will contribute to the goal ensuring 99 percent storage permanence by fixing CO_2 in stable products for indirect storage.

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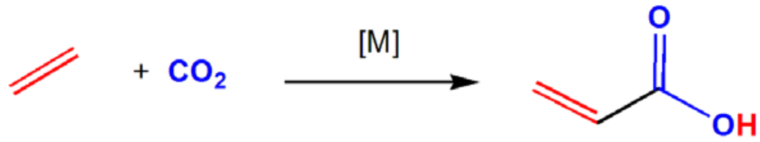
Project Overview:
Goals and Objectives

- Identify features for activation of molybdenum in CO_2 and ethylene coupling to acrylates.
  - Probe mechanism of zerovalent molybdenum complexes to determine the factors that control the reaction rate. (Complete)
- Validate reductive acrylate elimination
  - Use active species to assay the potential for reductive acrylate extrusion. (Complete)
- Develop and utilize an enhanced screening method for activity identification in acrylate formation.

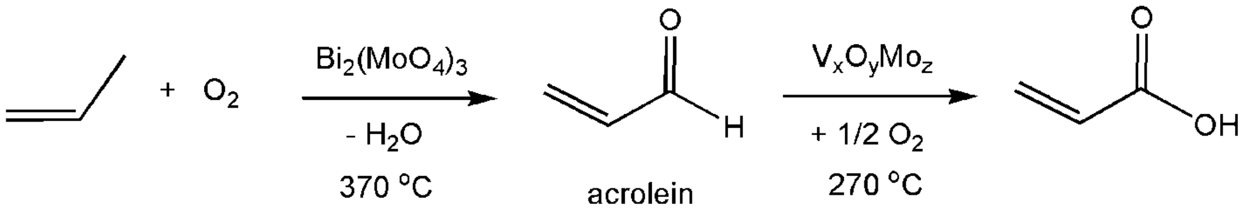
Guiding Motivations

Present & Future of Acrylate Synthesis

Proposed:



Current:



Guiding Motivations

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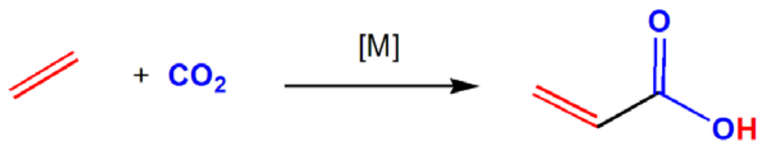
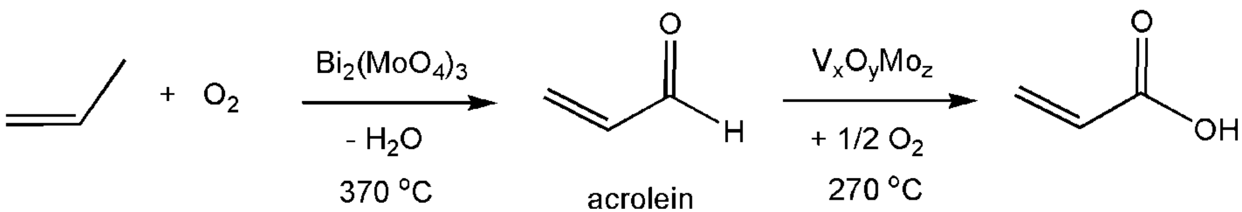


Current:



- Currently produce ~5 M tons 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 M 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

Which Metals Could Work?

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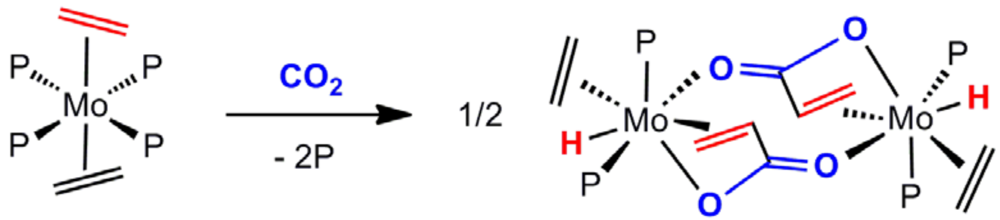
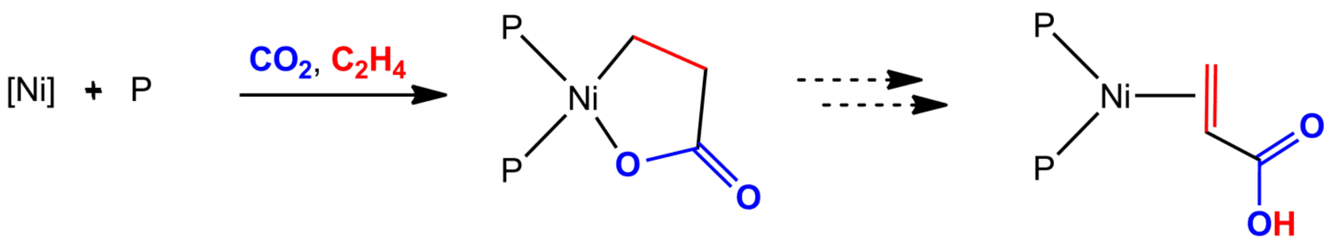
Prior Art-Molybdenum **(NETL-Project)**



P = PMe_3, PMe_2Ph,
$P(OMe)_3$, $P(OEt)_3$

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.

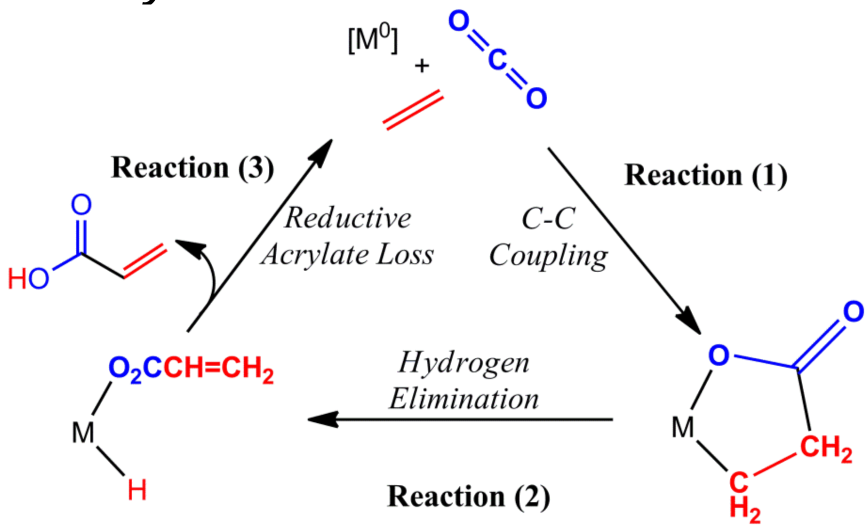
Prior Art-Nickel



Hoberg, H.; Schaefer, D. *J. Organomet. Chem.* **1983**, *251*, C51**.**
Limbach, M. *et al Chem. Eur. J.* **2012**, *18*, 14017; Limbach, M. *U.S. Patent Application* 13/040,043 Sep. 8 ,2011
Jin, D.; Bernskoetter, W. H. *et al. Organometallics.* **2013**, 2152*.*

Molybdenum

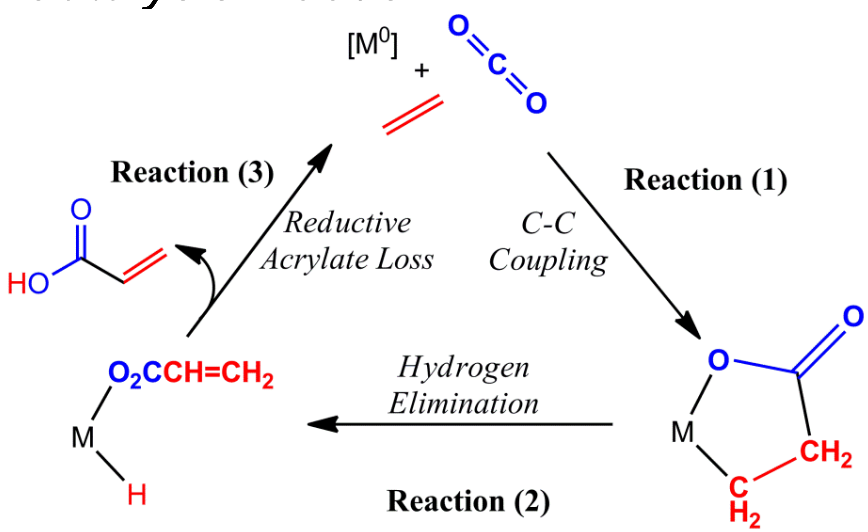
Catalysis Needs



- Molybdenum is quite capable of reactions 1, 2 & 3 individually
- Little is known about what makes molybdenum the “rare” success
- Identification of successful single-site molybdenum activity requires intensive fine chemistry assay

Molybdenum

Catalysis Needs



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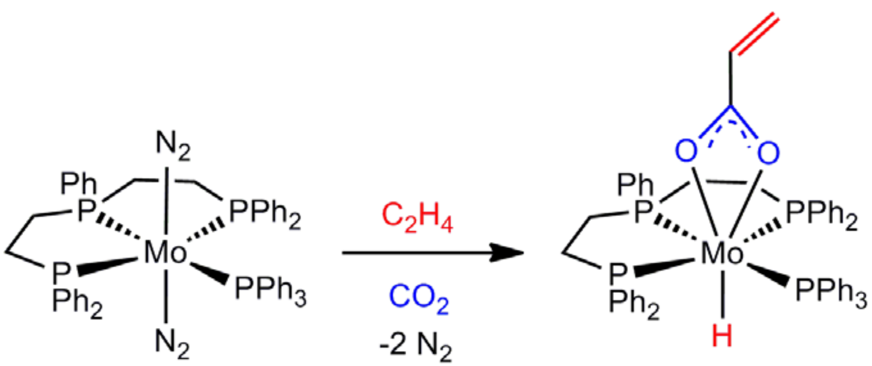
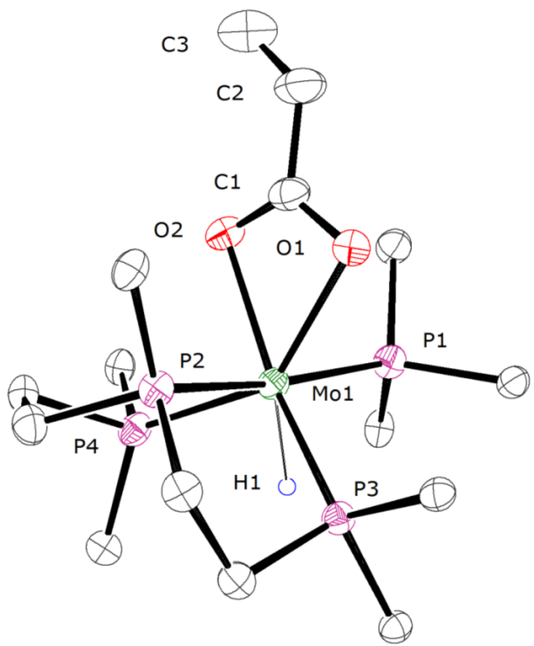
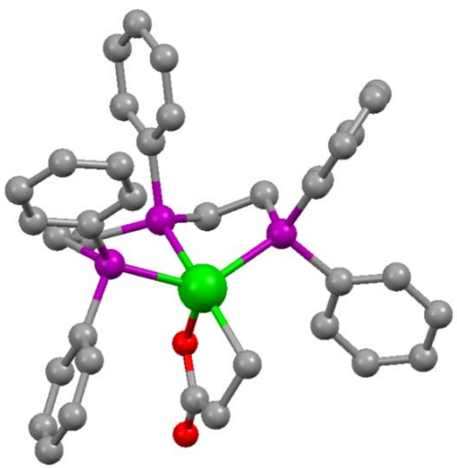
First New CO_2-Ethylene Acrylate in Decades

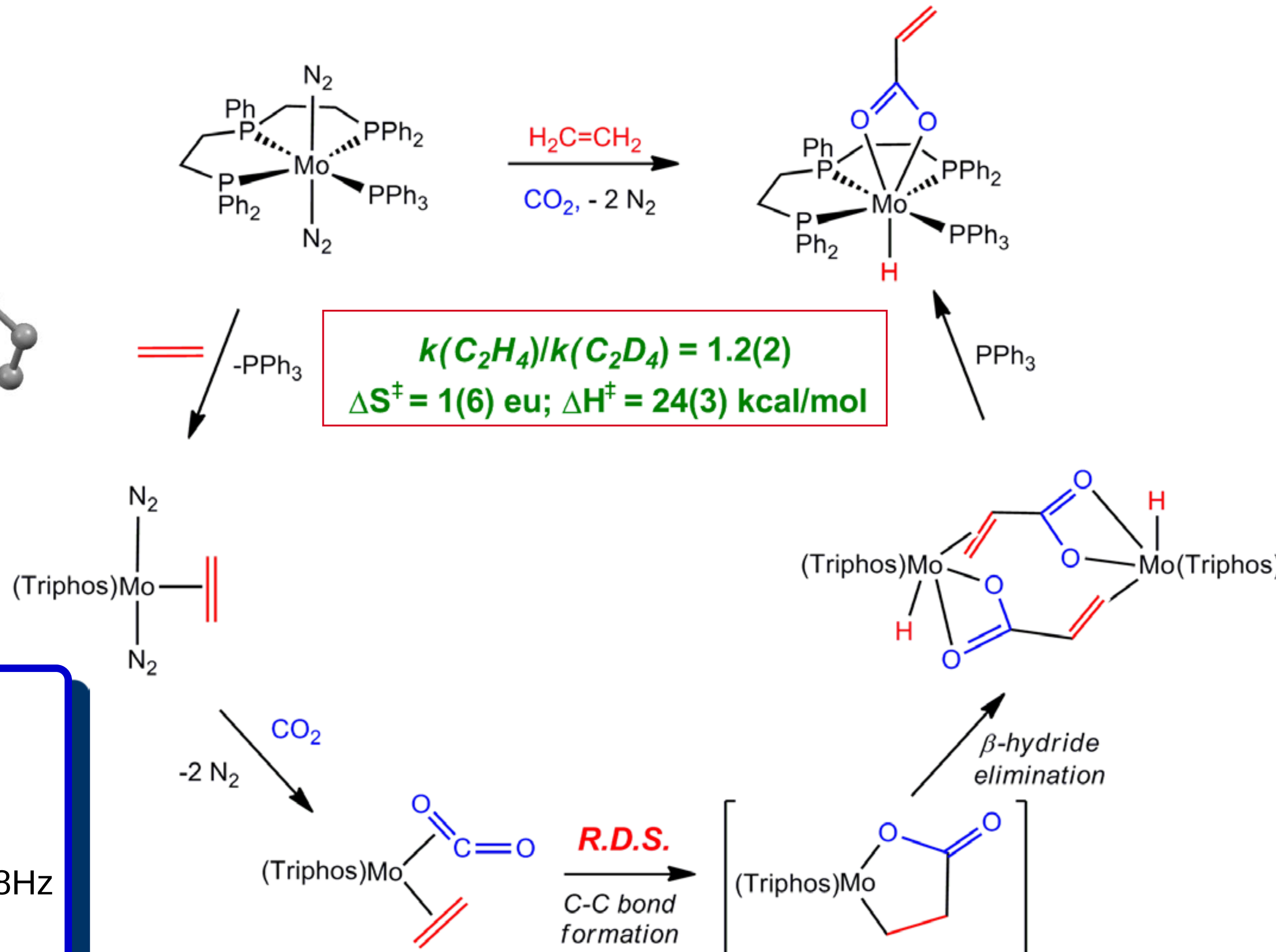




Bernskoetter, W.H.; Tyler, B. T. *Organometallics* **2011**, *30*, 520.

Mechanism of Action





^{1}H NMR: δ 0.25, m, C_2H_4

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

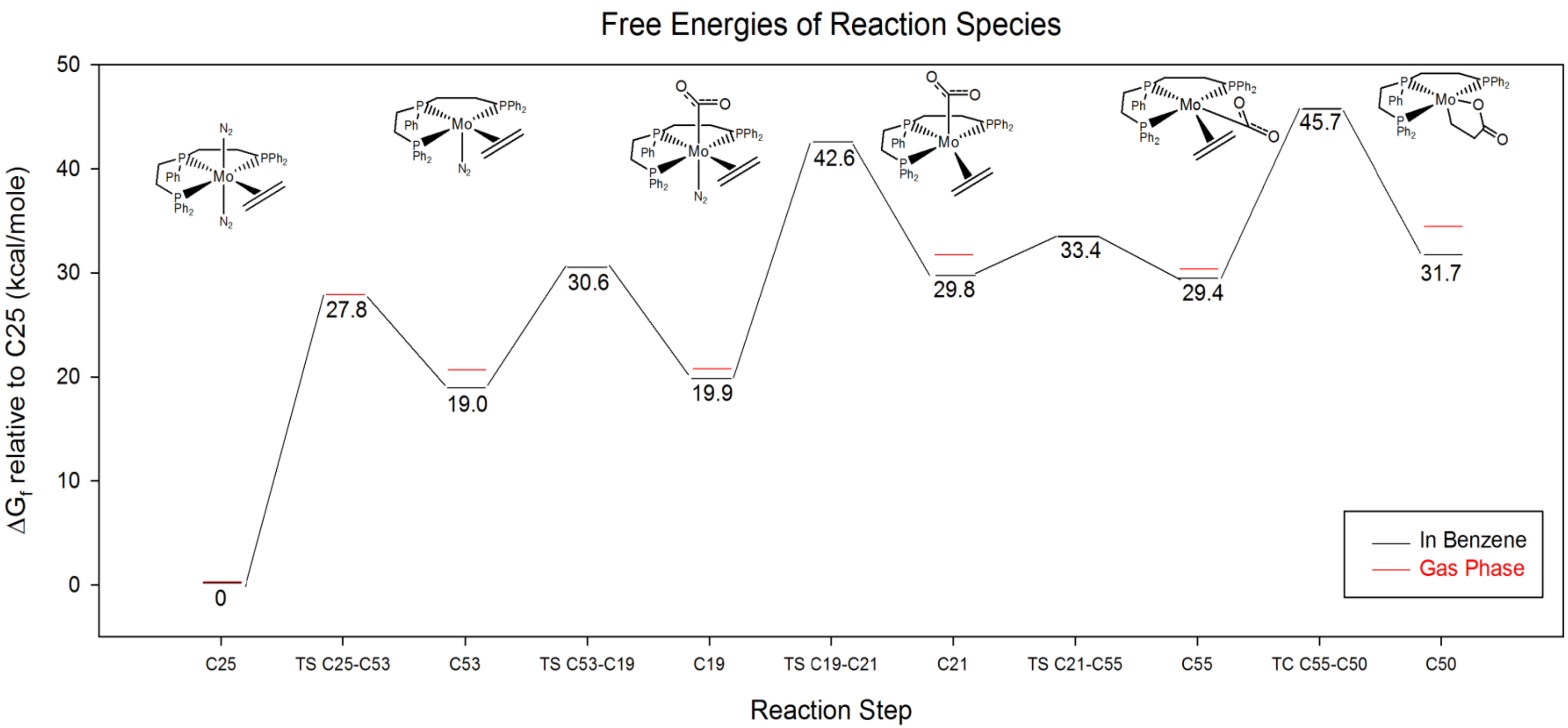
^{13}C NMR: δ 193.6, dt, 15, 28Hz

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

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

Mechanism of Action

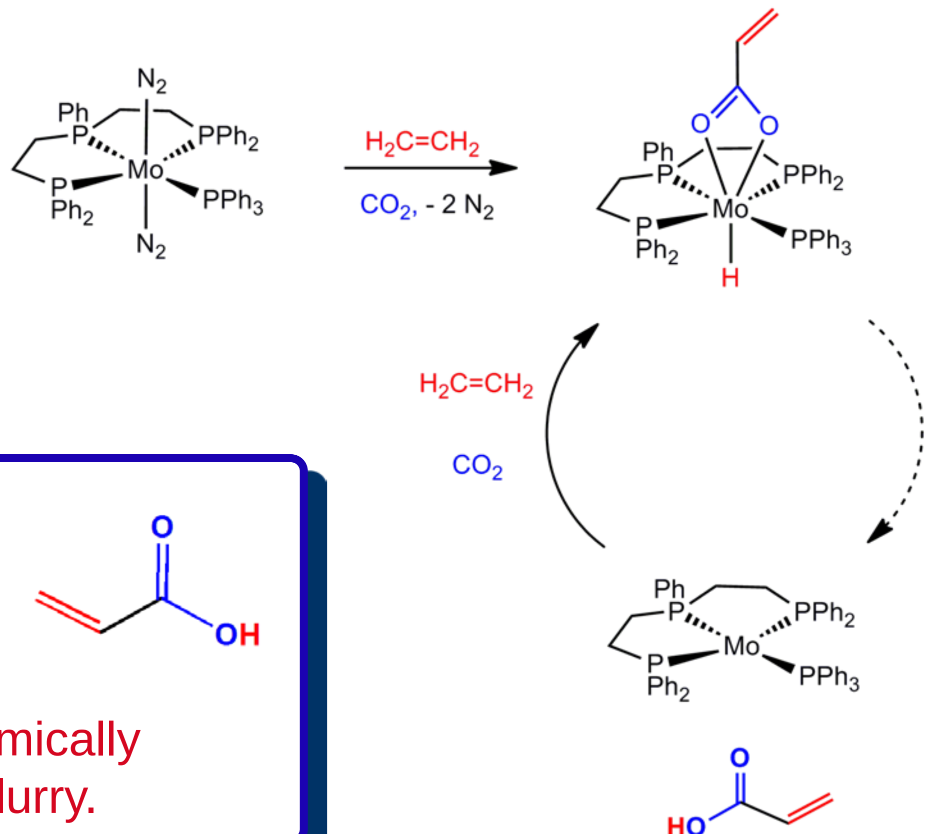
Computational Modeling



Viability of Elimination

Direct Elimination

Oxidation state = 2



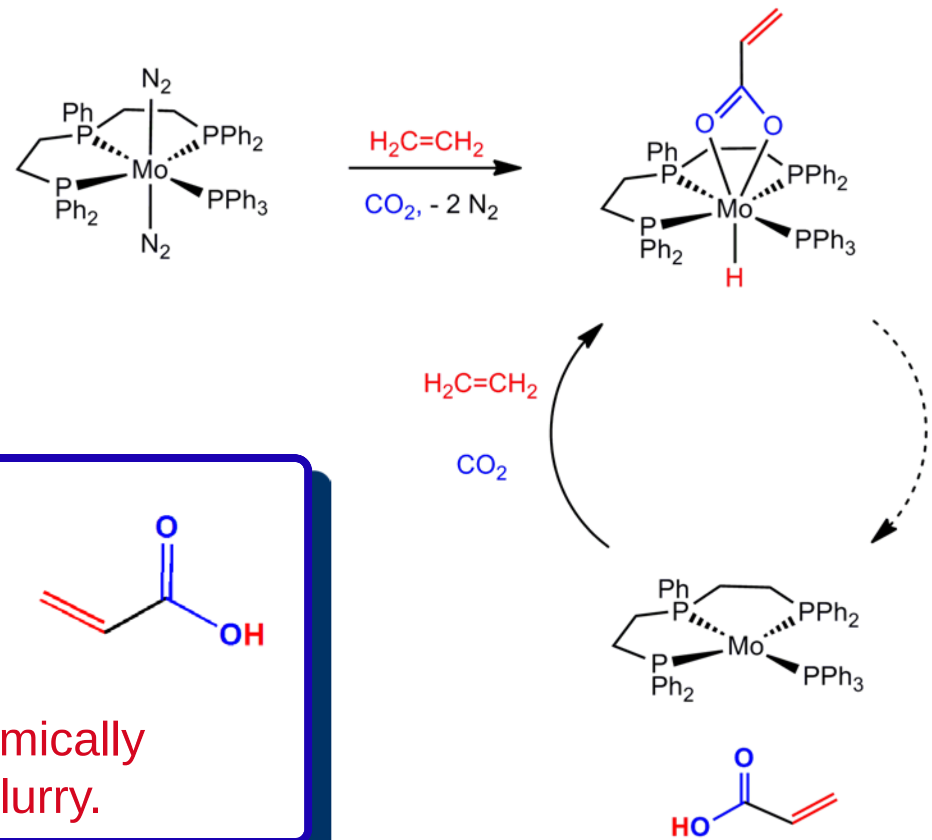
Overall thermodynamically feasible in solvent/slurry.

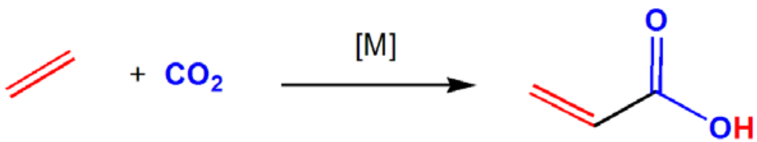
Oxidation state = 0

Viability of Elimination

Direct Elimination

…but pKa ~30-35



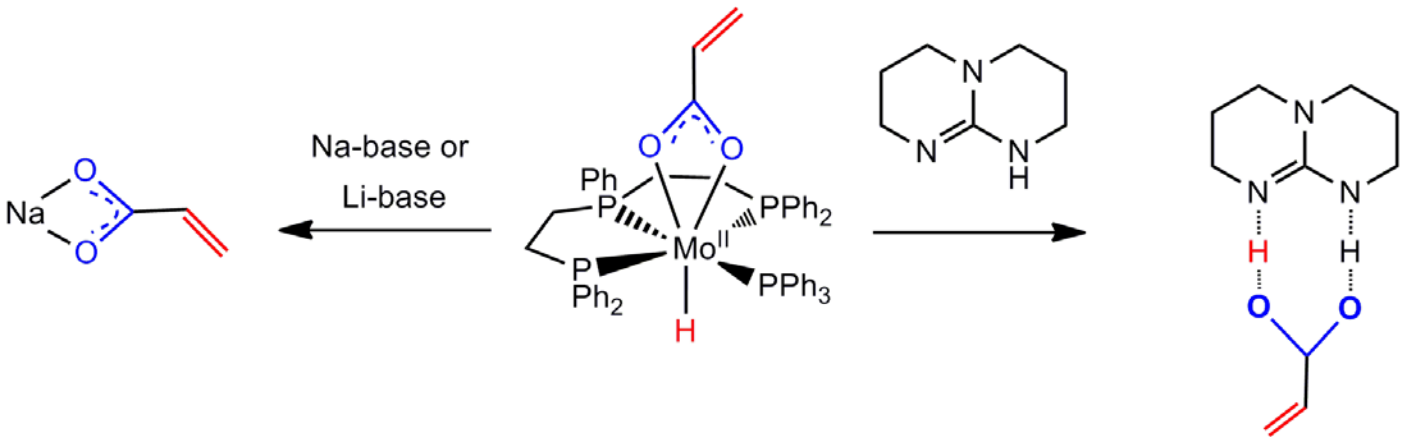


Overall thermodynamically feasible in solvent/slurry.

pKa ~13

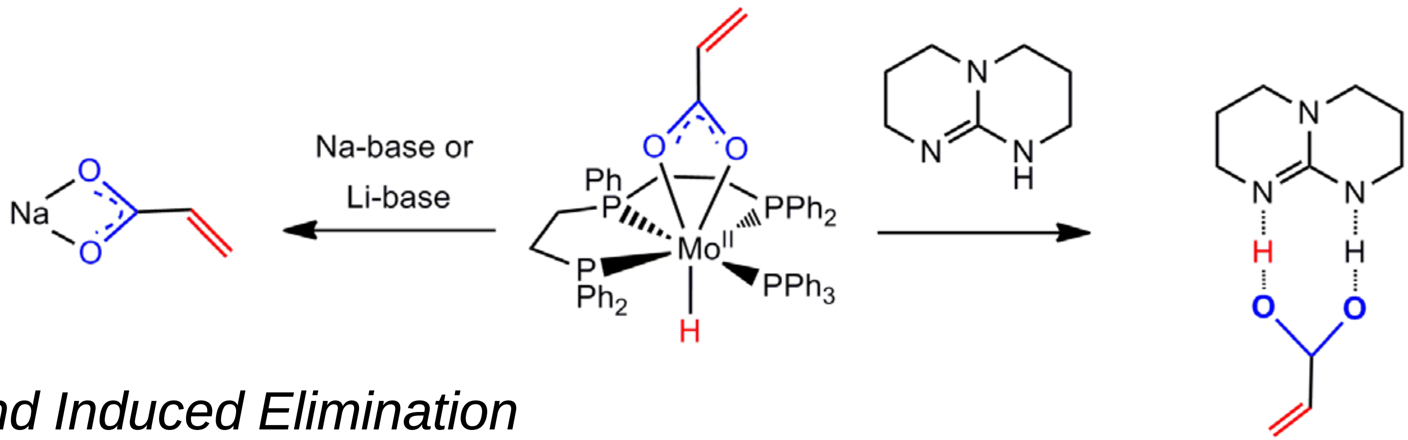
Viability of Elimination

Indirect Elimination-Base

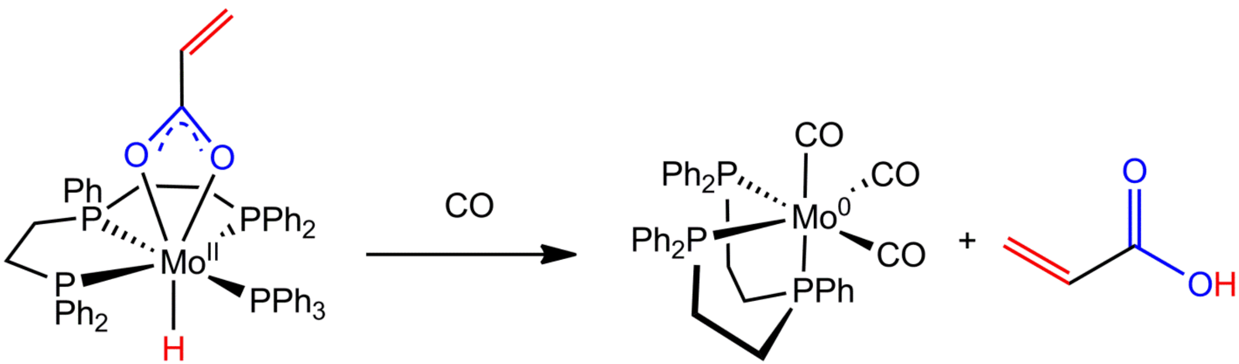


Viability of Elimination

Indirect Elimination-Base



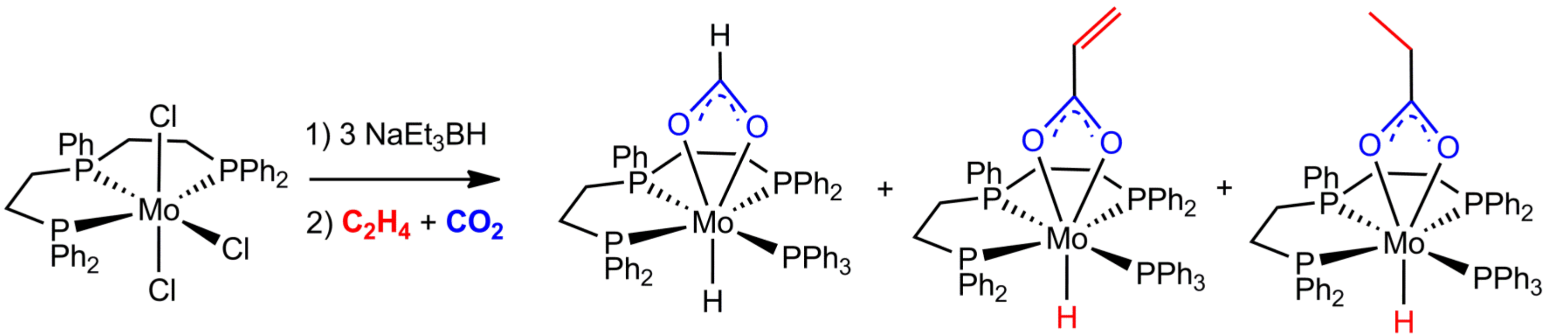
Ligand Induced Elimination



- Presence of carbon monoxide actually enables this process, not inhibit it
- Metal-carbonyls are frequently activated by photolysis for catalysis
- Probably the best lead for molybdenum induced acrylate formation

Need for Rate Enhancement

Enhanced Activity Screening Method



- Formate, propionate, and acrylate produced from single reaction

Zhang, Y., Bernskoetter *et al* *Organometallics* **2013**, *32*, 3969.

Need for Rate Enhancement

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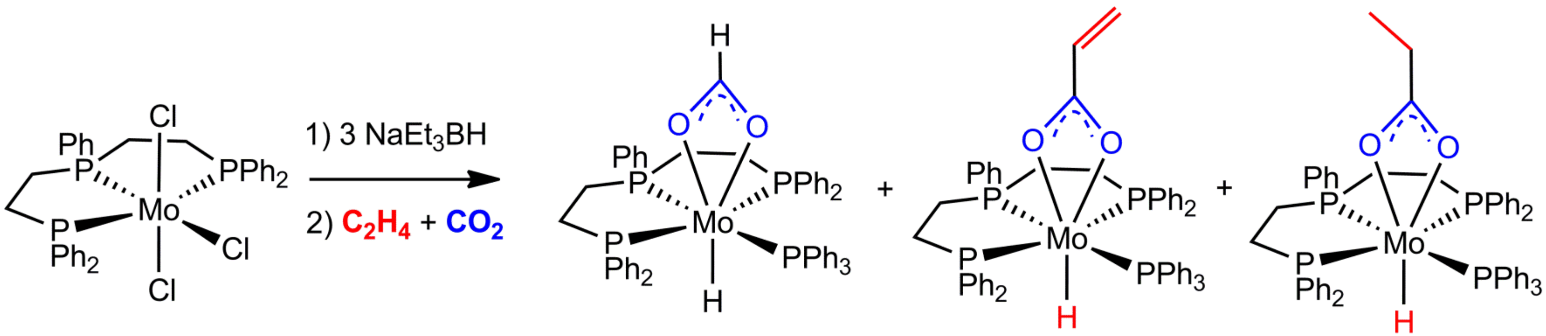

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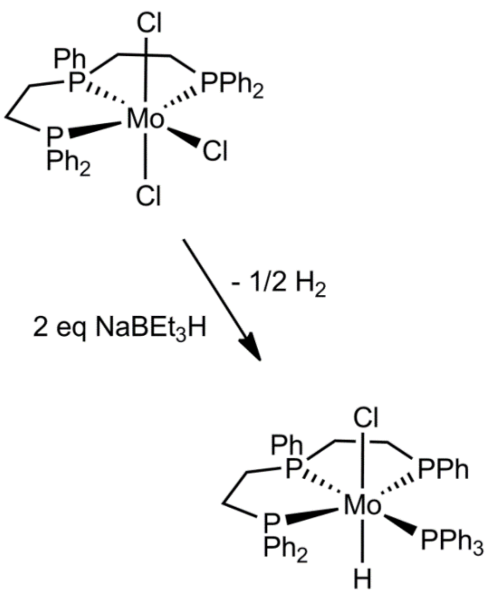

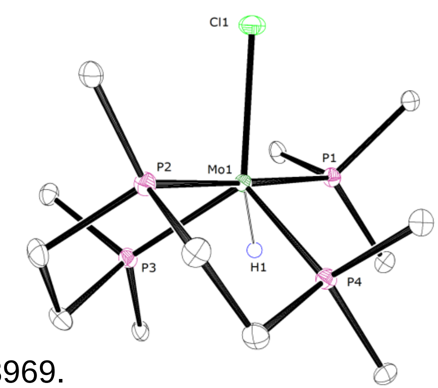

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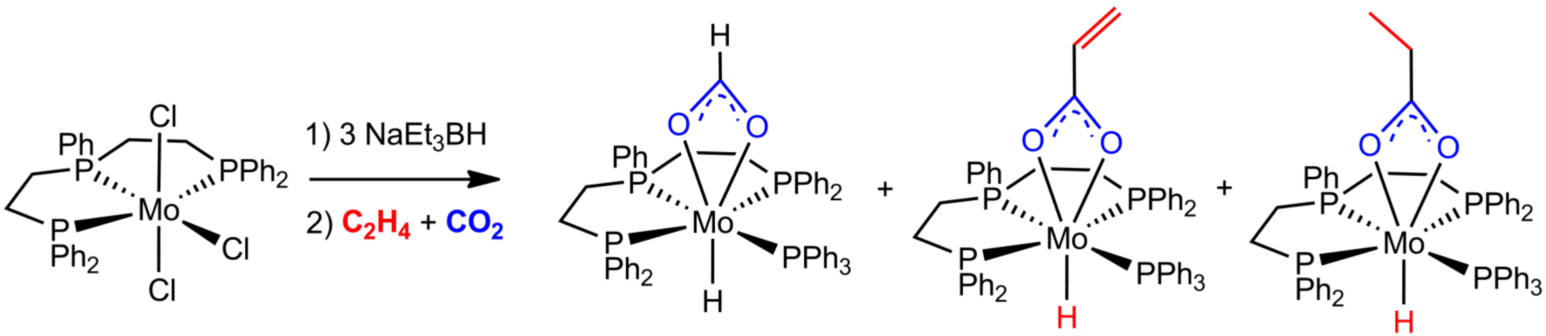

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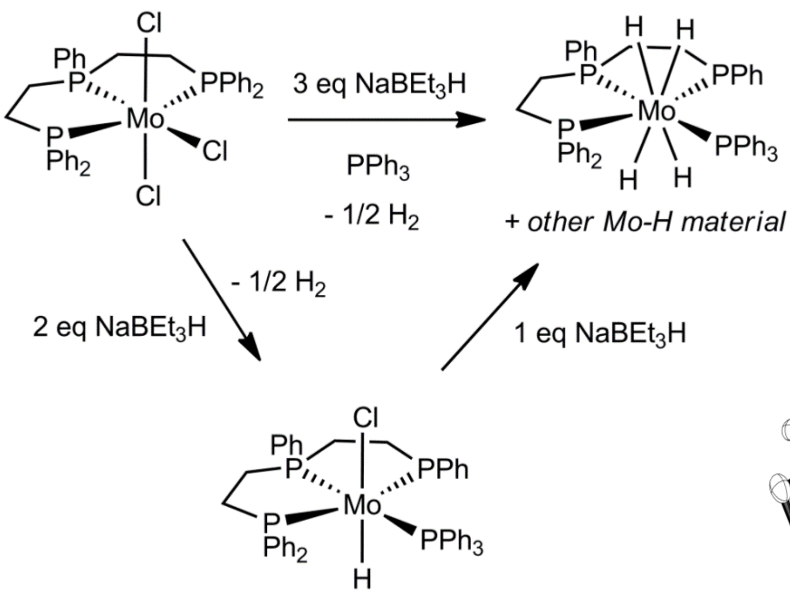

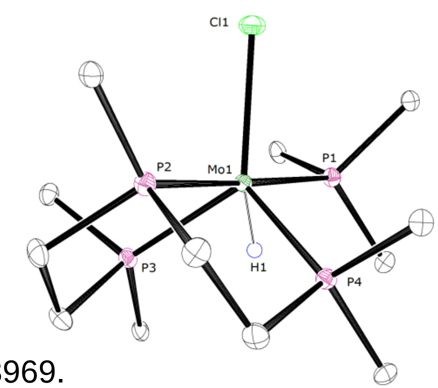

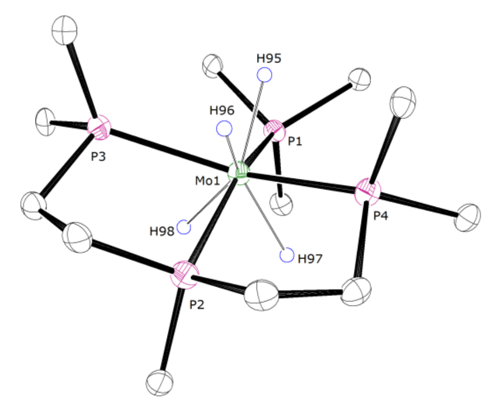

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Need for Rate Enhancement

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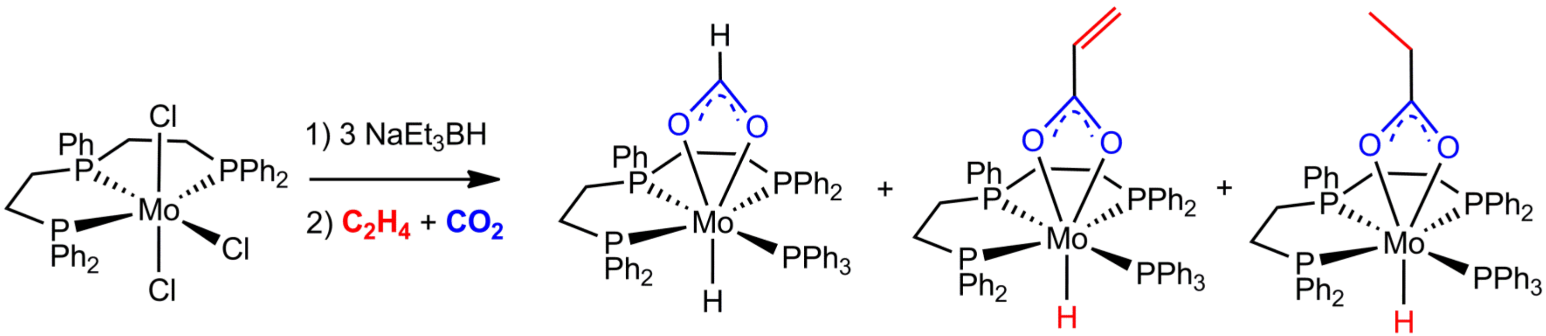

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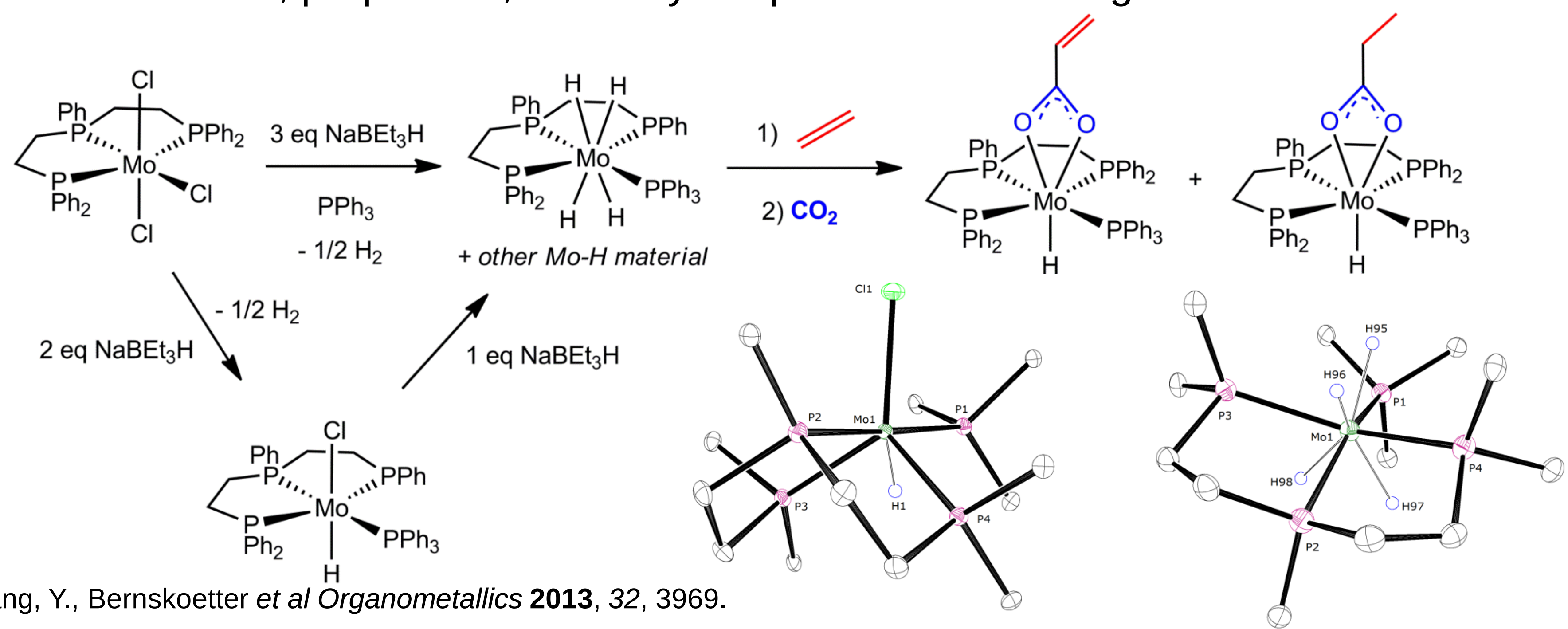

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Need for Rate Enhancement

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*Activity Results—**8 New Active Catalyst Targets***

Ligand	Observation	Rate
[bis(diphenylphosphino)ethyl-phenylphosphine]	Clear acrylate production detected	*5.2 x 10^{-5} s^{-1}*
[bis(dianisolephosphino)ethyl-phenylphosphine]	Clear acrylate production detected:	*2.54 x 10^{-5} s^{-1}*
[bis(di-m-xylyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected	*4.15 x 10^{-5} s^{-1}*
[bis(di-p-fluorophenyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected:	*3.2 x 10^{-5} s^{-1}*
[bis(di-p-trifluoroemethyl-phenyl-phosphino)ethyl-phenylphosphine]	Clear acrylate production detected:	*4.05 x 10^{-4} s^{-1}*
[bis(dipyrrolephosphino)ethyl-phenylphosphine]	No acrylate formation detected	
1,1,1-Tris(diphenylphosphinomethyl)ethane	No acrylate formation detected	
Methyl substited 1,4,7-Triazacyclononane	No acrylate formation detected	
[bis(di-tertbutyl-phosphino)ethyl-phenylphosphine]	Preliminary data suggest acrylate formation, additional characterization on-going	*TBD*
[bis(dicyclohexylphosphino)ethyl-phenylphosphine]	Preliminary data suggest acrylate formation, additional characterization on-going	*TBD*
N,N'-(2,4,6-Trimethyl)-oimidazolium	Preliminary data suggest acrylate formation, additional characterization on-going	*TBD*
N,N'-(2,6-Diisopropylphenyl-imidazolium	Preliminary data suggest acrylate formation, additional characterization on-going	*TBD*
N-Methyl-triazacyclononane	No acrylate formation detected	
1,3-Bis(di-tert-butylphosphinomethyl)benzene	No acrylate formation detected	
N,N'-Dimethyl-imidazolium	No acrylate formation detected	

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.
- Discovery of base and ligand induced reductive elimination pathways for acrylate removal
- Established an enhanced throughput screening method using sodium triethylborohydride for assessment of acrylate formation activity in molybdenum

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Future Plans

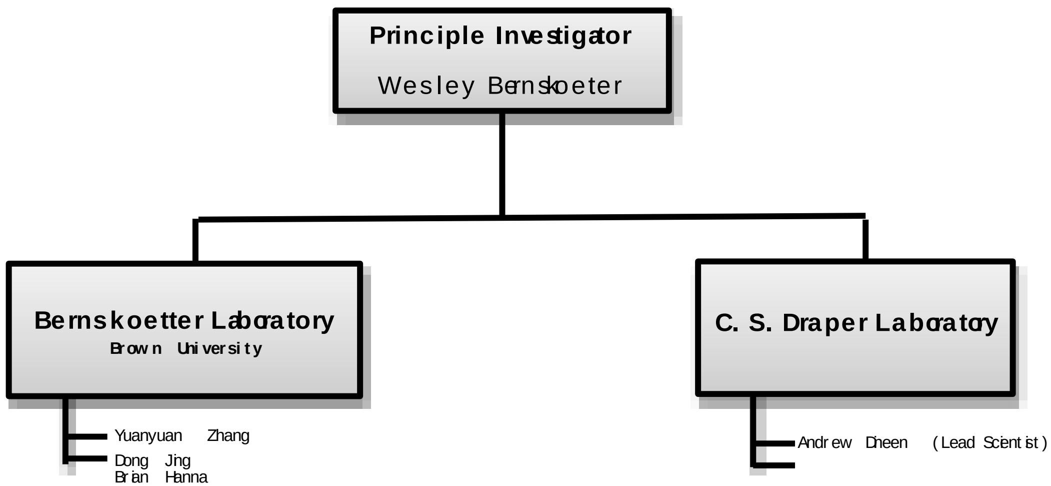
- Identify activation methods for CO or other ligand induced reductive elimination method.
- Complete screening of metal ligand pairs to optimize acrylate formation rate.

(Mo Targets Outside Current NETL Project)

- Heterogenize Mo catalyst as Nanoparticles
- Alternate Product Scope
  - Formic acid, propionic acid
  - Cyclic anhydrides

Appendix

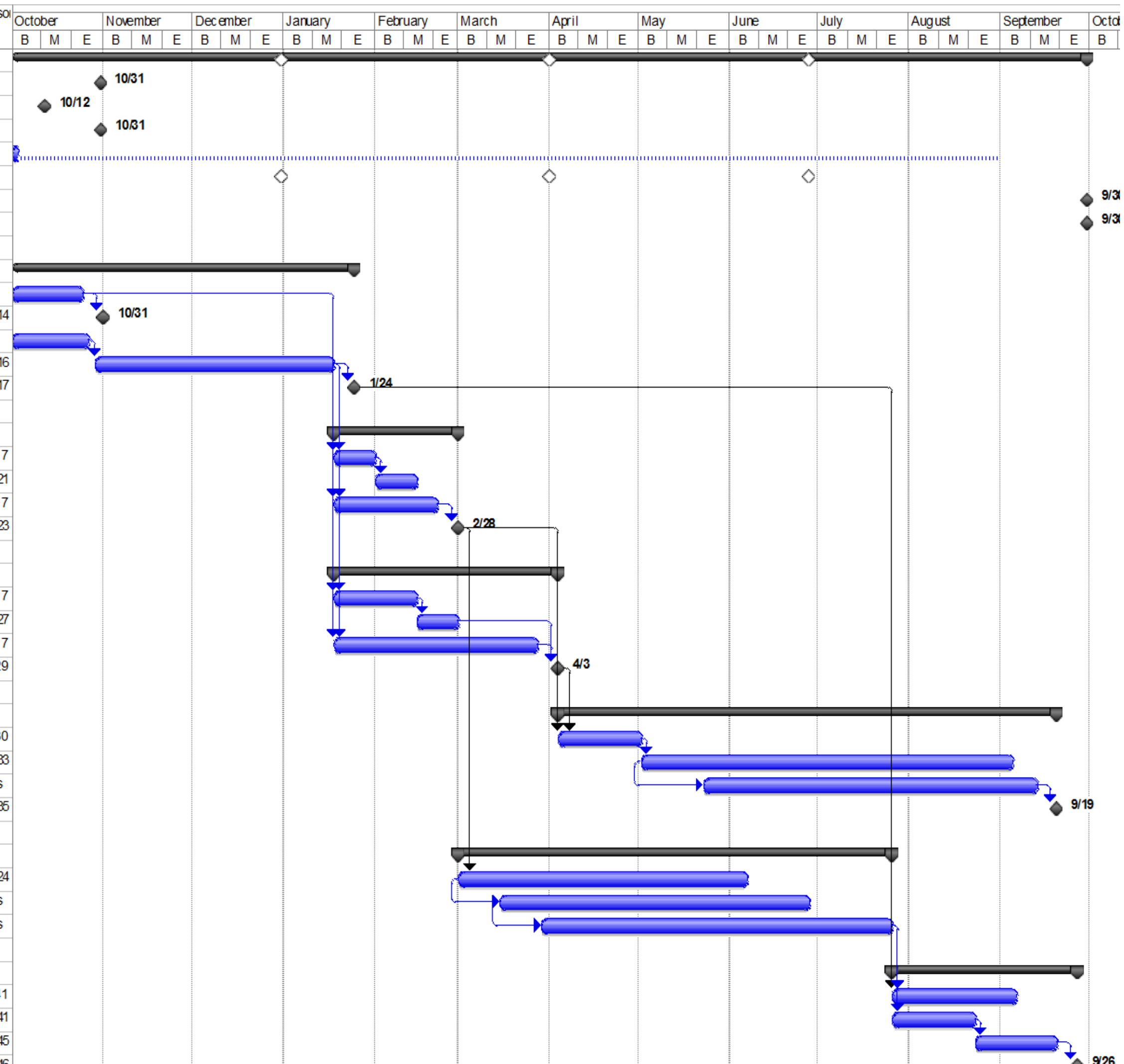
Organization Chart



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	edecesso
1	**1**	**Task 1 - Program Management and Planing**	**Mon 10/1/12**	
2	1.1	Finalize PMP	Wed 10/31/12	
3	1.2	Internal Kickoff	Fri 10/12/12	
4	1.3	External Kickoff	Wed 10/31/12	
5	1.4	RiskMonitoring IAW PMP	Mon 10/1/12	
6	**1.5**	**Quarterly Technical Reviews**	**Mon 12/31/12**	
10	1.6	Internal Program Review and Task Reassignment	Mon 9/30/13	
11	1.7	Program Closeout Meeting	Mon 9/30/13	
12				
13	**2**	**Task 2 - Prepare Molybdenum Target Complexes**	**Mon 10/1/12**	
14	2.1	Prepare and characterize tridentate Mo Complexes	Mon 10/1/12	
15	2.2	Report/presentation of tridentate Complexes	Thu 10/25/12	14
16	2.3	Computational anaysis of current Mo targets	Mon 10/1/12	
17	2.4	Prepare and characterize tetradentate Mo complexes	Mon 10/29/12	16
18	2.5	Report/Presentation on tetradentate complexes	Fri 1/18/13	17
19				
20	**3**	**Task 3- Analysis of Acrylate formation**	**Fri 1/18/13**	
21	3.1	Couple Mo Complexes to CO2 and C2H4	Fri 1/18/13	14,17
22	3.2	Measure Kinetics and derive Mechanism	Fri 2/1/13	21
23	3.3	Perform Computational valuation of reaction mechanisms	Fri 1/18/13	14,17
24	3.4	Report/ Presentation of Mechanistic Valuations	Fri 2/22/13	23
25				
26	**4**	**Task 4 - Factors for Acrylic Elimination**	**Fri 1/18/13**	
27	4.1	Conduct direct Acrylic Elimination Reactions	Fri 1/18/13	14,17
28	4.2	Conduct Microscopic Reversability Assays	Fri 2/15/13	27
29	4.3	Computational Analysis of Elimination reactions	Fri 1/18/13	14,17
30	4.4	Report/ Presentation of Acrylic Elimination	Thu 3/28/13	28,29
31				
32	**5**	**Task 5 - Desing, Preparation, and Assessment of Optimal Catalyst**	**Thu 4/4/13**	
33	5.1	Plan Synthesis of Optimal Catalyst	Thu 4/4/13	24,30
34	5.2	Execute synthetic plan	Thu 5/2/13	33
35	5.3	Conduct thermodynamic and Kinetic assessments	Thu 5/23/13	-15 days
36	5.4	Report/Present on optimal Catalyst	Fri 9/13/13	35
37				
38	**6**	**Task 6 - Alternative Reductive Preparation of Tridentate Mo**	**Fri 3/1/13**	
39	6.1	Computational Analysis of Reducing Agents	Fri 3/1/13	24
40	6.2	Synthesize Targets with Alternative Reducing Agents	Fri 3/15/13	-10 days
41	6.3	Generate Mo Complexes and and perform acrylate formation	Fri 3/29/13	-10 days
42				
43	**7**	**Task 7- Screening Aproach to CO2-Ethylene Coupling Activity**	**Fri 7/26/13**	
44	7.1	Computational Modelling of the Thermodynamics of Reduction and acry	Fri 7/26/13	18,41
45	7.2	Didentify and Develop Experimental Techniques to identify acrylate Form	Fri 7/26/13	41
46	7.3	Conduct Batch tests	Fri 8/23/13	45
47	7.4	Prepare/Report on Mo reduction	Fri 9/20/13	46



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, p. 10763-10768, available at: DOI:10.1039/C2DT31032E.

- Zhang, Y.; Hanna, B. S.; Dineen, A.; Williard, P. G.; Bernskoetter, W. H. 2013, Functionalization of Carbon Dioxide with Ethylene at Molybdenum Hydride Complexes. *Organometallics*, v 32, p. 3969-3979 DOI: 10.1021/om400448m