



Development of Catalyst Systems for the Selective Trimerization of Dienes

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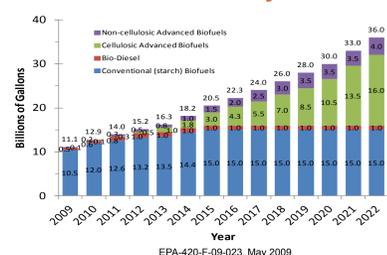
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Background and Introduction

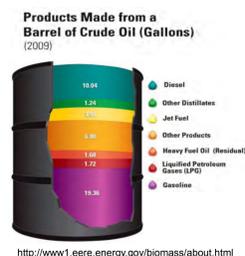
There is a Need for Biobased Fuels

- Sustainably attain energy security
- Reduce reliance on limited and foreign petroleum resources
- Minimize carbon footprint, especially by lowering GHG emissions in the transportation sector
- Maintain America's technological competitiveness
- Create green jobs
- Commercial and military specs and < \$3/gal

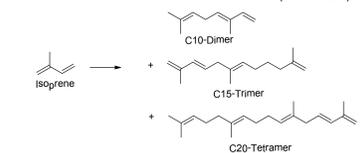
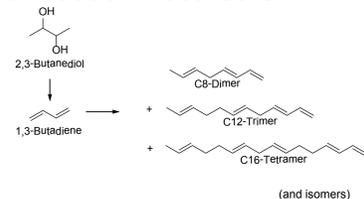
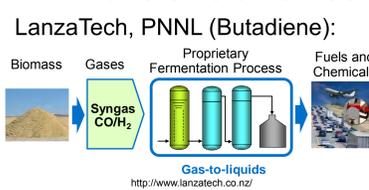
EISA Goal: 36 billion gallons of renewable fuel by 2022



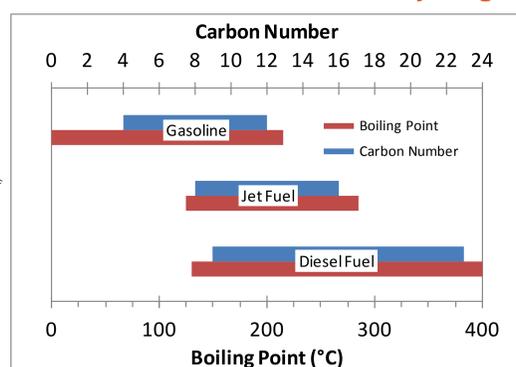
Biobased fuels impact the whole barrel



Processes Under Development Make Dienes, Which are Potential Fuel and Product Precursors



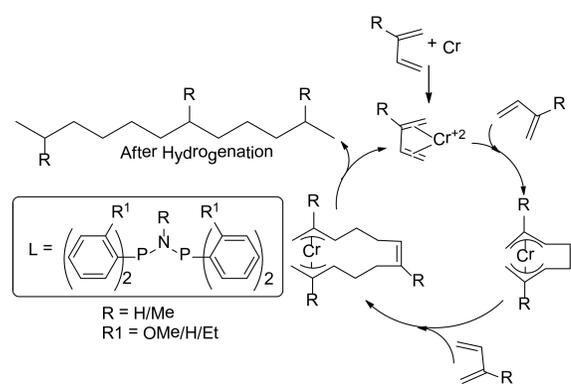
Jet and Diesel Blends are Primary Targets



Literature Survey On Oligomerization Of Isoprene

#	Ligand	Productivity g/(g Cr)h	(Trimer)			
			Total Trimer	Linear	Cyclic	Other
1		585	98	99	1	2
2		669	86	87	13	14
3		346	94	86	14	6
4		826	79	70	30	21
5		298	95	74	26	5
6		1483	65	87	13	35
7		1103	100	87	13	0

Postulated Diene Trimerization Mechanism



(1) Carter, A., S.A. Cohen, N.A. Cooley, A. Murphy, J. Scutt, and D.F. Wass, *Chem. Commun.* (2002) 858. (2) Dulai, A., C.L. McMullin, K. Tenza, and D.F. Wass, *Organometallics*, 30 (2011) 935. (3) Bowen, L.E., M. Charemsuk, T.W. Hey, C.L. McMullin, A.G. Orpen, and D.F. Wass, *Dalton Transactions*, 39:2 (2010) 560-567.

Approach

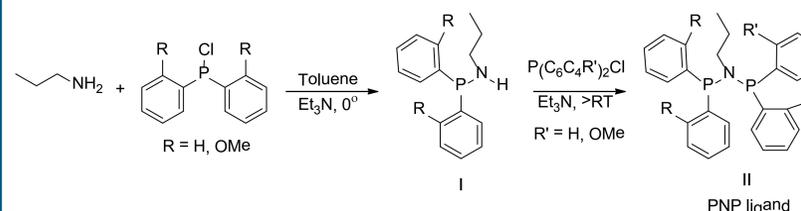
There is a Need for Further Research

- Homogeneous catalysts not always industrially practical
- Heterogeneous catalysts facilitate continuous processes and catalyst recovery
- Catalysts with the selectivity of homogeneous catalysts and the ease of use of heterogeneous catalysts would be advantageous
- Butadiene ≠ Isoprene; catalysts good for isoprene often are not good for butadiene. Steric and electronic factors are important, but not completely understood.

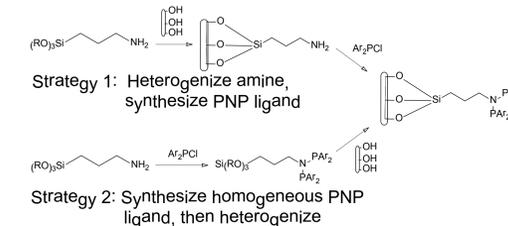
Our Proposed Research

- Prepare homogeneous oligomerization catalysts with (Ar)₂PN(R)P(Ar)₂ ligands (PNP ligands)
- Validate catalytic oligomerization
- Prepare heterogeneous analogs
- Determine activity and selectivity of heterogeneous catalysts; compare to homogeneous analogs
- Compare behavior of catalysts with symmetrical PNP ligands versus those with asymmetrical PNP' ligands
- Vary attachment method and surface environment
- Demonstrate a continuous process

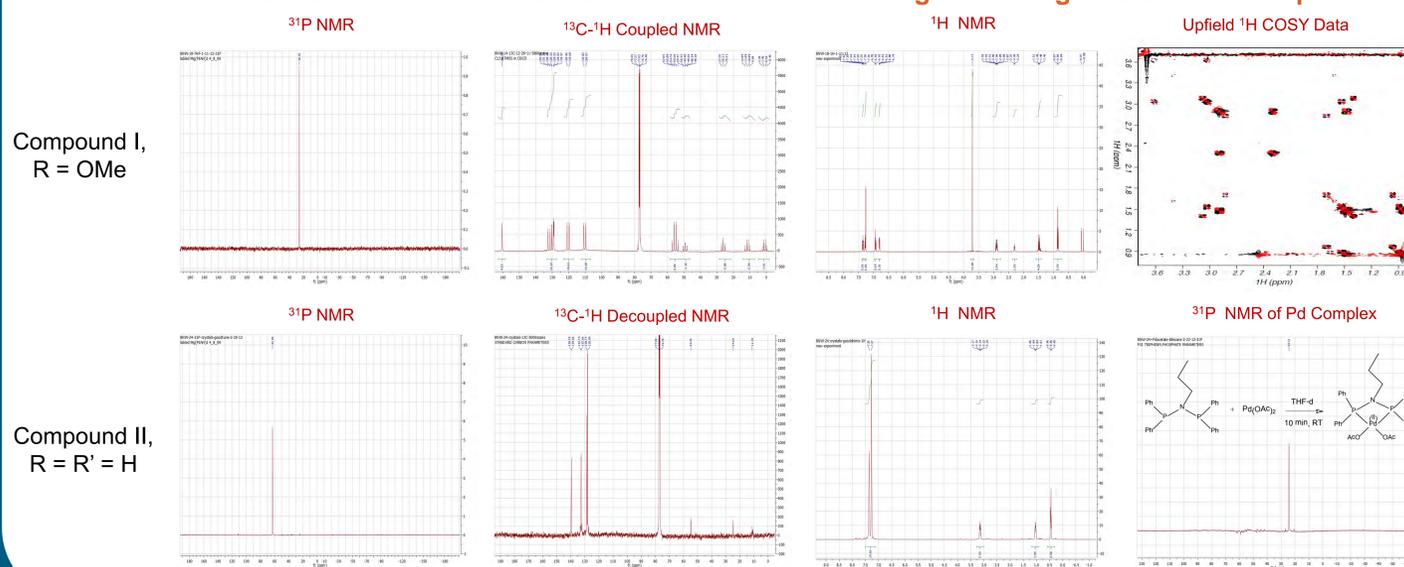
Current Results: Synthesis Of Homogeneous PNP Ligands



Future: Synthesis Of Heterogeneous PNP Ligand Analog



Multinuclear and 2-D NMR are Consistent with Desired Homogeneous Ligands and Pd Complex



Impact

This project has the potential to open new pathways to advanced biofuels by converting biochemically-derived dienes (butadiene and isoprene) to jet and diesel range hydrocarbons. This new pathway could help DOE and the nation meet EISA goals, reduce our dependence on foreign oil, and reduce green house gas emissions.

Acknowledgments



Homogeneous catalysts and their heterogenized analogs will be prepared to investigate steric and electronic effects in diene oligomerization to jet and diesel range hydrocarbons as fuel blendstocks.