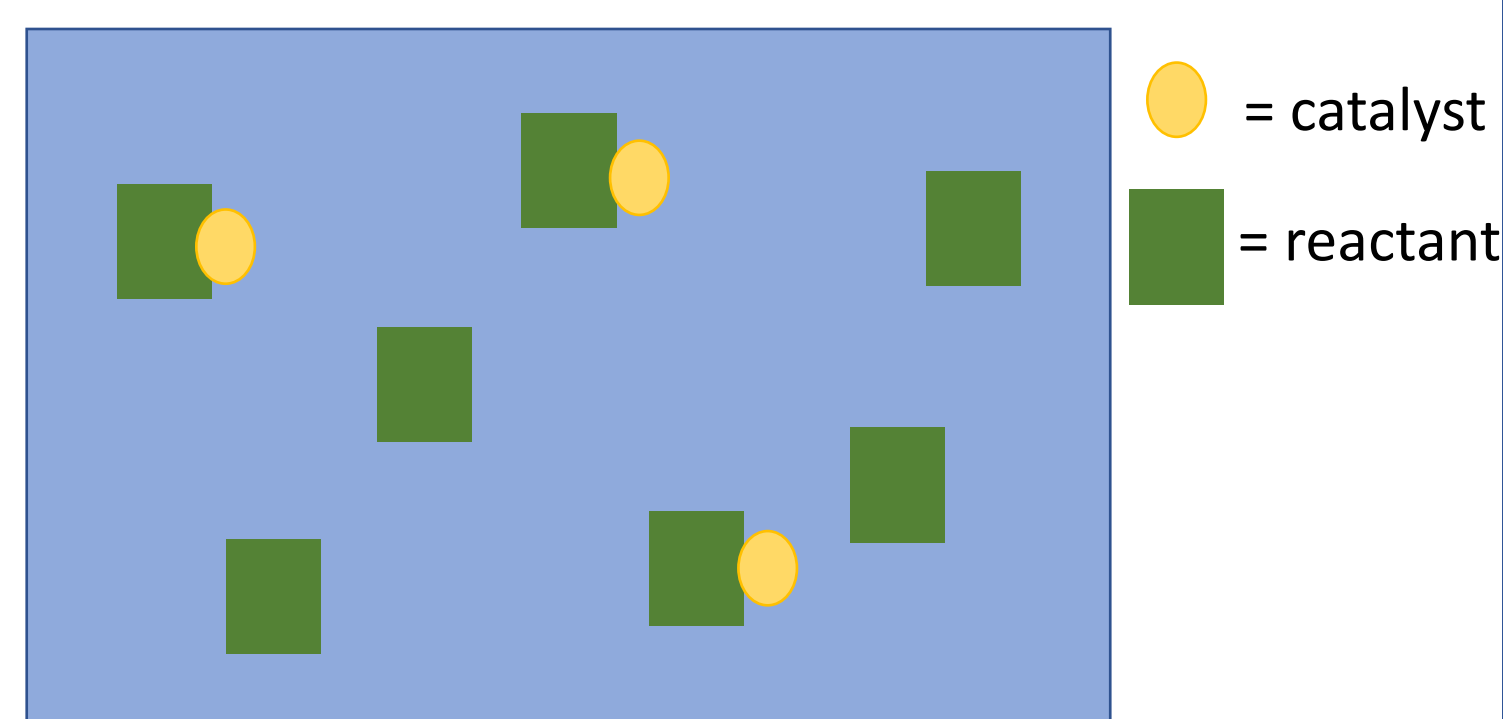


# Designer Catalysts: Synthesis and Activity of Nickel Compounds Towards Hydrosilylation

Parker Morris and Dr. Amanda Cook

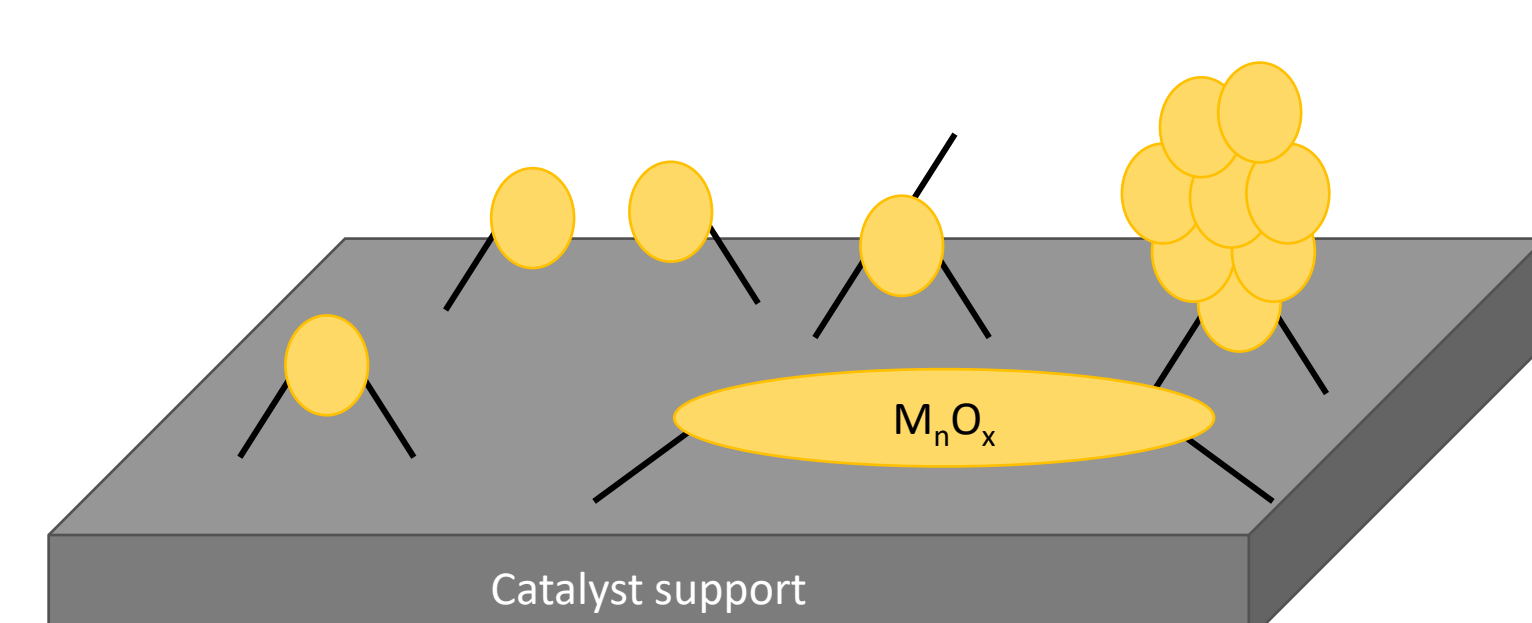
## Homogenous Catalysis

- In homogenous catalysis, the catalyst and the substrate are all dissolved in solution
- Pros
  - Higher percentage of active catalyst
  - Molecular control – generally easier to design/synthesize
- Cons
  - More difficult to recycle
  - Less tolerable to harsh conditions



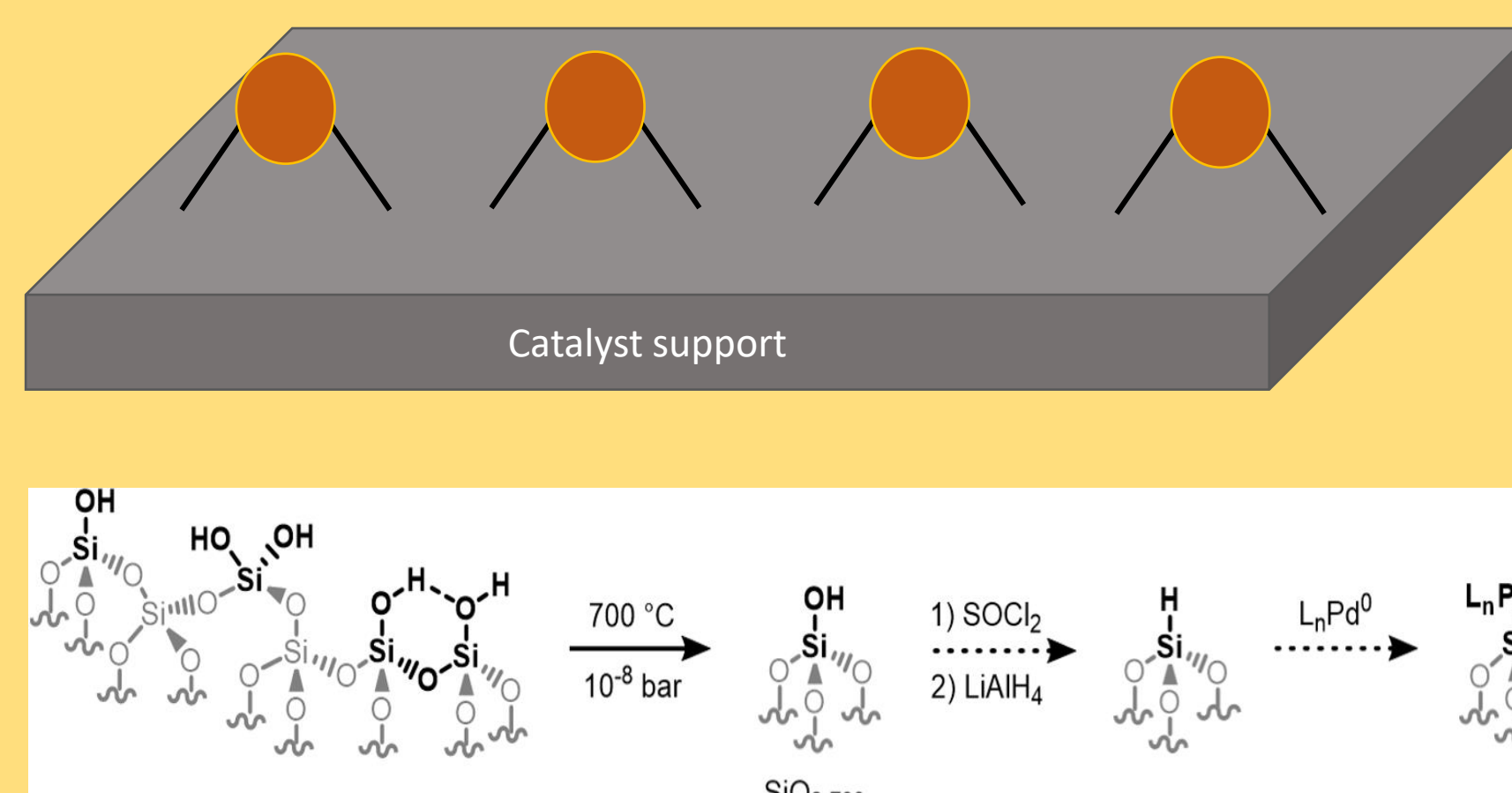
## Heterogenous Catalysis

- In homogenous catalysis your active catalyst is deposited on some sort of solid support, silica or carbon are common.
- Pros
  - Tolerable to harsh conditions
  - Easier to recycle – simply filter it out
- Cons
  - Limited molecular control
  - Potentially unknown active catalysts



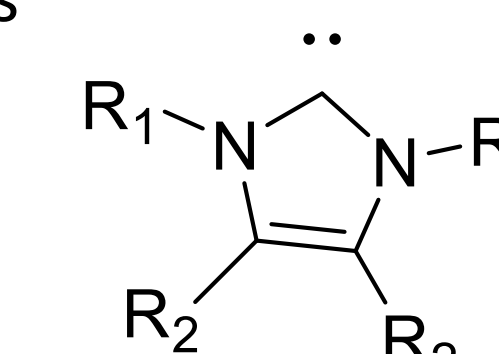
## Goals

- Combine the pros and the cons of both classes of catalysis by using Surface Organometallic Chemistry.
- Design and synthesize nickel complexes that promote hydrosilylation of alkenes
- Prove that the novel nickel complexes are superior catalysts than commercially available complexes



## Ligand Design

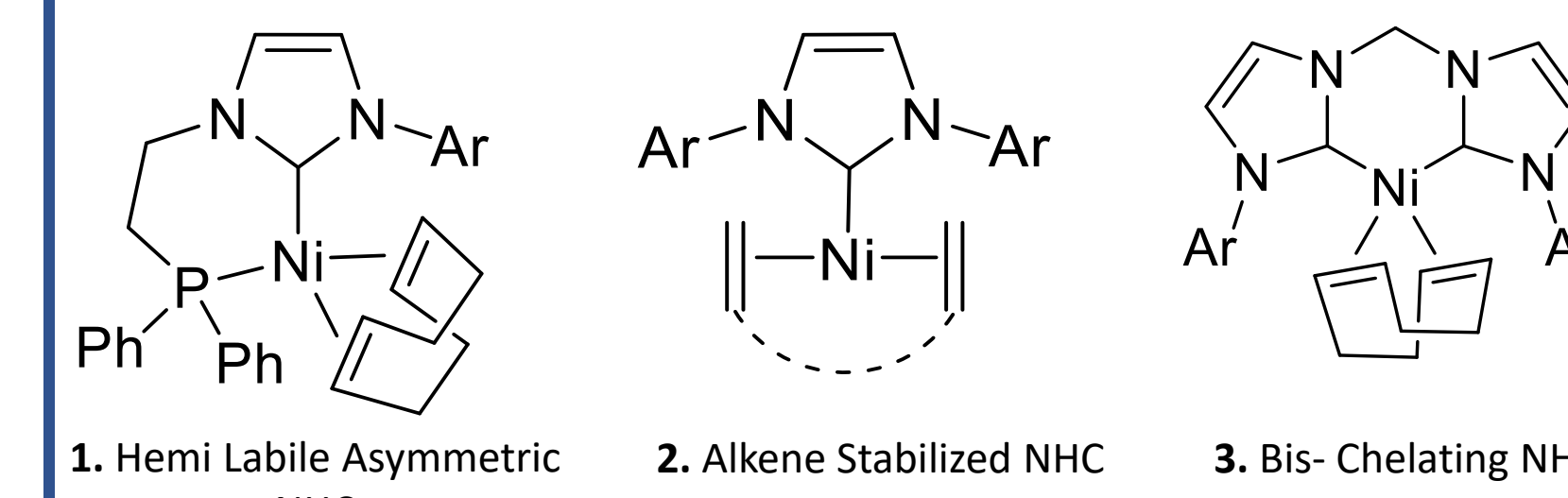
- Ligands are designed based on reactions shown in literature
- Two main catalytic ligands are N-heterocyclic carbenes (NHC) and chelating phosphines
- We investigated NHC's because they are easily tunable in terms of both electronics and sterics



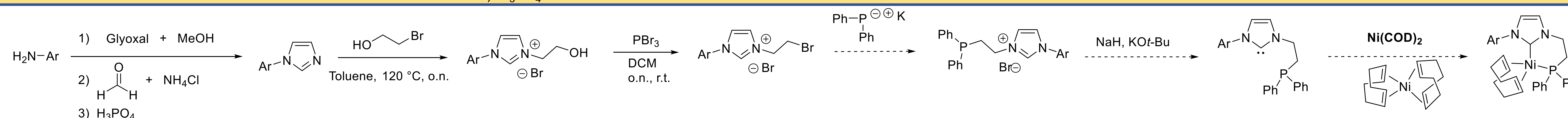
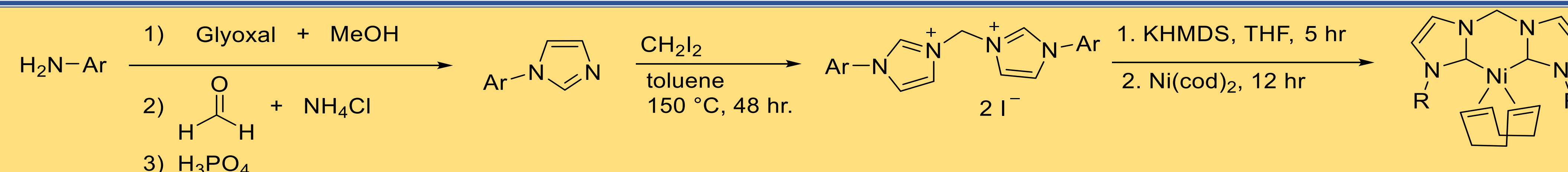
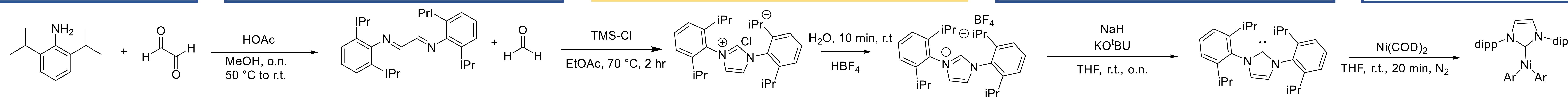
- Modulating the R<sub>1</sub> position would change sterics
- Modulating the R<sub>2</sub> position would change electronics

## Methods

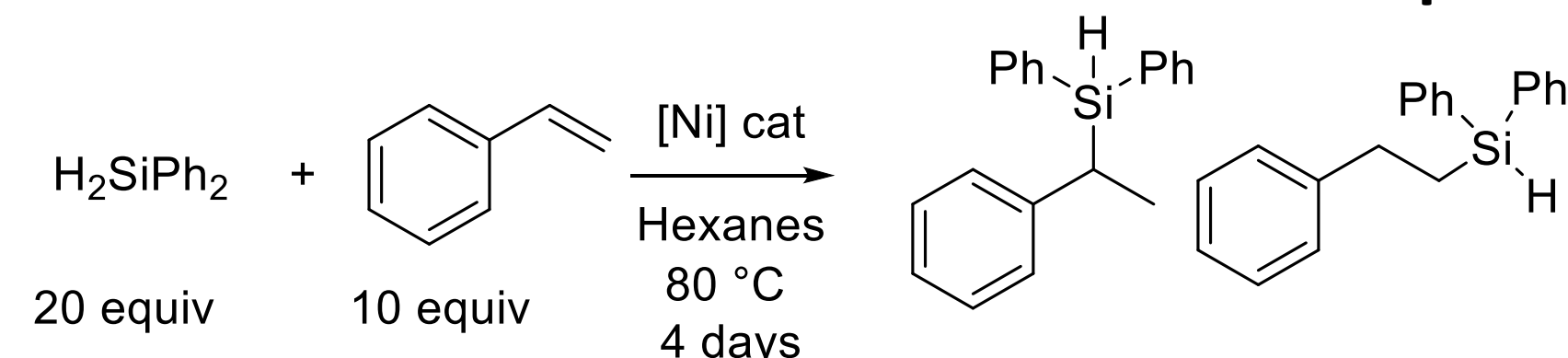
- Using traditional organic synthesis techniques, we look to synthesize 3 nickel complexes



- Once made, we will run NMR scale reactions with styrene and allylbenzene to determine their catalytic ability.
- We look to examine
  - Selectivity
  - Total yield



## Novel vs. Commercial Nickel Complexes



	N <sub>2</sub> /atm	Branch %	Linear %	Branch/linear	Total % Yield
NiCl <sub>2</sub>	atm	36	18	2.00	54
	N <sub>2</sub>	36	23	1.6	59
NiCl <sub>2</sub> · 6H <sub>2</sub> O	atm	32	18	1.6	50
Ni(acac) <sub>2</sub>	atm	50	27	1.8	77
	N <sub>2</sub>	42	37	1.1	79
(PPh <sub>3</sub> ) <sub>2</sub> NiCl <sub>2</sub>	atm	2.3	74	0.03	77
(PPh <sub>2</sub> ) <sub>3</sub> NiBr <sub>2</sub>	atm	4.5	59	0.08	63
(dppp)NiCl <sub>2</sub>	atm	43	29	1.5	72
(dppf)NiCl <sub>2</sub>	atm	41	23	1.8	63
	N <sub>2</sub>	4.8	58	25	2.3
Ni(BF <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	atm	38	18	2.1	56
	N <sub>2</sub>	38	27	1.4	65
(dme)NiCl <sub>2</sub>	N <sub>2</sub>	40	31	1.3	71
Ni(OAc) <sub>2</sub> · 4H <sub>2</sub> O	atm	38	23	1.7	61
NiBr <sub>2</sub> · 3H <sub>2</sub> O	atm	41	23	1.8	63
Ni(cod) <sub>2</sub>	N <sub>2</sub>	27	33	0.81	60
Ni(PPh <sub>3</sub> ) <sub>4</sub>	N <sub>2</sub>	0	100	0	100
hex-Ni-dippNHC	N <sub>2</sub>	52	25	2.1	77
styrene-Ni-dippNHC	N <sub>2</sub>	67	19	3.6	85

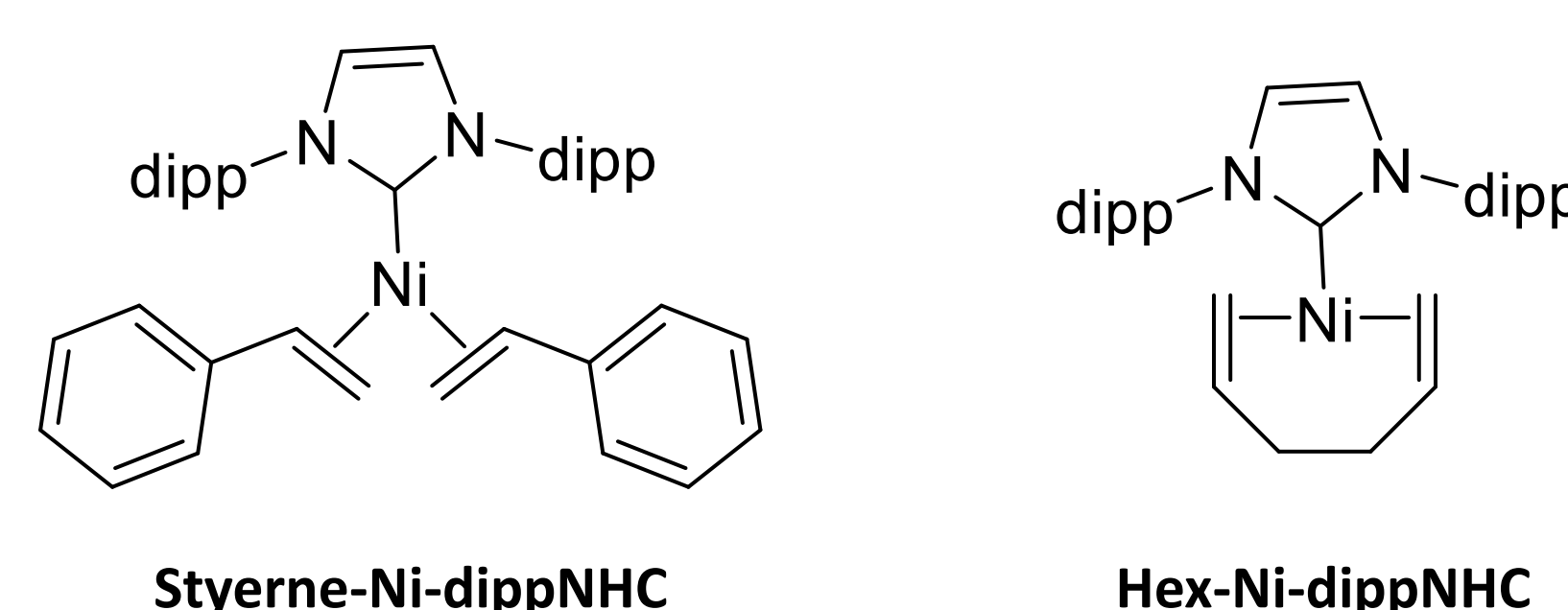
## Results/Conclusions

### Synthetic Conclusions

- Both the bis-chelating NHC and the alkene stabilized NHC were successfully synthesized
- The hemi-labile NHC proved limited by the substitution from bromine to phosphine
- Replacing the stabilizing alkene can be altered and doing so effects the product distribution

### Catalyst Screening Conclusions

- The catalysts made in lab out performed the commercial catalysts in terms of both selectivity and yield
- Sterics and/or lability have a direct relationship to overall yield and selectivity.
- More sterically hindering alkene stabilizers produce higher yield and higher selectivity
- Unexpectedly, Ni(PPh<sub>3</sub>)<sub>4</sub> had 100% linear yield and selectivity



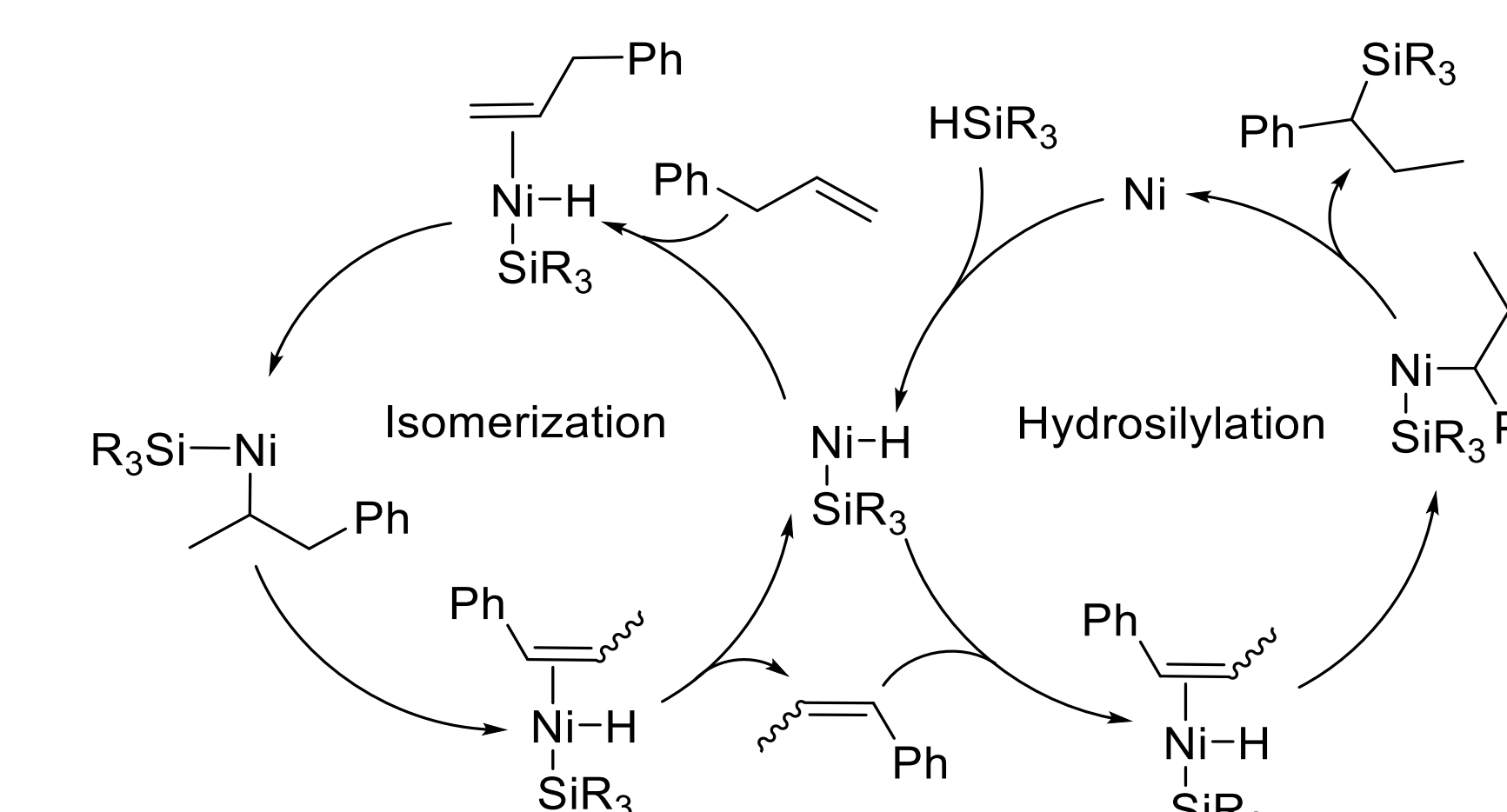
## Future Work

### Synthesis

- We look to modulate the NHC ligands using electron withdrawing and electron donating groups
- Continue to work towards the hemi-labile NHC

### Other

- Investigate the tandem catalysis of hydrosilylation and isomerization in a process called remote functionalization
- The catalytic cycle shown is proposed based on previous work that shows oxidative addition of the silane to the nickel center
- Optimize the solvent, temperature, and catalyst loading of the system
- Test the bis-chelating NHC for hydrosilylation catalysis



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