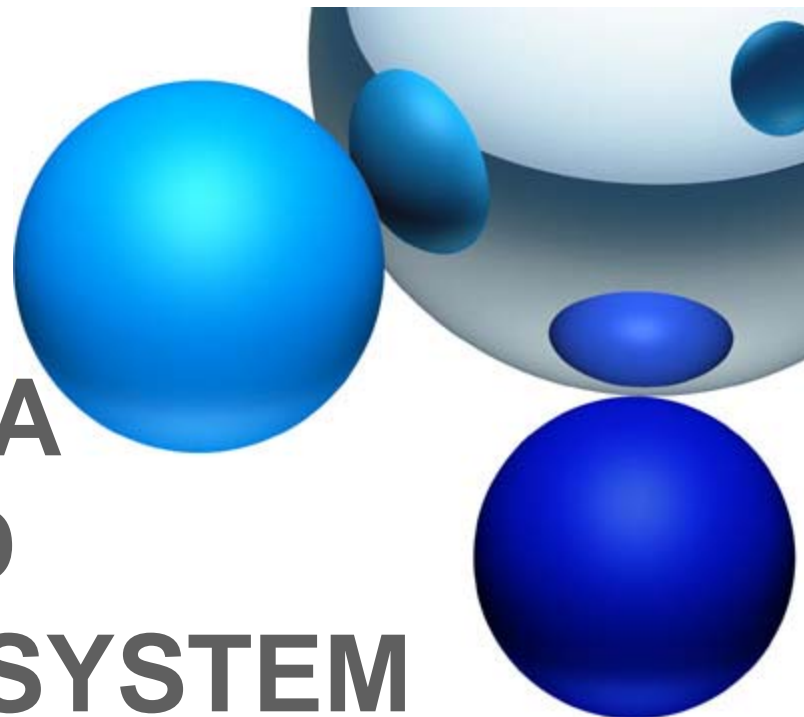


HOMOGENEOUS METATHESIS WITH A RUTHENIUM-BASED *IN SITU* CATALYST SYSTEM



Wynand Serfontein*, Manie Vosloo†, & Cathy Dwyer*



SASOL
reaching new frontiers

* *Sasol Technology Research & Development,
PO Box 1, Sasolburg, 1947*

† *North-West University,
P/Bag X6001, Potchefstroom, 2520*

In situ catalyst system: background



In Situ System = alkene + ligand + alkyne + RuCl₃ or RuBr₃

1. *PO Nubel, CL Hunt, J. Mol.Cat. A: Chem. 145 (1999), 323*
2. *US Patent 6,159,890, Dec 12, 2000*
3. *C van Schalkwyk, Die Katalitiese sintese van lineêre alkene via 'n metatesereaksie, PhD Thesis, PU vir CHO, 2001*

In situ catalyst system: background



In Situ System = alkene + ligand + alkyne + RuCl₃ or RuBr₃

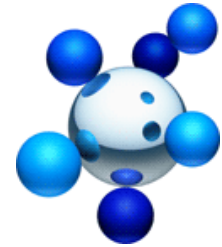
Used in this study: 1-octene, PCy₃, EP, Phoban-Cy, BDD (2-butyne-1,4-diol diacetate)

RuCl₃ dissolved in EtOH)

Some other alkynes and ligands (once-off for comparison)

- 1. PO Nubel, CL Hunt, J. Mol.Cat. A: Chem. 145 (1999), 323*
- 2. US Patent 6,159,890, Dec 12, 2000*
- 3. C van Schalkwyk, Die Katalitiese sintese van lineêre alkene via 'n metatesereaksie, PhD Thesis, PU vir CHO, 2001*

In situ catalyst system



WHY?

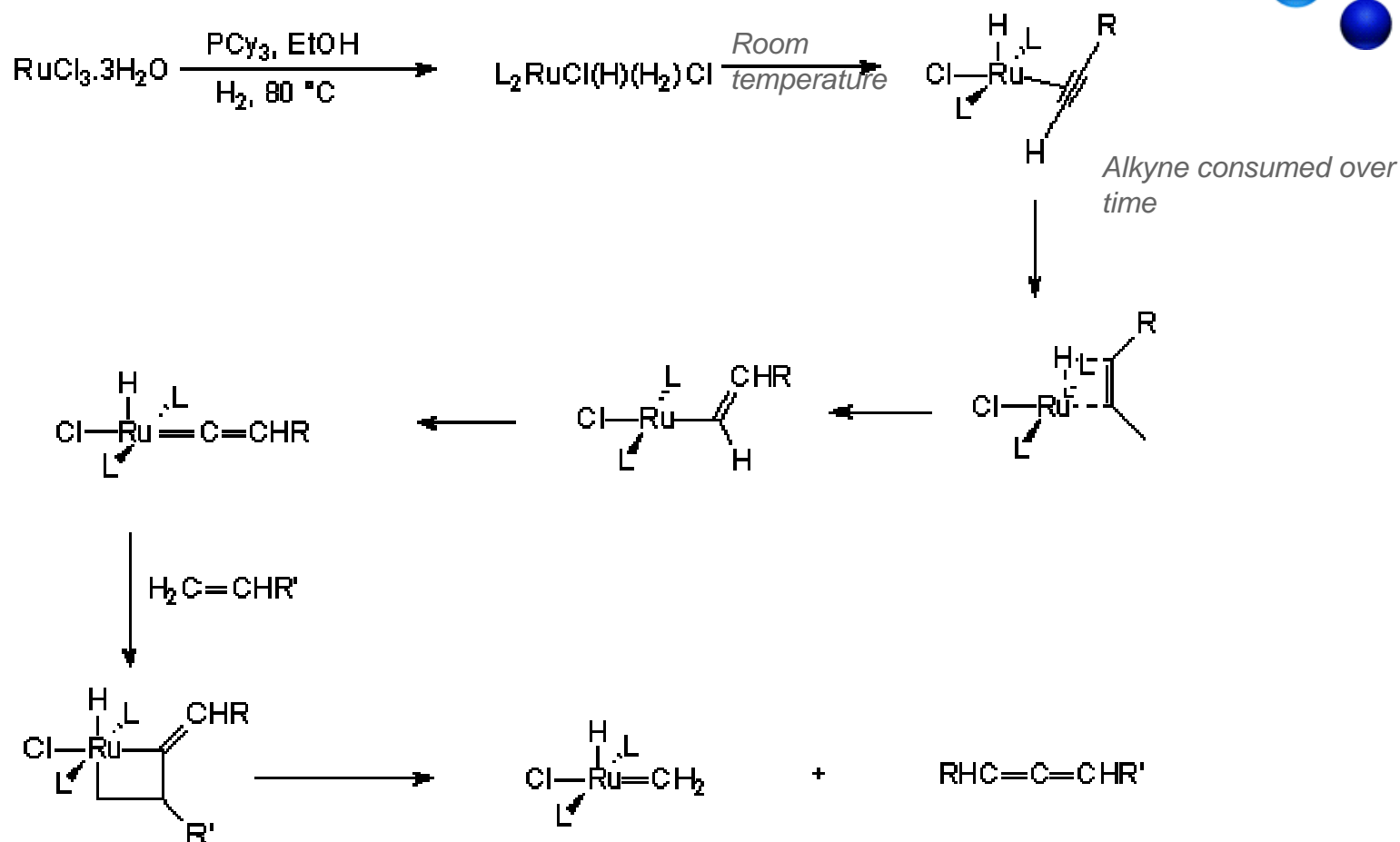
Cheap Ru precursor

BUT:

- *complex system - mechanism not yet confirmed, presumably via hydride intermediate;*
- *Slow, suggesting formation of metathesis catalyst is rate-determining*
- *Catalyst lifetime is longer than preformed catalysts, but lower TON*

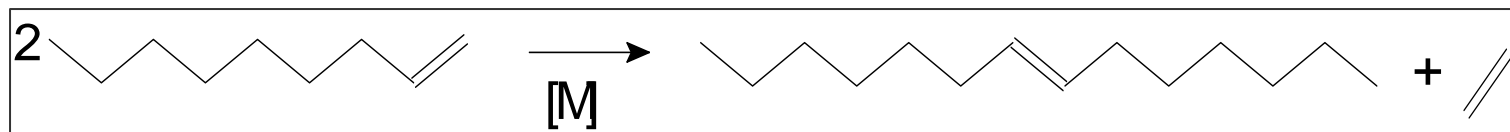
Further work by Sasol in this area focused on alternative ligands for in situ generation of the active catalyst from a cheap Ru precursor.

The mechanism



1. *C van Schalkwyk, HCM Vosloo, JM Botha, J. Mol. Catal. A: Chem., 2002, 190, 185*
2. *KJ Ivin and JC Mol, Olefin Metathesis and Metathesis Polymerisation, Academic Press, London, 1997*

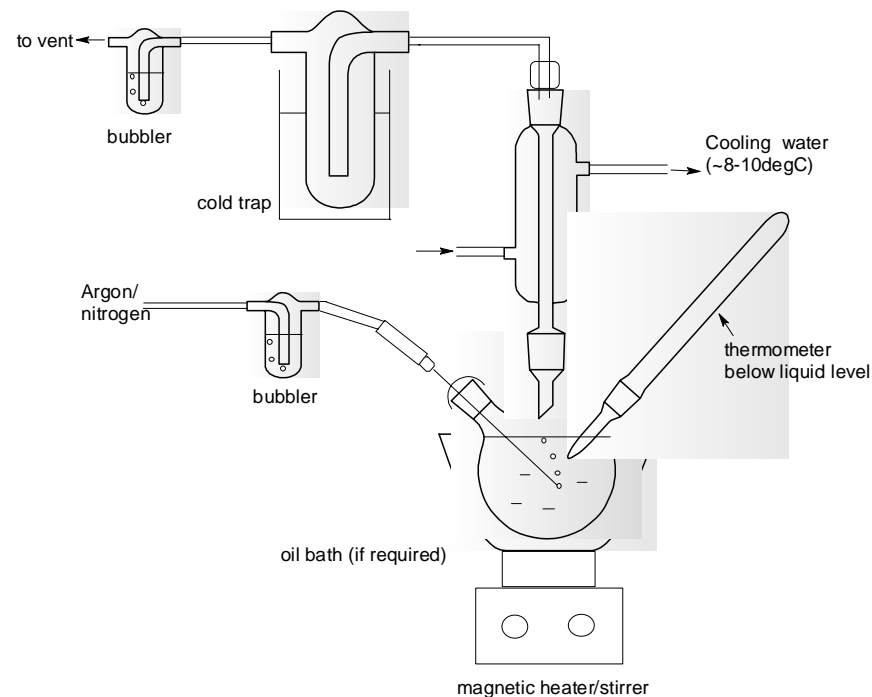
Our approach



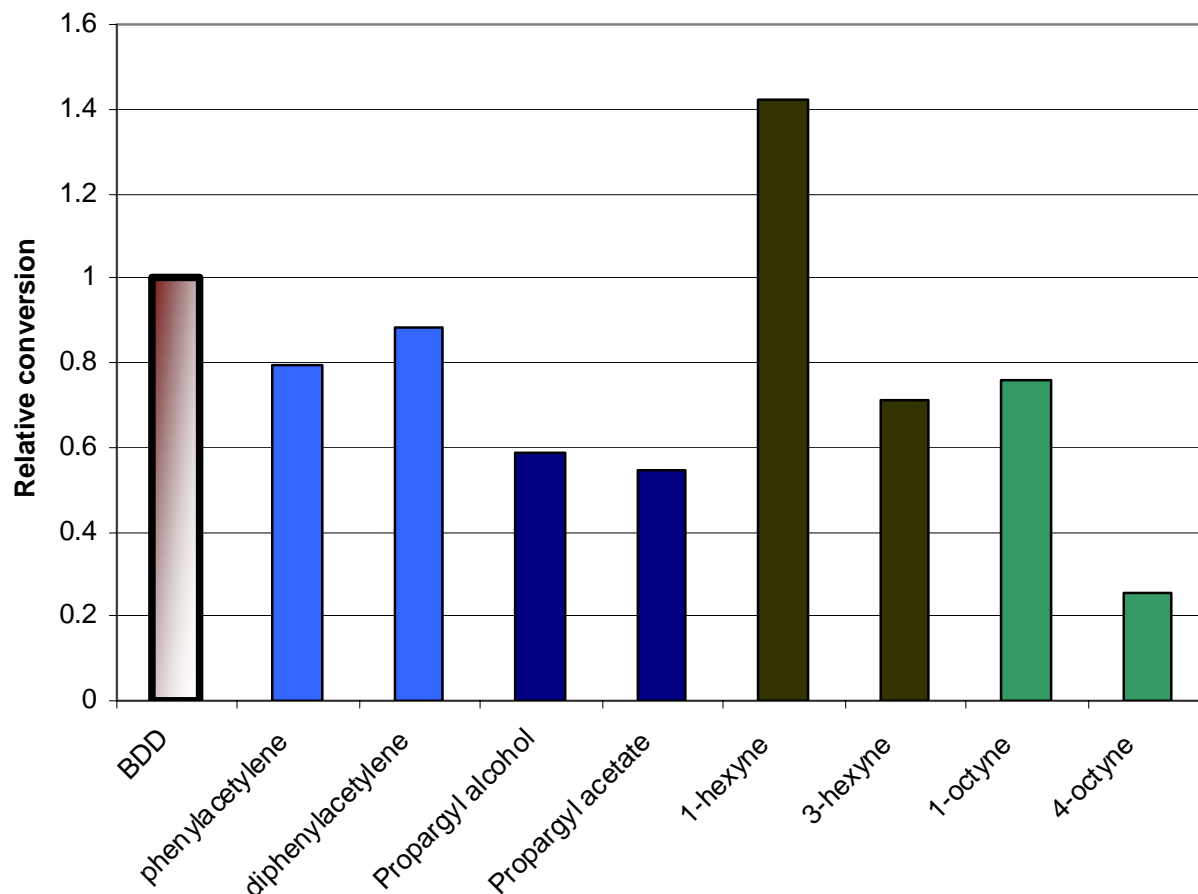
- *RuCl₃ dissolved in EtOH, left 24h.*
- *1-octene + ligand + alkyne + RuCl₃ sol + hydrogen sparge*
- *Alkyne and ligand dissolved in chlorobenzene.*
- *Base case molar ratio 9000 alkene:2.5 PCy₃:10 BDD:1 RuCl₃*

EXPERIMENTAL SETUP:

Open system with hydrogen sparge to generate active species and remove ethylene as formed



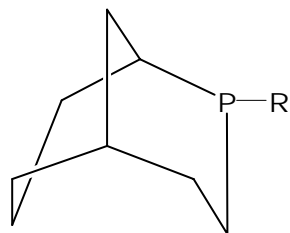
Metathesis yield vs alkyne type



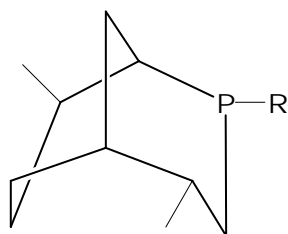
Conclusions:

1. *Shorter chain unfunctionalised alkynes better*
2. *Terminal alkynes better than internal alkynes (1 exception)*
3. *Functionalisation changes trend: can have same effect with different chain lengths.*

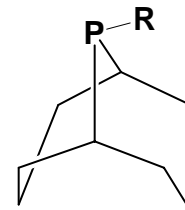
Some ligands tested



VCH derivative

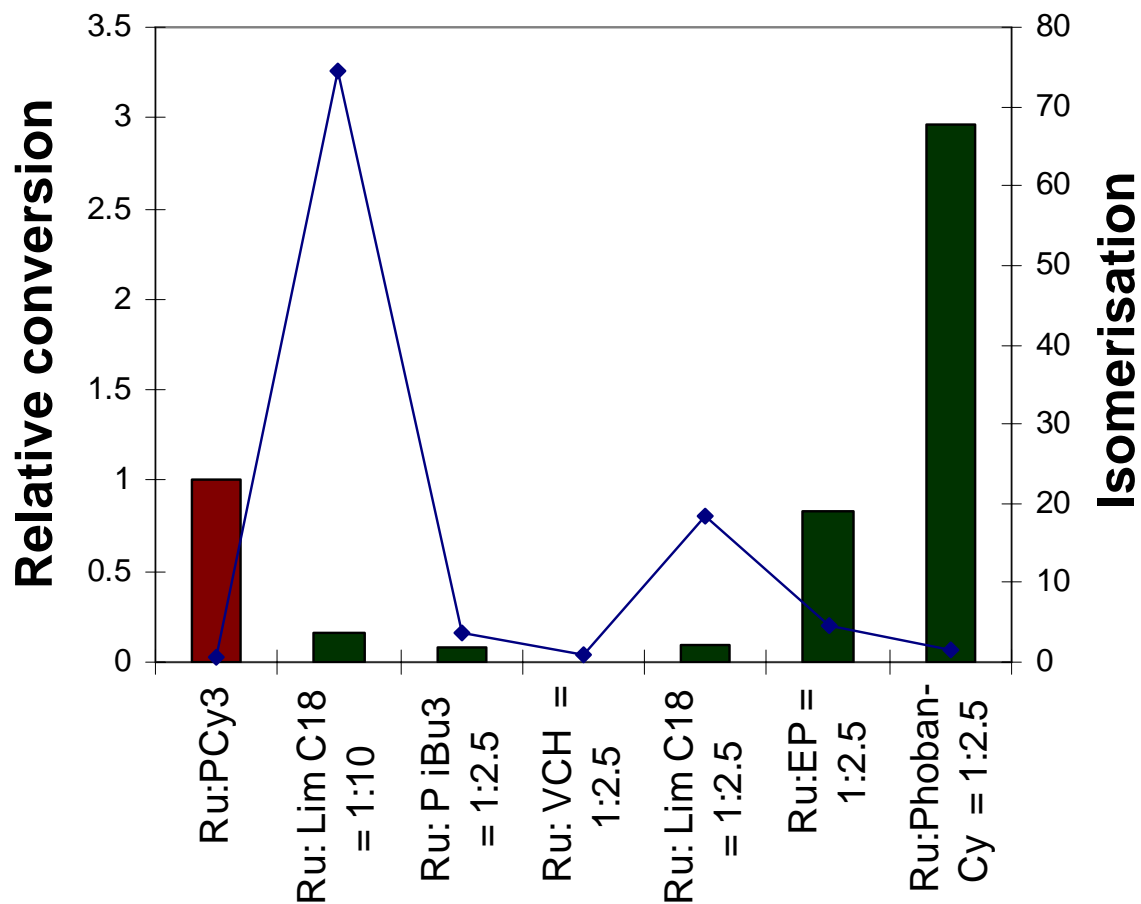


*Limonene derivative
(Lim)*



3,3,1-Phoban

Metathesis yield vs ligand type



100 ppm Ru

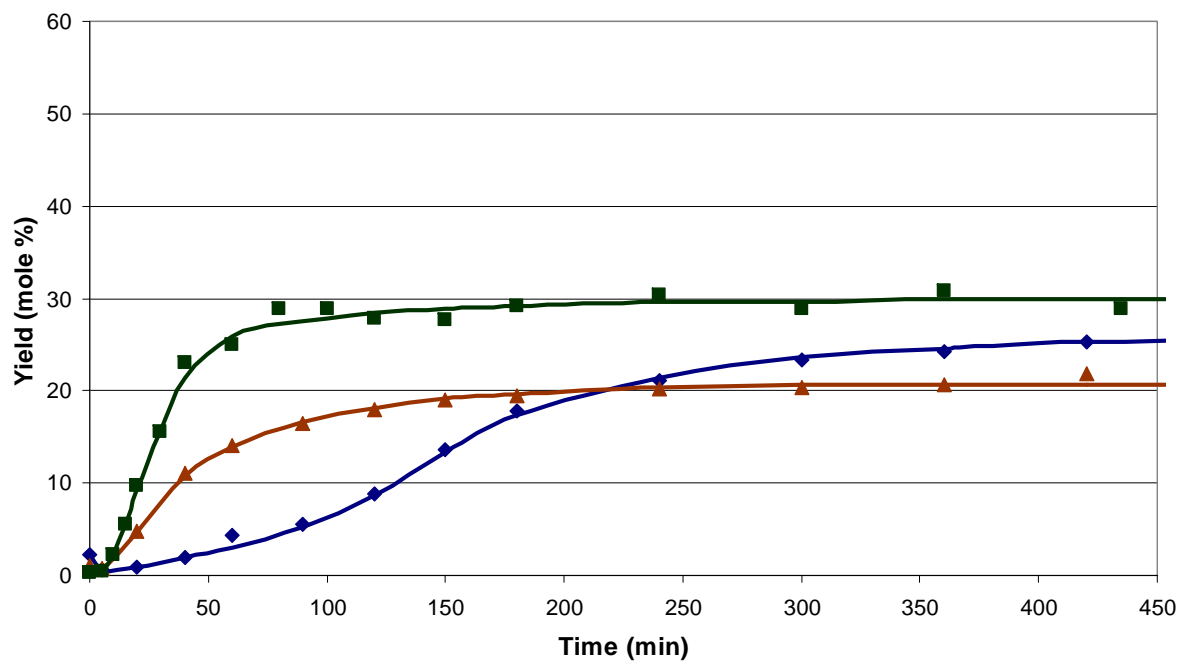
80 °C

Ru:BDD = 1:10

Conclusions:

1. Most ligands low activity, sometimes with high isomerisation
2. Different optimum conditions for different ligands
3. Exact nature of "ideal" ligand still unclear

Influence of temperature



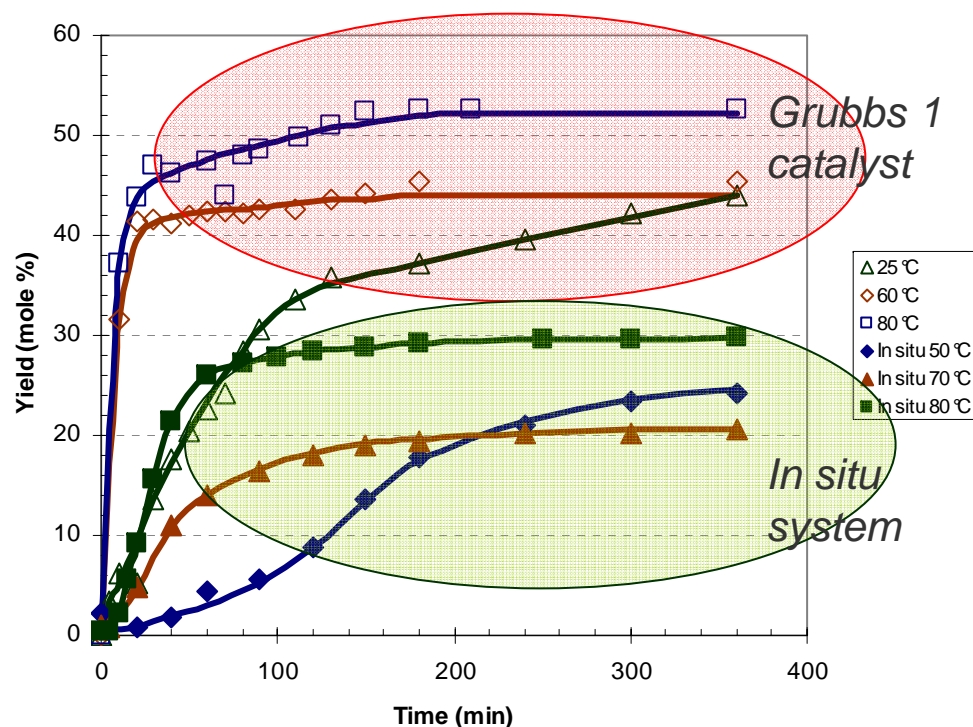
100 ppm Ru

Ru:PCy₃:BDD =
1:2.5:10

Conclusions:

1. *Higher temperature - higher overall yield.*
2. *Below 50 °C, the initial activity of the system is very low due to a temperature barrier for the formation of the catalytically active species.*
3. *The rate-limiting step - formation of the catalytically active species*
4. *High temperatures, high isomerisation*

Influence of temperature: Grubbs 1 catalyst and the In Situ system



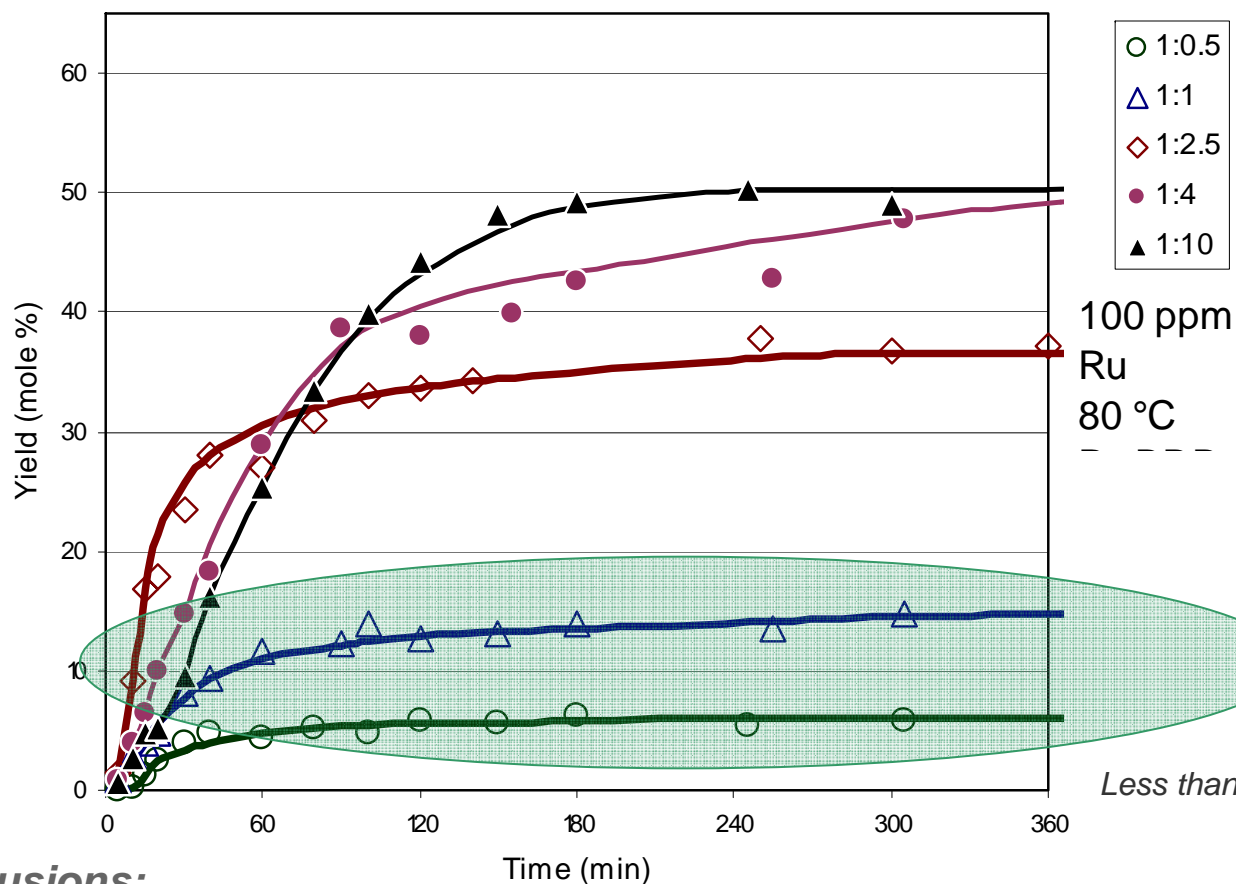
100 ppm Ru

Ru:PCy₃:BDD =
1:2.5:10

Conclusions:

1. G1 is both faster and affords higher yields than the in situ system under similar conditions

Influence of $Ru:PCy_3$ ratio

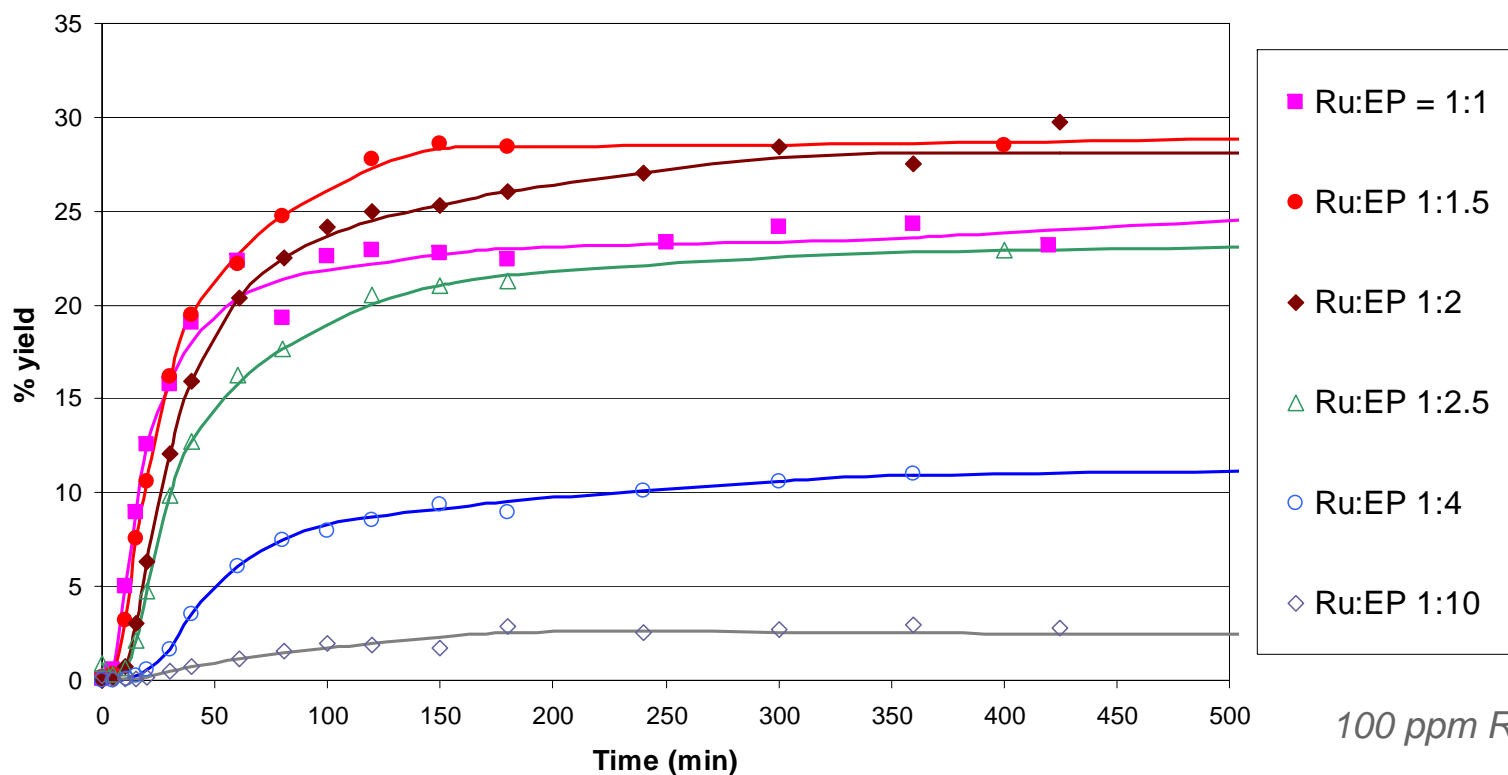


| Ru:L | % Isomerisation |
|-------|-----------------|
| 1:0.5 | 0.7 |
| 1:1 | 1.6 |
| 1:2.5 | 0.5 |
| 1:4 | 8.4 |
| 1:10 | 27.4 |

Conclusions:

1. An optimum $Ru:L$ ratio of 1 :2.5 was found using PCy_3 as ligand.
2. A higher $Ru:L$ ratio leads to a higher overall metathesis yield, BUT:
3. A too high ligand ratio leads to formation of unwanted side products (isomerisation/hydrogenation)

Influence of Ru:EP ratio



100 ppm Ru

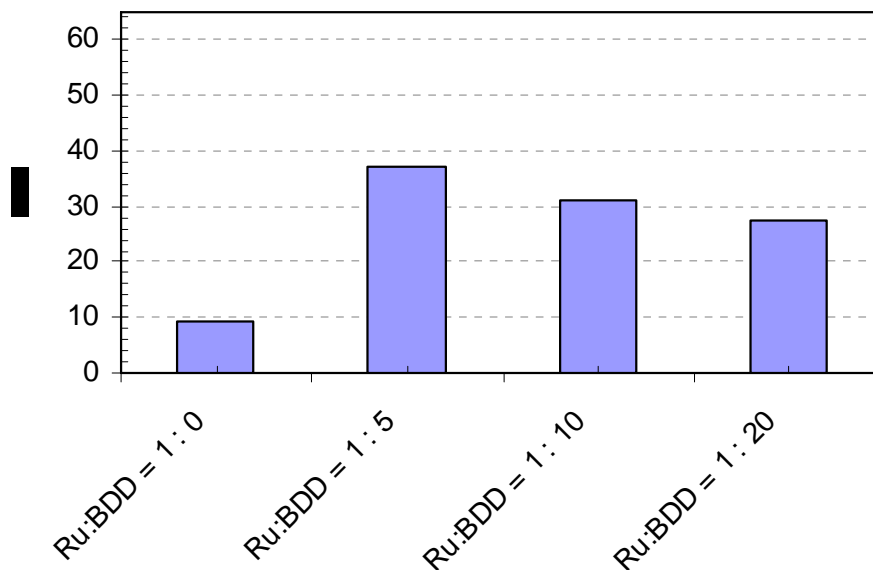
Ru:BDD = 1:10

Temp = 80 °C

Conclusions:

1. Optimal between Ru:EP = 1:1.15 and 1:2.0
2. Lower optimum ratio than PCy₃: 1.25 < 1.4 < 1:10, coordination strength effect

Ru:Alkyne ratio



| Ru:BDD | % Isomerisation |
|--------|-----------------|
| 1:0 | 67.4 |
| 1:5 | 11.4 |
| 1:10 | 0.5 |
| 1:20 | 1.3 |

100 ppm Ru

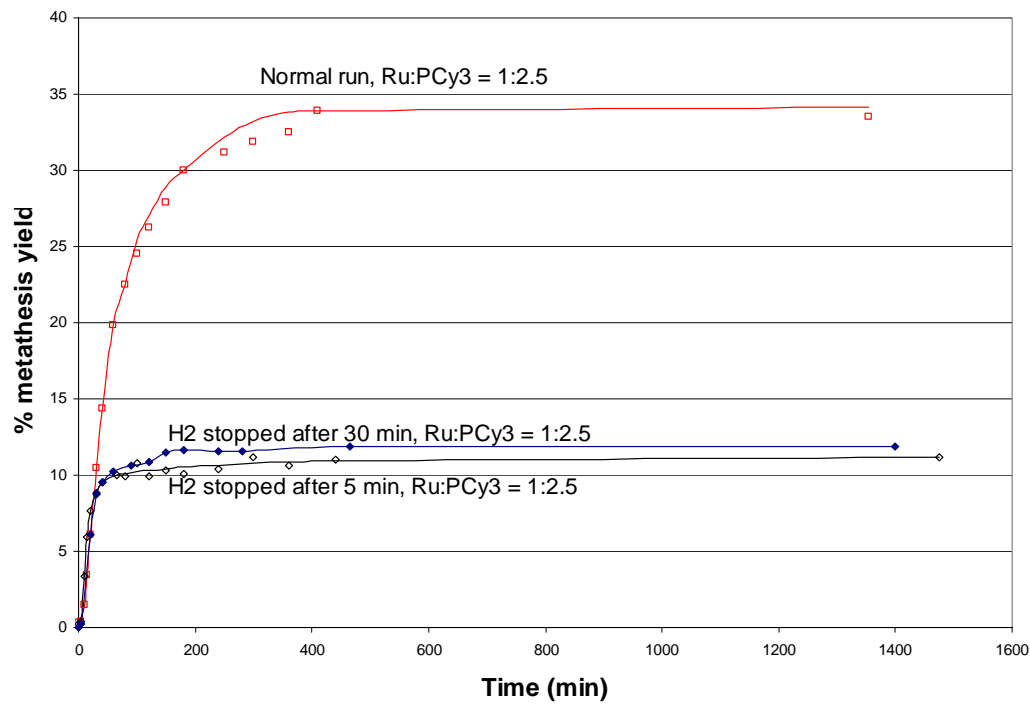
Ru:PCy₃ = 1:2.5

80 °C

Conclusions:

1. At an alkyne ratio of 1:5, a higher overall metathesis yield is offset by a higher yield of unwanted side products
2. The optimum Ru:alkyne ratio is 1:10
3. The alkyne is consumed as the reaction proceeds. This consumption results from a continuous formation of ruthenium carbene

Effect of continuous H₂ sparge



100 ppm Ru

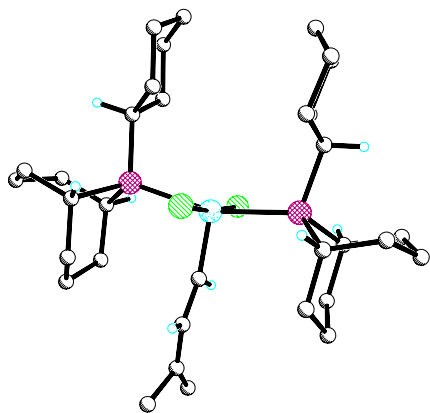
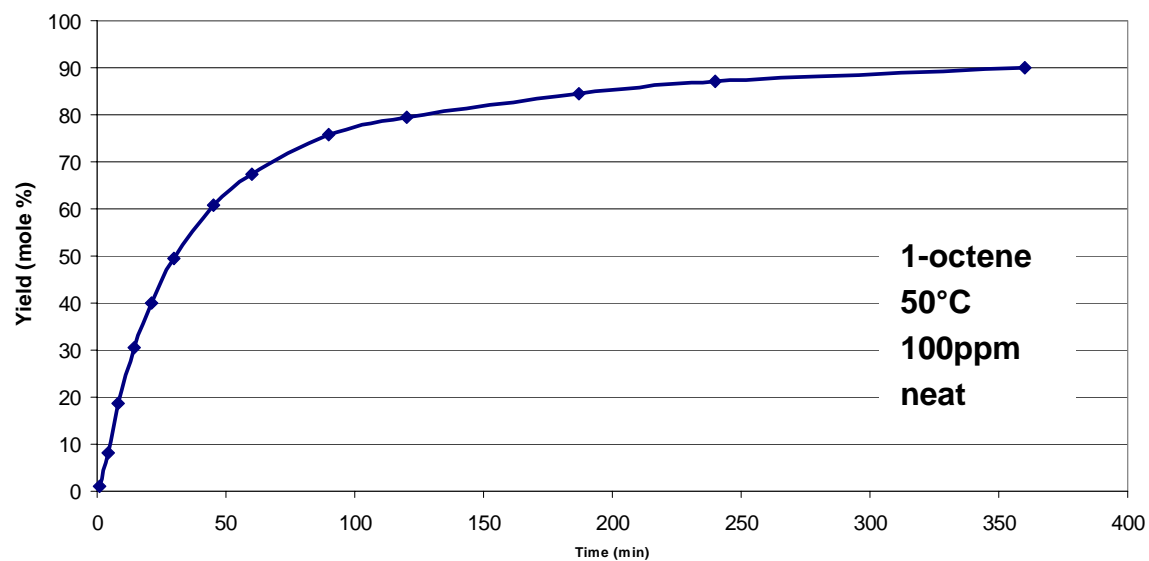
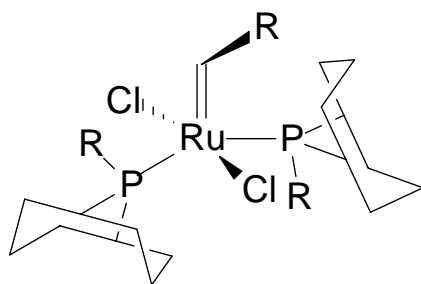
80 °C

Ru:PCy₃:BDD = 1:2.5:10

Conclusions:

A continuous hydrogen sparge needed for the formation of the intermediate hydride, followed by carbene formation

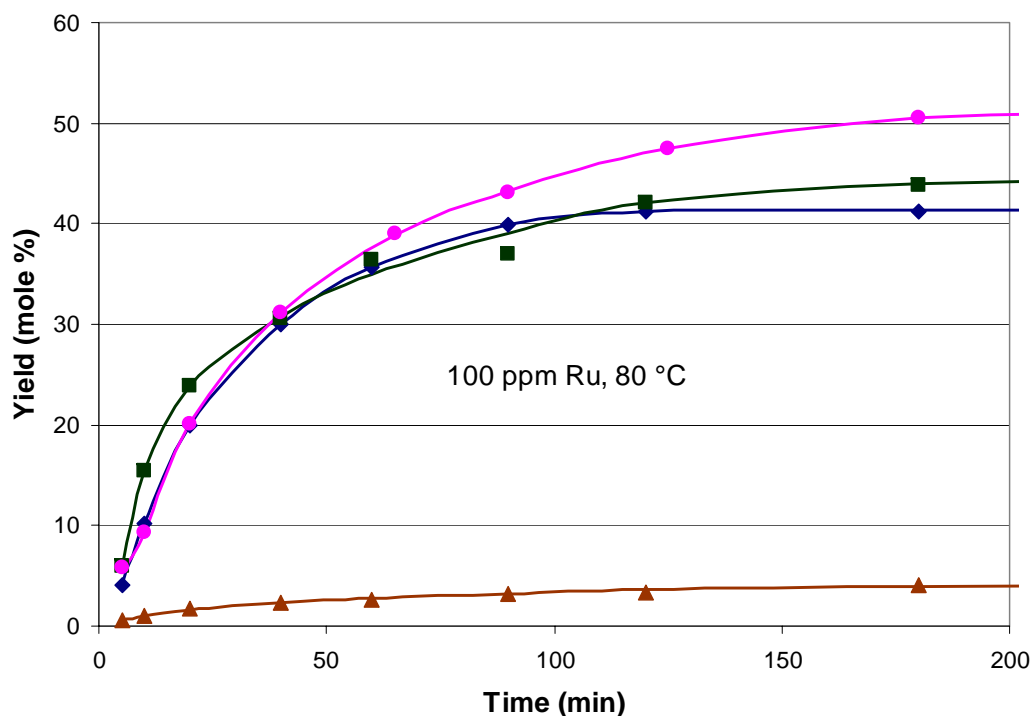
Phoban catalyst



Conclusions

1. *slower reaction,*
2. *MUCH slower decomposition: high TON*

What ligand ligand isomer?

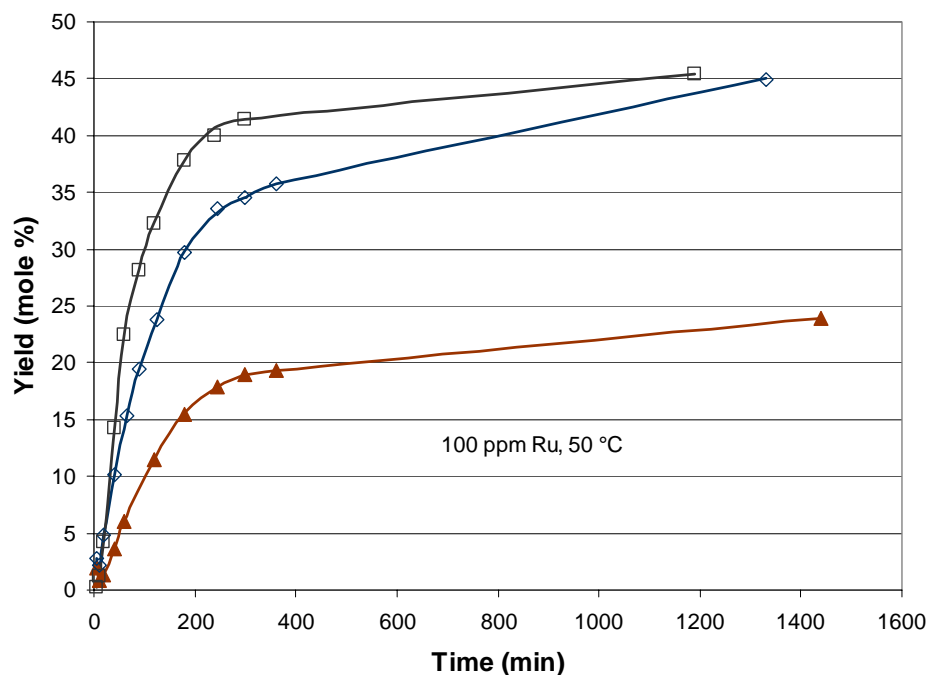


| Legend | Ru | 3,3,1 | 4,2,1 |
|--------|----|-------|-------|
| ◆ | 1 | 2.5 | 0 |
| ■ | 1 | 1.25 | 0 |
| ▲ | 1 | 0 | 1.25 |
| ● | 1 | 1.25 | 1.25 |

Conclusions:

1. Phoban-3,3,1 superior to phoban-4,2,1
2. With enough (1.25 eq) of phoban-3,3,1 present, can “top up” with phoban-4,2,1 under these conditions

What ligand ligand isomer?

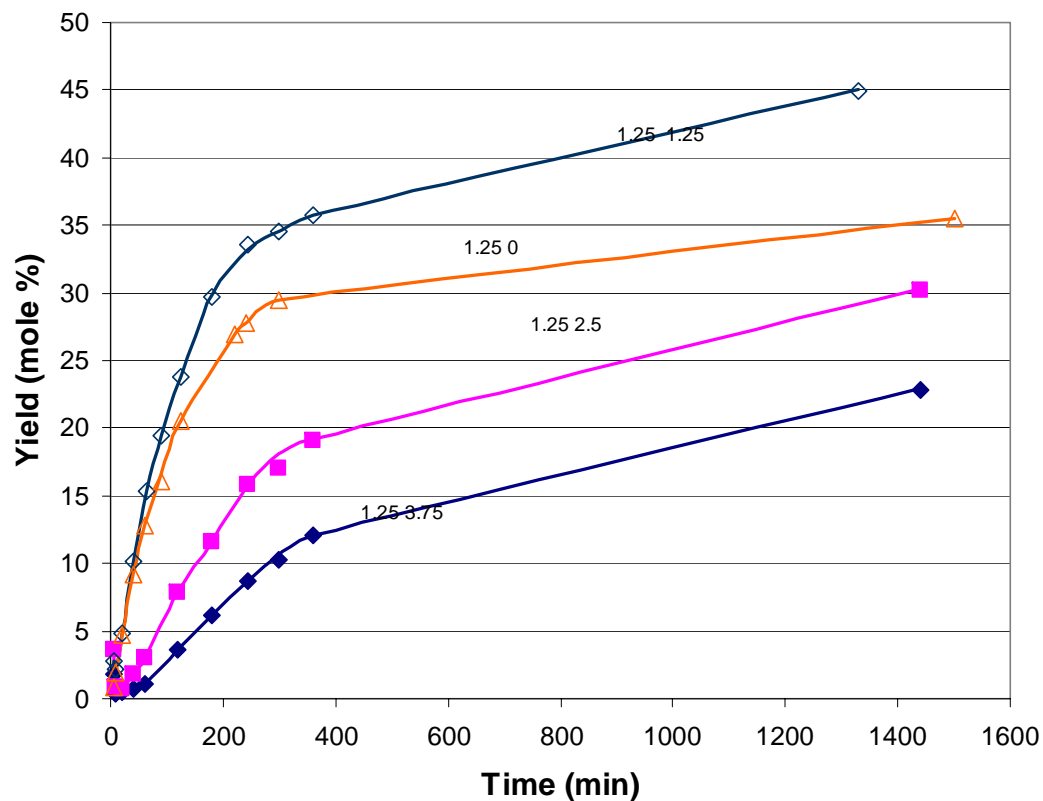


| Legend | Phoban-Cy isomer | | |
|--------|------------------|-------|-------|
| | Ru | 3,3,1 | 4,2,1 |
| ▲ | 1 | 0 | 2.5 |
| ◇ | 1 | 1.25 | 1.25 |
| □ | 1 | 2.5 | 0 |

Conclusions:

1. A high amount of phoban-4,2,1 only is not good enough to get similar conversion than with at least 1.25 eq phoban 3,3,1 present

Metathesis yield vs ligand amount

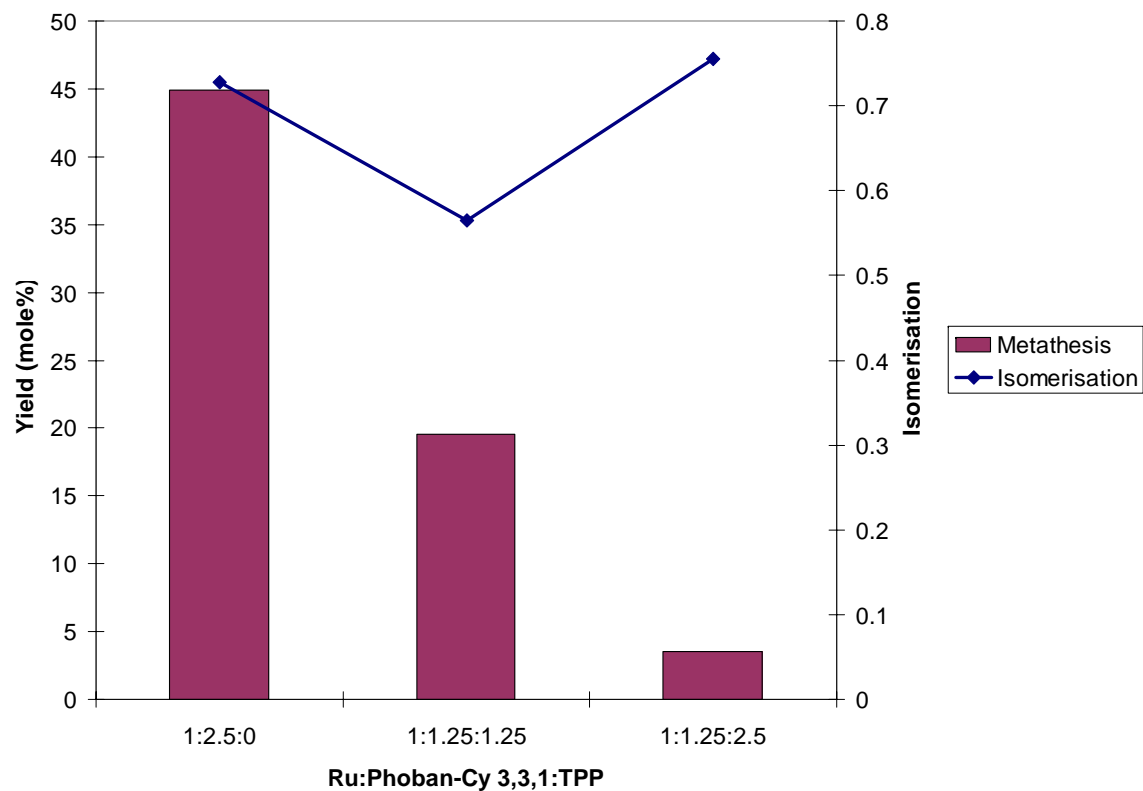


| Legend | Ru | Phoban-Cy isomer | |
|--------|----|------------------|-------|
| | | 3,3,1 | 4,2,1 |
| ◆ | 1 | 1.25 | 3.75 |
| ■ | 1 | 1.25 | 2.5 |
| ◇ | 1 | 1.25 | 1.25 |
| △ | 1 | 1.25 | 0 |

Conclusions:

1. An increase in total ligand suppresses both yield and initial rate

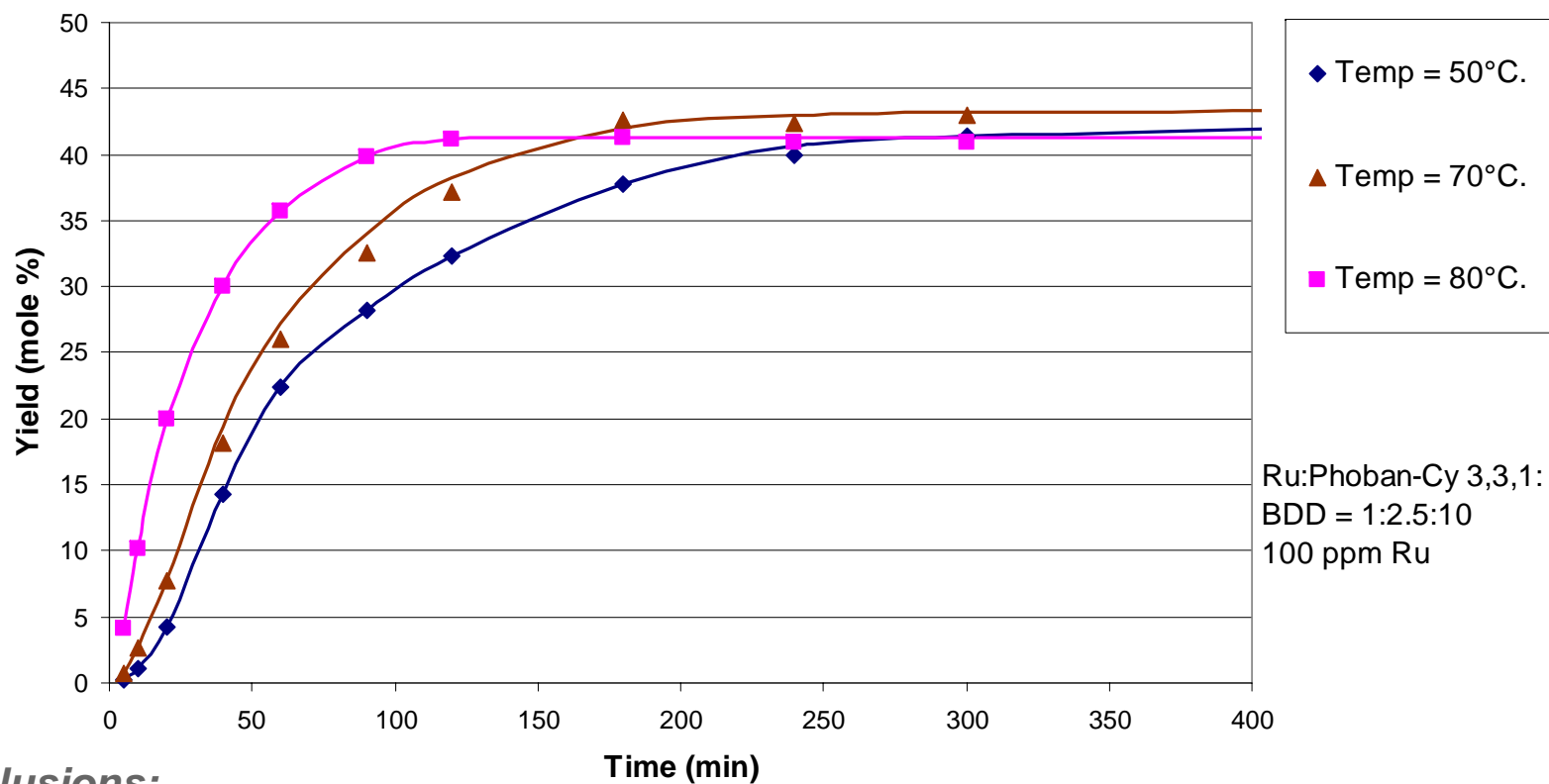
Phoban and TPP as mixed ligands



Conclusions:

1. Adding TPP reduced conversion

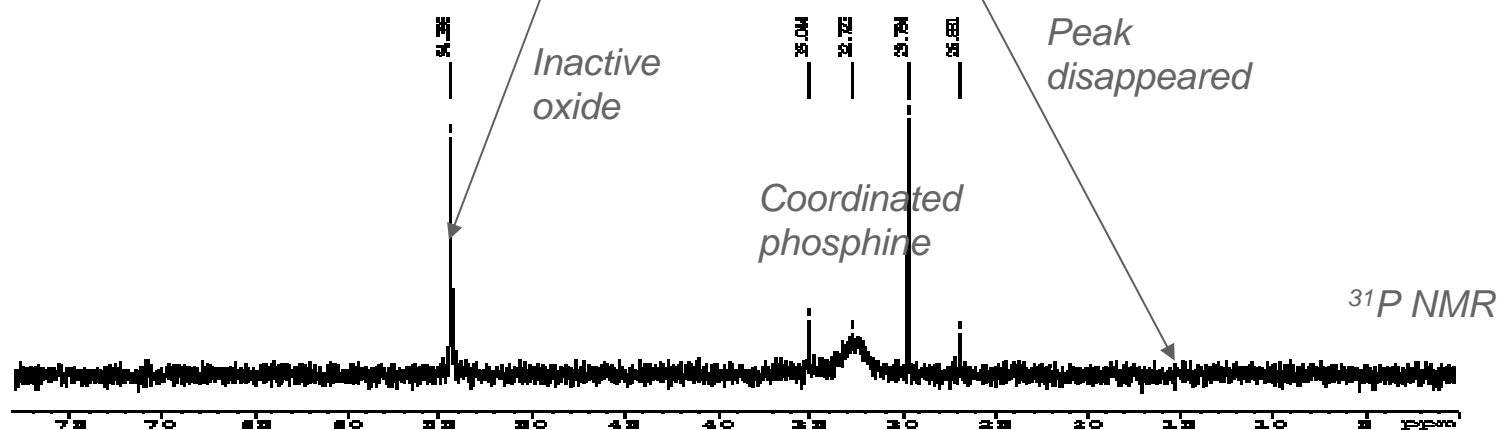
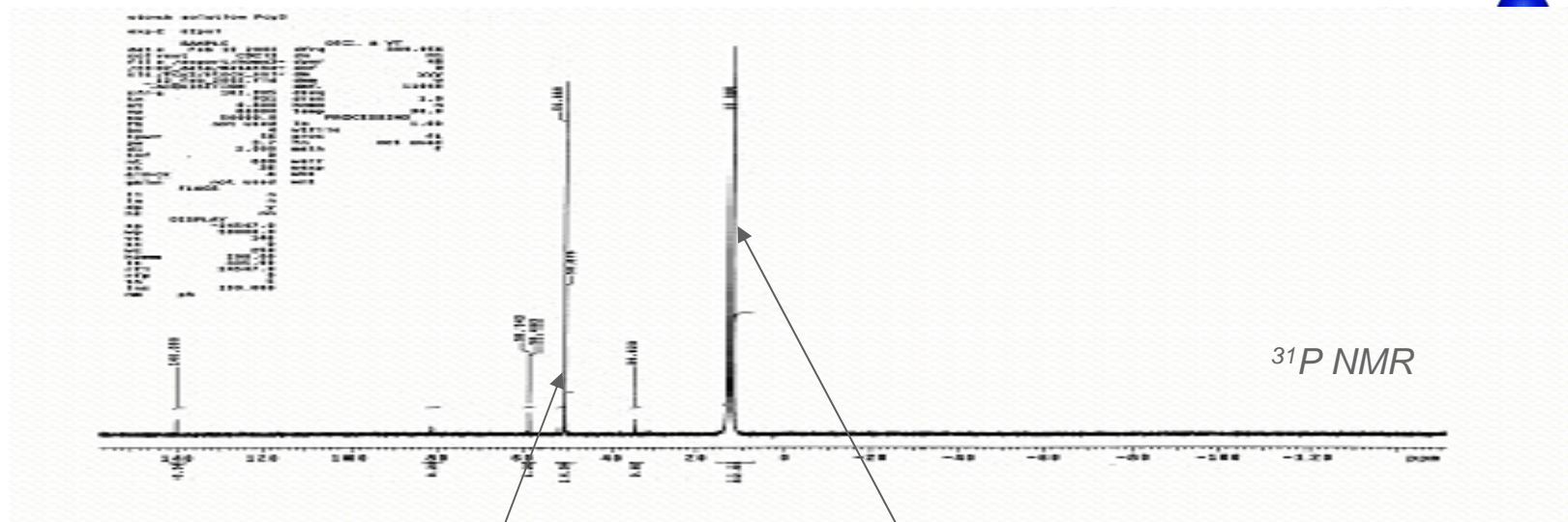
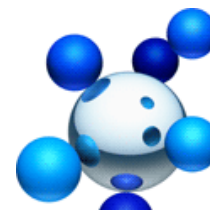
Effect of temperature



Conclusions:

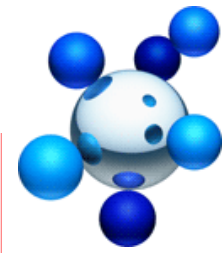
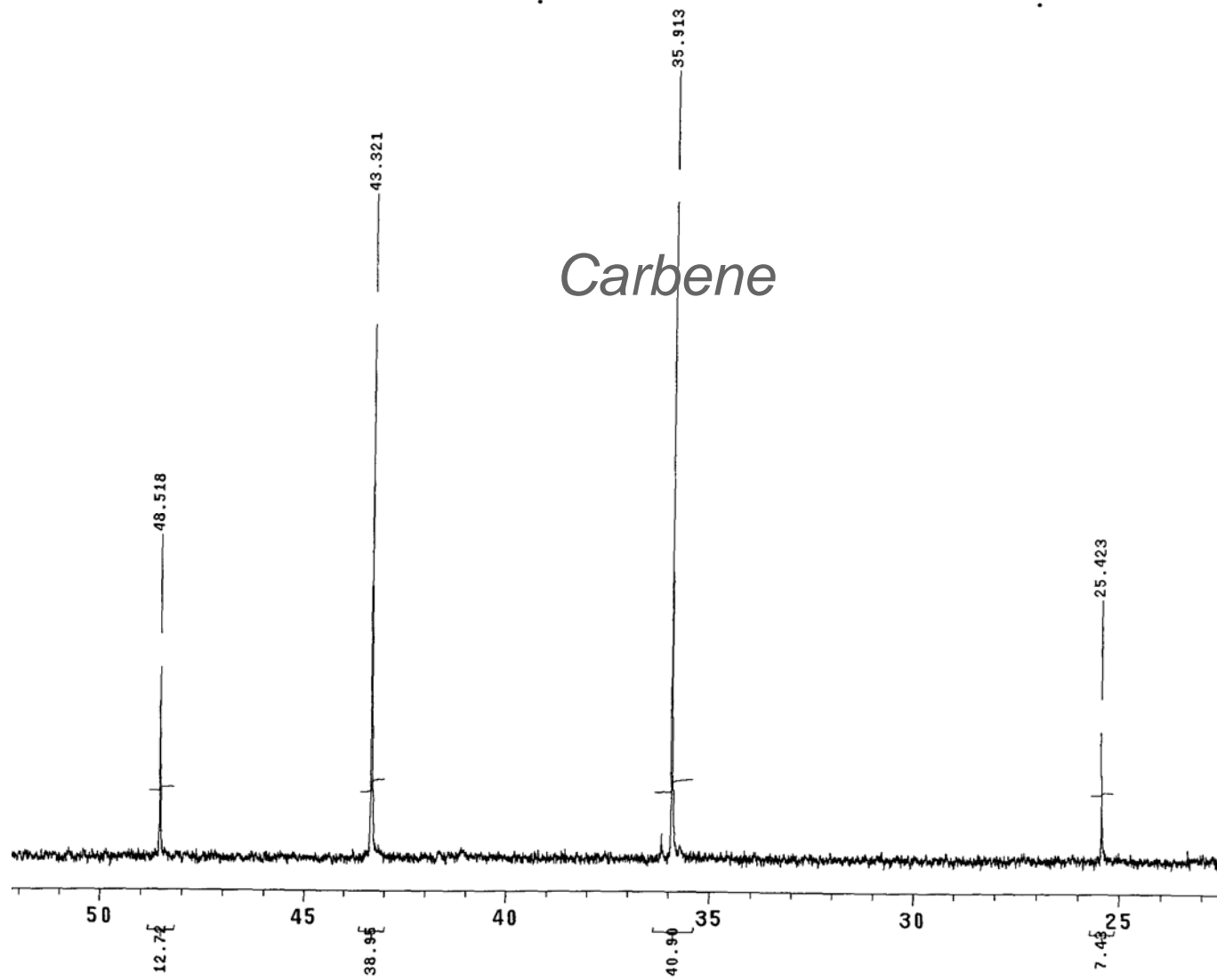
1. *Little difference between three temperatures*

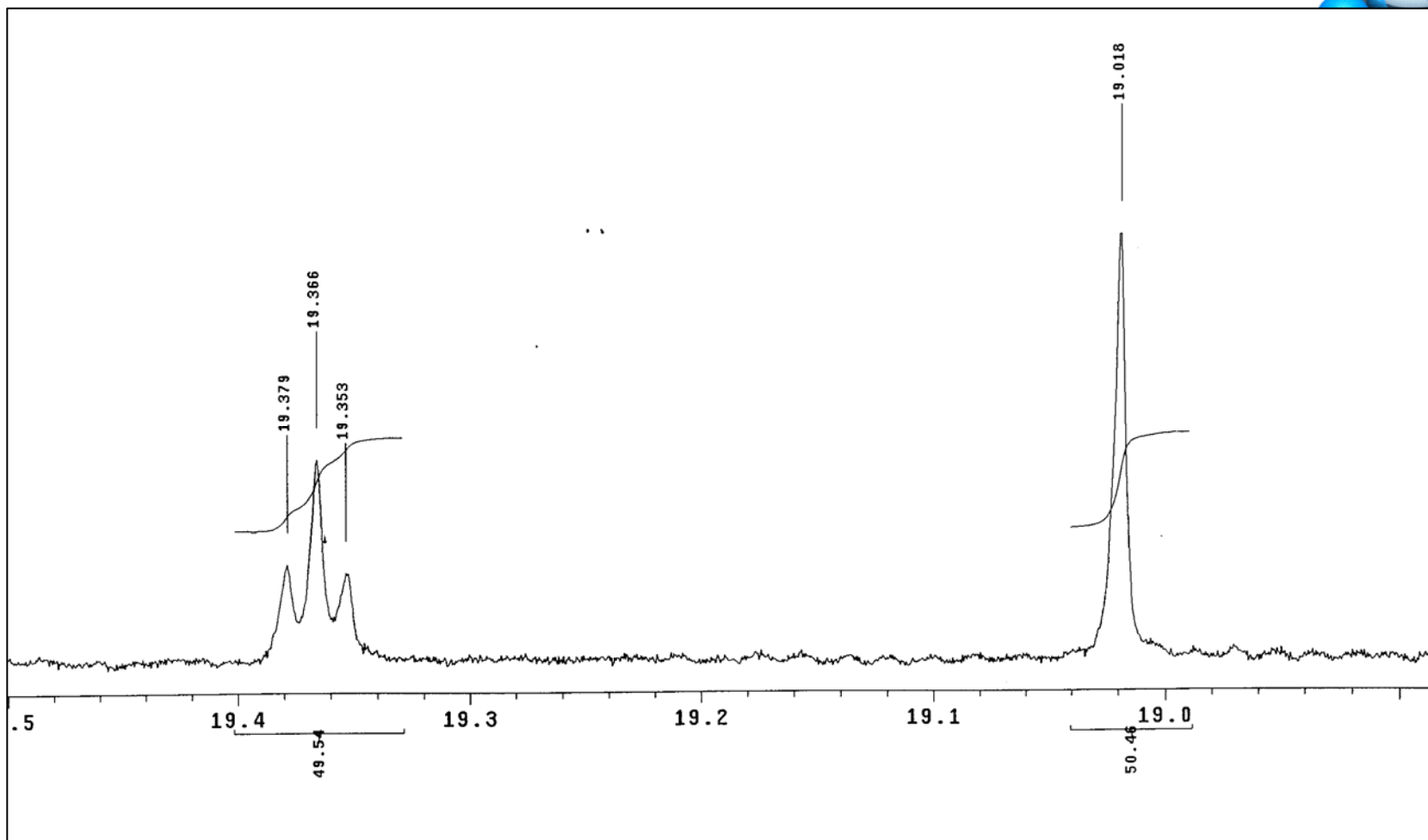
Interaction of reagents



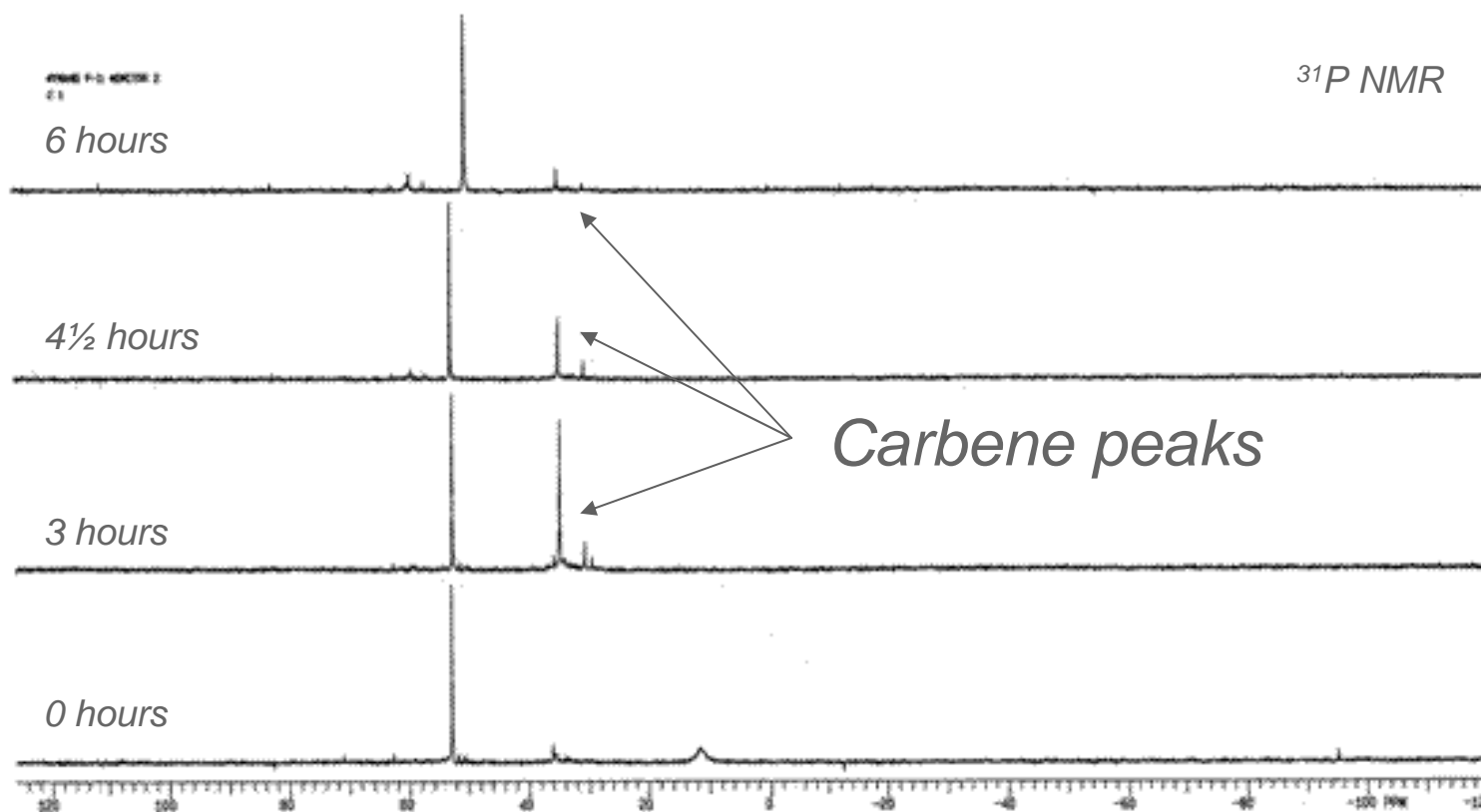
Conclusions:

1. Interaction between Ru and PCy_3 at room temperature – dictates order of addition.





Reaction progress



Conclusions:

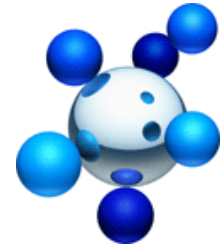
1. Catalyst deactivates over time, but also forms continuously during the reaction.

Conclusions



- 1 The system works best with the phoban-Cy 3,3,1 ligand*
- 2 Activity and turnover capability is lower than the preformed Grubbs catalysts*
- 3 Solvents not good for industry*
- 4 Useful tool for ligand screening*

Acknowledgements



- 1 Megan Kirk (Sasol) and André Joubert (UNW) for running the NMR analyses*
- 2 Charl van Schalkwyk for initial support and information*
- 3 Hendrik Hartman for IP support*
- 4 Wolfgang Meyer for helpful discussions*

