

● ISOM XVII, Pasadena, CA

**SASOL**  
reaching new frontiers



# ***Metathesis: An Industrial Perspective***



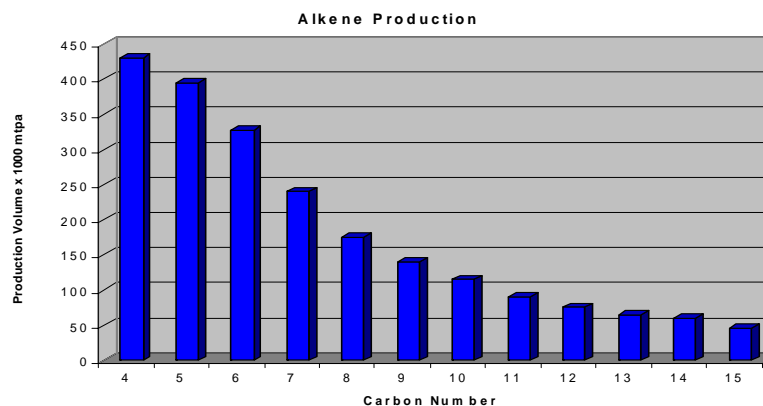
*Dr Cathy Dwyer  
Technology Manager: Chemicals  
Sasol Technology  
31 July 2007*

# Sasol's Interest in Metathesis...

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Coal/Gas → Syngas →



1-Alkenes  $\xrightarrow{\text{Metathesis}}$  Redistribute carbon number

- FT-derived olefins are a key strength for Sasol's chemicals businesses: allow for value addition beyond fuel alternative value
- HTFT provides large volumes of linear and branched  $\alpha$ -olefins
- Metathesis is a key integrating technology allowing redistribution of the product slate to preferred carbon numbers
- Industrial context – Homogeneous catalysts have yet to find application as catalysts for the large-scale cross-metathesis of olefin feedstocks derived from primary processes such as naphtha cracking and Fisher-Tropsch conversion of synthesis gas.

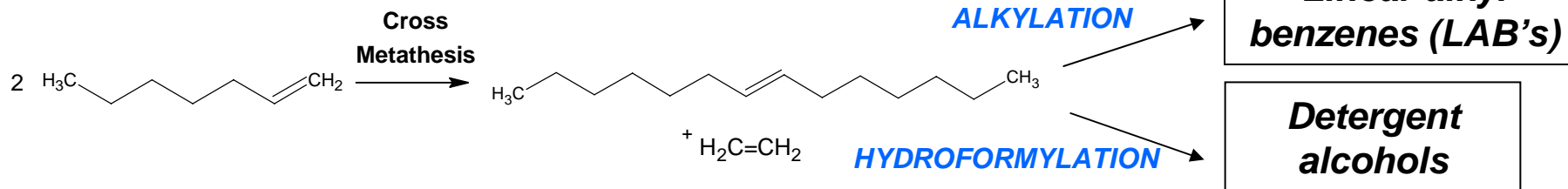
# LAB & DA FEEDS

## HETEROGENEOUS CATALYST SYSTEMS

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Self metathesis of a linear olefin, e.g.  $\alpha$ -C<sub>7</sub> to int-C<sub>12</sub>

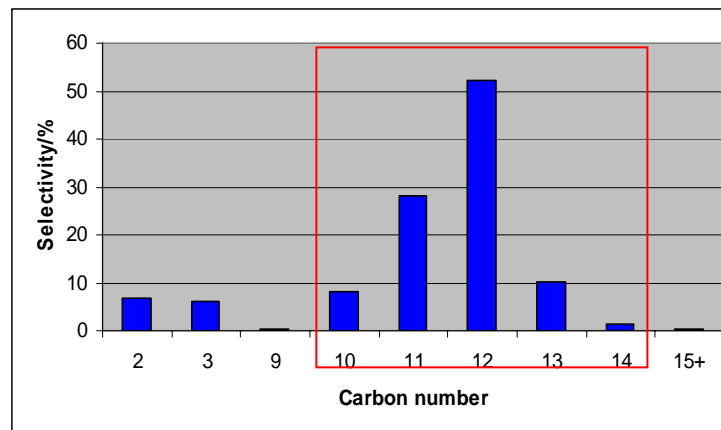


**High Temperature 8% WO<sub>3</sub>/SiO<sub>2</sub> catalyst**

- ◆ Reaction temperature > 350 °C; long catalyst lifetime > 1200 h
- ◆ Can convert branched isomers, and tolerate dienes, aromatics, oxygenates
- ◆ Robust catalyst - return to initial activity after regeneration

Successfully piloted

Selectivity to the C<sub>12</sub> product is not that high, but for this specific application, the whole C<sub>10-13</sub> fraction can be used as feed to either alkylation or hydroformylation, so it is not that critical



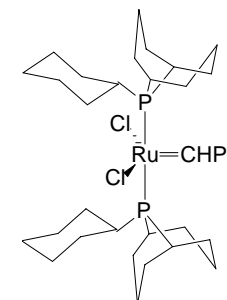
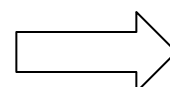
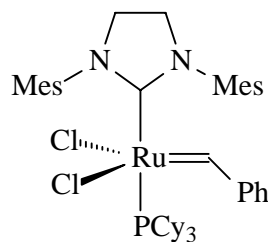
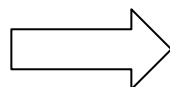
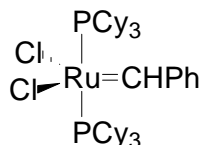
◆ **Mo and W systems:** Very poor lifetimes with FT-derived feed

- WO 01/046096, WO 01/002324, WO 04/016351
- Van Schalkwyk, Spamer et al. *Appl. Catal. A* **2003**, 255(2), 153-167; *Appl. Catal. A* **2003**, 255(2), 143-152; *Appl. Catal. A* **2003**, 255(2), 121-131

# LAB & DA FEEDS

## HOMOGENEOUS CATALYST SYSTEMS

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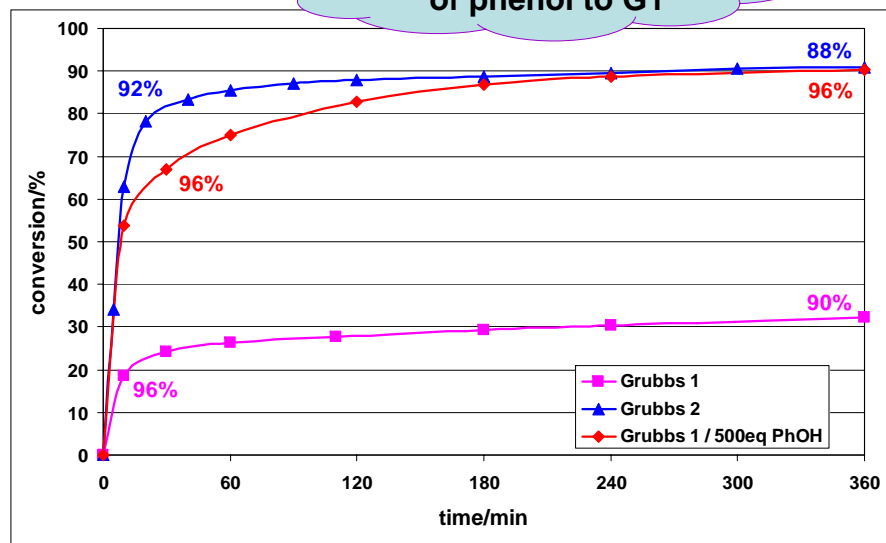


Grubbs 1  
SELECTIVE  
POOR LIFETIME

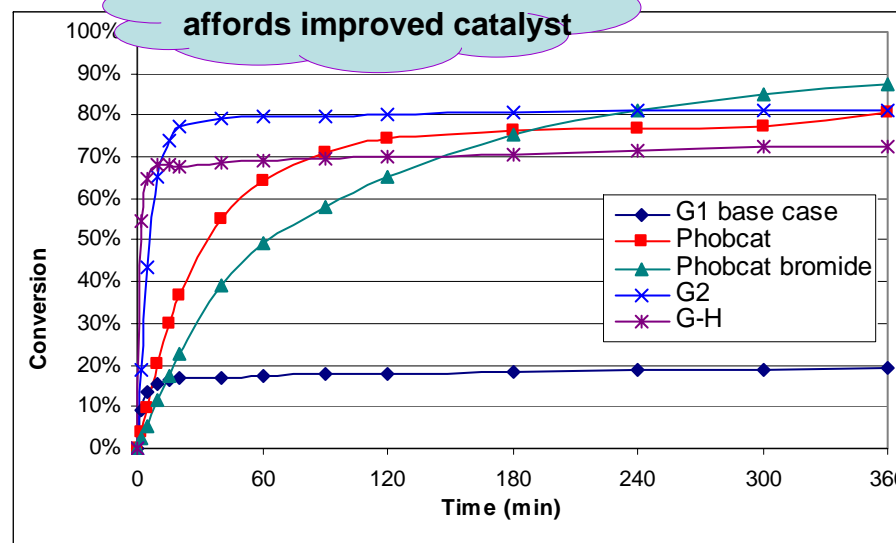
Grubbs 2  
SIDE REACTIONS  
IMPROVED LIFETIME

Sasol 'Phobcat'  
SELECTIVE  
GOOD LIFETIME

can be improved by addition  
of phenol to G1



ligand development  
affords improved catalyst

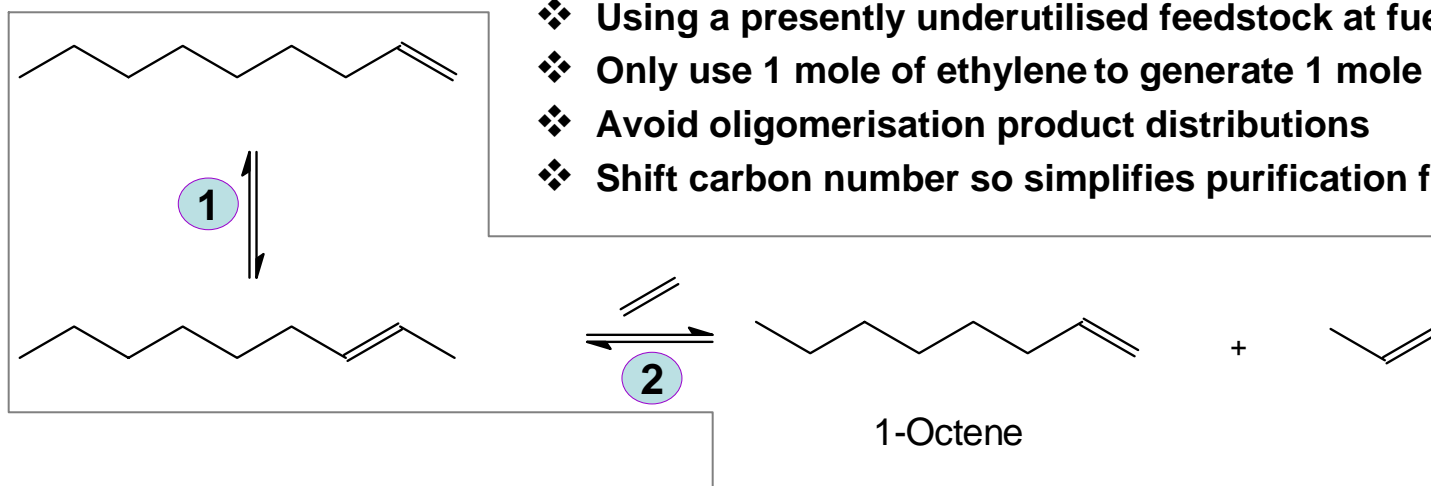


- G.S. Forman et al, *Organometallics* **2005**, 24,4528;
- Dwyer et al, *Organometallics* **2006**, 25, 3806.



# 1-NONENE → 1-OCTENE

## VIA SELECTIVE ISOMERISATION AND ETHENOLYSIS



- ❖ Using a presently underutilised feedstock at fuel alternative value
- ❖ Only use 1 mole of ethylene to generate 1 mole of 1-octene
- ❖ Avoid oligomerisation product distributions
- ❖ Shift carbon number so simplifies purification from FT components

### 1. Selective Isomerisation:

- **Difficult to maintain selectivity at high conversions, especially with heterogeneous catalysts; Best performance: HRuCl(CO)(TPP)<sub>3</sub>: 92% conversion at 96% selectivity; TON > 120000**

### 2. Ethenolysis:

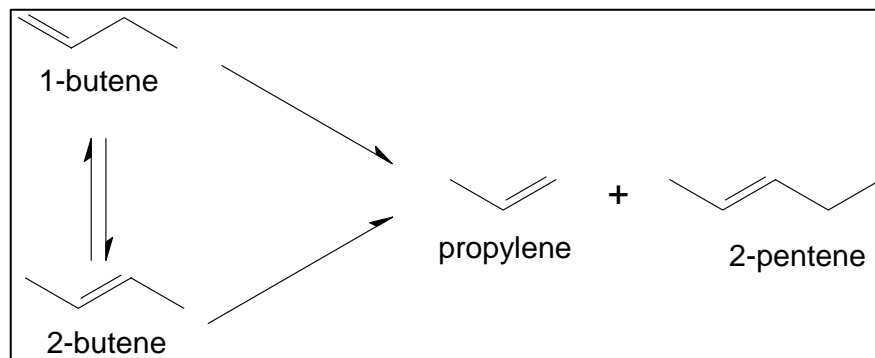
- **G1 Grubbs catalysts:** Good selectivity to ethenolysis products; Phoban catalyst has much better lifetime than PCy<sub>3</sub> analogue
- **G2 Grubbs catalysts:** Poorer selectivity to ethenolysis products; longer chain products favoured
- **cis-2-alkene reacts much more rapidly than trans isomer**

# BUTENE AUTOMETATHESIS

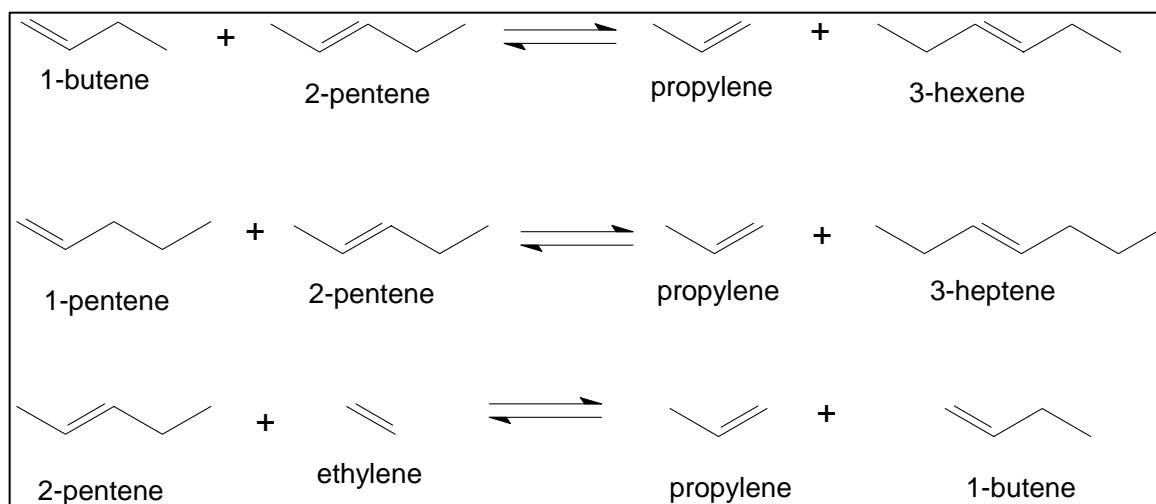
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## ● BUT ethylene can be costly so why use it??



Make use of the isomerising capability of the metathesis catalyst OR add an isomerising co-catalyst; as with SHOP, let the equilibrium reaction do the rest by recycling heavies to extinction



# CONCLUSIONS

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- Homogeneous Ru catalysts are (generally) more selective and highly active at mild conditions **BUT** catalyst lifetime and poison resistance still a concern;
- Heterogeneous W catalysts are robust, show excellent lifetime and can be regenerated, **BUT** suffer from poor selectivities (although this can be used to advantage);
- Other catalysts (Mo, Re...) are **not suitable** with typical Sasol feeds (impurities, oxygenates) and have not yet found favour in the rest of the industry
- Homogeneous catalysts are becoming more viable for large scale industrial processes (fundamental understanding leading the way towards development of improved catalysts) but there is still a way to go

**There is no such thing as a 'best metathesis catalyst'  
catalyst choice is ultimately dictated by the specific application**