

Organometallic Chemistry of Transition Metals : Curiosity Unbound

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CAST

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K. M. Sathe

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Sanjoy Kumar Chowdhury

Surojit Sur

Sunil K. Mandal

K. N. Jayaprakash

Vishwanath M. Swamy

Bikash C. Maity

Debasis Hazra

Tarun K. Maishal

T. Sureshkumar

Dilip Kumar Sinha Mahapatra

Anuradha Mukherjee

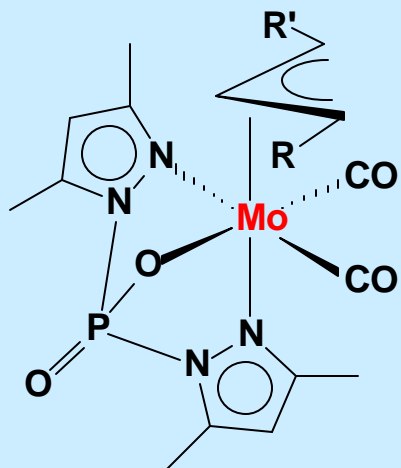
Debasis Samanta

Sudeshna Sawoo

Anwasha Pal

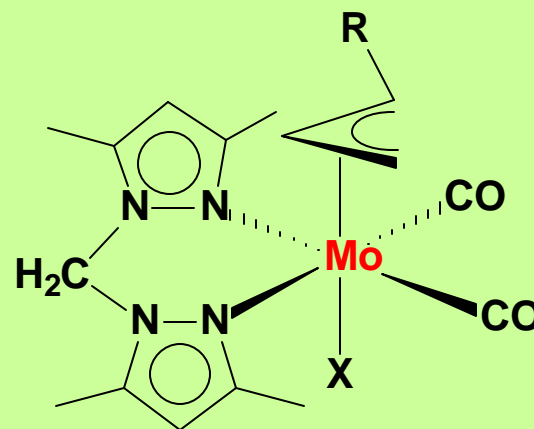
abroad
in India
current

Molybdenum η^5 -Complexes :
dynamic stereochemistry

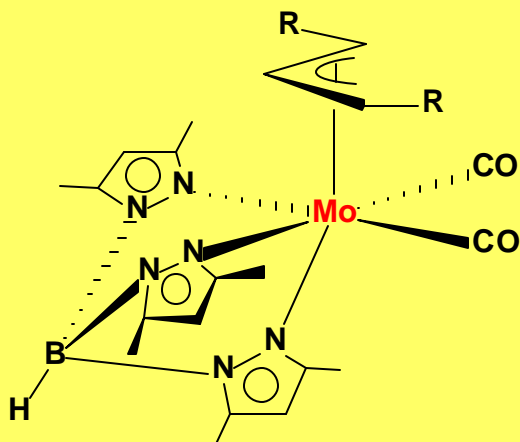


Vijaya
Organometallics, **1991**, 10, 2898

Sanjay, Vijaya
Organometallics, **1994**, 13, 4092

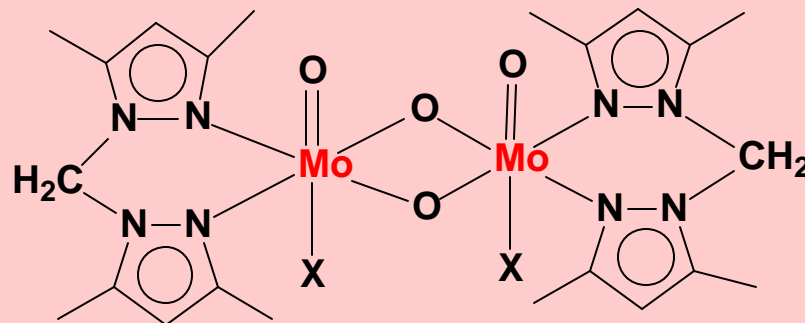


Vijaya
J. Organomet. Chem. **1991**, 409, 341



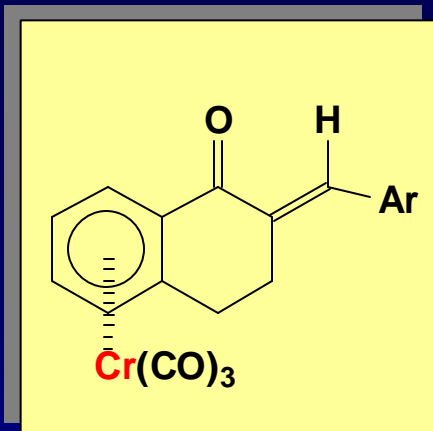
Sanjay, Malay, Vijaya
Organometallics, **1997** 16, 1806

Sanjay
Organometallics, **1997** 16, 2618



Vijaya, Malay
Inorganic Chemistry, **1993**, 32, 1301

Arene Chromium template :
remote stereoselection



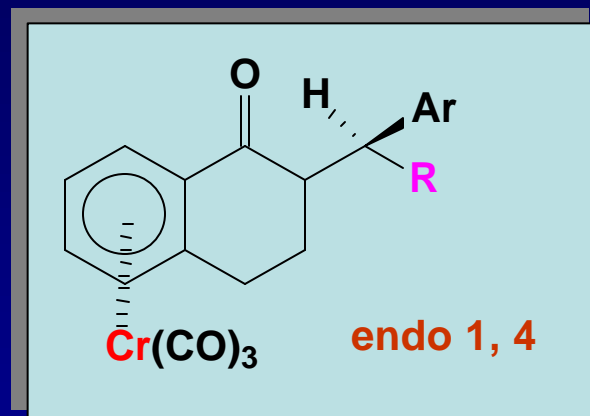
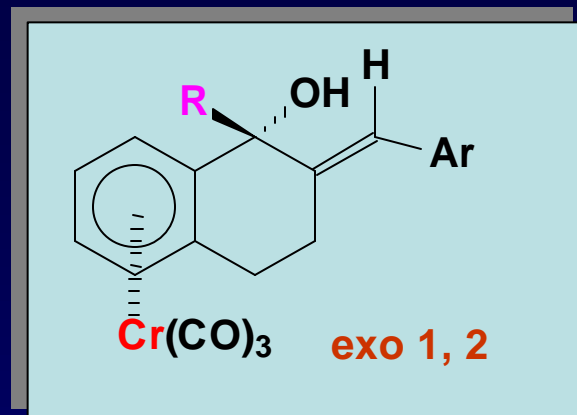
R-M

($\text{M} = \text{Li}$)

RM

$\text{M} = \text{Li}, \text{MgX}$

Lewis acid
(TiX_4 or MgX_2)



Surajit

J. Org. Chem., **1996**, 61, 8362

Sunil

J. Org. Chem., **1999**, 64, 2454

Swamy, Sunil

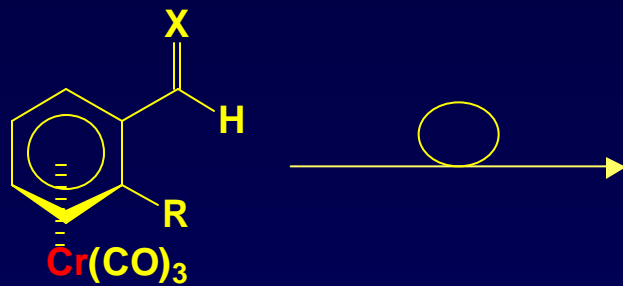
Tet. Lett., **1999**, 40, 6061

Sunil

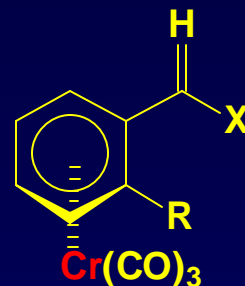
Jcs Perkin I, **2002**, 669

Account

J. Organomet. Chem, **2001**, 624, 18



Lewis acid promoted addition



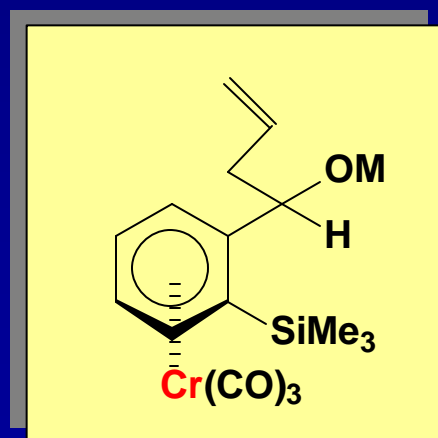
Swamy
Tet. Lett., 2000, 41, 6137

Bikash
Synlett., 2002, 504

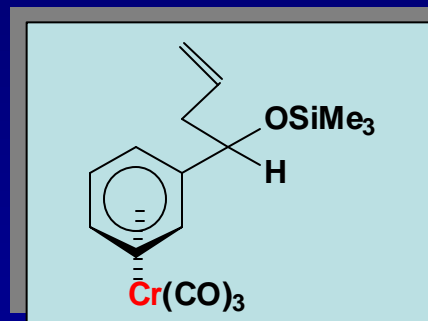
“Chelation Control”

Suresh
Organic Biomol. Chem., 2003, 1, 720

Counterion dependence of reaction path :

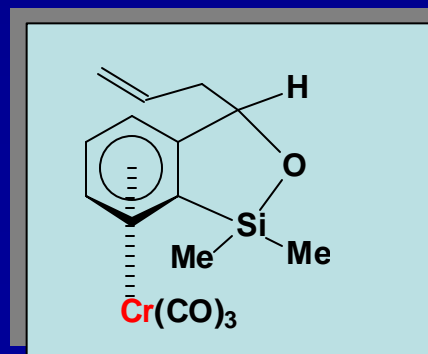


M=Li

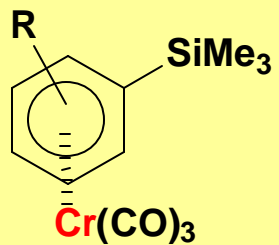


M = MgX

-CH₄

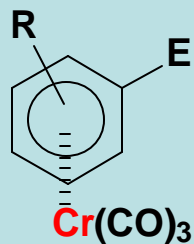


Suresh
Chem. Commun., 2002, 1924



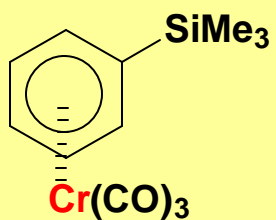
KH

EX



Sunil

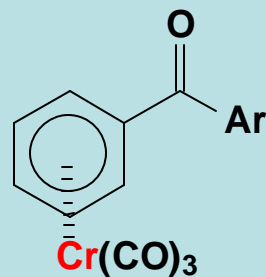
J. Org. Chem., 1998, 63, 1901



ArCHO

KH

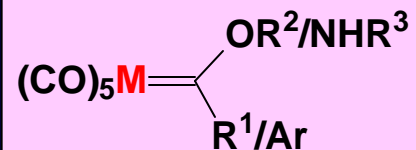
O_2



Sunil

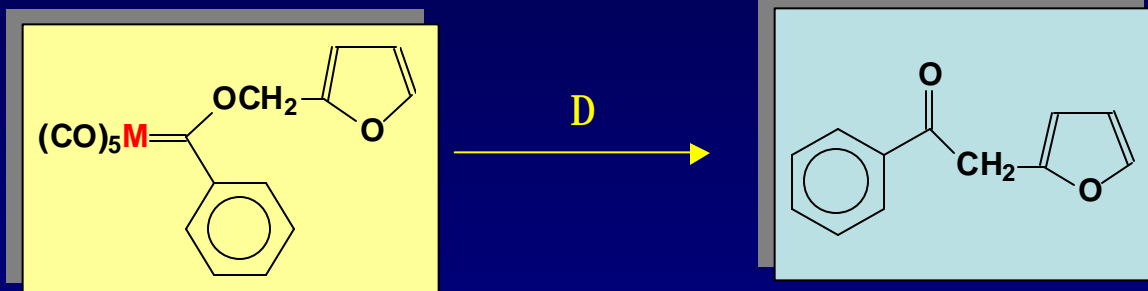
J. Org. Chem., 1998, 63, 5672

Fischer carbene complexes :
unusual reactivity



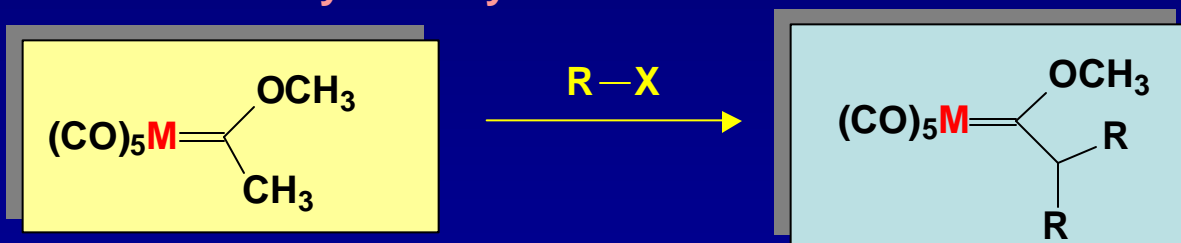
R = Alkyl
Ar = Aryl
M = W, Cr

Novel rearrangement



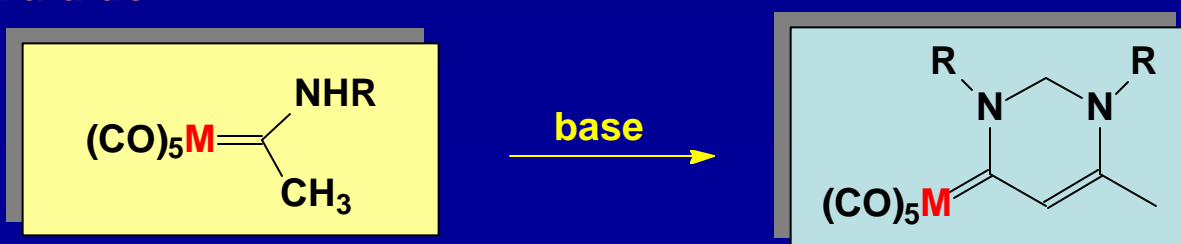
Malay, Milind
Chem. Commun, **1992**, 793
Milind, Malay, Rasidul
Organometallics, **1996**, 15, 2881

Phase transfer catalyzed alkylation



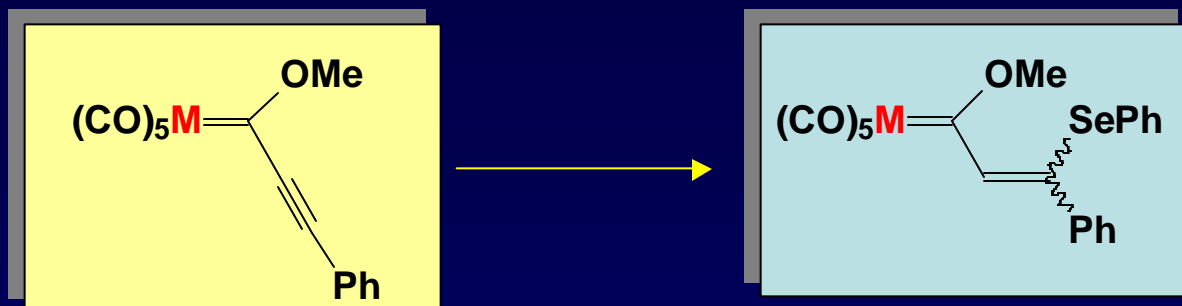
Rasidul
Organometallics, **1995**, 14, 547

Metala-aldol



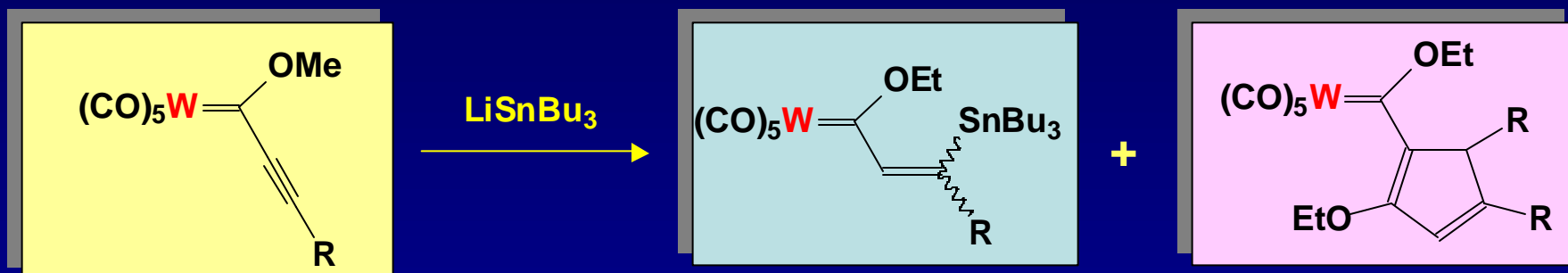
Rasidul, Sudhir
Organometallics, **1995**, 14, 3617

Chalcogenide tether



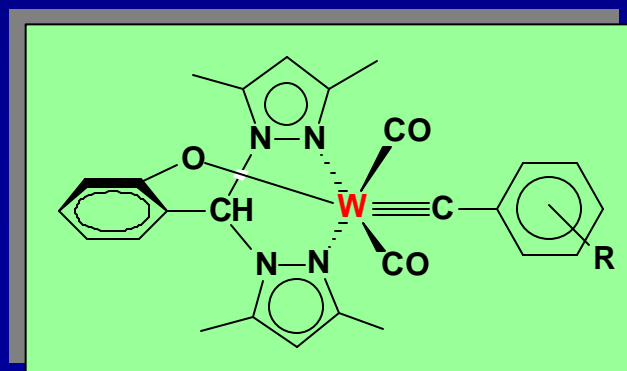
Dilip, Debasis (H)
J. Organomet. Chem., **2004**, 689, 3501

Tin-induced SET pathway



Dilip
J. Organomet. Chem., **2004**, 689, 3528

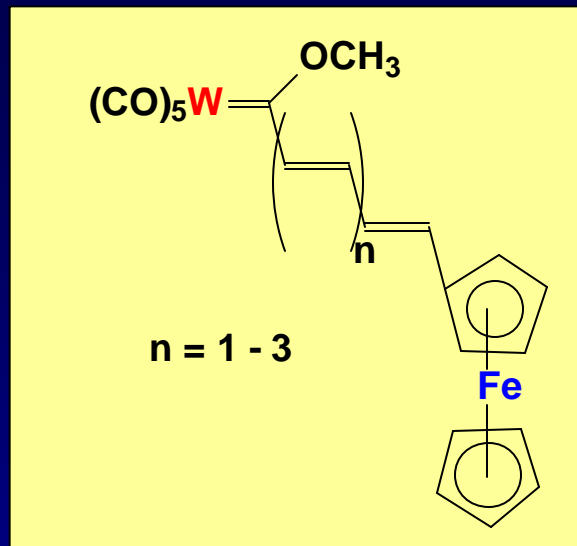
Air stable carbyne complex



Debasis (H), Dilip
J. Organomet. Chem., **2003**, 671, 52

Bimetallic variations

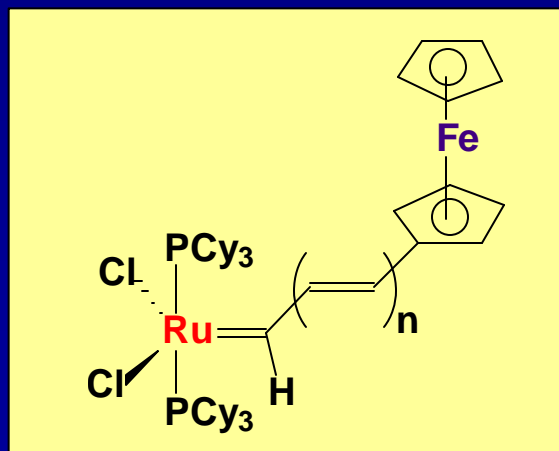
Organometallic “push-pull” system for NLO :



Jayaprakash

Organometallics, **1999**, 18, 3851

Modification of Grubbs' Catalyst :



Tarun

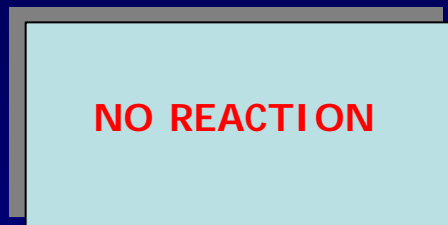
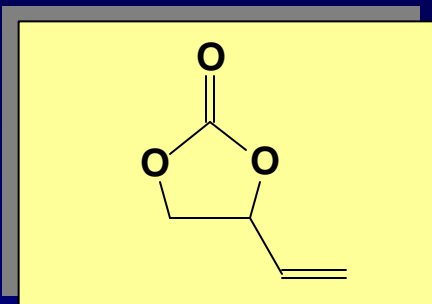
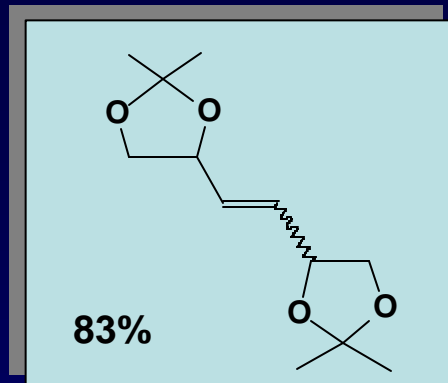
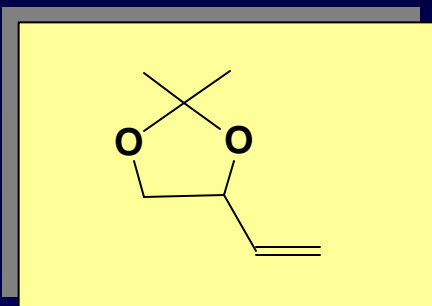
SynLett, **2002**, 1925

Tarun

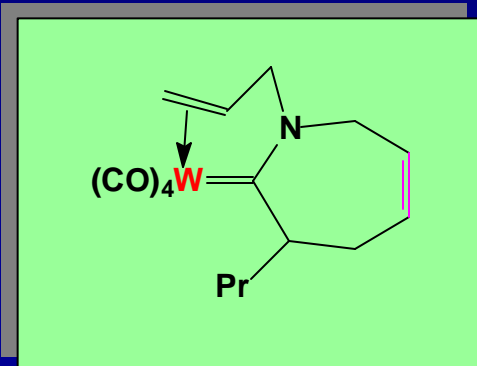
J. Organomet. Chem. **2005**, 690, 1018

Catalytic chemistry :

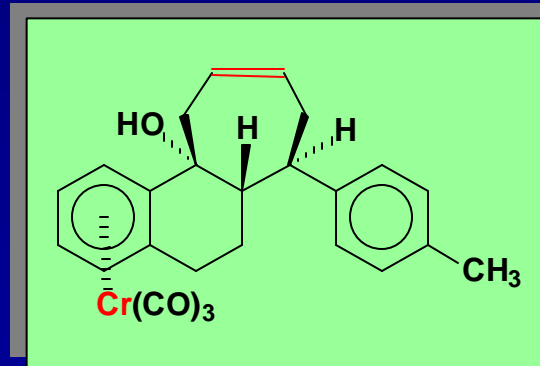
Ru and Pd



Tarun, Dilip, Kavita
Tet. Lett, **2002**, 43, 2263

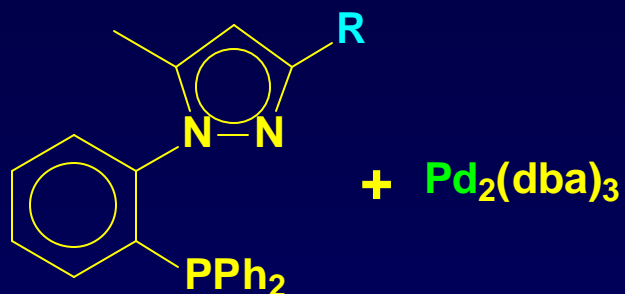


Debasis (H)
Ind. J. Chem. (Sect. A)
2003, 42A, 2398



Bikash, Swamy
Tet. Lett, **2001**, 42, 4373

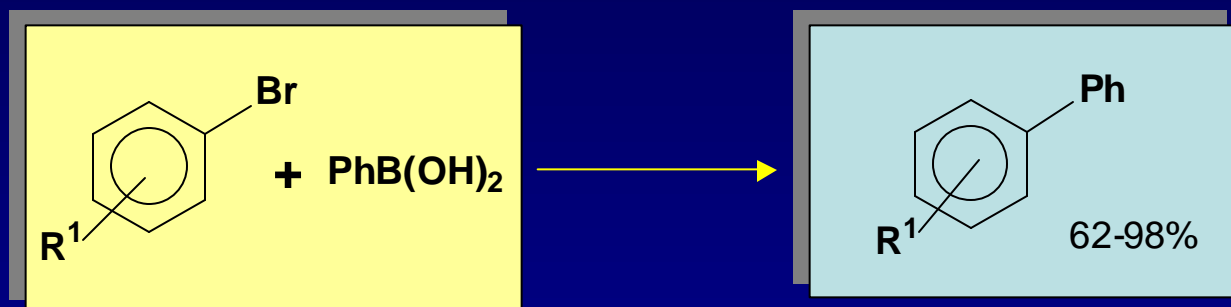
Monophosphine donor



Anuradha

Eur. J. Inorg. Chem. (in press)

Effective catalyst in promoting Suzuki reaction:



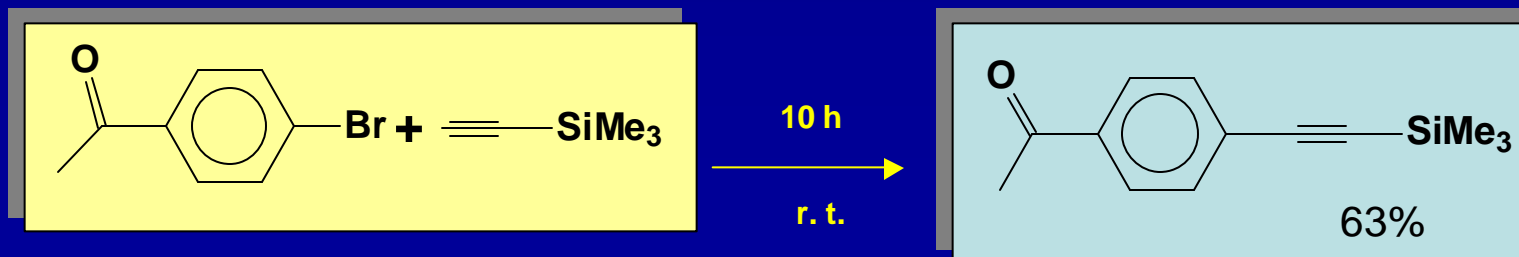
Can activate Ar-Cl
when $\text{R} = \text{Bu}^t$

- Mild condition: 4-6 h at r. t. or $< 60\text{ }^\circ\text{C}$
- Wide range of substitution is tolerated

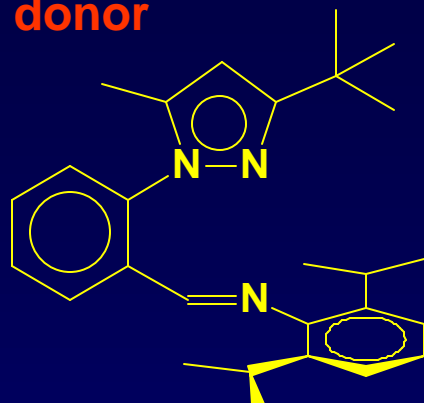
Anuradha

Tet. Lett., 2004, 45, 9525

When $\text{R} = \text{Bu}^t$: Effective catalyst for Sonogashira coupling at room temperature



Nonphosphine Schiff base donor

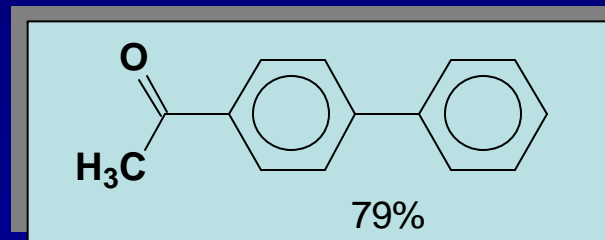
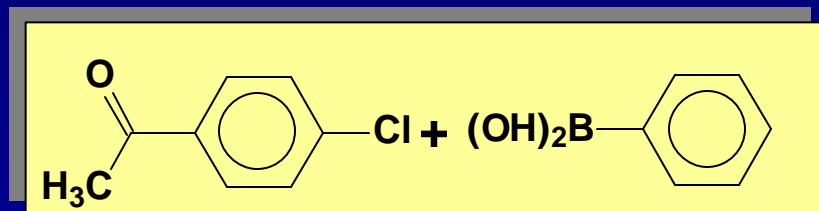
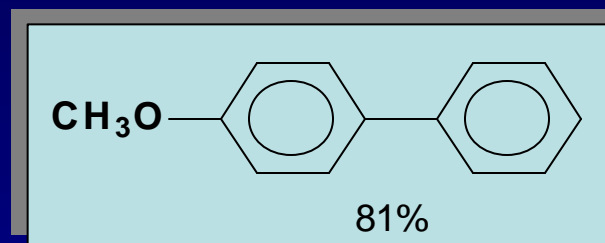
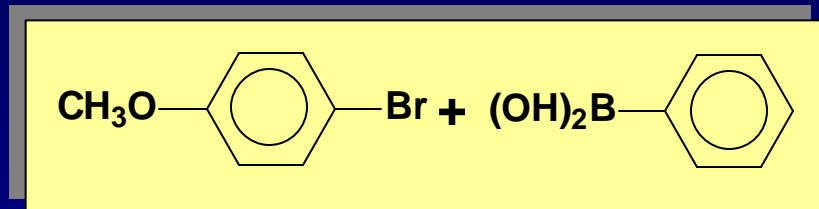


$\text{Pd}_2(\text{dba})_3$

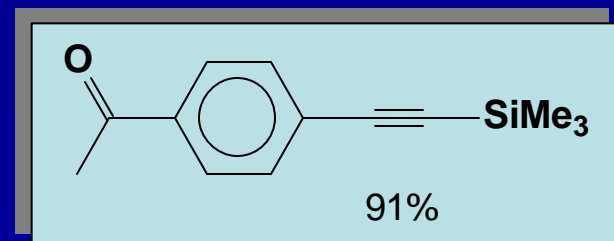
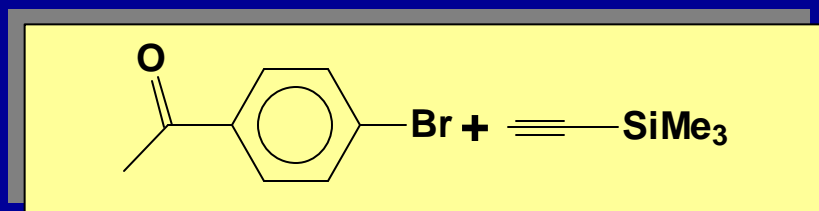
1:1

Anuradha
Tet. Lett. 2005, 46, 15.

Effective catalyst for Suzuki reaction:

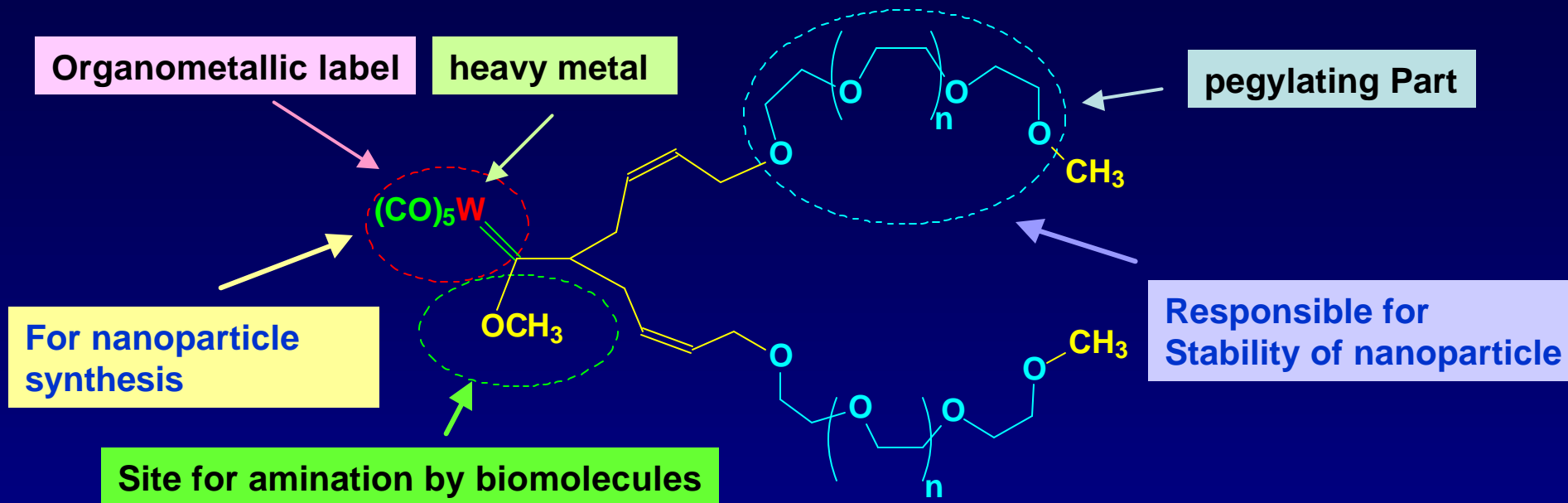


Effective catalyst for Sonogashira coupling:



Organometallic reagents/reactions for biomolecules and monolayers

Multifunctional water-soluble Fischer carbene complex






● For protein modification →

- As pegylating agent
- As nonradioactive labelling agent
- Incorporating heavy metal atom

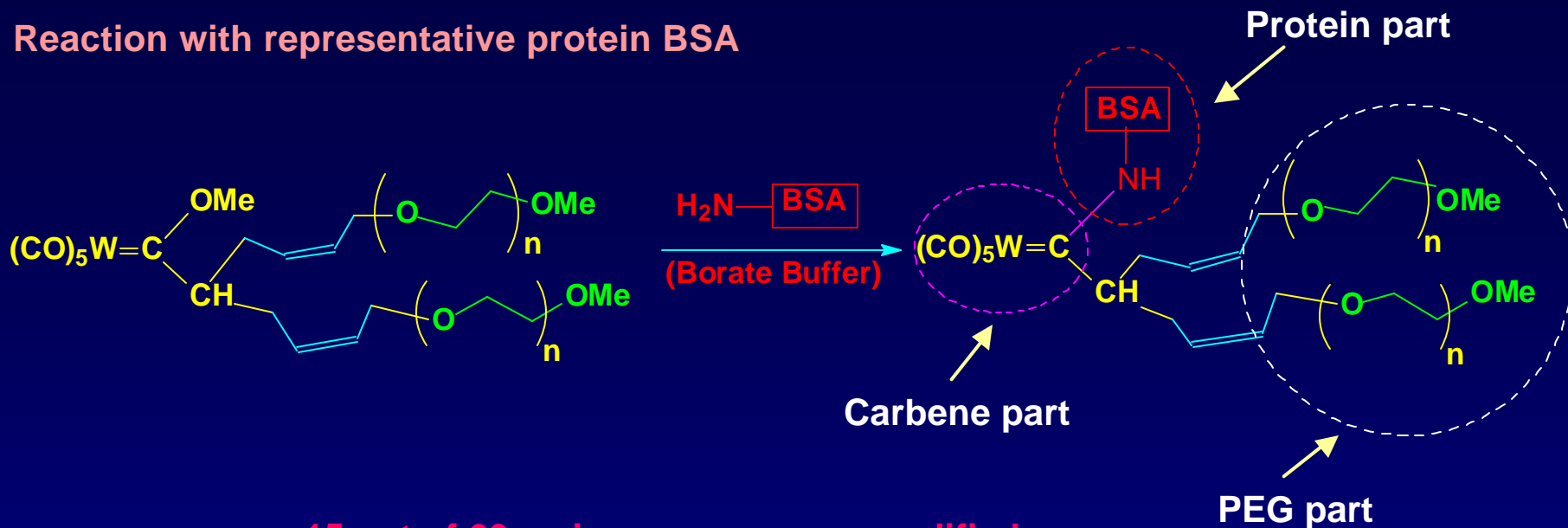
● For stable gold nanoparticle synthesis →

- Metal alkylidene part responsible for synthesis
- PEG part attributes stability

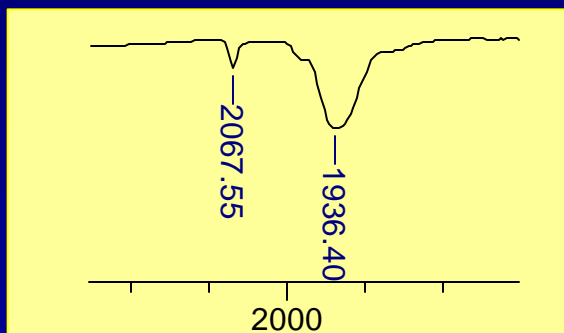
Protein modification:

- Pegylation of Protein / Drug by activated PEG  To increase stability
To decrease immunogenicity
To increase circulating lives
To increase efficacy of drug
- Non radioactive labeling (assay) of protein 
(In aqueous buffer) M(CO)₅ provides IR absorption window (2010 – 1900 cm⁻¹)
transparent to most organic functional group
- Heavy metal atom incorporation  May aid protein crystallography

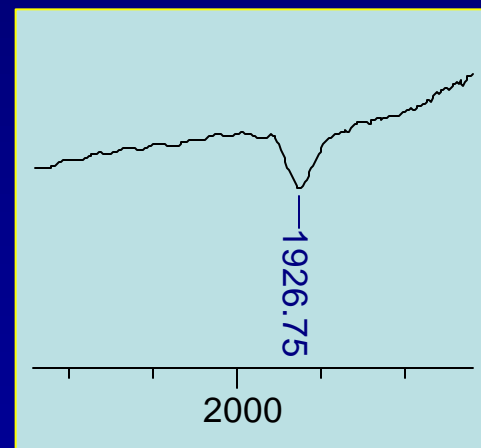
Reaction with representative protein BSA



15 out of 60 amino groups were modified



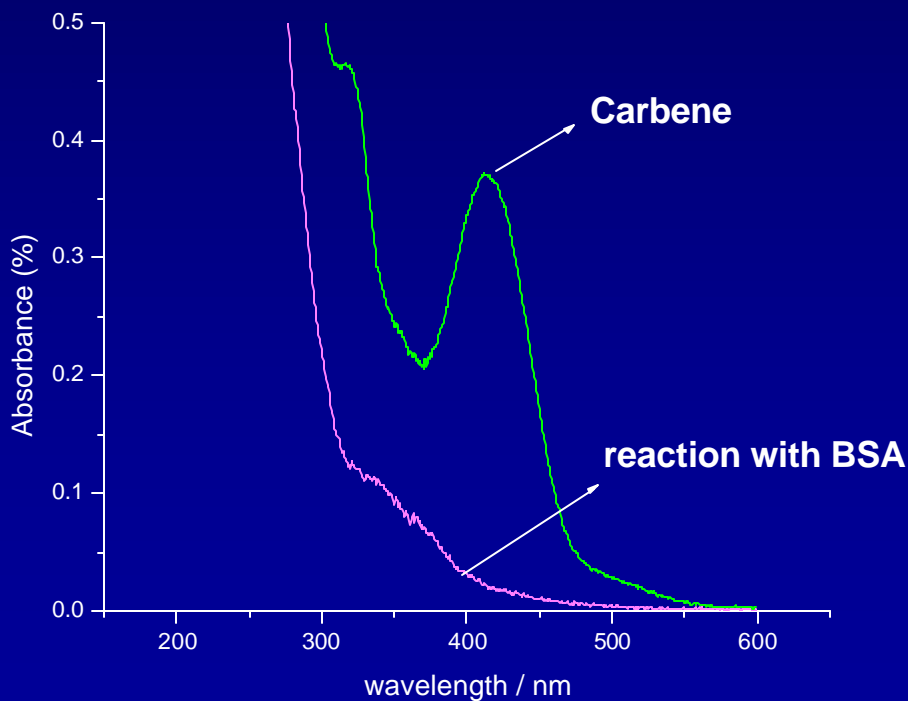
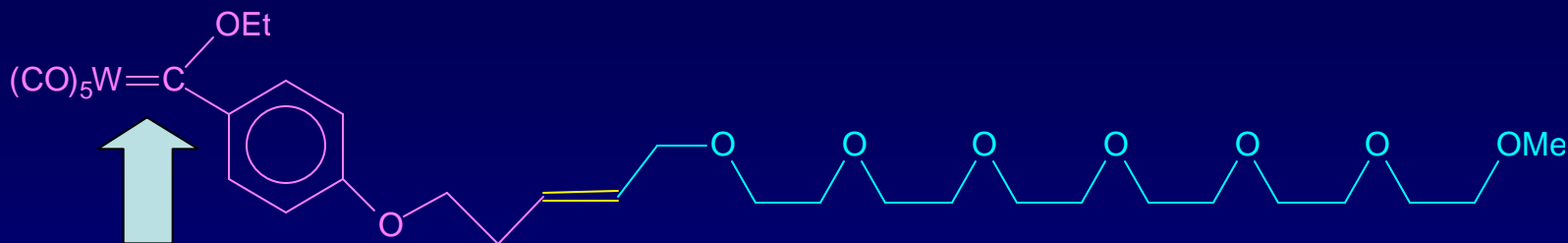
Before reaction with BSA



After reaction with BSA

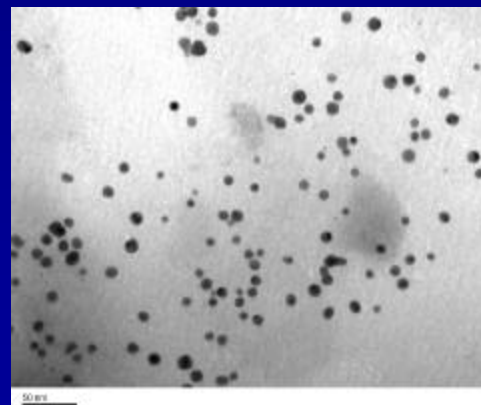
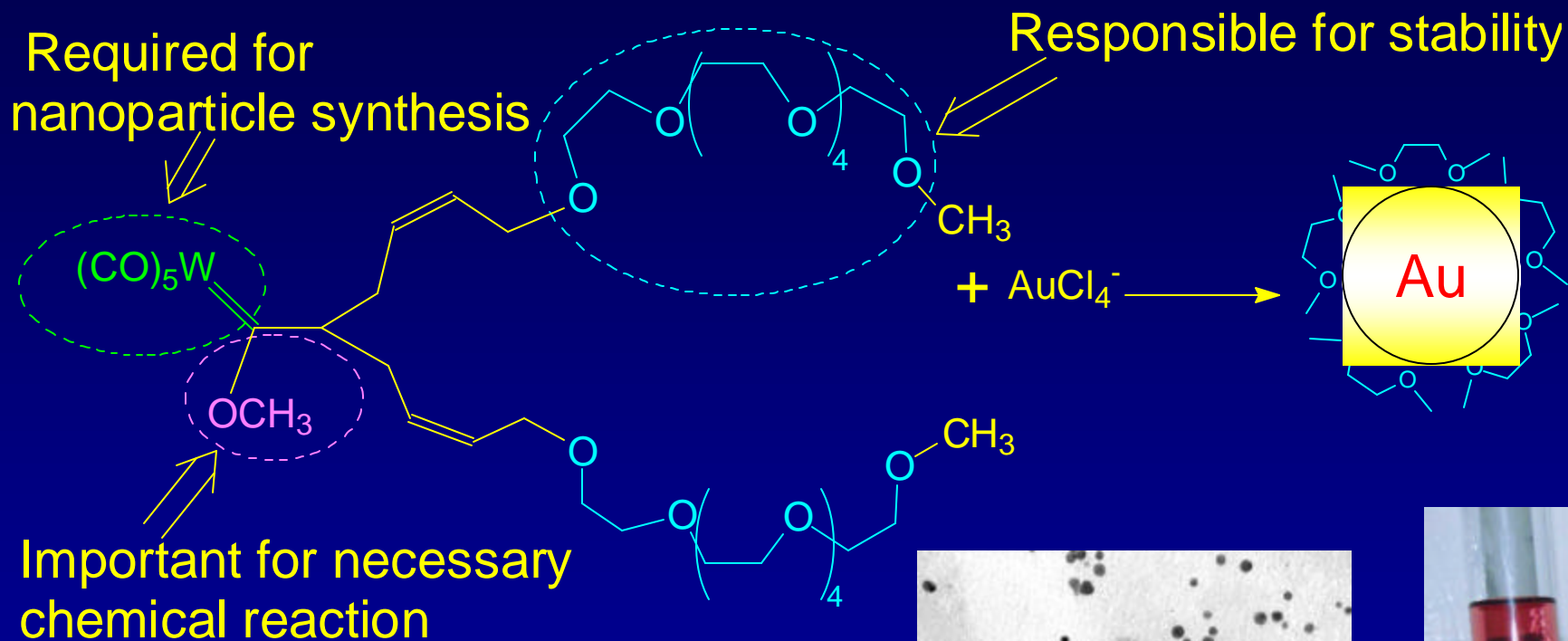
Phenyl carbene complex - the better choice :

- To monitor the reaction unambiguously by UV/vis Spectra
- To study by visual colour change



Reaction of BSA with carbene – UV/vis trace

Nanoparticle synthesis by water soluble carbene complex



50 nm

TEM micrograph



General strategy using Metathesis:



Design of organic component:

HS

Hydrophobic C_n

OEG Spacer



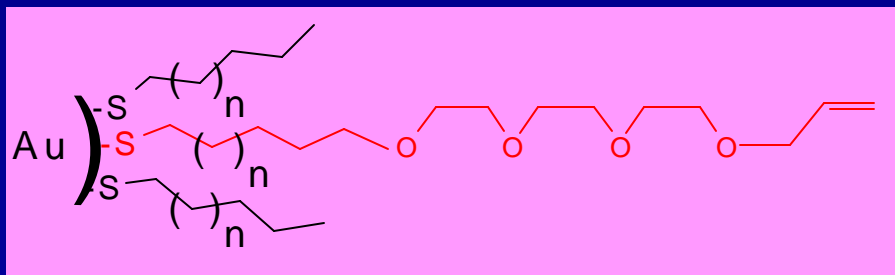
Reactivity with gold

Insertion in the SH- C_8H_{17} layer

Accessibility of the reactive groups

Metathesis reactivity

Model study was done with Gold nanoparticles



Debasis(S)
Chem. Commun, 2002, 1186

Acknowledgement:

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Collaborators : Dr. Vedavati G. Puranik
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Prof. Goutam Lahiri
Prof. Manju Ray
Prof. H. Nishihara
Prof. Francis Rondelez
Dr. Michèle Salmain

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C. S. I. R.

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Indian Oil Corporation

Reliance Industries Ltd.

Institut Curie

' Let me light my lamp,' says the star,

'And never debate

if it will help to remove the darkness'...

Rabindranath Tagore

(Fireflies 255)