Sigma Bond Metathesis

Reporter: Changliang Sun
Supervisor: Zhangjie Shi

Outline

- Introduction
- Mechanism
- Examples and Applications
- Summary and Outlook
- Acknowledgements

Introduction

The Nobel Prize in Chemistry 2005 :
"for the development of metathesis method in organic synthesis"

Yves Chauvin

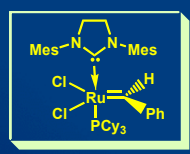
Robert H. Grubbs

Richard R. Schrock

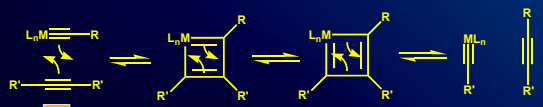
A Dance Changing Partners !

Introduction

Alkene Metathesis

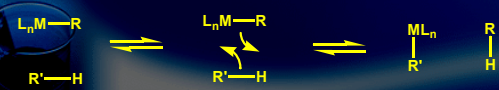


Alkyne Metathesis



$(RO)_3W{\equiv}C{-}t\text{-}Bu$

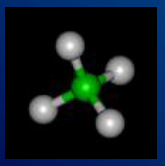
Alkane Metathesis



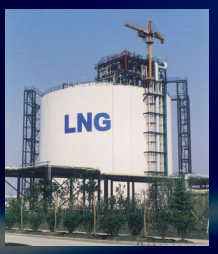
?

Introduction

Natural Gas

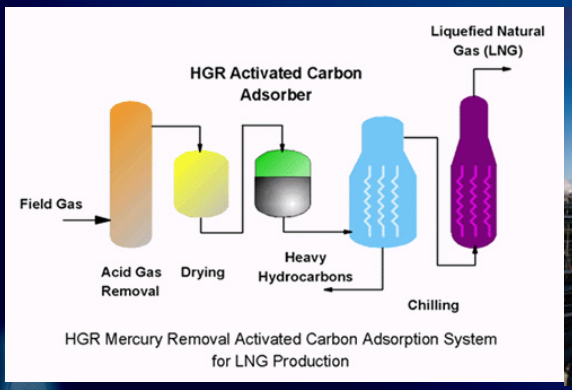


Methane



Liquefied Natural Gas

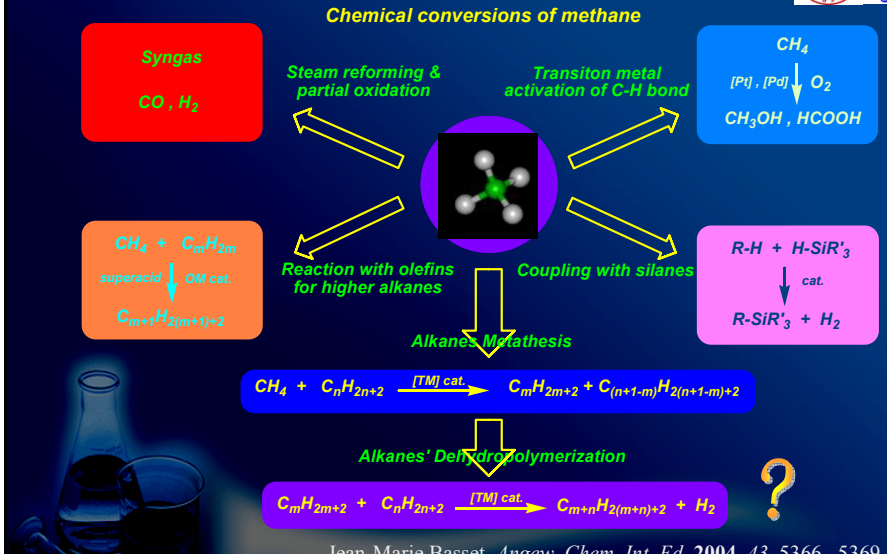
Introduction



HGR Mercury Removal Activated Carbon Adsorption System for LNG Production

CH_4 → higher alkanes

Introduction



Jean-Marie Basset, *Angew. Chem. Int. Ed.* **2004**, *43*, 5366 –5369

Introduction

Alkane Metathesis → Significant

↓

C-C , C-H Metathesis →
- Unreactive
- Non-selective
- Ineffective

↓

σ Bond Metathesis →
- General
- Direct
- Unique

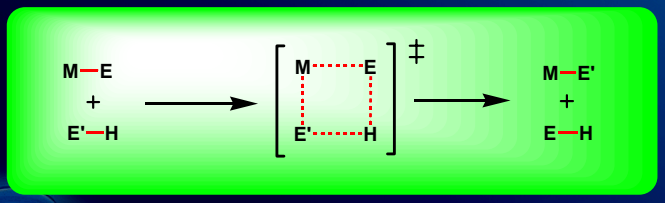
Outline

- Introduction
- Mechanism
- Examples and Applications
- Summary and Outlook
- Acknowledgements

Mechanism

General Define

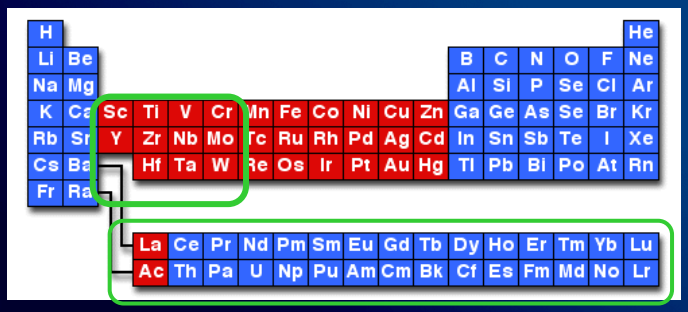
The idea of sigma bond metathesis was developed for the progress of σ bond cleavage and formation that catalyzed by alkyl or hydride complexes of 'early' transition metals with d^0 electronic configurations. Extensive experimental and theoretical studies have led to the concept of the general four-center transition state.



M= Sc , Y , Ln ; Ti , Hf , Zr , W , etc.

Mechanism

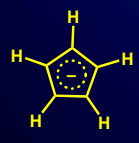
d^0 Metals



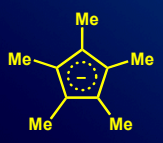
1. Electropositive, very easy to lose all their valence electrons---highest permissible oxidation state (d^0 configuration complexes).
   Oxidative addition and reductive elimination are impossible !
2. Electron-deficient metal center with one or more vacant orbitals would provide a low-energy means of approach for H-H, C-H bond to M-R bond.

Mechanism

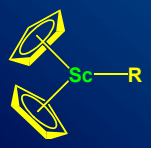
Ligand

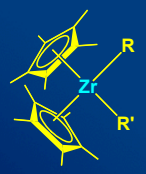


Cp



Cp*





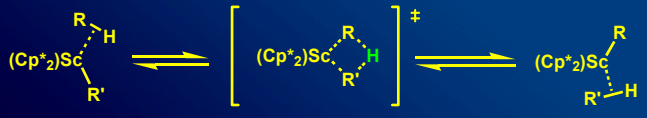
1. anionic ligands: necessary for d^0 metal center

2. η^5 ligands: more stable for the complex

3. bulky ligands: able to prevent dimerization or oligomerization
able to block approach of the π -orbital from substituted olefins.

John E. Bercaw *et al., J. Am. Chem. Soc.* **1987,** *109,* 203-219.

Mechanism



Three steps:

(i) Approach of the H-H or C-H bond to the vacant orbital of Cp^*_2ScR';

(ii) Formation of the transition state described above with H occupying the central β position in all cases;

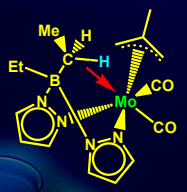
(iii) Departure of the new H-H or C-H σ bond from the opposite side of the orbital.

Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.
John E. Bercaw *et al., J. Am. Chem. Soc.* **1987,** *109,* 203-219.

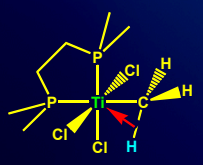
Mechanism

Agostic Interaction

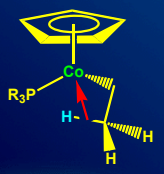
The word ***"agostic"*** is derived from the Greek word for "to hold on to oneself".(元结作用，抓氢作用) It most commonly refers to a C-H bond on a ligand that undergoes an interaction with the metal complex. Three-center, two-electron bridging interaction.
This interaction closely resembles the transition state of an oxidative addition or reductive elimination reaction. The bonding could also be described as closely resembling a sigma complex.



first example



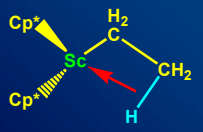
α-agostic interaction



β-agostic interaction

Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.***1974**, *96*, 754-760.

Mechanism



1. The C-H group acts as an electron donor in an interaction with an electron deficient metal center.

2. One condition for the interaction to be effective is that the hydrogen and the metal can be brought into contact without straining the system too much.

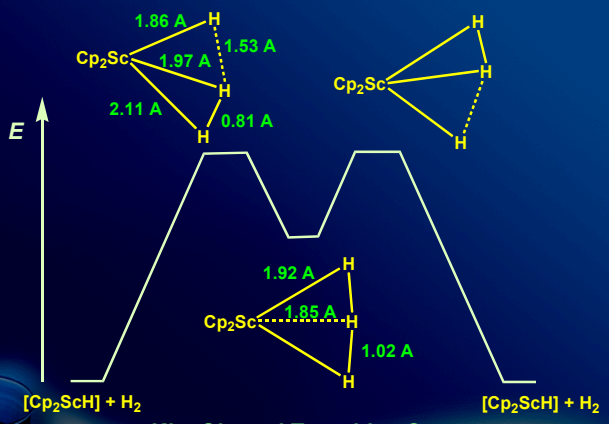
3. Typical agostic metal-hydrogen distances are 1.9-2.4 Å.

4. The determination of agostic bond strengths is often not possible at all and only approximate values are proposed. These difficulties lead to uncertain estimations of those interaction strengths between 1 and 20 kcal·mol^{-1}.

Jorg Grunenberg, *et al*., *Organometallics* **2006,** *25,* 118-121.
Bjorn O. Roos, *et al*., *J. Phys. Chem. A* **2007,** *111,* 6420-6424.

Mechanism

Transition State

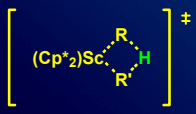


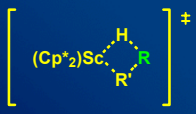
Kite-Shaped Transition State

T. Ziegler, E. Folga, A. Berces, *J. Am. Chem. Soc*. **1993,** *115*, 636.

Mechanism

Selectivity





?

Thermodynamic control ?

$Cp^*_2Sc\text{-}CH_3 + H\text{-}C_6H_5 \rightarrow Cp^*_2Sc\text{-}C_6H_5 + H\text{-}CH_3$ (1)

$Cp^*_2Sc\text{-}CH_3 + H\text{-}C_6H_5 \rightarrow Cp^*_2Sc\text{-}H + CH_3\text{-}C_6H_5$ (2)

$\Delta H^\theta = \Delta H^\theta_{(2)} - \Delta H^\theta_{(1)} = 4\ kcal \cdot mol^{-1}$

Consistent with the observed experimental results, but only slightly selective.
Many reactions with other substituents showed a roughly equal ΔH^θ values.

Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.
John E. Bercaw *et al., J. Am. Chem. Soc.* **1987,** *109*, 203-219.

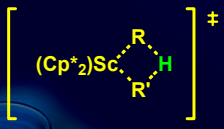
Mechanism

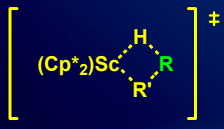
Steric effect control ?

A bulky R group, rather than H atom, seems favored at β position.
Even when R=Me, no C-C coupling product (ethane) was found !

Electronic effect control ?

Difference of electronegativity between C and H.
Much poorer overlap provided by the sp^3 C orbital of R in the crucial center β position results in an overriding, unfavorable electronic effect.





Unfavored

Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.

Outline

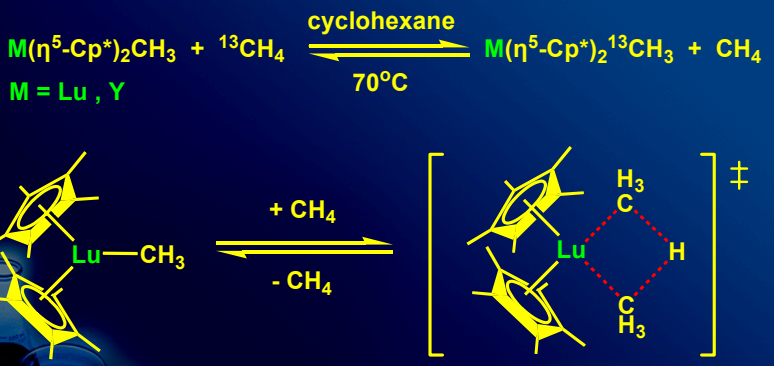
- Introduction
- Mechanism
- Examples and Applications
- Summary and Outlook
- Acknowledgements

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr
2. IVB Metals: Ti Zr Hf
3. VB Metals: V Nb Ta

Examples and Applications

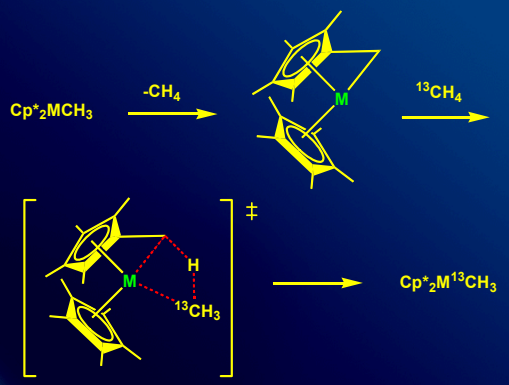
1. IIIB Metals: Sc Y La-Lu Ac-Lr



Patricia L. Watson, *J. Am. Chem. Soc.* **1983,** *105,* 6491-6493

Examples and Applications

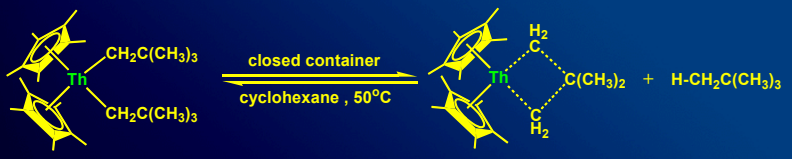
1. IIIB Metals: Sc Y La-Lu Ac-Lr

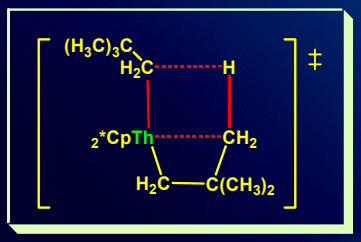


Aaron D. Sadow and T. Don Tilley , *J. Am. Chem. Soc.* **2003**, *125*, 9462-9475
Carol M. Fendrick and Tobin J. Marks , *J. Am. Chem. Soc.* **1984,** *108*, 425-437

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr

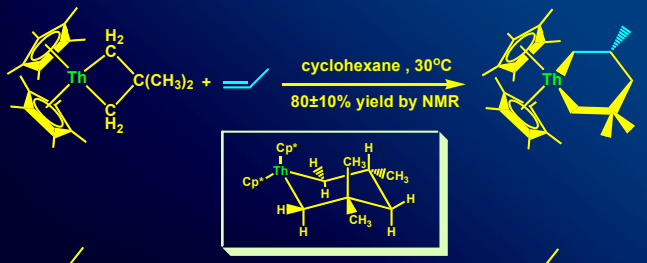


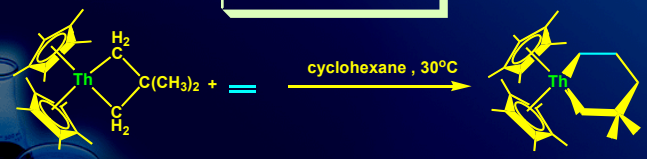


Carol M. Fendrick and Tobin J. Marks , *J. Am. Chem. Soc.* **1984,** *106*, 2214-2216

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr



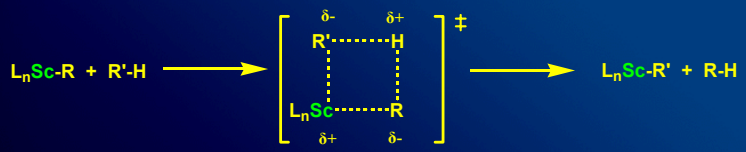


β-C elimination !

Carol M. Fendrick and Tobin J. Marks , *J. Am. Chem. Soc.* **1984,** *108*, 425-437

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr



R, R' = H, alkyl, alkenyl, aryl, alkynyl

An appropriate model for the transition states of such σ bond metathesis reactions must accommodate the observed order of reactivity of R-H bonds with Cp^*_2Sc-R' bonds :

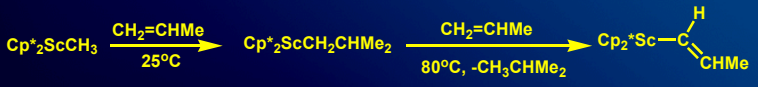
R = R' = H >> R = H, R' = alkyl >> R-H = sp C-H, R' = alkyl > R-H = sp^2 C-H, R' = alkyl > R-H = sp^3 C-H, R' = alkyl .

John E. Bercaw *et al., J. Am. Chem. Soc.* **1987,** *109,* 203-219.

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr

σ-bond metathesis



olefin insertion *σ-bond metathesis*

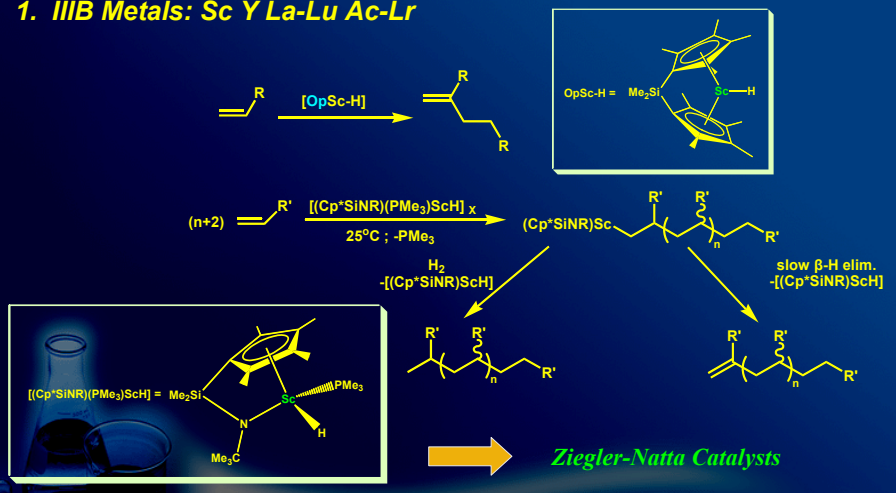
Bulky *Cp** ligands block approach of the π -orbitals from substituted olefins !

How about other less sterically encumbered ligands?

John E. Bercaw *et al., J. Am. Chem. Soc.* **1987,** *109,* 203-219.

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr



Ziegler-Natta Catalysts

John E. Bercaw, *Pure & Appl. Chem.*, **1990**, *62*, 1151-1154.

Examples and Applications

1. IIIB Metals: Sc Y La-Lu Ac-Lr

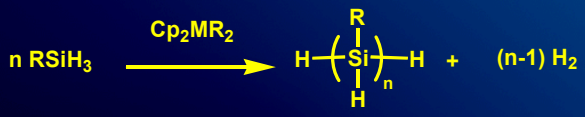
III B group metal complex catalysts:

- Initial investigation in σ bond metathesis
- Stoichiometric amount of complex, rather than catalystic reaction !
- Providing the general models of investigation on theoretical calculation.
- Unknown Lanthanide series and Actinium series……

Examples and Applications

2. IVB Metals: Ti Zr Hf

Catalytic dehydrogenative polymerization of silanes by Ti and Zr metallocene derivatives



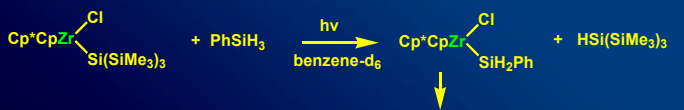
Significance:

A number of applications for polysilanes: photoresists, photoconductors, semiconductors, nonlinear optical meterials.
As an investigation ahead for methane (alkanes) dehydropolymerization, which probably shares the same mechanism.

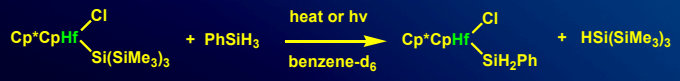
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989,** *111,* 3757-3158

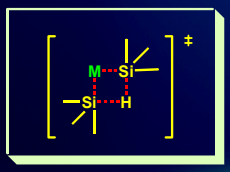
Examples and Applications

2. IVB Metals: Ti Zr Hf



Failed to isolate ! (-SiHPh-)$_n$ + [CpCp*ZrHCl]

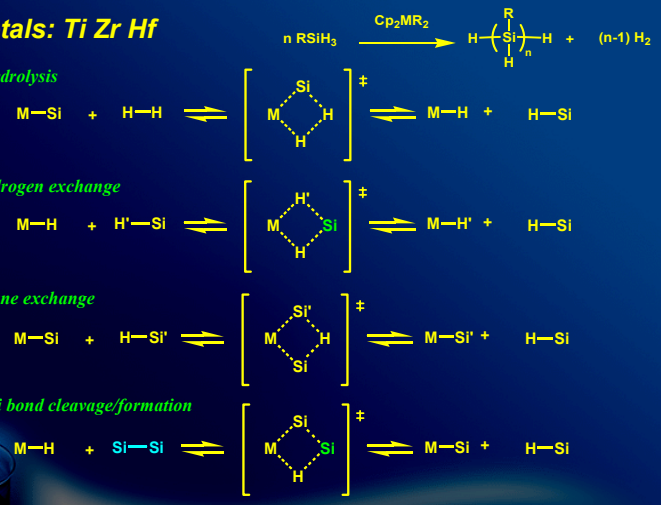




Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989,** *111,* 3757-3158

Examples and Applications

2. IVB Metals: Ti Zr Hf

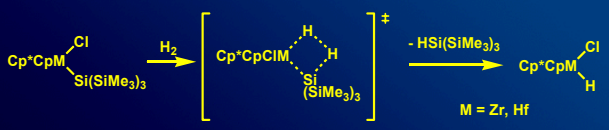


Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989**, *111,* 8043-8044

Examples and Applications

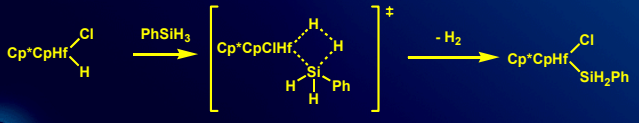
2. IVB Metals: Ti Zr Hf

Hydrolysis



H_2 should be excess absolutely !

Reverse



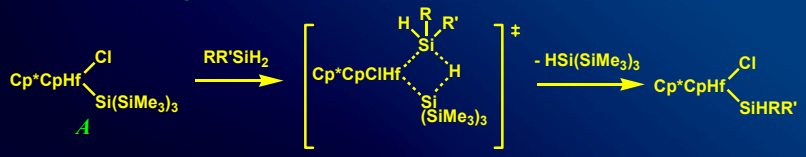
Silanes should be excess absolutely !

Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989**, *111,* 8043-8044

Examples and Applications

2. IVB Metals: Ti Zr Hf

Silane exchange



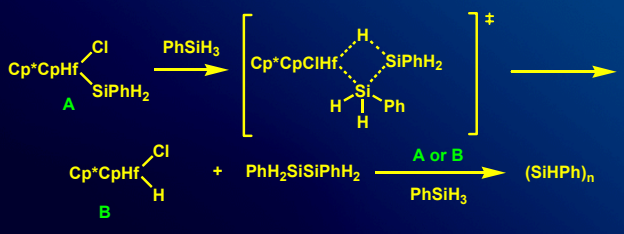
Occur when the starting complex possesses a bulky, easily displaced silyl group !
A : A good starting material !!!

Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989**, *111,* 8043-8044

Examples and Applications

2. IVB Metals: Ti Zr Hf

Si-Si bond cleavage/formation



$SiPhH_3$ should be excess absolutely !

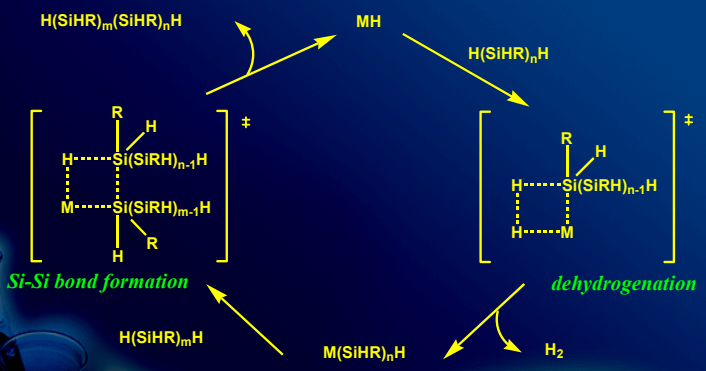
B is a crucial complex in this process !

Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989**, *111,* 8043-8044

Examples and Applications

2. IVB Metals: Ti Zr Hf

Dehydropolymerization Catalytic Mechanism



Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989,** *111,* 8043-8044

Examples and Applications

2. IVB Metals: Ti Zr Hf

Notes:

1. This polymerization involves step growth of polymer rather than chain growth. So the relatively low molecular weights are produced, and high monomer concentration and high vacuum to remove hydrogen can increased MW.

2. It is well-known that Si has an lower electronegativity to H and can form stable compounds with expanded 3d coordination spheres.
   So the Si atom can occupy the β position in transition state. But C atom seems very difficult !

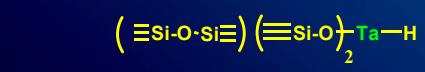
Electronegativity: ***Si: 1.9*** ***H: 2.2*** ***C: 2.5***

Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem. Soc.* **1992**, *114, 7047-1055*
Hee-Gweon Woo and T. Don Tilley, *J. Am. Chem.* Soc. **1989,** *111,* 8043-8044

Examples and Applications

3. VB Metals: V Nb Ta

The silica-supported transition metal hydrides:



$$C_nH_{2n+2} \longrightarrow C_{n+i}H_{2(n+i)+2} + C_{n-i}H_{2(n-i)+2}$$

with i = 1, 2, ...n-1 , but where i = 1 is generally favored.

Successful metathesis of alkanes !

V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99

Examples and Applications

3. VB Metals: V Nb Ta

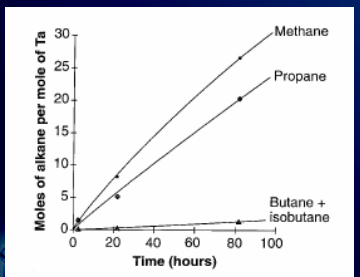
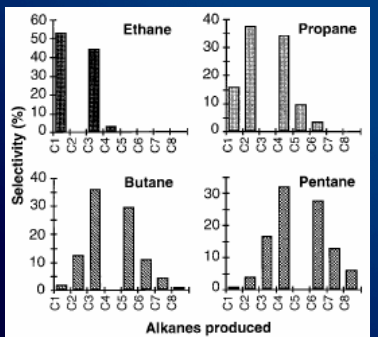


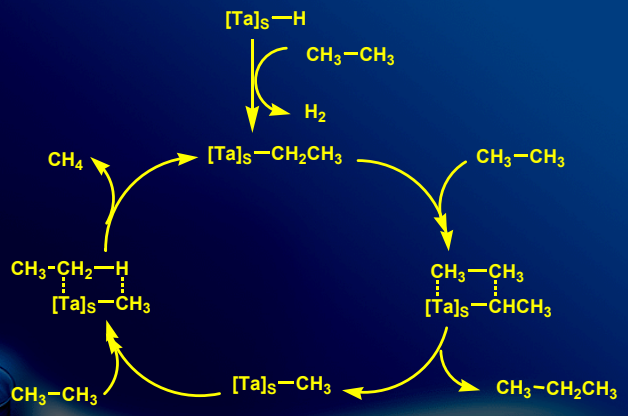
Fig. 1. Metathesis reaction of ethane catalyzed by the silica-supported $[Ta]_s$-H complex at 150°C under 1 atm (C_2H_6/Ta ratio, ~800).



V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99

Examples and Applications

3. VB Metals: V Nb Ta



V. Vidal, A. Theolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99

Examples and Applications

3. VB Metals: V Nb Ta

$$2\ C_2H_6 \xrightarrow[150^oC]{\text{cat.}} CH_4 + C_3H_8$$

ΔG^{θ} = - 8.2 kJ·mol^{-1} .(at 150° C driven by the formation of methane)

Reverse direction : $CH_4 + C_3H_8 \xrightarrow{\text{cat.}} 2\ C_2H_6$

$H_2 + C_3H_8 \longrightarrow CH_4 + C_2H_6$

$C_3H_8 \longrightarrow {}^1/_2\ C_2H_6 + {}^1/_2\ C_4H_{10}$

methane/propane = 1250:1

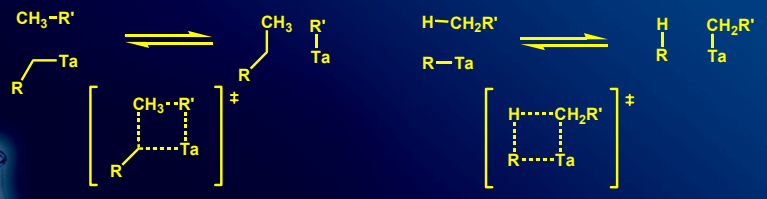
Jean-Marie Basset, *Angew. Chem. Int. Ed.* **2004**, *43*, 5366 –5369

Examples and Applications

3. VB Metals: V Nb Ta

$[(\equiv Si{-}O)_x Ta(=CHCMe_3)(CH_2CMe_3)_{(3-x)}]$

x=1, or 2



C-C bond activation *C-H bond activation(alkane exchange)*

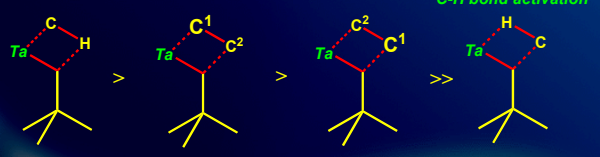
Jean Thivolle-Cazat, Jean-Marie Basset, *Angew. Chem. Int. Ed.* **2001**, *40*, 2331-2334

Examples and Applications

3. VB Metals: V Nb Ta

Entry	Alkane	NpH	NpMe	NpEt	NpPr	NpiPr	Total NpR in gas phase[a] [%]	TON[b]
1	ethane	76	24	< 1[c]	–[d]	–[d]	37	25 (46)
2	propane	70	26	4	< 1[c]	–[d]	48	58 (60)
3	butane	70	15	11	3	–[d]	48	55 (55)
4	isobutane	71	29	–[d]	–[d]	< 1[c]	51	33 (40)

C-H bond activation *C-C bond activation* *reverse C-H bond activation*



C^1 larger than C^2 *not absorved*

Jean Thivolle-Cazat, Jean-Marie Basset, *Angew. Chem. Int. Ed.* **2001**, *40*, 2331-2334

Examples and Applications

3. VB Metals: V Nb Ta

Notes:

- Silica-supported catalysts have special properties and have already been used in industrial applications.
- Selectivity needs more improvement.
- Still difficult for formation of higher alkanes.

Jean Thivolle-Cazat, Jean-Marie Basset, *Angew. Chem. Int. Ed.* **2001**, *40*, 2331-2334

Outline

Summary and Outlook

Sigma bond metathesis is a kind of mechanism applied in the progress of σ bond cleavage and formation that catalyzed by alkyl or hydride complexes of 'early' transition metals with d^0 electronic configurations.

Sc	Ti	V Cr
Y	Zr	Nb Mo
La	Hf	Ta W
Ac		

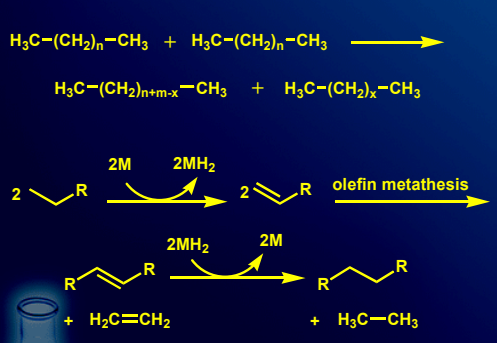
Initial investigation Stoichiometric reaction

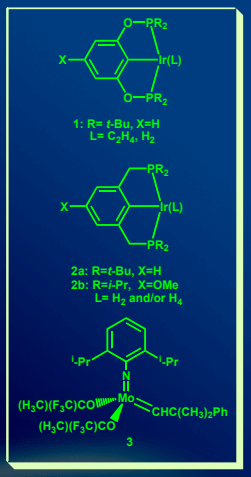
Dehydropolymerization of Silanes

Silica-supported alkane metathesis

Where is the future of sigma bond metathesis ?

Summary and Outlook



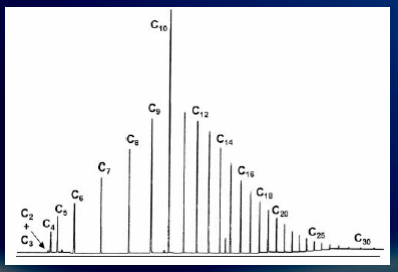


A new idea for alkane metathesis !

A. S. Goldman, *et al*, *Science* **2006**, *312*, 257 – 261.

Summary and Outlook

Ir catalyst	[TBE] (mM)	Time	*n*-Alkane concentration (mM)																	Total product (M)
			C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	[>C_{18}]	
1-C_2H_4 (9.5 mM)	0	3 hours	3.9	2.8	8.3	10	12	12	13	16	4980	15	11	9.3	7.2	6.0	4.6	2.1	1.3	1.9	0.14
		18 hours	5.4	9.7	39	43	43	48	55	64	4580	61	46	38	28	23	17	6.9	3.7	5.4	0.54
		7 days	26		101	117	118	115	140	163	3760	154	115	94	71	58	43	18	9.8	16.3	1.36
2a-H_2 (9.0 mM)	18	3 hours	16		61	86	98	122	142	152	3990	137	104	78	53	37	23	9.3	5.2	6.3	1.13
		11 days	39		207	299	327	382	427	446	1500	408	314	245	174	129	87	48	32	58	3.62
2b-H_4 (9.1 mM)	35	3 hours	15		81	117	134	146	172	181	3490	177	147	120	91	72	52	34	26	63	1.63
		18 hours	39		160	234	265	280	318	324	1870	317	271	226	176	145	110	76	61	194	3.20
		9 days	44		220	332	346	405	456	457	753	429	362	300	233	195	151	108	88	241	4.37

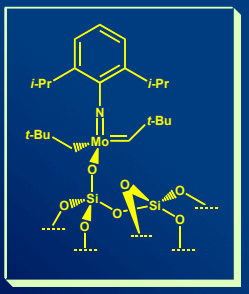


A. S. Goldman, *et al*, *Science* **2006**, *312*, 257 – 261.

Summary and Outlook

This system involves a single metal with dual properties in contrast to the Goldman–Brookhart system !

Alkane	TON[a]	Alkane selectivity[b]						
		C_1	C_2	C_3	C_4[c]	C_5[c]	C_6[d]	C_7[d]
ethane	2 (0.4)	35.9	n.a.[e]	62.0	1.5/0.8	n.o.[f]	n.o.	n.o.
propane	55 (9.9)	0.1	56.1	n.a.	35.3/2.7	5.2/0.7	0.6	<0.1
butane	90 (17.7)	<0.1	11.1	56.5	n.a./0.5	21.7/0.4	7.7	2.0
isobutane	3 (0.7)	1.0	35.9	17.1	7.0/n.a.	16.4/n.o	22.8	n.o.



There are also new methods to afford alkane metathesis, and sigma bond metathesis is just a kind of them !

C. Copret,* J. T.Cazat, and J.M. Basset, *Angew. Chem. Int. Ed*. **2006**, *45*, 6201 –6203

Summary and Outlook

"This represents a great step forward for 'green chemistry,' reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment,"

------ the committee's comment on 2005 Nobel Prize in Chemistry .

Next Nobel Prize in Organic Chemistry ?

Outline

- *Introduction*
- *Mechanism*
- *Examples and Applications*
- *Summary and Outlook*
- *Acknowledgements*

Acknowledgements

- *PKU, CCME, OPSS*
- *Prof. Zhangjie Shi*
- *All members in my group*
- *All professors and students here*