Multiple Metal-Carbon Bonds for Catalytic Metathesis Reactions

Nobel Lecture
December 8, 2005
Metal-carbon double and triple bonds in which the transition metal is in a "low oxidation state" were discovered by E. O. Fischer.

1964
"carbene"

1973
"carbyne"
Beta hydride elimination in an ethyl complex

\[
\begin{align*}
\text{M} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{H} \\
\text{L}_1 & \quad \text{M} & \quad \text{L}_3 \\
\text{L}_2 & \\
\end{align*}
\]

\[\rightarrow\]

\[
\begin{align*}
\text{M} & \quad \text{H} \\
\text{L}_1 & \quad \text{M} & \quad \text{L}_3 \\
\text{L}_2 & \\
\end{align*}
\]

\[+\]

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{C} & \quad \text{H} \\
\end{align*}
\]
Known Group 4 Peralkyl Complexes \((M = \text{Ti, Zr, Hf})\) in 1973.

All alkyls lack one or more hydrogen atoms on the atom \(\beta\) with respect to the metal.
The first relatively stable permethyl complex

\[
\text{WCl}_6 + 6 \text{AlMe}_3 \xrightarrow{\text{pentane}} \text{Me}_4\text{WMe}_4\text{Me}_4
\]

4 5 6 7 8
Ti V Cr Mn Fe
Zr Nb Mo Tc Ru
Hf Ta W Re Os

A. J. Shortland and G. Wilkinson


"*Note added in proof. Hexamethylrhenium (K. Mertis and G. Wilkinson) and pentamethyl[t]antalum (R. Schrock, DuPont, Wilmington, private communication) have recently been synthesized."

Geoffrey Wilkinson, Nobel Lecture, December 11, 1973
Synthesis of tantalum pentaalkyls

\[
\text{TaCl}_5 + 1.5 \text{ ZnMe}_2 \xrightarrow{\text{pentane}} \text{TaMe}_3\text{Cl}_2 \xrightarrow{2 \text{ LiMe}} \text{ether}
\]

Decomposes above 0 °C 

\[
\text{TaCl}_5 + 5 \text{ Me}_3\text{SiCH}_2\text{MgCl} \rightarrow 1/2 \text{Me}_3\text{SiCH}_2\text{MgCl}
\]

"It is assumed that a penta-alkyl complex cannot exist for steric reasons."

Neopentyls yield a stable product of α hydrogen abstraction.

J. Am. Chem. Soc. 1974, 96, 6796

Distills in a good vacuum at 75°C.
Alkylidenes can be deprotonated to yield tantalum-carbon triple bonds.

Alkylidenes decompose bimolecularly.

Bimolecular decomposition of alkylidenes, especially methylenes, is difficult to prevent, especially in electron deficient species.

Olefin metathesis and the Chauvin mechanism (1971)

\[
2 \text{RCH}=\text{CHR}' \rightleftharpoons \text{RCH}=\text{CHR} + \text{R'}\text{CH}=\text{CHR}' + \text{RCH}=\text{CHR}' - \text{RCH}=\text{CHR}'
\]

\[\text{M} = \text{Mo, W, or Re}\]
Alkyne metathesis and the metalacyclobutadiene mechanism

\[
2 \text{RC}≡\text{CR'} \rightleftharpoons \text{R'C}≡\text{CR'} + \text{RC}≡\text{CR}
\]

\[
\text{M}≡\text{CR} \quad \text{RC}≡\text{CR'} \quad \text{M}≡\text{CR'}
\]

(suggested by T. Katz; 1975)

\[
\text{M} = \text{Mo, W}
\]
Reaction of tantalum alkylidenes with olefins.

\[
\text{Cl}_2\text{Ta} = \text{CH-t-Bu} \quad 2 \text{RCH} = \text{CH}_2 \quad \text{Cl}_2\text{Ta} = \text{CH}_2 \quad + \quad 4 \text{olefins}
\]

\[
\text{CpCl}_2\text{Ta} \quad \text{CH-t-Bu} \quad \beta \text{H} \quad \text{RCH} = \text{CH}_2\text{t-Bu}
\]

\[
\text{CpCl}_2\text{Ta} \quad \text{CH}_2 \quad \beta \text{H} \quad \text{RCH}_2\text{CH} = \text{CH-t-Bu}
\]

\[
\text{CpCl}_2\text{Ta} \quad \text{CH}_2 \quad \beta \text{H} \quad \text{CH}_2 = \text{CHRCH}_2\text{t-Bu}
\]

\[
\text{CpCl}_2\text{Ta} \quad \text{CHR} \quad \beta \text{H} \quad \text{CH}_3\text{CHR} = \text{CH-t-Bu}
\]
Modification of Nb and Ta yields metathesis catalysts

\[ \text{M(CH-t-Bu)L}_2\text{Cl}_3 + \text{H}_2\text{C} = \text{CHR} \rightarrow \text{4 products of rearrangement} \]

of metallacyclobutanes

\[ \text{M} = \text{Nb or Ta} \]
\[ \text{L} = \text{PMe}_3 \]

\[ \text{M(CH-t-Bu)(O-t-Bu)}_2\text{Cl(PMe}_3) + \text{olefins} \rightarrow \text{also metathesis products} \]

(\sim 35 \text{ turnovers for cis-2-pentene})

Alkoxides "prevent reduction" and "promote metathesis."

An oxo neopentylidene complex of tungsten

\[
\begin{align*}
\text{L} & = \text{a phosphine, e.g. PEt}_3 \\
\end{align*}
\]
A sterically demanding diisopropylphenyl imido group might be a desirable "ancillary" ligand.

The OR group should be a sterically demanding tertiary alkoxide.
A sterically demanding diisopropylphenyl imido group might be a desirable "ancillary" ligand.

Hexafluoro-t-butoxide was chosen as a highly electron withdrawing alkoxide.
Synthesis of a tungsten neopentylidyne complex

Volatile yellow crystals.
Thermally stable, distilling at 75°C in a good vacuum.

(1978)
The tri-t-butoxide compound is a powerful catalyst for the alkyne metathesis reaction.

\[
2 \text{RC}≡\text{CR'} \rightleftharpoons \text{R'C}≡\text{CR'} + \text{RC}≡\text{CR}
\]
Metal-metal bonds and "metathesis" reactions.

(1982)
Synthesis of a tungsten imido alkylidene complex

\[
\text{W(NAr)(CH-t-Bu)(OR)}_2 \text{ species are } \text{"well-defined" catalysts for the metathesis of olefins and the activity can be varied systematically by varying OR.}
\]

\[
\text{OR = O-t-Bu, OCMe}_2\text{(CF}_3\text{), OCMe(CF}_3\text{)}_2, \text{ and various bulky phenoxides}
\]
Structure of \( \text{syn-W(NAr)(CH-t-Bu)(O-t-Bu)}_2 \)
Tungstenacyclobutanes can be isolated, but can be too stable toward loss of olefin.

Molybdacyclobutane intermediates lose an olefin more readily.
Two isomers (anti and syn) are available in any system through rotation about the M=C bond.
Olefin metathesis variations

RCM

- CH₂=CH₂

ROM/CM

+ RCH=CH₂

ROMP
(Ring-Opening Metathesis Polymerization)

Control!
Polymerization of bistrifluoromethylnorbornadiene via enantiomorphic site control.

When R = CH(CH₃)₂ the polymer structure has a relatively random (71% cis) structure.
Alkynes are polymerized to yield polyenes.

Soluble, highly conjugated (purple), and relatively air-stable; both rings observed in polymer made with Mo(NAr)(OR$_{p6}$)$_2$ catalyst.

>95% 5-membered rings produced with Mo(NAr)(O-t-Bu)$_2$ catalyst.
Ring-closing metathesis with Mo catalyst (4-5 mol%) 

\[
\text{(Catalyst} = \text{Mo(NAr)(CHCMe}_2\text{Ph)[OCMe(CF}_3\text{)]}_2\text{)}
\]

Synthesis of Fluvirucin-B\textsubscript{1}

Mo or W catalyzed alkyne metathesis reactions are useful in organic chemistry.

Olefins do not appear to react with M-C triple bonds.

Civetone

(Fürstner)
Other examples of alkyne metathesis in organic synthesis

Motuporamine C

PGE$_2$-1,15-lactone

Epothilone C

S-$(+)$-citreofuran
An enantiomerically pure Mo catalyst

Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A.; Schrock, R. R.
Asymmetric catalyst design; a modular approach

Imido Groups

Diolates

24 catalysts!
Asymmetric Ring-Closing Metathesis (ARCM)

R = i-Pr

- propylene
2 mol % cat
no solvent,
22 °C, 5 min
99% ee, 93%

- ethylene
2 mol % cat
no solvent,
60 °C, 4 h
>99% ee, 98%

33
Ring-Opening / Ring-Closing Metathesis

>99% ee, 76%
Ring-Opening / Cross Metathesis

Nitrogen-Containing substrates

5 mol %

22 °C
- ethylene
20 min
R = Me

>98% ee, 90% yield
Enantioselective synthesis of a tertiary ether in a drug

A bis amido alkylidene catalyst precursor.

Amido ligands deactivate the metal toward metathesis reactions.

*In situ* catalyst prepared with gives same ee (93-94%) as the isolated catalyst.
Dineopentyl species were examined as bisalkoxide catalyst precursors.

\[
\begin{align*}
\text{Ar} & = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3 \\
\text{OR} & = \text{OCH(CF}_3)_2, \text{OAdamantyl, OCMe}_3, \text{or OAr}
\end{align*}
\]

Preliminary results suggest that monoalkoxides are at least as active as bisalkoxides!

(Surprising since dineopentyl species are essentially inactive.)
"Well-defined" catalysts can be prepared on a silica surface.

Well-defined catalysts can be prepared on a silica surface using other "clean" neopentyl sources.

The principles of high oxidation state alkylidene and alkylidyne chemistry extend to Re(VII)

Olefins react with the Re=CHR bond selectively, not the Re≡C-t-Bu bond.
These Re species are active olefin metathesis catalysts.
Present and future challenges

1. **Prevent** catalyst decomposition completely and/or find ways to **regenerate** catalysts from decomposition products.

2. Find ways to generate and evaluate all catalysts **in situ** from one precursor.

3. Synthesize **new catalysts** and aim for **additional selectivity and efficiency** in metathesis reactions.
"Unsupported" M=M bonds are formed in bisalkoxide systems

![Structure diagram]

A W=W species (W=W = 2.49 Å) that does not contain bridging groups.