Fischer Carbyne and Schrock Alkyldyne

Fischer
- Doublet
- LX type
- 4e
- -1 lone pair covalent
- π-back bonding
- Weak donor L

Schrock
- Quartet
- X_3 type
- 6e
- -3 covalents
- Strong donor L

Alternative consideration:
- L_nM^- 
  + CR
  2e donor
  4e acceptor

Group Orbitals of $^+\text{CR}$ Fragment

$^+\text{CR}$ Fragment
$4e \pi$-acceptor
$2e \sigma$-donor

Carbyne Complexes, Fischer et. al.
1988, VCH
MOs of Fischer Carbyne

$$\text{L}_4\text{XM}$$
$$\text{d}^6$$
Group 6 M

$$\text{CR}$$
2e $\sigma$-donor
4e $\pi$-acceptor

$$\text{Br-W}$$
$$\text{Me}$$
$$\text{OC}$$
$$\text{CO}$$

18e, d$^4$, W(IV)

Carbyne Complexes, Fischer et. al. 1988, VCH
Consider

\[ \text{X}_3\text{M}^\ominus \qquad \text{d}^4 \]  
2e σ-donor, 4e π-acceptor  

Group 6 M

i.e.

\[ \text{X}_3\text{W}^- \qquad \text{+CPh} \]  
e count  
(Schrock)  
12e, d^4, W(VI)

Encyclopedia of Inorganic Chemistry,  
Electronic Structure of Organometallic Compounds,  
Albright, T. A.
Molecular Orbitals of L₃M(CR)

Carbyne Complexes, Fischer et. al. 1988, VCH
**A Brief History of Alkyne Metathesis**

First Heterogeneous Catalyst System (1968)

\[
\text{Me} \equiv \text{Et} \xrightarrow{\text{WO}_3 \text{ on silica} \ 350^\circ} \text{Me} \equiv \text{Me} + \text{Et} \equiv \text{Et} \sim 1 : 1
\]


First Homogeneous Catalyst System (1974)

\[
\text{Me} \equiv \text{Me} \xrightarrow{\text{Mo(CO)}_6, 160^\circ} \text{Me} \equiv \text{Me}
\]

\[
\text{Me} \equiv \text{Me} + \text{Me} \equiv \text{Me}
\]

\sim 1 : 1


Proposal of an Alkylidyne Complex Undergoes Metathesis (1975)

Experimentally studied by Schrock et. al.

\[
\text{Me} \equiv \text{Et} + \text{Et} \equiv \text{M} \xrightarrow{\text{Me} \equiv \text{Me}} \text{Me} \equiv \text{Me} \rightarrow \text{Me} \equiv \text{Me}
\]


Catalyst Deactivation by Dimerization and Ring Expansion

Many catalyst design criterion was established by Schrock et. al. in the 1980s by studying metal-alkylidyne complexes.

\[
\begin{align*}
2 \quad & \quad \text{RO} \quad \overset{\text{M}}{\text{\equiv}} \quad \text{R'} \quad \leftrightarrow \quad \text{RO} \quad \overset{\text{M}}{\text{\equiv}} \quad \text{M} \quad \overset{\text{OR}}{\text{\equiv}} \quad \text{OR} \\
\text{dimer} & \\
\end{align*}
\]

Bulky R and R' favors alkylidynes. The equilibrium is more sensitive to R than R'.

\[
\begin{align*}
\text{R'} & + \quad \text{Me} \quad \overset{\text{M(OR)₃}}{\text{\equiv}} \quad \text{Me} \quad \leftrightarrow \quad \text{R'} \quad \overset{\text{(RO)₃M}}{\text{\equiv}} \quad \text{Me} \\
\text{insertions} & \\
\text{M} & = \text{W, Mo} \\
\text{R} & = \text{alkyl or phenyl} \\
\text{R'} & = \text{alkyl} \\
\end{align*}
\]

Problem:
Polymerization of small alkyne by-products

Solution:
Alkyne by-product is more sterically bulky and insoluble to disfavor insertion. Removal of small alkynes by conducting the reaction under reduced pressure.

“Pseudopoiisoning” Effect

\[
\begin{align*}
\text{Et} &+ \text{M(OR)}_3 \\ \equiv &\rightleftharpoons \equiv \\
(\text{RO})_3\text{M} &\equiv \text{Aryl} \\ \equiv &\rightleftharpoons \equiv
\end{align*}
\]

unproductive

Alkyne reactivity depends on substituent
alkyl > aryl
\(e\)-rich aryl > \(e\)-deficient aryl

productive

catalyst is kinetically occupied

Especially relevant to alkyl
aryl substituted substrates

desired

Solution:
- Shifting the equilibrium in favor of active M-alkylidyne species.
- Remove dialkyl-substituted by-products (vacuum condition)
- Precipitation approach

Preparation of \((\text{Me}_3\text{CO})_3\text{W} \text{(CCMe}_3\text{)}\)

Bulky alkoxide ligand avoid dimerization of the catalyst.

\[
\begin{align*}
\text{WCl}_6 & \quad \xrightarrow{\text{LiCH}_2\text{CMe}_3} & (\text{CH}_2\text{CMe}_3)_3\text{W} \text{(CCMe}_3\text{)} \\
\text{WCl}_4 & \quad \xrightarrow{\text{LiNMe}_2} & (\text{Me}_2\text{N})_3\text{W} \equiv \text{W} \text{(NMe}_2\text{)}_3 \\
& & \xrightarrow{1. \text{Me}_3\text{COH}} (\text{Me}_3\text{CO})_3\text{W} \text{(CCMe}_3\text{)} \\
& & \xrightarrow{2. \text{Me} \equiv \text{CMe}_3} \text{First well-defined complex proven to promote alkyne metathesis (Schrock, 1981)}
\end{align*}
\]

Alkyl, thiolate and amide analogues showed little activity (lower electronegativity than O). Chloride forms bridge with metals readily.

Some examples of Mo Cat investigated by Schrock and Cummins

\[
\begin{align*}
\text{[OCMe(CF}_3)_2\text{]}_3\text{Mo} \text{(CCMe}_3\text{)} \\
(\text{o-PhC}_6\text{H}_4\text{)}_3\text{Mo} \text{(CPh)} \\
\text{TMS} \\
\text{Scope of these catalysts were not well established.}
\end{align*}
\]

Application to RCAM

\[ \text{[W(CCMe_3)(OCMe_3)_3]} \text{ (4-6 mol\%), 80 °C,} \]
\[ \text{1 atm, } \leq 0.02 \text{ M, } C_6H_5Cl, \text{ toluene, THF} \]
\[ \text{or} \]
\[ \text{in 1,2,4-trichlorobenzene (bp = 214 °C), 20 mbar} \]

\[ \begin{align*}
X &= \text{ether, ester, silyl ether, sulfonamide,} \\
   &= \text{carbamate, sulfoxide, enoate} \\
\end{align*} \]

\[ \text{2-19 h} \]
\[ \text{52-97% yield} \]

Thioether, basic nitrogen containing functional groups are not compatible.
Tolerate acidic proton of a secondary amide.

Curious Effect of Halogenated Solvents

Mo[N(tBu)(Ar)]₃ (2)

Secondary amide is not tolerated.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>additive</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂Cl₂</td>
<td>CH₂Cl₂</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>CH₂Cl₂</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>CHCl₃</td>
<td>CH₂Cl₂</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>CC₂</td>
<td>CH₂Cl₂</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>toluene</td>
<td>CH₂Br₂</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>CH₂I₂</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td>toluene</td>
<td>C₆H₅CHCl₂</td>
<td>78</td>
</tr>
<tr>
<td>8</td>
<td>toluene</td>
<td>C₆H₅CH₂Cl</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td>toluene</td>
<td>Me₃SiCl</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>toluene</td>
<td>[(Ar)(tBu)N]₃MoCl (3)ₖ</td>
<td>70</td>
</tr>
<tr>
<td>11</td>
<td>toluene</td>
<td>[(Ar)(tBu)N]₃MoBr (5)ₖ</td>
<td>79</td>
</tr>
</tbody>
</table>

ᵣ 25 equiv of the respective additive relative to 2 are used. ʙ Pure 3 was used as the catalyst instead of 2 + additive. ₖ Pure 5 was used as the catalyst instead of 2 + additive.

Major Components of the Molybdenum Species

Why is 3 not catalytically active?
Why are terminal alkynes not viable substrates?
“Deprotiometallacyclobutadiene”

\[
\text{M(C}^\text{Bu})(\text{OR})_3 + \text{R'C=CH} \rightarrow \text{RO-M-}'\text{Bu} \quad \text{RO-M-}'\text{Bu} \quad \text{- ROH} \rightarrow \text{RO-M-}'\text{Bu}
\]

Schrock et. al. J. Am. Chem. Soc. 1985, 107, 5987
Polyhedron 1995, 15, 3177

Mo[C_3(CMe_3)_2][OCH(CF_3)_2](py)_2
Cross Metathesis

![Cross Metathesis Reaction](image)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Homodimerization</th>
<th>ACM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1&lt;sup&gt;a&lt;/sup&gt; Mo(CO)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>F&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>59</td>
<td>14</td>
</tr>
<tr>
<td>NC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>58</td>
<td>15</td>
</tr>
<tr>
<td>OMe&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>68</td>
<td>0</td>
</tr>
<tr>
<td>COOMe&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;NC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>46</td>
<td>0</td>
</tr>
<tr>
<td>S&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;C≡CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Activated in situ with CH<sub>2</sub>Cl<sub>2</sub> in toluene at 80°C;  <sup>b</sup> Activated in situ with p-chlorophenol (30 mol%) in 1,2-dichlorobenzene at 140°C, cf. ref. 9d.

Fürtner, A., Mathes, C. *Org. Lett.* **2001**, *3*, 221
Cross Metathesis

Scheme 3. ACM of C-Silylated Alkynes with 5-Decyne (1.5 equiv) Catalyzed by 1 (10 mol %)/CH₂Cl₂ in Toluene at 80 °C

Scheme 1. ACM of Substrate 5 with a Set of Symmetrical Alkynes 9a–d (1.5 equiv) Catalyzed by 1 (10 mol %)/CH₂Cl₂ in Toluene at 80 °C

Application of RCM and RCAM to Macrocyclization

**RCM**  

17

18

epothilone C (19)

b)

**RCAM**  

56 (R = TBS)

complex 37, cat.

CH$_2$Cl$_2$/toluene

80%

57

58 R = TBS  
aq. HF

Epothilone C  
R = H

79% over both steps

epothilone C

a) amino pyridine (4-DMAP), CH$_2$Cl$_2$, RT, 12 h, 80%;  
b) [RuCHPh]Cl$_2$ (PCy$_3$)$_2$, CH$_2$Cl$_2$, RT, 12 h, 94% (Z:E = 1:1);  
c) HF, MeCN, Et$_2$O, RT, 12 h; 65%. 
- Active catalyst is generated in the presence of various phenols.
- Electron-deficient ligands make the catalysts more active e.g. p-nitrophenol (low cost)
- Catalyst is active in MeCN even though it is a coordinating solvent.
- Secondary amide and thiophene containing molecules can be used.
- Bulky ligand is not required. Apparently electronic factor dominates.
- Bulky ligands slows down both dimerization and metathesis presumably.

Effects of Alkyl Substituent and Ligand

R = Me gives polybutyne

Equilibrium ratio of 13:14 = 2:3 (established from both 13 and 14, respectively)

Optimal R = Et

Optimal Ligand = p-nitrophenol (cheaper)

---

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>Yield(%)</th>
<th>15</th>
<th>28</th>
<th>22</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Me</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Closed system, $d_8$-toluene, 20 °C, yield based on NMR spectral analysis.*

---

$t_{1/2}$ is the time required for the metathesis reaction to reach 50% of equilibrium conversion.

Equilibrium ratio of 13:14 = 2:3 (established from both 13 and 14, respectively)

## Homodimerization Substrate Scope

![Diagram of the reaction](image)

**Chemical Reaction:**

\[
\text{Ar} = 3,5\text{-xylyl}
\]

\[
\text{Ar} - \equiv - \text{CH}_3 \quad \xrightarrow{5 + \text{ligand} (10 \text{ mol} \%)} \quad \text{Ar} - \equiv \text{Ar} + \text{H}_3\text{C} - \equiv - \text{CH}_3
\]

### Substrate Scope

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>(t_{1/2}) (min)(^a)</th>
<th>Yield(%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>NC-\text{Ar-\equiv-CH}_3</td>
<td>NC-\text{Ar-\equiv-CH}_3-CN</td>
<td>17</td>
<td>&lt;8.0</td>
</tr>
<tr>
<td>b</td>
<td>F_3\text{C-\equiv-CH}_3</td>
<td>F_3\text{C-\equiv-CH}_3-CF_3</td>
<td>10</td>
<td>&lt;8.0</td>
</tr>
<tr>
<td>c</td>
<td>OHC-\text{Ar-\equiv-CH}_3</td>
<td>OHC-\text{Ar-\equiv-CH}_3-CHO</td>
<td>8.5</td>
<td>&lt;8.0</td>
</tr>
<tr>
<td>d</td>
<td>H_3\text{CO-\equiv-CH}_3</td>
<td>H_3\text{CO-\equiv-CH}_3-OCH_3</td>
<td>&lt;8.0</td>
<td>&lt;8.0</td>
</tr>
<tr>
<td>e</td>
<td>(H_3\text{C})_2\text{N-\equiv-CH}_3</td>
<td>(H_3\text{C})_2\text{N-\equiv-CH}_3-N(CH_3)_2</td>
<td>&lt;8.0</td>
<td>&lt;8.0</td>
</tr>
<tr>
<td>f</td>
<td>\text{S-\equiv-CH}_3</td>
<td>\text{S-\equiv-S}</td>
<td>10.5</td>
<td>&lt;8.0</td>
</tr>
</tbody>
</table>

---

\(a\) Closed system, d8-toluene, 20 °C, \(t_{1/2}\) is the time required for the reaction to reach 50% of final constant ratio of 10 to 12.

\(b\) Open driven condition, solvent 1,2,4-trichlorobenzene, 30 °C, 22 h, 1 mm Hg, yield based on isolated product.

\(c\) Ligand A ) \( R, R, R\text{-trifluoro-o-cresol} \)

\(d\) Ligand B ) \( p\text{-nitrophenol} \)
Precipitation strategy can be utilized to drive the equilibrium towards desired product such as 7. Aprotic, non-coordinating solvents are preferred.

Preparation of Shape-Persistent Macrocycles by PPT Strategy

Zhang, W.; Moore, J. S.


\[
\text{EtC≡Mo}[\text{NAr(tBu)}]_3 + p\text{-nitrophenol} \rightarrow \text{macrocyclization}
\]

\[
\begin{align*}
&\text{EtC≡Mo}[\text{NAr(tBu)}]_3 + p\text{-nitrophenol} \\
&30^\circ C, 22 h \\
&\text{Isolated Yield} \\
&\text{mg-scale} \quad \text{g-scale} \\
&2d \quad R = \text{CO}_2\text{Tg} \quad 76\% \quad <10\% \\
&2e \quad R = \text{CO}_2\text{Tg} \quad 81\% \quad 77\%
\end{align*}
\]
Catalyst Prepared from Nitrides by Metathesis with Alkynes

One major reason that MeCN cannot be used

- **36** and **38** are preferred thermodynamically.
- The formation of **38** is irreversible.
- Idea: in situ generation of catalyst by metal nitride/metal alkylidyne interconversion

Development Towards a Robust and Practical Precatalyst

\[
\begin{align*}
\text{Na}_2\text{MoO}_4 & \rightarrow \left[ \text{MoO}_2\text{Cl}_2(\text{dme}) \right] & \text{7} & \rightarrow & \text{8} \\
\text{Me}_3\text{SiO} & \text{Mo} & & & \text{Me}_3\text{SiO} \\
\text{N} & \text{SiMe}_3 & & & \text{N} & \text{SiMe}_3 \\
\text{distorted square pyramidal} & & & & & \\
\end{align*}
\]

Conditions: (a) TMSCl, 1,2-dimethoxyethane (DME), reflux; (b) LiHMDS, hexane, 64% (for two steps); (c) Ph$_3$SiOH (3 equiv), toluene, 80 °C, then pyridine (5 equiv), 81%. (bottom-right) Structure of complex 11 in the solid state.

## Scope

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>R = H (84%/76%)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>R = COOMe (70%)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>R = OMe (59%)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>R = SMEO (67%)</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td>68%&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td>61%</td>
</tr>
<tr>
<td>7</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td>81%&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Unless stated otherwise, all reactions were performed using complex 11 (20 mol %) in toluene at 80 °C. <sup>b</sup> Using 2 mol % 11. <sup>c</sup> At reflux.

11 can be weighed in air and used under dry air (need increased loading)

Incompatible: epoxide, aldehyde, acyl chloride

<sup>a</sup> Synthesis of gallicynoic acid I (17) by ACM. Conditions: (a) 9 (20 mol %)/Ph₃SiOH (40 mol %), toluene, 80 °C, 76%; (b) (i) LiOH, MeOH(aq)/1,4-dioxane; (ii) TBAF, THF, 61%. E = COOMe.

Fürstner et al. J. Am. Chem. Soc. 2009, 131, 9468
Typical Reaction Conditions for Homodimerization, CM, RCAM

(A) \textbf{15} (10 mol \%), \textit{MnCl}_2 (10 mol \%), \textit{MS} 5 \, \AA, toluene, 80 °C, 30 min, then addition of the substrate and reaction at 80 °C or 100 °C (for CM).

(B) \textbf{24} (2 mol \%), toluene, \textit{ambient temperature}, \textit{MS} 5 \, \AA.

(C) \textbf{25} (5 mol \%), \textit{MnCl}_2 (5 mol \%), toluene, 80 °C, 30 min; then addition of the substrate and \textit{MS} 5 \, \AA, and reaction at ambient temperature.

\textbf{15} is stable on bench top for storage.
Incompatible with aldehyde. Previous stoichiometric experiment showed its conversion to nitrile.

Roles of Molecular Sieve

Figure 7. Metathesis of 1-phenyl-1-propyne catalyzed by Mo(≡CPh)(OSiPh$_3$)$_3$(Et$_2$O) (24•Et$_2$O, 1 mol %) in toluene in the absence (blue triangles) or in the presence (blue squares) of powdered MS 5 Å at ambient temperature. Comparison with the plot obtained upon pretreatment of the catalyst with MS 5 Å, which was removed prior to the addition of the substrate (red circles). The yields were measured by GC against biphenyl as internal standard.

3 Å MS has no sig. effect (i.e. not equilibrium effect of H$_2$O)

Hypotheses:

“The small amounts of alkylidyynes, such as 16, formed in the mixture must be superbly active”

“12·L acts as a reservoir (slow release) (still show catalytic activity at 80 °C for days)"

The hypotheses were tested using 19 and 24.
Preparation of Molybdenum Alkylidyne Complexes

\[
\ce{Mo(CO)6 \xrightarrow{b,c)} [NMe4][Mo(CO)5(COPh)] \xrightarrow{d)} \ce{Br \xrightarrow{e)} \text{Ph} \xrightarrow{f)} \ce{Br_{12}MoBr_{12} \xrightarrow{g)} \text{Ph3SiO-Mo-O-SiPh3}}
\]

\[20 \quad 21 \quad 22 \quad 23 \quad 24\]

\(a\) Reagents and conditions: (a) Ph\(_3\)SiOLi (3 equiv), Et\(_2\)O, \(-40 \degree C \rightarrow \text{rt}\), then MeCN, 85%; (b) PhLi, Et\(_2\)O, reflux; (c) NMe\(_4\)Br, H\(_2\)O, 52% (over both steps); (d) oxalyl bromide, CH\(_2\)Cl\(_2\), \(-78 \degree C \rightarrow -15 \degree C\); (e) Br\(_2\), 1,2-dimethoxyethane (dme, 5 equiv), CH\(_2\)Cl\(_2\), \(-78 \degree C \rightarrow \text{rt}\), 88% (over both steps); (f) Ph\(_3\)SiOK (4 equiv), toluene; (g) Et\(_2\)O, 92%.

An Extraordinary Active Metathesis Catalyst

Equilibrium reached at ~ 25 min

Figure 4. Metathetic conversion of 1-phenyl-1-propyne to tolane catalyzed by 1 mol % of either Mo(≡CPh)(OSiPh₃)₃(Et₂O) (24·Et₂O) (blue triangles) or (tBuO)₃W≡CtBu (1) (red circles) in toluene at ambient temperature and ambient pressure. The yields were determined by GC using biphenyl as an internal standard.

Application of RCAM to the Synthesis of Lactimidomycin

Key steps: Ring closing alkyne metathesis and *trans*-hydrosilylation

Imidazolin-2-iminato Tungsten Catalyst


reaction conditions: hexane (25 mL), \( n(\text{substrate}) = 2.24 \text{ mmol} \), \( n(\text{catalyst}) = 2.2 \times 10^{-5} \text{ mol} \) (1 mol%), \( T = 293 \text{ K} \), \( p = 350 \text{ mbar} \).

hexane (4.5 mM)
2 h, 95%
- New (pre)catalysts are much more functional group tolerant and efficient.
- Bench top stable pre-catalyst has emerged (silanolate bound Mo complexes).
- The yields of cross-metathesis are generally moderate.
- RCAM and homodimerization are relatively mature.
- Three ways to drive the equilibrium of metathesis:
  (1) reduced pressure, (2) precipitation and (3) molecular sieve
- Mechanism of some pre-catalysts is still unknown (tris-amido Mo complex).
- Promising in the area of ADIMET and Shape Persistent Macromolecules.

RCAM, see Fürstner, Davies Chem. Commun. 2005, 2307.
Carbyne Complexes, Fischer et. al. 1988, VCH Verlagsgesellschaft Handbook of Metathesis: Catalyst Development, Grubbs, Ch 1.11