**General**

**Defintion and general view:**

How to define an \( \eta \)-coordination?

- Coordination via uninterrupted and contiguous series of atoms

Naming rules, see: F. A. Cotton* JACS, 1968, 6230

\[ (\eta^2\text{-allyl})-(\eta^4\text{-butadiene})-(\eta^5\text{-cyclopentadienyl})-\text{Mo(II)} \]

**Classification**

<table>
<thead>
<tr>
<th>VI</th>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
</tr>
<tr>
<td>d(^5)s(^1)</td>
<td>d(^5)s(^2)</td>
<td>d(^6)s(^2)</td>
<td>d(^7)s(^2)</td>
</tr>
<tr>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
</tr>
<tr>
<td>d(^5)s(^1)</td>
<td>d(^5)s(^1)</td>
<td>d(^6)s(^1)</td>
<td>d(^6)s(^1)</td>
</tr>
<tr>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
</tr>
<tr>
<td>d(^4)s(^2)</td>
<td>d(^5)s(^2)</td>
<td>d(^5)s(^2)</td>
<td>d(^5)s(^2)</td>
</tr>
</tbody>
</table>

**Stabilization:**

Activation:

- Stabilized cation
- Benzylic cation/anion/radical
- \( \eta^5 \)-diienyl complex
- \( \eta^6 \)-diienyl complex
- Ligand insertion
- Nu:

Protection:

- Protecting group for alkene
- Protecting group for alkene

Geometry:

- Reaction face
- Blocked face
- Distortion
- Break the symmetry

**Organization of this group meeting**

Included: \( \eta^5 \)-complex (Os, Re, W, Mo); \( \eta^6 \)-complex (Fe); \( \eta^5 \)-complex (Cr, Fe, Ru, Rh, Mo, Mn)

Not included: Activation of alkene/alkyne, allylic compounds, etc.

**Part I**

- early transition metals

**Part II**

- late transition metals

**Part III**

- summary

References:


Related context: metal-carbonyl complex; dearomatization.
**η-Complex I: Activation of Diene and Arene**

**η² and η-complex of iron: preparation and properties**

**Formation of η²-Fe complex**

from 1,3-diene

\[
Fe_2(CO)_9 \rightleftharpoons Fe(CO)_4 + Fe(CO)_5
\]

R¹ \ R² \ R³

CO

Fe(CO)₃R³

from 1,4-diene (2 steps from arene)

R¹ \ R² \ R³

regioselectivity?

regio-mixtures

A. J. Birch* JCS Perkin 1, 1973, 1802

from 1,3-diene

R¹ \ R² \ R³

Fe(CO)₃

A. J. Birch* JCS A, 1989, 332

a carbonyl insertion/elimination process

**Formation of η²-Fe complex**

from iron-diene complex - hydride abstraction (most used)

R¹ \ R² \ R³

oxidant

ambient temp.

oxidants: Ph₃C⁺X⁻

L = CO/PR₃/P(OR)₃, etc.

MeO₂C

TrBF₄

decomplexation

S. V. Ley* JCS Perkin 1, 1997, 1125

**Decomplexation**

oxidative decomplexation: CuII/CAN/DDQ/N-oxide/I₂/MnO₂ etc.

photolysis in existence of other ligands.

carbonyl insertion

**Reactions of η²-Fe complex**

stabilizing the cyclobutadiene

CO on iron involved nucleophilic attack

R. Pettit* JACS, 1965, 3293

M. L. Snapper* JACS, 2007, 486

M. L. Semmelhack* JACS, 1983, 2497

R L Li normally attack CO on iron

42-100%

K. Narasaka* Chem.Lett, 1997, 4095
**η^-Complex I: Activation of Diene and Arene**

### η^2 and η^3-complex of iron: preparation and properties

**Reactions of η^2-Fe complex**

- **diene-complex for stereocontrol - limited to concerted reaction**
  - dihydroxylation
  - facile hydration

- **difunctionalization**
  - (±)-trichodermol
  - ~14 steps

**Reactions of η^3-Fe complex**

- **nucleophilic addition**
  - vicinal quaternary centers possible

- **Nu scope:** enolate, ArLi, R Cu, R_2 CuLi, RNH_2, alkyn-Li, e-rich Ar...

### Catalytic ene reaction

- trans- Fe(0): Fe(acac)_3 with DIBAL
- *rationalization: CH_3OBn tends to lie on pseudoequatorial position

### Reaction with alkene - limited to intramolecular system

- **η^2-Fe complex**
  - nucleophilic addition
  - CO, Bu_2O

- **η^3-Fe complex**
  - reaction with alkene - limited to intramolecular system

- **(OC)Fe**
  - **O**
  - **(OC)Fe**
  - **Me**
  - **H**
  - **Fe**(OC)_3
  - **Ph**
  - **(OC)Fe**
  - **Me**
  - **H**
  - **Nu**
  - **(OC)Fe**
  - **Me**
  - **O2N**
  - **Fe**(OC)_3
  - **Me**
  - **H**
  - **H**
  - **MeO_2C**
  - **Fe**(OC)_3
  - **Me**
  - **H**
  - **O**

### Other Reactions

- **Facile hydration**
  - KHCO_3/H_2O
  - 95%

- **Difunctionalization**
  - (-)-methylshikimate
  - A. J. Birch JOC, 1988, 278

- **Diene-complex for stereocontrol**

**A.J. Pearson** JACS, 1984, 6065

**A.J. Pearson** JOC, 1989, 4663

**A. J. Pearson** JACS, 2003, 638

**JACS, 1987, 2200**

**TL, 1991, 635**

**TA, 1998, 3781**

**A. J. Pearson** JACS, 1984, 6065

**A.J. Pearson** JACS, 2003, 638
**η-Complex I: Activation of Diene and Arene**

### Preparation and general properties

Cr-arene complex can be prepared by refluxing Cr(CO)₆ in solvents like nBu₂O/THF.

#### Rules for coordination:
1. Sensitive to steric effect.
2. Possess directing effect.
3. Prefer e-rich arene.

#### Other ways:
- Photolysis
- Other Cr source: Cr(CO)₃L₃, L could be NH₃/MeCN/pyr/cod/PR₃, etc.

### Other Mn-arene complex

Mn(OC)₃MeO, MeO

#### Mn-based complexes:
- **Mn(CO)₅**
- **Mn-Cp**

#### Reaction of metal-arene complex

**Direct lithiation**

Classical directing effect: CONR₂ > SO₂NR₂ > NHCOR > CH₂NR₂ > OMe > NMe₂ ~ F

After coordination: F > CONR₂ > NHCOR > CH₂NR₂ > OMe > CH₂OR > NMe₂

**SNAr reaction** - facile way to form C(sp²)-X bond

**Catalytic S_NAr with RhCp complex** - the only example

### Decomplexation

For Cr: I₂ enough for decomplexation, Ph₃C⁺ not.

For Fe: really hard, using DDQ/CAN/Jones, I₂ doesn't work.

For Ru: hv/sunlight in MeCN.

### Ligand exchange

- **Cr(CO)₃** → **Cr(CO)₃N**
- **Cr(CO)₃** → **Cr(CO)₃HO**
- **Cr(CO)₃** → **Cr(CO)₃F**

Major ~90%, Minor ~10%

---

**References:**
- JACS, 1982, 171
- TL, 1988, 171
- TL, 1992, 4049
- R. P. Houghton*, JCS Perkin1, 1984, 925
- A. P. J. J. Corpus, JOC, 1999, 1819
η-Complex I: Activation of Diene and Arene

Reaction of metal-arene complex
addition/oxidation - methods for substituted arene

regioselectivity (arene and heterocycle)

- meta-sub for \( R = \text{EDG} \)
- ortho-sub for \( R = \text{EWG} \)

\[
\begin{align*}
    \text{OMe} & \quad \text{Cr(CO)}_3 \\
    \text{Me} & \quad \text{CN} \\
\end{align*}
\]

nucleophile scope when \([M] = \text{Cr(CO)}_3\)
no rxn:

\[
\begin{align*}
    \text{O} & \quad \text{Li} \\
    \text{Me} & \quad \text{MgBr} \\
\end{align*}
\]
only active lithium reagents work

\[
\begin{align*}
    \text{Me}_2\text{CuLi} & \quad \text{Me}-\text{MgBr} \\
\end{align*}
\]

nucleophile scope when \([M] = \text{Mn(CO)}_3^+\)

\[
\begin{align*}
    \text{O} & \quad \text{Li} \\
\end{align*}
\]

nucleophile scope when \([M] = \text{CpRu}^+/\text{FeCp}^+\)

\[
\begin{align*}
    \text{O} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

Anisole as substrate

- 50-86% yield
  - dr > 20:1

\[
\begin{align*}
    \text{Me} & \quad \text{CN} \\
\end{align*}
\]

example

- L = chiral phosphine, low ee.

\[
\begin{align*}
    \text{O} & \quad \text{Me} \\
\end{align*}
\]

side reaction - 1,5-H-shift (stepwise):

\[
\begin{align*}
    \text{TBAF} & \quad \text{DDQ} \\
\end{align*}
\]

chiral auxiliary

\[
\begin{align*}
    \text{Ph} & \quad \text{OMe} \\
\end{align*}
\]

chiral base

\[
\begin{align*}
    \text{Ph} & \quad \text{OMe} \\
\end{align*}
\]

meta-subs for \( R = \text{EDG} \)

- ortho-subs for \( R = \text{EWG} \)

- C4 functionalization without directing?

\[
\begin{align*}
    \text{LiR} & \quad \text{I}_2 \\
\end{align*}
\]

\[
\begin{align*}
    \text{Me} & \quad \text{CN} \\
\end{align*}
\]

dearomatization

\[
\begin{align*}
    \text{OMe} & \quad \text{Me} \\
\end{align*}
\]

\[
\begin{align*}
    \text{Me} & \quad \text{CN} \\
\end{align*}
\]

\[
\begin{align*}
    \text{Me} & \quad \text{CN} \\
\end{align*}
\]
Reaction of metal-arene complex
asymmetric dearomatization
chiral base for asymmetric synthesis

1. nBuLi
2. CuCl, BrR
then TMSCI, HMPA
hv, air
H3O+

45%-53%

(+)-Ptilocaulin

then
TMSCI, HMPA

acetone, air

77%

73%

side rxn: Nu attack on ligands

accelerating Pd catalyzed cross coupling

atropisomers for aryl-aryl coupling

enantiopure

SynLett, 1995, 1040
**Junchen Tang**  
**Baran Lab Group Meeting**  
**02/08/2020**

### η-Complex I: Activation of Diene and Arene

#### Preparation and Properties

$[\text{dihapto-complex}]\, ([\text{Os}^{II}/\text{Re}(I)/\text{W}(0))]$

**Preparation and properties**

**NH$_3$**

- **E$_{1/2}$ ~ -0.8 V**
- **L = $\sigma$-donor (H$_2$O/pyr/Cl)**
- **Selectivity**

**Reactions of Os(II)-arene complex - based on effect of aromatic substrate**

- **Phenol as substrate**
- **Application in steroid chemistry**

**Anisole as substrate**

**Interesting examples for type 1**

**Type 2**

**Tandem cyclization based on type 1 and type 2**

**31% from anisole**

**From benzylic alcohol**

**D. W. Harman** JACS, 1999, 6199
Reactions of Os(II)-arene complex - based on effect of aromatic substrate
aniline as substrate - synthon of γ-cyclohexenone enolate

hydrogenation - all cis

Reactions of Re(I)-arene complex - more electron rich
**Reactions of W(0)-arene complex**

*preparation of W(0)-arene complex*

\[ \text{Br} \rightarrow \text{W(NO)} \rightarrow \text{PMe}_3 \rightarrow \text{Cu(OTf)}_2 \rightarrow \text{decomplexation} \]

\[ E_{1/2} = -0.13 \text{ V} \]

**known complexes**

all mixtures are:

- air stable and mixture of diastereoisomer

**Reactions of Mo(0)-arene complex**

Mo(0) possesses a weaker metal-arene bond

**η-Complex I: Activation of Diene and Arene**
Summary

Characters of Cr(0)/Mn(I)/Fe(II)/Ru/Rh arene complexes

Characters of Fe-diene/dienyl complexes

Characters of Os(II)/Re(I)/W(0)/Mo(0) dihapto complexes