Cyclopentadienyl Complexes

Sandwich compounds
Structures
• Accidental discovery!
• Two groups in 1951
  – (a) Miller and
  – (b) Pauson and Kealy
• Properties don’t match the properties of the expected cpd nor the properties of the structure proposed by Pauson and co..
Proposed structures of Wilkinson / Woodward and Fischer

Sandwich Structure

Double cone

Diamagnetism
Chemical behaviour
Xray analysis
• Fischer and Wilkinson enter a “historic race” to make the Periodic Table of metallocenes!

• It ends in a Nobel Prize in 1973 for both!!
• Cp is $[C_5H_5]^-$: \[ \textcolor{red}{4n+2} \quad n=1 \]

• Pentamethyl cyclopentadienyl group is also popular $[C_5\text{Me}_5]^-$ = Cp*

• It is essentially an anionic group $R^-$ but has the ability to coordinate multiple (5) C atoms to the metal.
  - Allyl had 3 C atoms
  - Cp has 5 C atoms

A line in the centre implies
All 5 C atoms are bonded!
Preparation of metallocenes

Aromatic anion

Aromatic anion

CH₂⁻
Transmetallation

- TlCp is easily made and can be stored. So it is considered a convenient source of cyclopentadienyl complexes!
- Tl is toxic and so should be handled with care!

- CpMgBr and CpLi can be used as well.
- CpLi can be made from CpH and Li sand.
Direct Reaction

- Ferrocene can be made from FeCl$_3$ and Fe powder with Et$_3$N and CpH under reflux conditions.
- The amine removes the HCl that is generated!
- Fe reduces the Fe(III) to Fe(II)

Alt: Fe and Et$_3$N·HCl at a higher temp.

Always, CpH is freshly prepared from cracking C$_{10}$H$_{10}$ (CpH)$_2$
Bonding

\[ \text{4s} \]

\[ \text{4p}_x \]
\[ \text{3dz}^2 \]

\[ \text{3dyz} \]
\[ \text{3dxz} \]

\[ \text{Dxy, } dx^2-y^2, \]

\[ \text{4py} \]
Energy Levels
Cyclopentadienyl MO
Mix and Match
Remember there are two Cp rings!
MO Energy diagram of Ferrocene
Electron Count! Iron is the best!
## Properties!

<table>
<thead>
<tr>
<th>Metallocene</th>
<th>Color</th>
<th>upe</th>
<th>Exper. B.M</th>
<th>Expected B.M</th>
<th>Interplanar distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCp₂</td>
<td>Purple</td>
<td>3</td>
<td>3.84</td>
<td>3.87</td>
<td></td>
</tr>
<tr>
<td>CrCp₂</td>
<td>Red</td>
<td>2</td>
<td>3.2</td>
<td>2.83</td>
<td>361</td>
</tr>
<tr>
<td>MnCp₂</td>
<td>Amber</td>
<td>5</td>
<td>5.81</td>
<td>5.92</td>
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<tr>
<td>FeCp₂</td>
<td>Orange</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
<td>332 (dash)</td>
</tr>
<tr>
<td>CoCp₂</td>
<td>Black</td>
<td>1</td>
<td>1.76</td>
<td>1.73</td>
<td>340 (dash)</td>
</tr>
<tr>
<td>NiCp₂</td>
<td>green</td>
<td>2</td>
<td>2.86</td>
<td>2.83</td>
<td>360 (dash)</td>
</tr>
</tbody>
</table>
Ferrocene: Most stable, 300+ °C
Sublimes and is used for making carbon nanotubes!
Bond distance is shortest for Fe (18 electron system)
Magnetic properties are predictable!!

\[ \text{Co(Cp)₂}^+ \] should be a very stable system! It is

\[ \text{Mn(Cp)₂}^- \] is not as stable as it should be because, Cp- is lost!
Look at the MO diagram.
• Bonding mode should depend on the electron count!

Many of the $M^{2+}$ structures are slipped from the centre

• But most structures are fluxional.
Importantly, the Cp is a ligand which can adjust the electron donation. By sliding the metal along the line shown by the arrow.
• Ferrocenes can be oxidized and protonated.
• Fe(Cp)\(_2\) is oxidized with AgBF\(_4\) to produce a [Fe(Cp)\(_2\)]\(^+\) species. It leaves behind silver metal.
• H\(^+\) can be added to ferrocene to give [Fe(Cp)\(_2\)]H\(^+\)
Aromaticity

- Acetyl chloride / AlCl₃
Aromaticity

- Lithiation
Group 4 Transition Metal Sandwich Complexes: Still Fresh after Almost 60 Years†

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\[(C_5H_5)_2\text{Ti}\] The “mystery-cene”

1956 Wilkinson group reports formation of bright green paramagnetic solid. It transforms to a brown solid spontaneously!

Much later, Watt, Baye and Drummond said that titanocene was diamagnetic and had a molecular weight of 346! Twice what is expected for \[(C_5H_5)_2\text{Ti}\]
14 years after Wilkinson, in 1970, a strong band at 1230 cm\(^{-1}\) is identified as a Ti-H bond in the titanocene. Britzinger and Bercaw suggest the structure: 
\[((\text{C}_5\text{H}_5)\text{C}_5\text{H}_4\text{TiH})_2\]

20 years later, 1976: LT NMR spectrum of the compound confirms the presence of Ti-H bond

Finally in 1992, the crystal structure of titanocene is confirmed. It is not what Wilkinson proposed, it was a dimer with a Ti-H bridge.
X-ray structure of titanocene
Arene Sandwich Complexes
Hein (1919) mixed ArMgX and Metal CrCl$_3$ to make Cr(Ar)$_3$ and accidentally made a compound that analyzed for Cr(ArH)$_2$.
More rational approach
Fischer Hafner (1955) synthesis

• Mix Al (powder) + 3 CrCl$_3$ + 6ArH
• Forms 2 [(ArH)$_2$Cr $]^+$ + AlCl$_4^-$
• What is obtained is the Cr(+1) complex !!
• Used AlCl$_3$ and Al as catalysts! Later used Na$_2$S$_2$O$_8$ as a reductant to generate the Cr(0) species in good yield
Limitations of F-H synthesis

- Does not work with all metals

\[ MX_n + Al + AlCl_3 \]
Limits on the aromatic rings

• Ar-X where X = any group with a lone pair of electrons

• The lone pair complexes with AlCl$_3$ and stops the reaction.
Cyclotrimerization of alkynes

- Me-C≡C-Me is trimerized with some metals in a template synthesis to give an arene:

\[
(C_6H_5)_3Cr(THF)_3 + \text{Me-C≡C-Me} \rightarrow \frac{1}{2} \text{Cr(C}_{12}H_{16})_3
\]

1) THF, 20 °C
2) H₂O, O₂
Reduction and substitution

- $\text{MCl}_n(\text{THF})_{6-n} + n\text{LiC}_{10}\text{H}_8$

- This METHOD WORKS for Cr, Mo, and V
Surprise! Surprise!

\[
\text{ZrCl}_4(\text{THF})_2 + 4\text{LiC}_{10}\text{H}_8
\]
Metal atom ligand vapor co-condensation

- Works even when the electron count is bad Cr, Ti, Zr, Hf, Nb, Y, Gd,
- Eg. Ti(g) + 2 C₆H₆

\[ \text{Ti (g) + benzene} \xrightarrow{\text{vapor}} \text{LN}_2 \xrightarrow{1) \text{CC, -196 }^\circ\text{C}} \xrightarrow{2) \text{warm up}} \text{product} \]
Schematic Representation of Metal Vapor Synthesis

Ligand

High Vacuum

high current

“\text{M} + \text{ArH} \rightarrow \text{LN}_2

Liquid N$_2$
coling
Metal atom ligand vapor co-condensation CC

- Coordinating arenes: Chlorobenzene, dimethylamino benzene

\[
\text{Ti (g) + Chlorobenzene} \rightarrow \text{1) CC, -196}^\circ\text{C} \rightarrow \text{2) warm up}
\]
Metal atom ligand vapor co-condensation

- Works even with sterically inaccessible phenyl groups: Biphenyl, \textit{tri-}t-butylbenzene
Metal prefers aromatic centers!
Bonding and Structure
MO treatment
Bonding

- Dxy, dx²-y²,
- 3dxy
- 3dxy
- 4py
- 4px
- 3dxz
- 3dz²
- 4p₂

Metal along the z axis!
Frost’s Energy level diagram
Benzene MO
Top view of MO’s (down z axis)

- Three nodes
- Two nodal planes
- One nodal plane
- Zero nodes except for plane of benzene ring
Remember there are two arene rings!
Mix and Match

px
pz
dz²
dxz
MO Interaction diagram of bis-benzene chromium (Eclipsed Geometry)

- b2g
- b1u
- e2g
- e2u
- e1g
- e1u
- a1g
- a2u
- a1g
- dx^2-y^2, dxy
- dz^2
- dyz, dxz
- 3d
- 4s
- 4p
Electron Count!
Chromium is the Best!

b2g  b1u

e2g  e2u
e1g  e1u

a1g  a2u

3d  4s  4p
dX^2-Y^2, dXY
dyz, dxz
dz^2
• Cr bears a +Ve charge of 0.7 e
• Benzene bears -0.35 e
• Attributed to Cr transferring electrons through $\delta$ bonding

• Bond energy of bis benzene chromium is 170 kJ mol$^{-1}$
• Ferrocene has a value of 260 kJ mol$^{-1}$

• Look at some structures of these molecules!
• Structures of a few arene complexes!
## Properties!

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</tr>
</thead>
<tbody>
<tr>
<td>$(\text{C}_6\text{H}_6)_2\text{Ti}$</td>
<td>red</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_6)_2\text{V}$</td>
<td>Dark Red</td>
<td>1</td>
<td>1.68</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_6)_2\text{Cr}$</td>
<td>brown</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>322</td>
</tr>
<tr>
<td>$(\text{C}_6\text{Me}_6)_2\text{Fe}$</td>
<td></td>
<td>2</td>
<td>3.08</td>
<td>2.83</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_6\text{Me}_6)_2\text{Co}$</td>
<td>Black</td>
<td>1</td>
<td>1.86</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>$(\text{C}_6\text{Me}_6)_2\text{Ni}$</td>
<td></td>
<td>2</td>
<td>3.00</td>
<td>2.83</td>
<td></td>
</tr>
</tbody>
</table>
Reactions of arene complexes
Is the aromaticity retained?

\[ \text{Cr} \quad \text{nBuLi / TMEDA} \quad \text{Cr} \]

\[ \text{AlCl}_3 + \text{CH}_3\text{COCl} \quad \rightarrow \quad \text{CrCl}_3 \]

End up with CrCl₃
Ligand exchange

Benzene ring on $(C_6H_6)_2Cr$

is not labile

but annelated

rings exchange
\( \eta^4 \) complexes

-\( \eta^4 \) and \( \eta^6 \)

1. Ru(0) - 8
   1Ar - 6

2. 2H\(^-\) units are added

3. \( \eta^4 \) and \( \eta^6 \)
Neutral complexes can be made by reducing the Ru$^{2+}$ cation which is a 18 electron complex with Na/ NH$_3$

X-ray reveals complete bond localization and bending, NMR shows a dynamic structure!
Hetero-Sandwiches
Electron Counting

• CpMC₆H₆ what would be M?
  – 6 electrons from the arene
  – 5 from the Cp (neutral method)
  – M has to give 7 electrons! M=Mn

• CBDMC₆H₆ What should be M
  – 4 from Cyclobutadiene CBD
  – 6 from Arene
  – 8 from metal! M=Fe
Cyclopropenyl rings

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Br} & \quad \text{Ni(CO)}_4 \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]
Cyclobutadiene sandwich!

1. Li metal
2. NiBr$_2$
Cycloheptatrienyl

\[
\begin{align*}
C_5H_5MCl_4 + C_7H_8 & \xrightarrow{\text{Mg / THF}} \quad \text{5-Coordinate complex}\quad \text{M = V, Nb, Ta} \\
MCl_4 + C_7H_8 & \xrightarrow{\text{iPrMgBr}} \quad \text{2BF}_4^-
\end{align*}
\]
Beyond 7 it is difficult for d group metal ions but lanthanides and actinides like U can form complexes!

\[ [\text{C}_8\text{H}_8 ]^{2-} + \text{UCl}_4 \rightarrow \text{U} \text{C}_8\text{H}_8 \]
Summary

• 18 electron rule holds good!

• Possible to have some reactions of the benzene ring

• One can make hetero sandwiches!
Sandwich Complexes

Half, Bent, Open and Multi
The Possible Existence of Transition-metal Complexes of cyclo Butadiene.

By

H. C. LONGUET-HIGGINS and L. E. ORGEL.

• “The possibility that the unstable cyclobutadiene molecule can be stabilised by combination with a suitable transition-metal ion is investigated by use of molecular-orbital theory.”

• “complexes of the type MnX_2(C_4H_4), where M is nickel, palladium, or platinum and X is a univalent ligand, may be stable,”

• “Ni(CN)_2(C_4H_4) is an intermediate in the Reppe synthesis of cyclooctatetraene.”
Synthesis of 4 membered rings...

\[
\text{Sn} + \text{NiBr}_2 \rightarrow \left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \\ \text{Ph} \\ \text{NiBr}_2 \\ \text{Ph} \\ \text{Ph} \end{array} \right]_2
\]

\[
\text{Cl} + \text{Fe}_{2}\text{(CO)}_9 \rightarrow \text{OC} \text{Fe} \text{CO} + \text{FeCl}_2
\]
Crystal structure of a CBD complex

Synthetic routes

\[(\text{Fe(CO)}_5) + \text{Ph} \rightarrow \text{Fe(0)} \text{Ph} \text{Ph} \text{Ph} \text{Ph} \text{OC} \text{OC} \text{CO} \]
Reactivity
Aromatic Behavior!
Other half sandwich complexes

\[ \text{Fe(CO)}_5 + \text{C}_5\text{H}_6 \rightarrow \text{Fe}^{(\text{II})} \]

\[ \text{OC} - \text{H} - \text{H} - \text{CO} \]

\[ 3 \times 2 = 6 \text{ ionic} \]

\[ 2 \text{ Fe}^{(\text{II})} \rightarrow \text{Fe} - \text{Fe} \]

\[ \text{OC} - \text{CO} \]
Mn - Mn $\xrightarrow{\text{Na/Hg}}$ 

\[ \begin{array}{c}
\text{Fe} \\
\text{OC} \\
\text{CO} \\
\text{Fe} \\
\text{OC} \\
\text{CO}
\end{array} \xrightarrow{\text{Na/Hg}} 2 \left[ \begin{array}{c}
\text{Fe} \\
\text{OC} \\
\text{CO}
\end{array} \right]^{-} \]

\[ \text{Na}^{+} \]

RX

\[ \text{Fe} \]

\[ \begin{array}{c}
\text{OC} \\
\text{R} \\
\text{CO}
\end{array} \xrightarrow{\text{-NaX}} \]

\[ \text{Fe} \]
\[
\text{Mn} + 3 \text{CO, 200 bar} \rightarrow \text{Mn}_\text{Cycamtrene} \]

15 h 100 C
\[
\text{[RhCl(RhClCO)OC] + 2 TlCp} \rightarrow 2 \text{[RhOC(CO)OC]} + 2 \text{TlCl}
\]
CpTO!
The organic metal oxide!
Arene half sandwiches
Templated synthesis of Piano stool complexes

$$\text{AlR}_3 + \text{CrCl}_3 + \text{CO} \rightarrow \text{Piano stool complex}$$
$\eta^7$ complexes are possible!

$\text{Mo(CO)}_6 + \text{C}_7\text{H}_8 \xrightarrow{\text{Ethyl cyclohexane}} \text{[Ph}_3\text{C}^+][\text{BF}_4^-]

\begin{align*}
\text{Mo} & \quad \text{CO} \\
\text{OC} & \quad \text{CO} \\
\text{OC} & \quad \text{CO}
\end{align*}

+ [ ]

\[ \phi_3\text{CH} \]

\[ \text{BF}_4^- \]
C$_3$H$_3$ half sandwiches

\[ \text{Ni(CO)$_4$} \rightarrow \text{Pyridine} \]

\[ 3 \times \text{C}_3\text{H}_3 = 3 \]
\[ 2 \times 2 \times \text{Py} = 4 \]
\[ \text{Br} = \frac{1}{10} \]
\[ \text{Ni} = 18 \]
$\eta^2$ arene complexes

1.51 angstroms

1.33

1.36

1.48

Pt

PPh$_3$

Ph$_3$P

16 v.e.
Mixed Sandwiches to half sandwiches!
Bent Metalloccenes

dry, dry and d_{2}^2 ← empty

Cp_{4} Ti

\[ \text{Fe} \]

\[ \text{Zr} \]

\[ \text{Mg} \]

H

H

H

H
Bent titanocenes

Catalysis, fluxional behaviour
Open Sandwiches

• Acyclic version of cp- is $C_5H_7^-$

(η⁵-Pentadienyl)-tris(trimethylphosphine)-iron tetrafluoroborate
GEVDOA from CSDS
Synthesis of Open Metallocene

Synthesized in 1988 by Ernst
Structure of Open Metallolocene

Ruthenium analog of the open metallocene

Ruthenium vs. Iron
What is the difference?
Trimethylenemethane

\[ \text{Cl} \quad \text{Fe}_2(\text{CO})_9 \quad \text{or Na}_2\text{Fe}(\text{CO})_4 \]

\[ \text{Fe}_2(\text{CO})_9 \]
Structure of TMM-Fe(CO)$_3$

- Note Inverted umbrella structure
- Staggered orientation of tmm!
Exotic Sandwiches

• Hetero atom containing “bread”
  – C-H is converted to N
  – C-H is replaced by P
  – CH- is replaced by S!
• Thiophene
CC with pyridine!

Cr (g) + Me₃SiN·SiMe₃ → 1) CC, -196 °C → 2) warm up → Me₃SiCrN·SiMe₃

O₂ → benzene + H₂O → Reducing agent
$P_5$ Sandwich!

$(\eta^5\text{-Ethyltetramethyl-cyclopentadienyl})-(h^5\text{-cyclopentaphosphorus})\text{-iron}$

GEVRUU from CSDS
Multimetal Sandwich

\[ \text{Ni} \quad \xrightarrow{\text{C}_8\text{H}_8} \quad \text{Ni} \]

-40 deg. C
Multidecker Sandwiches
• What is the use of making sandwich complexes?

• Observed in the mass spectrometer and later synthesized.
Inverse Sandwich
COT as an inverse sandwich synthon

YUHRUO from CSDS
Inverse and Exotic!

(μ²-(η¹⁰-Cyclopentaphosphorus))-bis(η⁵-pentamethyl-cyclopentadienyl)-di-chromium DOMYAF from CSDS
Summary

• The sky is the limit!

• 18 electron rule is a great guiding principle

• The complexes are useful as catalysts as the “bread” is flexible and can change hapticity!
Reactivity Changes of Coordinated Ligands
Modified Ligand Reactivity

General features of M-olefin bonding.

- Removal of electron density from olefin $\pi$ by metal.
- Population of the $\pi^*$ orbital of the olefin/polyene by metal 'd' electrons.
- 1. Nucleophilic addition enhanced / Electrophilic reactions suppressed
- 2. Photochemical type of reactivity.
Oxidation of Dienes with Pd

\[
Pd(0) + O_2 + HOAC \longrightarrow Pd(OAC)_2 + H_2O
\]

Involves a nucleophilic attack on the coordinated olefin!!
Oxidation of alkenes at the allylic position

\[ \text{PdCl}_2 \] + \[ \text{H} \] \rightarrow \begin{array}{c} \text{Pd} \\ \text{Cl} \end{array} + \begin{array}{c} \text{Pd} \\ \text{Cl} \end{array} + \text{HCl} \]

\[ \eta^3 \text{Nu} \]

\[ L = \text{PPh}_3 \]

\[ \text{NuH} \]

\[ + \text{HCl} \]
Allylic complex is a “chem”eleon

Fe allyl complexes behaved as allyl anion

Ni(0) / Pd(0) based coupling is almost like allyl radical coupling

Ru(IV) allyl complexes behaved as if they were allyl cations

CpFe(CO)₂CH₂-CH=CH₂
Modified Ligand Reactivity

General features of M-olefin bonding.

• Unavailability for usual reactions common for double bonds.
• Loss of conjugation in a polyene.

3. Protection from hydrogenation or Enhanced reactivity of other D.B.

4. Alternate reactions due to 1,2,3.
Protection of an alkyne!
Different Reactivity for the arene

Nucleophilic Substitution

Increased Acidity

Increased Hydrolysis

Steric hindrance
The source of anchimeric assistance
Reduced Nucleophilic Attack!

- Cr bears a +Ve charge of 0.7 e
- Benzene bears -0.35 e
- Attributed to Cr transferring electrons through $\delta$ bonding

Dilithio and Monolithio Cpds are formed
Enhancing nucleophilic attack
Metal effect
Half Sandwich complexes
Ligand effect
Nucleophilic substitution

\[
\text{F} \quad \text{R}_2\text{NH} \quad \text{NR}_2
\]

\[
\text{Cr} \quad \text{H}^+ \quad \text{F}^-
\]
Nucleophilic substitution

Two step addition elimination

Martin Semmelhack
Nucleophilic substitution

$\text{Cr} \hspace{1cm} \text{H}$

$\text{R}^-$

$\text{Cr}^{-}$

$\text{I}_2$ oxidation

X-ray crystallography of the intermediate carried out!
Different Reactivity for the arene

Steric hindrance

Nucleophilic Substitution

Increased Acidity

Increased Hydrolysis

Cr
\[
\text{Br(CH}_2\text{)}_3\text{Br} 
\rightarrow \text{NaH / DMF} 
\rightarrow \text{CH}_2\text{COOMe} 
\rightarrow \text{Ar} - \text{CH} - \text{COOMe} 
\rightarrow \text{COOMe} 
\]
Cr(CO)$_6$ ▶ racemic mixture

\[ \text{(OC)$_3$Cr} \]

\[ \text{R(+)} \text{ isomer separated by chromatography} \]

Chiral Indanone!
Reduced aromaticity

Reduction!
Makes it 18 ve species
Electrophilicity reactivity index
• Nucleophilic attack occurs preferentially at even coordinated polyenes

• Nucleophilic addition to open coordinated polyenes is preferred over closed polyene ligands

• In the case of even polyenes, nucleophilic attack always occurs at the terminal carbon atom.
DMG rules

Even and odd polyenes are present. Rule 1 says that the even polyene will be attacked by the nucleophile. Rule 2 says it will be the open polyene.
• For odd polyenyls, attack at the terminal carbon atom occurs only if the metal is a relatively strong electron withdrawing fragment
DMG rules

Only odd polyenes are present. Rule 3 says that the odd open polyene will be attacked by the nucleophile. Rule 4 says it will be at the center position.
DMG rules

Odd polyenes are present. Open is to be attacked but it is attacked on the terminal
Altered Reactivity of coordinated ligands
How does the reactivity change?

a. Change in selectivity.
b. Rate of reaction decreases.
Asymmetric Catalysis
Summary

• Altered reactivity: primarily enhanced and directed nucleophilic attacks!
• Metal oxidation state makes a difference
• Ligands like CO enhance reactivity \(\textit{NO}\)
• Protection of triple / double bonds
• Reduction of aromaticity / conjugation
• Steric effects that introduce “facial” selectivity