Organometallic Chemistry – Solutions

Give the denticity and hapticity of the ligands in the following complexes:

Just because this complex is drawn with the iron centre bound to two distinct alkene units doesn’t mean this ligand binds twice through two $\eta^2$ centres, it binds once through one $\eta^4$ centre.

Provide electron-counts (using both the ionic and covalent methods) for the following complexes:

I’ve always preferred the ionic method but I suppose I should probably do this properly…
Note that both methods are the same here. No non-octet binding atoms.
This is ferrocene. Ferrocene's cool. Cyclopentadienyl (cp) ligands can be quite difficult to understand. The look like this:

They're made from cyclopentadiene:

Why did I set this one again?
Pretty complicated here – still 18 electrons though. You might be noticing a pattern…

Why might this be?

It's the top left of the d-block therefore quite electropositive, therefore complexes tend to be very ionic in character.

Comment on the stability of all the complexes you've electron-counted so far in this worksheet.

Both $16e^- \rightarrow$ square planar therefore stable

Everything else – not square planar; $18e^-$, hence stable too!
Just looking at the complexes themselves, you should convince yourself that the
electron counts, co-ordination numbers and rhodium oxidation states are all correct.

Looking first at how we can determine the ox. state.
Assume 16 electrons: (square planar)

\[
\begin{align*}
\text{Ph}_3\text{P} & \hspace{1em} \text{Rh} \hspace{1em} \text{Cl} \\
\text{Ph}_3\text{P} & \hspace{1em} \text{PPh}_3
\end{align*}
\]

With the ionic method each ligand here will have contributed \textbf{two} electrons

Therefore 16 - 8 → 8 electrons left
Rhodium configuration: \text{s}^2\text{d}^7 → 9 electrons
Therefore Rh must have a charge here of 1+
Therefore Rh (I)

To check, let’s do a covalent electron count:

\[
\begin{align*}
\text{Rh}^0: \text{s}^2\text{d}^7 - 9 \text{ electrons} \\
3 \times \text{PPh}_3 & \hspace{1em} 6 \text{ electrons} \\
\text{Cl} & \hspace{1em} \text{-1 electron}
\end{align*}
\]

\[= 16 \text{ electrons overall} \]

Co-ordination number → 4 (4 ligands, innit)

\[
\begin{align*}
\text{H} & \hspace{1em} \text{PPh}_3 \\
\text{Ph}_3\text{P} & \hspace{1em} \text{Rh} \hspace{1em} \text{H} \\
\text{Ph}_3\text{P} & \hspace{1em} \text{Cl}
\end{align*}
\]

Ox. state ?
Octohedral - therefore 18 electrons assumed
ionically - 6 ligands - 12 electrons

\[18 - 12 = 6 \text{ electrons}; \text{ Rh in P.T. has s}^2\text{d}^7 = 9 \text{ electrons} \]

\[9 - 6 = 3; \text{ therefore must be Rh(III)} \]
electron counting (again, covalently, to check this makes sense)

C.N. = 6; 6 ligands

Convinced yourself again that the co-ordination numbers, electron counts and metal oxidation states given are correct.

By determining the co-ordination number, electron-count and metal oxidation state, convince yourself this is true for the following equilibrium:
Therefore CN → -1; e⁻ → -2; ox. state: no change

(not doing the full e⁻ count for you, sorry)

Determine them for yourself.

\[
\begin{align*}
\text{Assume 18 electrons} & & \text{PPh₃ neutral donor} \\
\text{6 ligands - 12 electrons} & & \text{therefore electron count must be 18-2} \\
\text{therefore Rh(III)} & & \text{(nothing else has changed)} \\
\text{Electron count - 18 electrons} & & \text{Rh(III) - d}^6 \text{ - 6 elec.} \\
\text{CN = 6} & & \text{2 x PPh₃ - 4 elec.} \\
\end{align*}
\]

Therefore the rules:

\text{ox. state → no change, CN → -1, e⁻ count → -2}
Work through the catalytic cycles at the end of the catalysis resource of this series and:

- Assign co-ordination numbers, metal oxidation states and electron counts for all the individual steps.
- Comment on the reactivity of each individual organometallic complexes - do you expect them to be reasonably stable or highly reactive? In what direction do you expect the equilibrium to lie based on this?
- Can you identify some other geometries certain complexes might exist in? Would these be more or less stable? Why?
- Use the knowledge you’ve learnt in this work sheet to comment on the feasibility of any alternative catalytic cycles you might have proposed.

I’m going to try an answer all of these (except 4, which I won’t address) as one single answer.
Example 1:

1 = 16 e⁻ square planar; stable
2 = 18 e⁻ octahedral; stable
3 = 16 e⁻ square-based pyramid; unstable
4 = 18 e⁻ octahedral; stable
5 = 16 e⁻ square-based pyramid; unstable
6 = 18 e⁻ octahedral; stable
Therefore 3 and 5 are most unstable. Equilibrium arrows will lie away from these and towards 2, 4 and 6. 3 and 5 could also exist in trigonal bipyramidal configuration.

Example 2:

bridged complex exists in equilibrium with unbridged form (this is easier to electron count)

<table>
<thead>
<tr>
<th>Ionic</th>
<th>Covalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co^{2+}: s^1d^7 - 8 electrons</td>
<td>Co^{0}: s^2d^7 - 9 electrons</td>
</tr>
<tr>
<td>4 x CO - 8 electrons</td>
<td>4 x CO - 8 electrons</td>
</tr>
<tr>
<td>Co(CO)_4^{2-} - 2 electrons</td>
<td>• Co(CO)_4 - 1 electrons</td>
</tr>
<tr>
<td>= 18 electrons overall</td>
<td>= 18 electrons overall</td>
</tr>
</tbody>
</table>
Anyway:

18 e, CN = 5, Co(I)

1. Each μ² CO counts as 0.5

H-H

ox. add

red. elim

18 e, CN = 5, Co(I)

Note how ox state is unchanged here. It’s the Co-Co bond that is oxidised - this might not be immediately clear.

OC-Co-H

18 e, CN = 6, Co(III)

OC-Co

OC

16 e, CN = 4, Co(I)

H-H

ox. add

red. elim

alkyl migration

18 e, CN = 5, Co(I)

OC-Co

OC

16 e, CN = 4, Co(I)

OC-Co

OC

18 e, CN = 5, Co(I)

Note how ox state is unchanged here. It’s the Co-Co bond that is oxidised - this might not be immediately clear.

OC-Co

OC

16 e, CN = 4, Co(I)

OC-Co

OC

18 e, CN = 5, Co(I)

Note how ox state is unchanged here. It’s the Co-Co bond that is oxidised - this might not be immediately clear.

OC-Co

OC

16 e, CN = 4, Co(I)

OC-Co

OC

18 e, CN = 5, Co(I)

Note how ox state is unchanged here. It’s the Co-Co bond that is oxidised - this might not be immediately clear.
1 = 18 e\(^-\) (on each Co) → stable
2 = 18 e\(^-\) square-based pyramid → stable
3 = 16 e\(^-\) not square-planar → unstable
4 = 18 e\(^-\) square-based pyramid → stable
5 = 16 e\(^-\) square planar → stable
6 = 18 e\(^-\) square-based pyramid → stable
7 = 16 e\(^-\) not square planar → unstable
8 = 18 e\(^-\) octahedral → stable

Therefore 3 and 7 are very unstable. Equilibria will lie away from these species. *They will likely re-arrange to more stable square planar configurations.*

‘Fraid this is all I’m doing. If this doesn’t answer your questions, please ask a teacher.