Study Notes on EAN Rule

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EAN Rule:

Introduction:

Organometallic compounds are the chemical species in which one or more carbon atoms of an organic functional group are directly bound to metal. In a broader sense, the term organometallic compounds also include:

1. Metal carbonyl compounds such as Tetracarbonylnickel (0), $Ni(CO)_4$ although carbon monoxide is not an organic group.

2. Analogs with boron-carbon bonds, for example, trimethylboron (III), $(CH_3)_3B$, as well as the derivatives with silicon-carbon bonds, for example, Tetraphenylsilicon (IV), $(C_6H_5)_4Si$, although both boron and silicon are not metals in the true sense of the term.

However, the name organometallic compounds do not include:

1. The traditional ionic compounds such as sodium cyanide, Na^+CN^-

2. The compounds that are formed by the combination of an organic moiety and a metal but contain no metal-carbon bond, for example, diacetatocopper (II), $[Cu(OOCCH_3)_2]$ and tetraethoxytitanium(IV), $[Ti(OC_2H_5)_4]$. These compounds, no doubt, contain a metal ion and an organic moiety, but they have metal-oxygen bonds rather than metal-carbon bonds in their structures. Such derivatives may be designated as metal-organic compounds, but not as organometallic compounds.

Some of the complexes which obey the EAN Rule are as follows:

$\left[Co(NH_3)_6\right]^{3+}$

$Co(III) = 24e^-$

$6NH_3 : 6\times 2e^- = 12e^-$

$\underline{36e^-}$

$\left[Fe(CN)_6\right]^{4-}$

$Fe(II) = 24e^-$

$6CN : 6\times 2e^- = 12e^-$

$\underline{36e^-}$

$\left[Cr(C_6H_6)_2\right]$

$Cr(0) = 24e^-$

$2C_6H_6 : 2\times 6e^- = 12e^-$

$\underline{36e^-}$

$\left[Fe(C_5H_5)_2\right]$

$Fe(0) = 26e^-$

$2C_5H_5 : 2\times 5e^- = 10e^-$

$\underline{36e^-}$

$\left[CoF_6\right]^{3-}$

$Co(III) = 24e^-$

$6F : 6\times 2e^- = 12e^-$

$\underline{36e^-}$

$\left[NiCl_4\right]^{2-}$

$Ni(II) = 28e^-$

$4Cl : 4\times 2e^- = 8e^-$

$\underline{36e^-}$

$\left[Zn(CN)_4\right]^{2-}$

$Zn(II) = 28e^-$

$4CN^- : 4\times 2e^- = 8e^-$

$\underline{36e^-}$

$\left[Pd(NH_3)_6\right]^{4+}$

$Pd(IV) = 42e^-$

$6NH_3 : 6\times 2e^- = 12e^-$

$\underline{54e^-}$

$\left[Rh(H_2O)_6\right]^{3+}$

$Rh(III) = 42e^-$

$6H_2O : 6\times 2e^- = 12e^-$

$\underline{54e^-}$

$\left[Ru(NH_3)_5(N_2)\right]^{2+}$

Ru(II) $= 42e^-$
$5NH_3 : 5 \times 2e^- = 10e^-$
$N_2 = 2e^-$
$\underline{54e^-}$

$\left[PtCl_6\right]^{2-}$

Pt(IV) $= 74e^-$
$6Cl : 6 \times 2e^- = 12e^-$
$\underline{86e^-}$

$\left[IrCl_6\right]^{3-}$

Ir(III) $= 74e^-$
$6Cl : 6 \times 2e^- = 12e^-$
$\underline{86e^-}$

Which is expressed to be more stable : $\left[Cu(NH_3)_4\right]^{2+}$ or $\left[Cu(CN)_4\right]^{3-}$?

The stability of the two complexes may be gauged on the basis of EAN rule.

$\left[Cu(NH_3)_4\right]^{2+}$

Cu(II) $= 27e^-$
$4NH_3 : 4 \times 2e^- = 8e^-$
$\underline{35e^-}$

$\left[Cu(CN)_4\right]^{3-}$

Cu(I) $= 28e^-$
$4CN : 4 \times 2e^- = 8e^-$
$\underline{36e^-}$

The $\left[Cu(CN)_4\right]^{3-}$ complex obeys the EAN rule and, therefore, is more stable.

Metals or metal ions with an odd number of electrons cannot satisfy the EAN rule. This is because each ligand normally donates two electrons to the metal. If the metal has an odd atomic number, the total number of electrons in the complex would also be odd, irrespective of the number of ligands. The noble gas configuration requires an even number of electrons.

Such complexes tend to satisfy the EAN rule by varied options. Consider, for example, the complex species, $\left[Mn(CO)_5\right]$.

$\left[Mn(CO)_5\right]$

Mn $= 25e^-$
$5CO : 5 \times 2e^- = 10e^-$
$\underline{35e^-}$

There are a total of 35 electrons in this complex – one less than that demanded by EAN rule. For this reason, this complex is so unstable that it does not exist. However, it may accept an electron from a reducing agent and form an anion, $\left[Mn(CO)_5\right]^-$ which obeys the EAN rule.

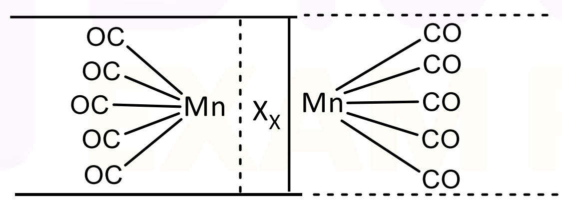
$\left[Mn(CO)_5\right]^-$

Mn	$=25e^-$
$5CO : 5 \times 2e^-$	$=10e^-$
Negative charge	$= 1e^-$
	$36e^-$

Alternatively, it may combine with an alkyl radical (R) or a halide radical (X).

$\left[Mn(CO)_5\right]$		$\left[Mn(CO)_5X\right]$	
Mn	$=25e^-$	Mn	$=25e^-$
$5CO : 5 \times 2e^-$	$=10e^-$	$5CO : 5 \times 2e^-$	$=10e^-$
$R^{\bullet}$	$= 1e^-$	$X^{\bullet}$	$= 1e^-$
	$36e^-$		$36e^-$

Another option is that two $\left[Mn(CO)_5\right]$ units, each possessing an odd electron, dimerize. One electron on each manganese atom is involved in the formation of metal-metal bonds.



Mn	$=24e^-$	Mn	$=24e^-$
$5CO : 5 \times 2e^-$	$=10e^-$	$5CO : 5 \times 2e^-$	$=10e^-$
$Mn - Mn$ bond	$= 2e^-$	$Mn - Mn$ bond	$= 2e^-$
	$36e^-$		$36e^-$

There is thus a noble gas configuration around each manganese. This means that each $\left[Mn(CO)_5\right]$ unit obeys EAN rule.

Hexacarbonylvanadium (0), $V(CO)_6$ is not a very stable complex. It decomposes at 350 K. This is because it does not obey the EAN rule.

V	$= 23e^-$
$6CO : 6 \times 2e^-$	$=12e^-$
	$35e^-$

The complex does not dimerize, first because too much energy is required to rearrange octahedral geometry and second coordination number around vanadium would increase to seven causing, in turn, steric over crowdedness. Nevertheless, the complex readily reacts with sodium

$$Na + V(CO)_6 \rightarrow Na^+[V(CO)_6]^-$$

The resulting anion follows the EAN rule.

$[V(CO)_6]^-$

$$\begin{aligned} &V && = 23e^- \\ &6CO: 6\times 2e^- && = 12e^- \\ &\text{Negative charge} && = \underline{1e^-} \\ & && \underline{36e^-} \end{aligned}$$

Similarly, $[Co(CO)_4]$ which does not follow EAN rule is non-existent, but $[HCo(CO)_4]$,$[Co(CO)_4]^-$ and $[Co_2(CO)_8]$ species, which obey the rule, are stable.

$$[HCo(CO)_4] \xleftarrow{H^+} \text{and} [Co(CO)_4] \xrightarrow{Na} Na^+[Co(CO)_4]^-$$

$\downarrow$ Dimerization

$[Co_2(CO)_8]$

Each $[Co(CO)_4]$

$$\begin{aligned} &Co && = 26e^- \\ &4CO: 4\times 2e^- && = 8e^- \\ &Co-Co \text{ bond} && = \underline{2e^-} \\ & && \underline{36e^-} \end{aligned}$$

$$\begin{aligned} &Co && = 23e^- \\ &4CO: 4\times 2e^- && = 8e^- \\ &H^\bullet && = \underline{1e^-} \\ & && \underline{36e^-} \end{aligned}$$

$$\begin{aligned} &Co && = 27e^- \\ &4CO: 4\times 2e^- && = \underline{8e^-} \\ & && \underline{35e^-} \end{aligned}$$

$$\begin{aligned} &Co && = 27e^- \\ &4CO: 4\times 2e^- && = 8e^- \\ &\text{Negative charge} && = \underline{1e^-} \\ & && \underline{36e^-} \end{aligned}$$