carry excess energy, which can be lost as heat. Down-conversion mechanisms can be integrated into the solar cell design to convert these high-energy photons into multiple lower-energy photons, effectively utilizing a wider range of the solar spectrum and reducing energy losses due to thermalization. This approach helps improve the overall efficiency of solar cells and enhances their power conversion capabilities.

X-ray florescence

X-ray Fluorescence (XRF) is an analytical technique that investigates the interaction between X-rays and a material to determine its elemental composition. XRF is suitable for solids, liquids, and powders, and in most circumstances is non-destructive. It is a very useful method to determine the chemical/elemental composition of metals, ceramics, paintings, glass, and materials related archeology, geology, and forensic science. This technique studies secondary X-rays (florescence) emitted from a material that has been excited by being bombarded with high energy X-rays or gamma rays.

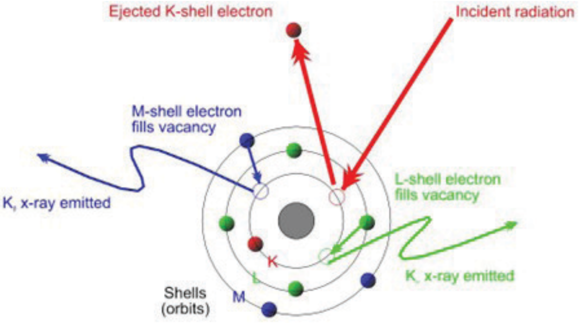

Figure 11. XRF observed by ejecting an electron in the K-shell

In this case (Fig. 11) high energy X-ray photons are made to collide with electrons of a targeted atom to ionize its electrons. Incident radiation removes an electron in the K-shell. The vacancy created in the in the lower K-shell is filled by moving an electron in a higher L-shell (or M-shell) with the emission of X-rays (XRF). The observed XRF is characteristic to the element.

Student Corner

Nucleophilic Attack on Coordinated Ligands

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Reactions of nucleophiles with transition metal complexes are useful in the preparation of new metal complexes. Unsaturated ligands such as C≡O, isonitriles, olefins, dienes, and arenes are not normally reactive towards nucleophiles. When these ligands or molecules are coordinated to an electron-deficient metal they become activated towards nucleophilic attack.

The factors which facilitate nucleophilic attack on a coordinated ligands are (i) formal positive charge on the metal, (ii) coordination of π acceptor ligands, (iii) the metal should be coordinatively saturated. and (iv) high reactivity of the nucleophile.

Nucleophilic attack on C≡O

Nucleophiles such as hydride, alkyls, alkoxides, hydroxide and amines can attack the carbon of metal carbonyls without prior coordination to the metal. For example,

1. Attack of hydride ion (H^-) on C≡O produces a formyl (CHO) group in (**1**).

   ($L = CO, PPh_3$; $M = Cr, W, Fe$; $n = 4, 5, 6$)

$$H^- + [LM(CO)_n]$$
$$\downarrow$$
$$[L(OC)_{n-1}M\text{-}C(=O)H]^- \ \mathbf{(1)}$$

2. Attack of an alkyl/aryl reagent produces an acyl group as in (**2**).

$$R^- + [LM(CO)_n]$$
$$\downarrow$$
$$[L(OC)_{n-1}M\text{-}C(=O)R]^- \ \mathbf{(2)}$$

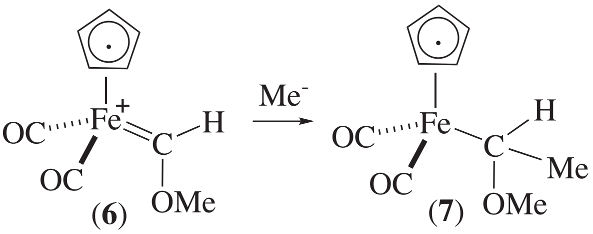
3. HO^- attacks C≡O in (**3**) to give hydroxy- carbonyl complexes (**4**), which lose CO_2 to form metal hydrides (**5**).

$$\begin{tikzcd}
HO^- + [L_nM(CO)]\ (\mathbf{3}) \arrow[d] \\
{[L_nM\text{-}C(=O)OH]^-(\mathbf{4})} \arrow[d] \\
{[L_nMH]^-(\mathbf{5}) + CO_2}
\end{tikzcd}$$

4. Similarly, alkoxides (RO^-) can attack a coordinated C≡O to generate an alkoxy carbonyl (CO_2R) group.

Nucleophilic attack on carbene ligands

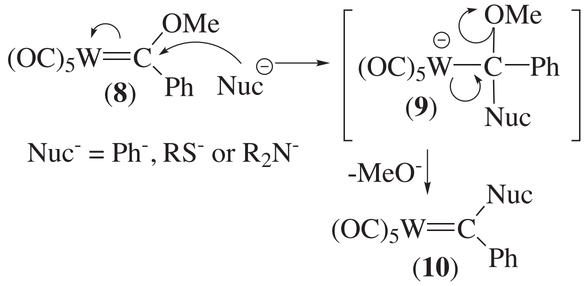
Carbene complexes have M=C bonds. This carbene-carbon of a Fischer carbene is electrophilic. It can be attacked by a suitable nucleophile as shown scheme 1.



Scheme 1. Conversion of (**6**) to (**7**)

Here, Me^- adds on to the carbene-carbon of $[(\eta^5\text{-}Cp)(OC)_2Fe{=}CH(OMe)]^+$ (**6**) to produce $[(\eta^5\text{-}Cp)(OC)_2FeCH(Me)(OMe)]$ (**7**).

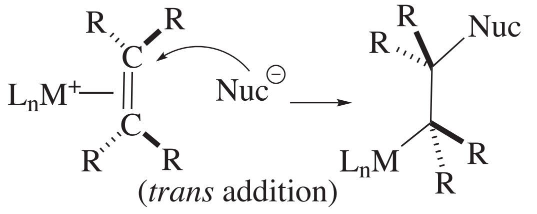
Neutral carbene complexes can react with a nucleophile by either addition or addition-elimination as shown in scheme 2. Addition of nucleophile (Nuc^-) to (**8**) gives the anionic intermediate (**9**) which eliminates OMe^- to give the neutral complex (**10**).



Scheme 2. Addition-elimination reaction of (**8**)

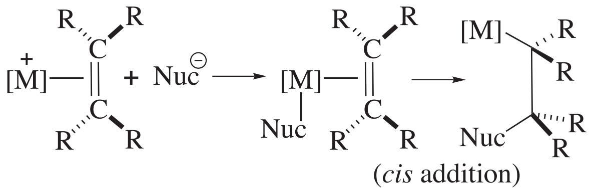
Nucleophilic attack on alkene and alkyne ligands

Alkenes coordinated to transition metals in higher oxidation states are susceptible to nucleophilic attacks. Intermolecular addition of Nuc^- to a coordinated alkene ($R_2C{=}CR_2$) is shown in scheme 3. Note that the metal and the nucleophile end up in *trans*-positions.



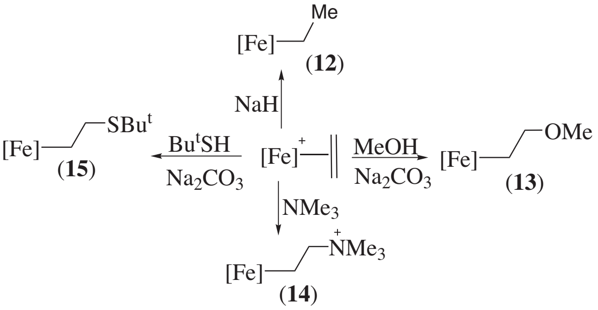
Scheme 3. *trans*-Addition of Nuc^- to a coordinated olefin

Some nucleophiles may attack the metal centre first and then the nucleophile migrates on to alkene to generate the *cis* product (scheme 4).



Scheme 4. *cis*-Addition of Nuc^- to a coordinated olefin

Some nucleophilic addition reactions of $[(\eta^5\text{-}Cp)(OC)_2Fe(\eta^2\text{-}CH_2{=}CH_2)]^+$ ion (**11**) are given in scheme 5. $[Fe] = Cp(OC)_2Fe$.



Scheme 5. Addition reactions of (**11**)

The scheme 5 illustrates the following reactions.

(a) Nucleophilic addition of H^- to ethene generates a neutral ethyl complex $[(\eta^5\text{-}Cp)(OC)_2FeCH_2CH_3]$ (**12**).

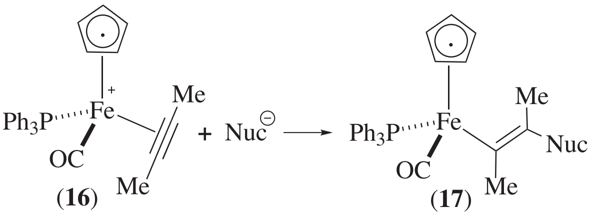
(b) Attack of MeO− gives the complex $[(\eta^5\text{-}Cp)(OC)_2FeCH_2CH_2OMe]$ (**13**).

(c) NMe_3 attacks ethene giving the cation $[(\eta^5\text{-}Cp)(OC)_2FeCH_2CH_2NMe_3]^+$ (**14**).

(d) Attack of Bu^tS^- produces the complex $[(\eta^5\text{-}Cp)(OC)_2FeCH_2CH_2SBu^t]$ (**15**).

Similarly, cationic alkyne complexes undergo nucleophilic attack in a *trans*-fashion to give stable σ-vinyl metal complexes. Note that metal fragment and the Nuc end up trans to each other.

Nucleophiles (Nuc$^-$) can attack the coordinated dimethyl acetylene ligand of [(η^5-Cp)(OC)(Ph_3P)Fe(η^2-MeC≡CMe)]$^+$ ion (**16**) to give the complexes of the type [(η^5-Cp)(OC)(Ph_3P)FeC(Me)=CMe(Nuc)] (**17**).



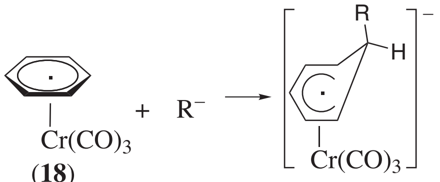
(**16**) (**17**)

Nuc$^-$ = R$^-$, H$^-$, CN$^-$, PhS$^-$, $^-$CH(CO_2Et)$_2$, MeC≡C$^-$

Scheme 6. Addition reactions of (**16**)

Nucleophilic attack on polyene and polyenyl ligands

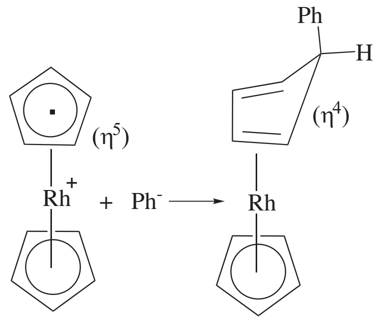
Let us first consider nucleophilic attack on a coordinated polyene (conjugated π-systems), *e.g.*, benzene (scheme 7). Reaction of LiR with [Cr(CO)$_3$(η^6-C_6H_6)] (**18**) gives the complex anion [Cr(CO)$_3$(η^5-C_6H_6R)]$^-$ (**19**). This is a nucleophilic addition reaction. Hapticity of the arene-ligand has reduced by one unit (η^6→η^5) whilst the complex has acquired one negative charge. Generally nucleophilic addition reactions are regiospecific and R$^-$ reaches the arene from the *exo*-face (*i.e.*, from the opposite side to the metal center).



(**18**) (**19**)

Scheme 7. Addition of R$^-$ to (**18**)

Cyclopentadienyl ($C_5H_5^-$) is a polyenyl ligand widely used with most transition metal centers. The addition of Ph$^-$ to [Rh(η^5-C_5H_5)$_2$]$^+$ (**20**) gives [(η^4-C_5H_5Ph)Rh(η^5-C_5H_5)] (**21**).



(**20**) (**21**)

Scheme 8. Addition of Ph$^-$ to cation (**20**)

Green-Davies-Mingos rules

Generally nucleophilic addition is selective, and attack takes place at a particular ligand. The following rules are applied to predict the product when metal centre contains more than one polyene/polyenyl ligand. These rules apply only to reactions of 18e-complexes under kinetic control.

Rule 1

Nucleophilic attack occurs at polyenes preferentially than polyenyls.

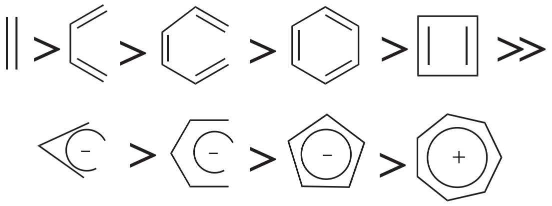
Rule 2

Open-ligands are more reactive than closed-ligands.

Rule 3

Open polyenes are always attacked at the terminal carbon. Open polyenyls are usually attacked at the terminal carbon, but non-terminal if the metal has strong electron donating groups.

The reactivity of polyene/polyenyl ligand is follows.



Note that reactivity of even systems > odd systems and open systems > closed systems.

Problems

1. Using Green-Davies-Mingos rules draw the structures of the products if each of the following complexes is reacted with the nucleophile Y$^-$.
   (a) [Ru(η^5-C_5H_5)(η^6-C_6H_6)]$^+$
   (b) [Ir(η^5-C_5H_5)(η^5-C_6H_7)]$^+$
   (c) [W(η^5-C_5H_5)(η^6-C_6H_6)]$^+$
   (d) [W(η^6-C_6H_6)(η^3-C_3H_5)(dppe)]$^+$
   (e) [W(η^5-C_5H_5)(η^4-C_5H_6)(dppe)]$^+$
   (f) [WMe(η^5-C_5H_5)$_2$(η^2-CH_2=CH_2)]$^+$
   (g) [W(η^5-C_5H_5)$_2$(η^3-C_3H_5)]$^+$
   (dppe = $Ph_2PCH_2CH_2PPh_2$)