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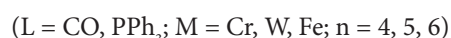
The factors which facilitate nucleophilic attack on a coordinated ligands are (i) formal positive charge on the metal, (ii) coordination of π acceptor ligands, (iii) the metal should be coordinatively saturated. and (iv) high reactivity of the nucleophile.

Nucleophilic attack on $C\equiv O$

Nucleophiles such as hydride, alkyls, alkoxides, hydroxide and amines can attack the carbon of metal carbonyls without prior coordination to the metal. For example,
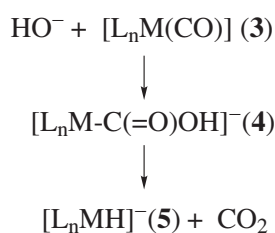
1. Attack of hydride ion (H^-) on $C\equiv O$ produces a formyl (CHO) group in (**1**).

    (L = CO, PPh$_3$; M = Cr, W, Fe; n = 4, 5, 6)

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

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

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

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

$$HO^- + [L_nM(CO)] \; (3)$$

$$\downarrow$$

$$[L_nM\text{-}C(=O)OH]^- \; (4)$$

$$\downarrow$$

$$[L_nMH]^- \; (5) + CO_2$$

4. Similarly, alkoxides (RO^-) can attack a coordinated $C\equiv O$ to generate an alkoxy carbonyl (CO_2R) group.
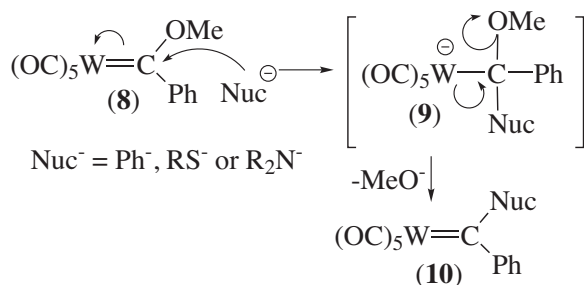
Nucleophilic attack on carbene ligands

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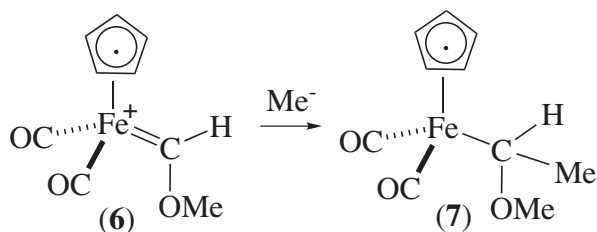
Scheme 1. Conversion of (**6**) to (**7**)

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**).

$Nuc^- = Ph^-$, RS^- or R_2N^-

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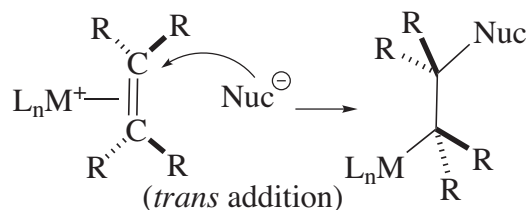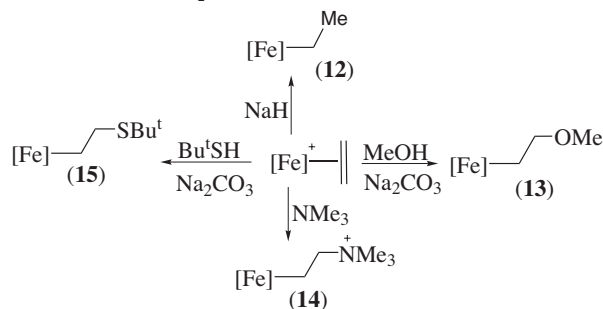
Scheme 3. *trans*-Addition of Nuc^- to a coordinated olefin

Some nucleophiles may attack the metal centre first and then the nucleophile migrates on to alkene to generate the *cis* product (scheme 4).
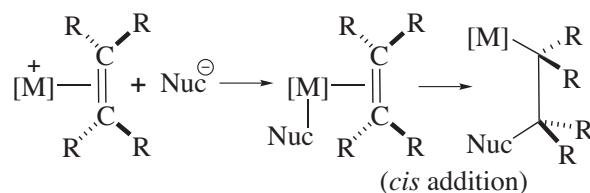
Scheme 4. *cis*-Addition of Nuc^- to a coordinated olefin

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] = $Cp(OC)_2Fe$.
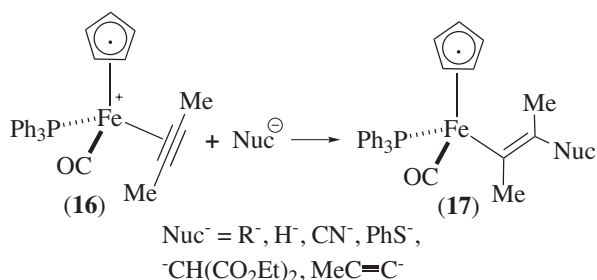
Scheme 5. Addition reactions of (**11**)

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 $[(\eta^5\text{-Cp})(OC)(Ph_3P)Fe(\eta^2\text{-MeC}\equiv\text{CMe})]^+$ ion (**16**) to give the complexes of the type $[(\eta^5\text{-Cp})(OC)(Ph_3P)FeC(Me)=CMe(Nuc)]$ (**17**).

Nuc⁻ = R⁻, H⁻, CN⁻, PhS⁻,
⁻CH(CO₂Et)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 $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ (**18**) gives the complex anion $[Cr(CO)_3(\eta^5\text{-}C_6H_6R)]^-$ (**19**). This is a nucleophilic addition reaction. Hapticity of the arene-ligand has reduced by one unit ($\eta^6 \rightarrow \eta^5$) 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).
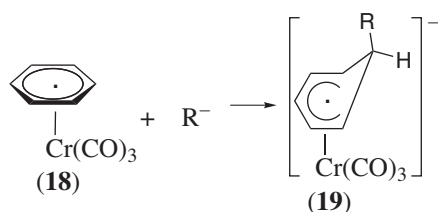
Scheme 7. Addition of R⁻ to (**18**)

Cyclopentadienyl ($C_5H_5^-$) is a polyenyl ligand widely used with most transition metal centers. The addition of Ph⁻ to $[Rh(\eta^5\text{-}C_5H_5)_2]^+$ (**20**) gives $[(\eta^4\text{-}C_5H_5Ph)Rh(\eta^5\text{-}C_5H_5)]$ (**21**).
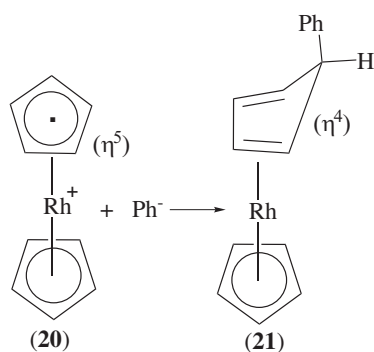
Scheme 8. Addition of Ph⁻ to cation (**20**)

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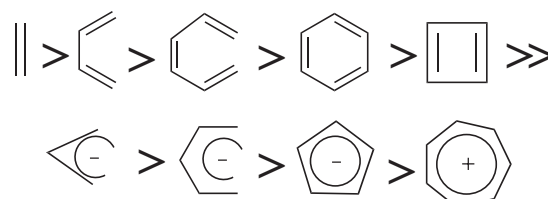
Note that reactivity of even systems > odd systems and open systems > closed systems.

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) $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$

    (b) $[Ir(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)]^+$

    (c) $[W(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$

    (d) $[W(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)(dppe)]^+$

    (e) $[W(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)(dppe)]^+$

    (f) $[WMe(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}CH_2=CH_2)]^+$

    (g) $[W(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-}C_3H_5)]^+$

    (dppe = $Ph_2PCH_2CH_2PPh_2$)