Transition Metal Aryl and Alkyl Complexes

(iv) **Insertion:**

- Insertion of Multiple Bonded molecule in M-H Bond

$FeH(CO)_2(\eta^5\text{-}C_5H_5) + CH_2=CHCN \rightarrow Fe\{CH(CH_3)CN\}(CO)_2(\eta^5\text{-}C_5H_5)$

$CoH(CO)_4 + C_2F_4 \rightarrow Co(CF_2CF_2H)(CO)_4$

$[RhH(NH_3)_5]^{2+} + C_2H_4 \rightarrow [Rh(C_2H_5)(NH_3)_5]^{2+}$

- Insertion of Unsaturated molecules in M-M Bond

$Co_2(CO)_8 + C_2F_4 \rightarrow (CO)_4Co\text{-}CF_2CF_2\text{-}Co(CO)_4$

- Insertion of Unsaturated Molecule in M-C Bond:

Trans $PtCl(CH_3)(PEt_3)_2 + CO \rightarrow$ Trans $PtCl(COCH_3)(PEt_3)_2$

(v) **Elimination Reaction:**

- Elimination of CO from Acyl Compound:

$Li[Co(CO)_4] + F_3C\,COCl \rightarrow Co(CO\,CF_3)(CO)_4 + LiCl \rightarrow CO(CF_3)CO)_4 + CO$

- Elimination CO_2 from Carboxylates:

$Ni(CO_2Ph)_2(biby) \xrightarrow{Heat} NiPh_2(biby) + CO_2$

$K_2PtCl_4 + 2\,TlO_2C\,Ph + 2Py \rightarrow$ Trans-$Pt(Ph)_2(Py)_2 + 2KCl + 2TlCl + CO_2$

- Elimination of SO_2 from Sulphonate:

$Fe(SO_2R)(CO)_2\,\eta^5\text{-}C_5H_5 \xrightarrow{Heat} FeR(CO)_2\,\eta^5\text{-}C_5H_5 + SO_2$

$[Pt(SO_2Ph)Cl(PR_3)_2 \xrightarrow{Heat} PtCl(Ph)(PR_3)_2 + SO_2]$

$IrCl_2(SO_2C_6H_4Me)(CO)(PR_3)_2 \xrightarrow{Heat} IrCl_2(C_6H_4Me)(CO)(PR_3)_2 + SO_2$

(vi) **Oxidative addition/ Metal-Atom Reactions:** Co-condensation of Organic Halides with Metal Vapour.

$2M + 2\,C_6H_5Br \xrightarrow{-196°C} M(C_6H_5)_2 + MBr_2 \xrightarrow{PhMe} M(C_6H_5)_2(\eta^6\text{-}C_6H_4Me)$

(M = Co or Ni)

$2M + 2\,C_6H_5X + 2PEt_3 \rightarrow M(C_6H_5)_2(PEt_3)_2 + MX_2$

M = Reactive Metal Powder (Fe, Co, Ni, Pd Or Pt)

$Pd + C_6H_5I + bipy \rightarrow Pd(C_6H_5)(Bipy)(I)$

(vii) **Cyclic Metallation:** Alkyl groups linked with N or P-coordinated ligands show Cyclic Metallation by oxidative addition involving breaking of sp^3-hybridised C-H bond and formation of M-C bond.

$FeCl_2(PMe_3)_3 + PMe_3 \xrightarrow{Na/Hg} [FeH\{CH_2PMe_2\}(PMe_3)_3] + 2NaCl$

7. Group 11 – d^9 Metals: Cu [Oxidation Number +1: Coordination Number: 1 Example: $[CuR]_4$ (R=Ph, $Me_2C_6H_3$), Coordination Number: 2(sp) Example: $[CuMe_2]^-$; Oxidation Number +2: Coordination Number: 2(sp) Example: CuR_2 ($R=CH_2CH_2PMe_3$), Coordination Number: 3(sp^2) Example: $Cu(Mes)_3^-$], Ag [Oxidation Number +1: Coordination Number: 1 Example: $[Ag(Mes)]_5$, Coordination Number: 2(sp) Example: $[Ag\{C(SiMe_3)_3\}_2]^-$] and Au [Oxidation Number +1: Coordination Number: 1 Example: $[Au(Mes)]_5$, Coordination Number: 2(sp)

Transition Metal Aryl and alkyl Complexes.

Example [$AuMe_2$]. Oxidation Number +2 Coordination Number 2(sp) Example Au[CH_2(Si Me_3)](L). Oxidation Number +3 Coordination Number 3(sp^2) Example $AuPh_3$, Coordination Number 4(sp^3) Example [$AuMe_4$]] are present in this group. The general method of their synthesis are

(i) **Halide Exchange reaction**

$$2\,CuCl + ZnR_2 \xrightarrow[10^\circ C]{ROR} 2\,[CuR]_n + ZnCl_2$$

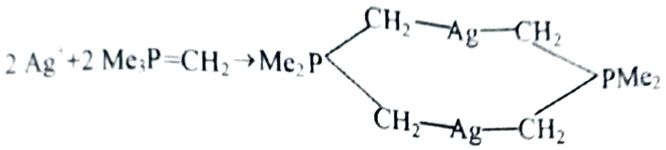
$$CuCl + 2\,Li\,Me \xrightarrow{ROR} Li\,(Cu\,Me_2) + Li\,Cl$$

$$4\,CuI + 4\,Li\,(CH_2\,Si\,Me_3) \rightarrow [Cu\,(CH_2\,Si\,Me_3)]_4 + 4\,Li\,I$$

$$AuCl(L) + Mg\,RCl \rightarrow AuR(L) + MgCl_2\ (R = (SiMe_3)_3;\ L = Me, Ph, P_r\,)$$

$$5Au\,Cl(CO) + 5Mg\,Br(Mes) \xrightarrow{THF} [Au\,(Mes)]_5 + 5\,Mg\,BrCl + 5CO$$

(ii) **Ylide synthesis**:

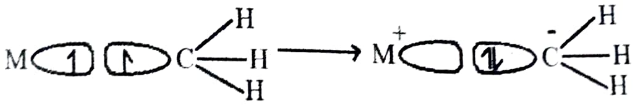


$$2\,Ag^+ + 2\,Me_3P{=}CH_2 \rightarrow Me_2P\langle\,CH_2{-}Ag{-}CH_2\,;\,CH_2{-}Ag{-}CH_2\,\rangle PMe_2$$

Stability of Transition Metal Hydrocarbyls: Transition metal σ–analogues are generally much less stable compared to main group hydrocarbyls. Alkyl and aryl groups are one electron donor monohapto-ligands similar to hydrogen and halogens, which combine with metal atom sharing their unpaired electron to form metal-alkyl or metal-aryl complexes.

Nature of the bond may vary from purely ionic to purely covalent on the basis of electronegativity of the metal.

- **Ionic**: Alkyls and aryls of Mn, Zn and Eu-hydrocarbons are anions or specifically crarbanions, formed by transfer of electron from valence shell of strongly electropositive metal to valence shell of carbon, pairing the unpaired electron present in alkyl or aryl radical.



Methyl Free Radical Methyl Carbanion

- **Covalent:** Covalent alkyls or aryls are formed by overlapping of metal orbital having unpaired electron with the valence orbital of alkyl or aryl radicals containing unpaired electron.

Methyl Free Radical

In hydrocarbyls of transition metals, carbon is always negative compared to metal atom, due to its higher electronegativity, making M-C bond polar. This polarity depends on the nature of the hydrocarbon radical also in addition to electronegativity of metal atom. Electronegativity of