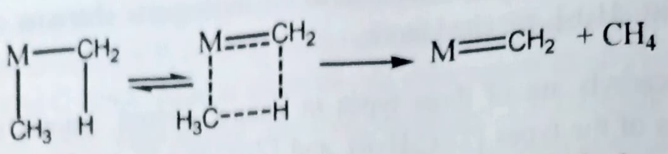
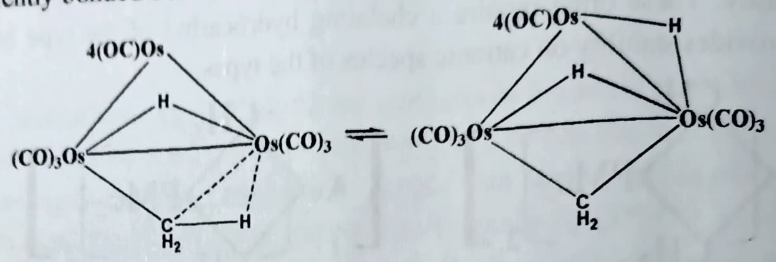
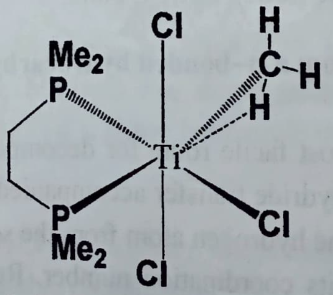
benzyls and neopentyls, especially of titanium and tantalum are known to decompose by this mechanism.



Another mechanism of α-elimination involves "agnostic" hydrogens (C-H-M), which are actually covalently bonded both to a carbon atom and a transition metal atom.

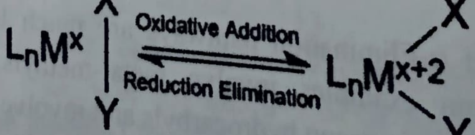


Crystallographic analysis shows that, when a methyl group is attached to a d°-metal centre, having less than 18-electron environment, one of the C-H bonds of that methyl group gets distorted to the extent that it gets into the bonding distance with the metal. Such strong interactions between metal and C-H group are known to play key role towards cyclometallation and alkene polymerization reactions.



iii. γ-elimination: It has been observed for some main group hydrocarbyls, but it's rare in transition metal chemistry.

2. Intermolecular reductive elimination: It is reverse of oxidative addition reaction. Both the oxidation state and coordination number of the central metal are reduced by two units. Hence, this pathway would be confined to metals with stable oxidation states differing by two units, which is more common for the later transition metals.



Examples: $AuMe(PPh_3) \rightarrow Au(PPh_3) + C_2H_6$

$PtH(R)(PPh_3)_2 \rightarrow Pt(PPh_3)_2 + RH$

$Au(CH_2SiMe_3)(PPh_3) + MeI \rightarrow AuIMe(CH_2SiMe_3)(PPh_3) \rightarrow AuI(PPh_3) + SiEtMe$

Transition Metal - Aryl & Alkyl Complexes.

3. **Homolytic fission of M-C bond** These are common pathways for decomposition of main group alkyls, but several transition metal alkyls also follow it.

$Zr(CH_2Ph)_4 \rightarrow Zr + 2Ph\text{-}CH_2CH_2Ph$

Characteristic Reactions: Reactivity of σ-bonded transition metal organometallics depend upon the nature of the metal as well as on the other ligands present.

1. **Metal-Carbon Bond Cleavage:** Transition metal alkyls are weakly nucleophilic and decompose in presence of proton. Nucleophilic reaction on alkyls in oxidative conditions will also come in this category. Example:

$TiMe_4 + 4\,MeCOOH \xrightarrow{ROR} Ti(O_2CMe)_4 + 4CH_4$

$Zr(CH_2SiMe_3)_4 + 4\ 2,6\text{-}C_6H_5Pr_2OH \rightarrow Zr(2,6\text{-}Pr_2C_6H_5O)_4 + 4\,SiMe_4$

$CrPh_3(THF)_n + \text{Acetyl Acetone} \rightarrow Cr(Acac)_3 + 3\,C_6H_6 + n\,THF$

$Cis\text{-}[PtCl_2(PEt_3)_2] \xleftarrow[-2CH_4]{2HCl} Cis\text{-}PtMe_2(PEt_3)_2 \xrightarrow[-CH_4]{HCl} Cis\text{-}[PtCl(Me)(PEt)_2]$

$MnMe(CO)_5 + Br_2 \rightarrow MeBr + MnBr(CO)_5$

$TiMe_4 + 4I_2 \rightarrow 4\,MeI + TiL_4$

$CoMe_2(PMe_3)_3 + X_2 \rightarrow CoX(Me)(PMe_3)_3 + MeX$

2. **Elimination of alkene with proton transfer (β–Decomposition):**

$PtCl(CH_2CH_3)(PEt_3)_2 \rightarrow PtHCl(PEt_3)_2 + C_2H_4$

$Cu(CH_2CH_2CH_2CH_3)(PBu^n_3) \rightarrow C_2H_5CH=CH_2 + CuH(PBu^n_3)$

$MnCH_2CH_3(CO)_5 + Ph_3C^+BF_4^- \rightarrow Ph_3CH + [(CO)_5Mn(C_2H_4)](BF_4)$

3. **Replacement reactions:**

$[PdMe_2(bipy)] + 2\,C_3H_7I \rightarrow [Pd(C_3H_7)_2(bipy)] + 2\,CH_3I$

$M(CH_2Ph)_4 + 2\,EtOH \rightarrow M(CH_2Ph)_2(OEt)_2 + 2PhCH_3\ (M = Ti \text{ or } Zr)$

$ZrMe_2(\eta^5\text{-}C_5H_5)_2 + MeOH \rightarrow ZrMe(OMe)(\eta^5\text{-}C_5H_5)_2 + CH_4$

4. **Adduct Formation:**

$[MnR_2]_n + TMEDA \rightarrow MnR_2(TMEDA)\ R = CH_2CMe_3, CH_2SiMe_3 \text{ or } CH_2(Me_2Ph)$

$TiMe_2 + dmpe \rightarrow TiMe_2(dmpe)_2$

$TaMe_5 + dme \rightarrow TaMe_5(dme)$

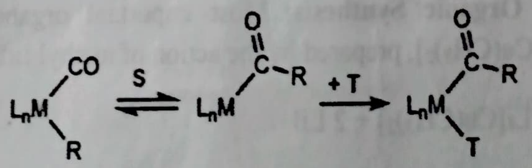
$[Mn(CH_2SiMe_3)_2] + 2\,LiCH_2SiMe_3 \rightarrow Li_2[Mn(CH_2SiMe_3)_4]$

5. **Redistribution:**

$Cis\text{-}PtMe_2(PEt_3)_2 + Cis\,PtCl_2(PEt_3)_2 \rightarrow 2\,Cis\text{-}PtCl(Me)(PEt_3)_2$

6. **Insertion Reactions:** Unsaturated ligands insert itself into M-C bond giving new products.

i. **CO insertion:**



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