E-Content

E-notes for M.Sc (Semester IV) Students

INORGANIC Spl.

Title:- Transition Metal –Alkyl & Aryl Complexes

Dr. Arun Kumar Pandey
Assistant Professor
GUEST
(Dept. of Chemistry)
Maharaja College, Ara

E-mail Id:- dr.arunkumarpandey01@gmail.com

E-content
PG Dept. of Chemistry
Maharaja College, ARA

M.Sc. Semester (IV)
Paper: EC-1a

Transition metal-alkyl and -aryl complexes

Organometallic Compounds are Organic Compounds of metals, with metal-carbon bond. Their chemistry functions as a bridge between organic and inorganic chemistry. They possess ionic or covalent, localised or delocalised bonding between one or more carbon atoms of organic group or molecule and transition metals or lanthanides or actinides or main group metal atoms. Organic compounds are hydrocarbons or their derivatives, hence organometallic compounds are generally those compounds which have one or more hydrocarbon group(s)/radical(s) directly linked to metal atom. Therefore, metal-carbides, metal-carbonates, metal-cyanides, metal-carboxylates, metal-carbonyls, should not be included in organometallic compounds. Metal carbonates and metal carboxylates are not organometallic compounds, as they do not have metal-carbon bond. While, although metal-carbides and metal-cyanides have metal-carbon bond, they are not organic compounds.

Compounds of metals with alkyl radicals are called 'Metal-alkyls', while those with aryl radicals are known 'Metal-aryls'.

Nomenclature: Names of metal-alkyls and metal-aryls are derived as, first naming the ligands in alphabetic order followed by the name of the metal with oxidation state in parenthesis, in reference to Werner's and IUPAC rules of naming. For example: $[Zn(C_2H_5)_2]$ will be Diethyl Zinc(II) and $[Me_3PtCl]$ is Chloro trimethyl Platinum(IV).

Classification and Types: On the basis of nature, bonding and structure, organo-transition metal compounds are classified into following three groups:

1. Ionic
2. σ-Bonded covalent
3. π-Bonded covalent compounds

Ionic Organometallic compounds are generally formed by strongly electropositive s-block metals, though alkyl and aryl compounds of Mn, Zn and Eu also show sufficient ionic property. Here hydrocarbon radical is present in the form of carbo-anion and is bond with non-directional electrostatic forces. These compounds resemble with alkali and alkaline earth halide and hydrides.

Transition metal organometallic complexes can be divided into two broad groups, for convenience:

(a) σ–bonded organometallics (σ–hydrocarbyls): Here, one single carbon atom of the ligand is linked directly to the metal through σ–bond.

(b) π–bonded organometallics: These are formed between metal atom and ligands such as CO, RNC, :CRR_1, CR, RC≡CR and other unsaturated types.

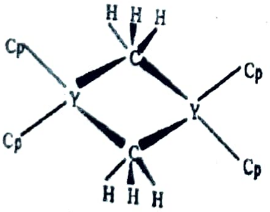
Transition Metal. Aryl and Alkyl Complexes

Metals having 18 electrons or nearly 18 electrons sub-shell (d-block metals of group 11-12 and p-block metals of group 13-16) form stable σ–bonded covalent organometallic compounds, whereas σ–bonded organometallics of transition metals with incomplete d-orbitals are generally unstable. Transition metals with unsaturated sub-shells form π-bonded covalent organometallic compounds with hydrocarbon radicals.

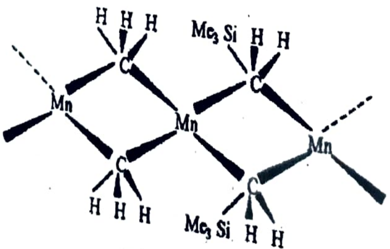
Types of Organo Transition Metal Alkyls and Aryls:

In alkyl and aryl derivatives of transition metal complexes, metal atom and alkyl or aryl radical share one electron each to give normal 2-electron-2-center M-C σ–bonded organometallics. Alkyl or aryl radicals are monohapto (η^1) ligands (one electron donors). Organo-transition metal alkyls and aryls are classified on several bases. Such as:

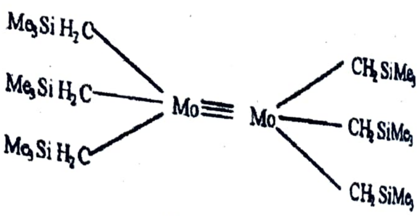
1. **Types of ligands present**: (a) Homoleptic [MR_n]: Metal hydrocarbyls, where all the organic groups/ligands on the metal atom are same. Example: [$TiMe_4$], [$Ti\{CH(SiMe_3)_2\}_3$], [VPh_6] etc. (b) Heteroleptic [$MR_{n-a}X_a$]: Metal hydrocarbyls, where the groups attached to the central metal atom are of more than one type. Example: [$TiMe_{4-x}L_x$], [$ZrMe_2(\eta^5-C_5H_5)_2$], [$ZrMe_x(OPh)_{4-x}$] etc.
2. **Nature of ligands**: (a) Alkyl Organometallics: Complexes with alkyl radicals are called metal-alkyls. Example: [$Ti(Me)_4$], [$Hf(CH_2{}^tBu)_4$], [WMe_6] etc. (b) Aryl Organometallics: Complexes with aryl radicals are termed as metal-aryls. Example: [$Sc(Ph)_3$], [$LaPh_4$]$^-$, [$V(Ph)_6$]$^{4-}$, [$Hf(CH_2Ph)_4$] etc. Further these can be classified into (i) Symmetrical: Similar alkyl or aryl ligands present. Example: [$TiMe_4$], [$Sc(Ph)_3$] etc. (ii) Unsymmetrical: Two or more types of either alkyl or aryl ligands present. Example: [$Ti(Me)_3(Bu)$] etc. (iii) Mixed: Both alkyl and aryl ligands are present in the complex. Example: [$WMe_2(CH_2Ph)_4$] etc.
3. **Number of metal atoms**: (a) Mononuclear: One metal centre is there. (b) Polynuclear: More than one metal centre is present. Here, metal atoms are linked together by either bridging alkyl or aryl groups or direct M-M single/multiple bonds or by both M-M bond and bridging alkyl or aryl. Examples:



[$Cp_2Y(\mu-CH_3)_2YCp_2$]



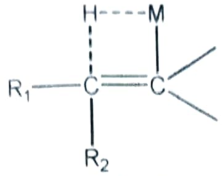
[$Mn(\mu-CH_2SiMe_3)_2$]$_n$



$Mo_2(CH_2SiMe_3)_6$]

Synthesis Paths: Alkyl and aryl derivatives of transition metals are difficult to prepare due to high instability compared to their main group metal analogues as they tend to decompose through various pathways, such as β–hydrogen elimination. Hence, Large number of alkyls of various transition metals was synthesized using alkyl radicals having no β–hydrogen [Example: $PhCH_3$, $CH_2C(CH_3)_3$ etc.]. [$M(CH_3)_n$] are abundant. Thus, stability of metal benzyls

$[M(CH_2C_6H_5)_n]$ and metal neopentyls $[M\{CH_2C(CH_3)_3\}_n]$ can be explained. Comparative stability of derivatives like $[Cr\{C(CH_3)_3\}_4]$ can be explained by the influence of steric hindrance in inhibiting the approach for β–hydrogen in crowded tert-butyl/isopropyl groups to the central metal atom. $[M(CH_2SiMe_3)_n]$ derivative are more stable than analogous neopentyls $[M(CH_2CMe_3)_n]$ as substitution of β–carbon atom in ligand by silicon precludes possibility of β–hydrogen elimination as the formation of C=Si analogue of the alkene is rather unlikely. Other similar examples of this type are CH_2GeR_3, CH_2SnR_3 etc. as well as 1-norbornyl, (where the resulting bridge head alkene is highly unstable).



Decomposition of metal alkyls through β–hydrogen elimination involves formation of intermediate hydridoalkene complex, where coordination number of the metal increases. If coordination sites of the metal are already saturated by other ligands, then formation of hydridoalkene complex would be difficult. Examples: $[Mo(CH_2CH_3)(CO)_3(\eta^5\text{-}C_5H_5)]$, $[Mn(CH_2CH_3)(CO)_5]$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^5\text{-}C_5H_5)]$ etc. These stabilizing ligands are generally of π–bonding/π–acid type, but they could also be lewis bases, like ammonia in $[Rh(C_2H_5)(NH_3)_5](ClO_4)_2$ or bis-salicylaldehyde-ethylenediimine (salen) in $[Co(C_2H_5)(salen)]$. Hence, for synthesis of transition metal alkyls and aryl complexes by stabilizing them, following measures need to be taken off:

(a) Use of alkyl (or aryl) radicals with no β-hydrogen.

(b) Use of radicals like t-butyl or isopropyl having crowded β-hydrogen atoms (where reach of metal atom is difficult to β-hydrogen).

(c) In place of β-carbon, use of radicals, with silicon, germanium and tin atoms (where no tendency of hydrogen elimination is present).

(d) Use of stabilizing ligands

Now, below are categorical representations of synthesis methods for transition metals of different groups.

1. **Group 3 - d^1 Metals**: Sc [Oxidation Number +3: Coordination Number: 3(sp^2) Example: $Sc(Ph)_3$], Y [Oxidation Number +3: Coordination Number: 3(sp^2) Example: $Y(Ph)_3$, 4(sp^3) Example: $Y(^tBu)_4$], Lanthanides [Oxidation Number +3: Coordination Number: 3(sp^2) Example: $[M(CH_2PMe_3)_3]^{3+}$, 4(sp^3) Example: $[M^tBu_4]^-$ (M = Sm, Er, Yb or Lu), 6(d^{2}sp^3) Example: $[MMe_6]^{3-}$] and actinides [Oxidation Number +4: Coordination Number: 4(sp^3) Example: $Th(CH_2Ph)_4$, 6(d^{2}sp^3) Example: $[UMe_6]^{2-}$] elements are present in this group. General methods for synthesis are:

(i) **Halide-Carbanion exchange**: Substitution of halide ion from metal halides by Carbanion ion. Example:

$$M\,Cl_3 + 3\,Li\,CH_2\,Si\,Me_3 \xrightarrow{THF} [M\,(CH_2\,Si\,Me_3)_3]\,(thf)x + 3\,Li\,Cl$$

(M = Sc, Y, Tb, Er, Tm, Yb, Lu. x = 0, 2, or 3)

$$M\,Cl_3 + 3Li\,CH\,(Si\,Me_3)_2 \rightarrow [M\,\{CH\,(Si\,Me_3)_2\}_3] + 3\,Li\,Cl$$

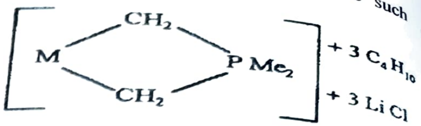
$$MCl_3 + 6LiMe + 3TMEDA \xrightarrow{Et_2O} [MMe_6]^{3-}[Li(TMEDA)]_3^{3+} + 3LiCl$$

M = Lanthanide metal

(ii) **Ylide synthesis**: Chelating ligands stabilizes transition metal-alkyl bond. One such important example is the use of phosphorous ylide. Example:

$$MCl_3 + 3\,Me_3P=CH_2 \longrightarrow M(CH_2PMe_3)_3\,3Cl^- \xrightarrow{3\,Li\,Bu}$$

(M = Lanthanide)



2. **Group 4 - d^2 Metals:** Ti [Oxidation Number +2: Coordination Number: 2(sp) Example: $Ti(CH_2Ph)_2$; Oxidation Number +3: Coordination Number: 3(sp^2) Example: $Ti(CH_2SiMe_3)_3$, 5(dsp^3) Example: $TiCl_2R(Py)_2$ (R = Me, Ph); Oxidation Number +4: Coordination Number: 4(sp^3) Example: $TiMe_4$, 4(dsp^2) Example: $TiMe_2(DMPE)_2$, 5(dsp^3) Example: $[TiMe_5]^-$], Zr [Oxidation Number +4: Coordination Number: 4(sp^3) Example: $ZrMe_4$] and Hf [Oxidation Number +4: Coordination Number: 4(sp^3) Example: $Hf(CH_2{}^tBu)_4$, 6(d^{2}sp^3) Example: $[HfMe_6]^{2-}$] are present in this group. General methods for synthesis are:

(i) **Halide exchange**:

$$M\,Cl_4 + 4\,Li\,Me \xrightarrow[80^\circ C]{ROR} M\,(Me_4) + 4\,Li\,Cl\ (M = Ti\ Or\ Zr)$$

$$M\,Cl_4 + Mg\,(CH_2\,Ph)_x \xrightarrow[-60^\circ C]{ROR} M(CH_2Ph)_4 + MgClx\ (M = Ti,\ Zr\ Or\ Hf)$$

$$M\,Cl_4 + 4\,Li\,CH_2\,Si\,Me_3 \xrightarrow{Et_2O} M\,(CH_2SiMe_3)_4 + 4LiCl\ (M = Ti,\ Zr\ Or\ Hf)$$

$$Ti\,Cl_3 + Mg\,(R)\,Br \xrightarrow[30^\circ C]{Py} Ti\,Cl_2\,(R)\,(Py)_2 + Mg\,(Br)\,Cl\ (R = Me,\ Ph)$$

$$Ti\,Cl_3(\eta^5 - C_5\,h_5) + 3\,Li\,Me \xrightarrow[30^\circ C]{ROR} Ti\,Me_3\,(\eta^5\text{-}C_5\,H_5)_2 + 3\,LiCl$$

$$Ti\,Cl_2\,(dmpe)_2 + 2\,Li\,Me \xrightarrow{ROR} Trans\ Ti\,Me_2\,(dmpe)_2 + 2\,LiCl$$

(ii) Transmetallation: *These reactions are opposite to halide exchange reactions giving heteroleptic alkyls or aryls.*

$$2\,Ti\,Cl_4 + Zn\,Me_2 \rightarrow 2\,Ti\,Cl_3\,Me + Zn\,Cl_2$$

$$Ti\,Cl_4 + Al\,Me_3 \rightarrow Ti\,Cl_3\,Me + Al\,Me_2\,Cl$$

$$Ti\,Cl_4 + Pb\,R_4 \rightarrow Ti\,Cl_3\,R + Pb\,(R)_3\,Cl\quad (R = Me\ Or\ Et)$$

(iii) Metal hydride alkane insertion:

$$Zr\,(H)Cl(\eta^5\text{–}C_5\,H_5)_2 + LiPh \rightarrow Zr(Cl)(Ph)(\eta^5\text{–}C_5\,H_5)_2 + LiH$$

3. **Group 5 - d^3 Metals:** V [Oxidation Number +2: Coordination Number: 4(dsp^2) Example: *Trans*-$VMe_2(dmpe)_2$, 6(d^{2}sp^3) Example: $[VPh_6]^{4-}$; Oxidation Number +3: Coordination Number: 3(sp^2) Example: $V(CH_2SiMe_3)_3$; Oxidation Number +3: Coordination Number: 6(d^{2}sp^3) Example: $VPh_3(THF)_3$; Oxidation Number +4: Coordination Number: 4(dsp^2) Example: VMe_4], Nb [Oxidation Number +4: Coordination Number: 4(sp^3) Example: $Nb(C_6F_5)_4$; Oxidation Number +5: Coordination Number: 5(dsp^3) Example: $NbMe_5$; Oxidation Number +5: Coordination Number: 6(d^{2}sp^3) Example: $[NbPh_6]^-$] and Ta [Oxidation Number +5: Coordination

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Number 5(dsp³) Example TaMe₅, Oxidation Number +5 Coordination Number 6(d²sp³) Example [TaPh₆]⁻] are present in the group. General methods for synthesis are

(i) **Halide exchange**

$$VCl_2(dmpe)_2 + Li\,me \xrightarrow{ROR} Trans{-}V(Me)_2(dmpe)_2 + 2\,LiCl$$

$$VCl_3(THF)_3 + Li\,Ph \rightarrow VPh_3(THF)_3 + 3\,Li\,Cl$$

$$VCl_4 + 4\,Li\,R \rightarrow VR_4 + 4\,Li\,Cl\ (R = Me, Ph)$$

$$VCl_3(NMe_3)_2 + 3\,Li\,CH(SiMe_3)_2 \rightarrow V[CH(Si\,Me_3)_2]_3 + 3\,Li\,Cl + 2NMe_3$$

$$VCl_4 + 4\,Mg(CH_2Ph)X \xrightarrow[-60^\circ C]{ROR} V(CH_2Ph)_4 + 4MgXCl$$

$$VCl_4 + 4\,Li(CH_2SiMe_3) \longrightarrow V(CH_2SiMe_3)_4 + 4LiCl$$

$$Ta\,Cl_2Me_3 + 2\,Li\,Me \xrightarrow[+78^\circ c]{Et_2O} TaMe_5$$

(ii) **Transmetallation**:

$$Nb\,Cl_5 + ZnR_2 \xrightarrow{Pentane} NbCl_3R_2 + ZnCl_2$$

$$2TaCl_5 + 3ZnR_2 \xrightarrow{Pentane} 2TaCl_2R_3 + 3ZnCl_2$$

$$(R{=}Me, CH_2, Si\,Me_3)$$

4. **Group 6 - d⁴ Metals:** Cr [Oxidation Number +2: Coordination Number: 4(dsp²) Example: *Trans*-CrMe₂(dmpe)₂, 6(d²sp³) Example: [Cr₂Me₈]⁴⁻; Oxidation Number +3: Coordination Number: 3(sp²) Example: Cr(CH₂Ph)₃, 4(sp³) Example: [CrPh₄]⁻, 6(d²sp³) Example: CrPh₃(THF)₃; Oxidation Number +4: Coordination Number: 4(sp³) Example: CrMe₄, 6(d²sp³) Example: [CrMe₆]²⁻], Mo [Oxidation Number +2: Coordination Number: 5(dsp³) Example: Mo(CH₂Ph)(CO)₃(η¹–C₅H₅); Oxidation Number +3: Coordination Number: 6(d²sp³) Example: (Mo₂Me₁₀)⁴⁻; Oxidation Number +4: Coordination Number: 4(sp³) Example: Mo(CH₂Ph)₄] and W [Oxidation Number +3: Coordination Number: 6(d²sp³) Example: W₂Me₈²⁻; Oxidation Number +4: Coordination Number: 4(sp³) Example: W(CH₂Ph)₄, 6(d²sp³) Example: WPh₆²⁻; Oxidation Number +5: Coordination Number: 5(dsp³) Example: W(Ph)₅; Oxidation Number +6: Coordination Number: 6(d²sp³) Example: WMe₆] are present in the group. General methods for synthesis are:

(i) **Halide exchange method:**

$$CrCl_2(dmpe)_2 + 2\,Li\,Me \xrightarrow{ROR} Trans{-}Cr\,Me_2(dmpe)_2 + 2\,Li\,Cl$$

$$CrCl_3 + 3\,Li\,CH(Si\,Me_3)_2 \longrightarrow Cr\{CH(Si\,Me_3)_2\}_3 + 3LiCl$$

$$CrCl_3 + 6\,Li\,Me \xrightarrow[-18^\circ c]{Dioxane} Li_3[Cr\,Me_6]_3 + 3LiCl$$

$$WCl_6 + 6AlMe_3 \rightarrow WMe_6 + 6\,AlClMe_2$$

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(ii) **Transmetallation:**

$CrCl_3(THF)_3 + AlR_3 \xrightarrow{THF} CrRCl_2(THF)_3 + AlR_2Cl$, (R = me, Et, Pr or 'Bu)

$WCl_6 + MR \rightarrow WCl_5R$ (MR = $HgMe_2$ (Ether), R = Me

= $ZnMe_2(CH_2Cl_2$ in Ether) R = Me

= $ZnPh_2$ (in Ether) R = Ph

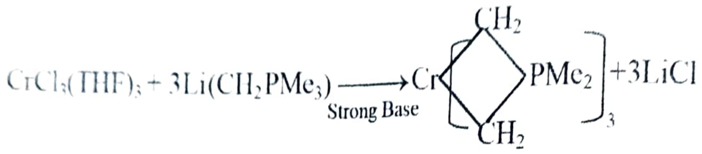
= $SnMe_4$ (in Hexane) R = Me

(iii) **Reaction of Anionic Metal Complexes with Organic Halides:** Sodium salts of carbonilate are generally used in the synthesis of molybdenum hydrocarbyls. Example:

$Na[Mo(CO)_3\ \eta^5\text{-}C_5H_5) + PhCH_2Cl \rightarrow Mo(CH_2Ph)(CO)_3(\eta^5\text{-}C_5H_5) + NaCl$

(iv) **Ylide synthesis:**

$Cr(CO)_5(PPh_3) + Ph_3P{=}CH_2 \rightarrow Cr(CH_2PPh_3)(CO)_5 + PPh_3$



5. **Group 7 - d^5 Metals:** Mn [Oxidation Number +1: Coordination Number: 6(d^2sp^3) Example: $Mn(CF_3)(CO)_5$; Oxidation Number +2: Coordination Number: 4(sp^3) Example: $MnMe_2(dmpe)_2$; Oxidation Number +3: Coordination Number: 4(sp^3) Example: $[Mn(CH_2CMe_2PPh_3)_3]_2]$ and Re [Oxidation Number +3: Coordination Number: 4(sp^3) Example: $Re_2(\mu\text{-}SiMe_3)_2(CH_2SiMe_3)_4$, 6($d^2sp^3$) Example: $Re_2Me_8^{2-}$; Oxidation Number +4: Coordination Number: 6(d^2sp^3) Example: $Re_3(CH_2SiMe_3)_{12}$; Oxidation Number +6: Coordination Number: 6(d^2sp^3) Example: $ReMe_6$] are present in the group.

General methods for synthesis are:

(i) **Halide exchange**:

$MnCl_2 + 4LiMe \xrightarrow[ROR]{} Li_2[MnMe_4] + 2LiCl$

$MnCl_2 + 2LiMe \xrightarrow{dmpe} Trans\text{-}MnMe_2(dmpe)_2 + 2LiCl$

$MnCl_2 + 4LiCH_2SiMe_3 \rightarrow Li_2[Mn(CH_2SiMe_3)_4] + 2LiCl$

$2MnCl_2 + 4MgCl[CH_2C(Ph)Me_2] \xrightarrow{ROR} [Mn\{CH_2C(Ph)Me_2\}_2]_2 + 4MgCl_2$

$3ReCl_4(THF)_4 + 6MgR_2 \rightarrow Re_3R_{12} + 6MgCl_2$

(ii) **Reactions of anionic metal complexes with organic halides**:

$Na[Mn(CO)_5] + CH_3I \rightarrow MnCH_3(CO)_5 + NaI$

$Na[Mn(CO)_5] + CF_3COCl \rightarrow Mn(COCF_3)(CO)_5 + NaCl$

(iii) **Insertion of unsaturated compounds in M-C bond**:

$MnPh(CO)_5 + PPh_3 \rightarrow Mn\{(CO)Ph\}(CO)_4(PPh_3)$

$MnCH_3(CO)_5 + CO \rightarrow Mn\{CO)CH_3\}(CO)_5$

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(iv) **Elimination of CO from acyl-compounds**:

$$Mn(COC_6H_4Me)(CO)_5 \xrightarrow{Energy} Mn(C_6H_4Me)(CO)_5 + CO$$

6. **Group 8, 9, 10 - d^6 , d^7 , d^8 Metals, respectively:** Fe [Oxidation Number +2: Coordination Number: 2(sp) Example: $Fe(Mes)_2$ MeS = Mesitylene, 4(sp^3) Example: $FePh(Co)_2(\eta^1\text{-}C_5H_5)$], Co [Oxidation Number +1: Coordination Number: 5(dsp^3) Example: $Co(CF_2CF_2H)(CO)_4$; Oxidation Number +2: Coordination Number: 4(sp^3) Example: $CoPh_2(dipy)$; Oxidation Number +3: Coordination Number: 3(sp^2) Example: $[CoPh_2(\eta^6\text{-}C_6H_4Me)]$, 6($d^2sp^3$) Example: $[Co(C{=}CR)_6]^{3-}$; Oxidation Number +4: Coordination Number: 4(sp^3) Example: CoR_4, 6(d^2sp^3) Example: $[Co(CH_2Ph)(CN)_5]^{2-}$], Ni [Oxidation Number +2: Coordination Number: 2(sp) Example: $NiBu_2$, 4(sp^3) Example: $NiMe_4^{2-}$; Oxidation Number +3: Coordination Number: 3(sp^2) Example: $NiPh_2(\eta^6\text{-}C_6H_4Me)$, Oxidation Number +4: Coordination Number: 6(d^2sp^3) Example: $[Ni(CH_2Ph)(CN)_5]^{2-}$], Ru [Oxidation Number +2: Coordination Number: 6(d^2sp^3) Example: $Ru(CH_3)(I)(CO)_2(PPh_3)_2$], Rh [Oxidation Number +3: Coordination Number: 3(sp^2) Example: $Rh(Mes)_3$, 6(d^2sp^3) Example: $[Rh(Et)(NH_3)_5]^{2+}$], Pd [Oxidation Number +2: Coordination Number: 4(sp^3) Example: $[Pd({>}CH_2SPh)_2]_4$], Ir [Oxidation Number +3: Coordination Number: 6(d^2sp^3) Example: $IrMe(Cl)(I)(CO)(PPh_3)_2$], Pt [Oxidation Number +2: Coordination Number: 4(dsp^2) Example: $PtMe_2(PPh_3)_2$] etc. are present here. General methods for synthesis are:

(i) **Halide exchange:**

$$FeCl_2(dmpe)_2 + 2\,LiMe \xrightarrow{ROR} FeMe_2(dmpe)_2 + 2LiCl$$

$$NiCl_2(PEt_3)_2 + 2MgBr(Mes) \rightarrow 2\,MgBrCl + Ni(Mes)_2(PEt_3)_2 \xrightarrow{Vacuum} Ni(Mes)_2 + 2\,PEt_3$$

$$NiCl_2(Py)_2 + 2Mg(CH_2SiMe_3)Cl \rightarrow Ni(CH_2SiMe_3)_2(Py)_2 + 2\,MgCl_2$$

$$RhCl_3(SC_4H_6) + 3Mg(Mes)Br \rightarrow Rh(Mes)_3 + SC_4H_6 + 3\,MgBrCl$$

$$PdCl_2(L)_2 + 2\,LiPh \rightarrow PdPh_2(L)_2 + 2\,LiCl;\ (L - \text{Bidentate})$$

$$4\,PdCl_2(PhCN)_2 + 8\,Li(CH_2SPh) \rightarrow \{Pd(CH_2SPh)_2\}_4 + 8\,LiCl + 8\,PhCN$$

$$PtCl_2(PEt_3)_2 + 2\,LiMe \rightarrow PtMe_2(PEt_3)_2 + 2\,LiCl$$

(ii) **Transmetallation:**

$$PtCl_2(PR_3)_2 + HgPh_2 \xrightarrow{EtOH} trans\text{-}Pt(Ph)Cl(PR_3)_2 + Hg(Ph)Cl$$

$$PtCl_2(1,5\text{-}Cod) + SnMe_4 \xrightarrow[100^\circ C]{C_2H_2Cl_4} PtMe\,Cl(1,5\text{-}Cod) + SnClMe_3$$

$$Pt(O_2CCF_3)_2(PMe_2Ph)_2 + SnMe_4 \rightarrow trans\text{-}PtMe(O_2CCF_3)(PMe_2Ph)_2 + Sn(O_2CCF_3)Me_3$$

(iii) **Reaction of anionic metal complexes with organic halides:**

$$Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)] + PhF \rightarrow [Fe(Ph)(CO)_2(\eta^5\text{-}C_5H_5)] + NaF$$

$$Na_3[CO(CN)_5] + PhCH_2Br \rightarrow Na_2[Co(CH_2Ph)(CN)_5] + NaBr$$

$$Na[Co(CO)_4] + CH_2\text{-}CH{=}CH_2Br \rightarrow Co(CH_2\text{-}CH{=}CH_2)(CO)_4 + NaBr$$

$$\downarrow$$

$$Co(CO)_3(\eta^3\text{-}C_3H_5) + CO$$

(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:

$$Trans\ Pt\,Cl(CH_3)(PEt_3)_2 + CO \rightarrow Trans\ Pt\,Cl(COCH_3)(PEt_3)_2$$

(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:

$$Ni(CO_2Ph)_2(biby) \xrightarrow{Heat} Ni\,Ph_2(biby) + CO_2$$

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

- 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.

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

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)

Example: $[AuMe_2]^-$; Oxidation Number +2: Coordination Number: 2(sp) Example: $Au[CH_2(SiMe)_3](L)$; 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**:

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

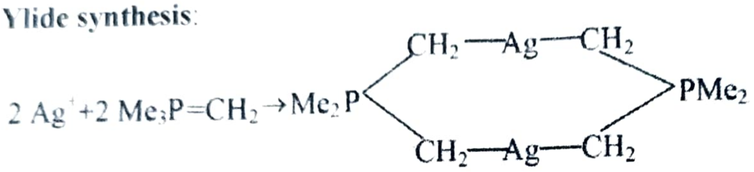
$$CuCl + 2\,Li\,Me \xrightarrow{ROR} Li\,(Cu\,Me_2) + Li\,Cl$$

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

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

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

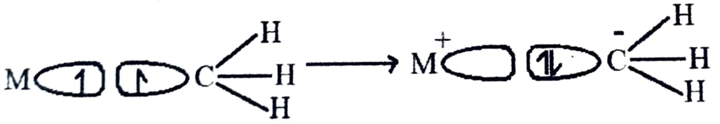
(ii) **Ylide synthesis**:



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

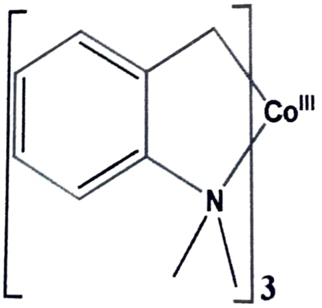
Transition Metal Aryl + Alkyl Complex

hydrocarbon radical depends on the presence/absence of hydrogen atoms in that group. Presence of excess of hydrogen on the group makes it rather more positive, while absence of hydrogen or presence of electronegative F, Cl or O atom makes hydrocarbon radical more negative increasing the stability of M-C bond. Thus in summary, in comparison to alkyl or aryl compounds, fluoro alkyls or fluoro aryls have higher stability. Example: $CF_3Co(CO)_5$ is far more stable than $CH_3Co(CO)_5$. Fluorine makes M-C bond more polar by attracting electrons towards it increasing ionic contribution in that bond. Upon increase of positive charge on metal, d-orbitals get contracted which helps in increasing better overlap between bonding metal d-orbitals and ligand orbitals.

One important phenomenon takes place during synthesis of transition metal hydrocarbyls, which is the change of the nature of alkyl (or aryl) carbon from electrophilic to nucleophilic. Increase in M→L back-bonding (π–bonding) tendency is feasible with the increase in electroneutrality. This eventually increases stability of these compounds. Presence of CO, CN, pyridene etc. ligands (which help M→L π–bonding in transition metal alkyls or aryls) increases their stability, for example $Mn(CH_2CH_3)(CO)_5$, $Mo(CH_2CH_3)(CO)_3(\eta^5\text{-}C_5H_5)$ etc. are quite stable.

Most important characteristic of transition metal σ–hydrocarbyls is their coordinative unsaturation, leading to instability through facile decomposition paths. On the other hand, thi unsaturation also explains their tendency to act as Lewis acids with a variety of donors. Presenc of these ancillary ligands adds extra comparative stability on these derivatives. Examples $TiMe_4$(biby); $TaMe_5$(dme); CoMe(diphos)$_2$, [diphos = 1,2-bis (diphenylphosphino) ethane] $MMe_2(dmpe)_2$ [M=Ti, V, Cr, Mn and Fe, dmpe = 1,2-bis (dimethylphosphino) ethane $NiEt_2$(bipy) and $Ln(CH_2SiMe_3)_3(THF)_n$ [Ln = lanthanide metal, n = 2 or 3] are more stable tha uncoordinated σ–hydrocarbyls.

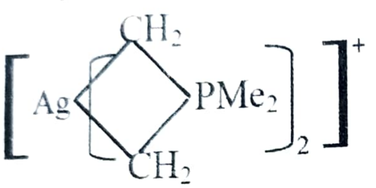
Chelating hydrocarbyls e.g. o-$CH_2C_6H_4NMe_2$ etc. tends to provide stability to σ–bond derivatives by blocking the available coordination sites.

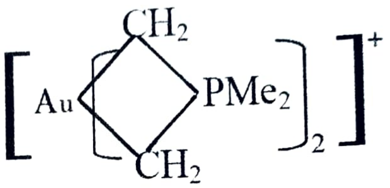


Metal-alkyl/aryls tend to satisfy their coordination environment by forming polynuclear spec via alkyl or other bridging ligands or via multiple M-M bonding too. Association thro bridging would obviously be hindered by sterically crowded ligands, resulting in mononuc species. Though these complexes would formally be coordinatively unsaturated, still they wil thermally stable, due to steric crowding of the ligands which will inhibit any approach of reac species. Example: $[Ti\{CH(SiMe_3)_2\}_3]$, $[Cr\{CH(SiMe_3)_2\}_3]$ etc.

Coordinative unsaturation increases upon lowering of the oxidation state of the metal, leading to greater associative tendency. For example, compared to the monomeric character of $Ti(C_6H_5)_4$, the polymeric nature of $\{Ti(C_6H_5)_2]_n$ are cited more.

Transition metal σ–hydrocarbyls are of three types in nature: neutral, anionic and cationic. Stability of anionic species of the types $[Ti(C_6H_5)_5]^-$ and $[Zr(C_6H_5)_6]^{2-}$ can be explained as the central metal atoms are coordinatively less unsaturated than in their corresponding neutral species $[Ti(C_6H_5)_4]$ and $[Zr(C_6H_5)_4]$, respectively. With same logic, cationic species are expected to form not so easily. These often require a chelating hydrocarbyl of the type $Me_3P{=}CH_2$ for example, which provides stability on cationic species of the types:

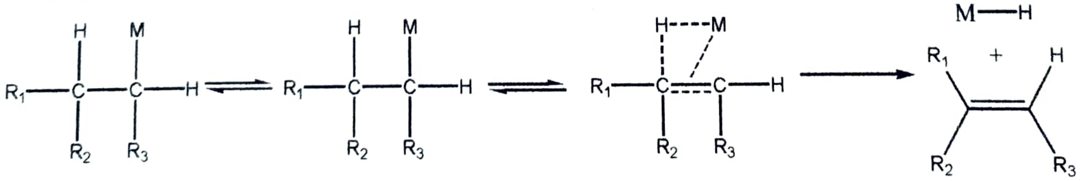




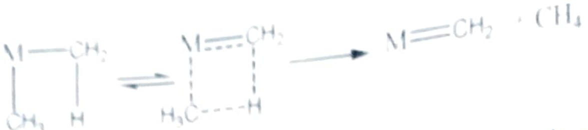
Decomposition Pathways: Transition metals σ-hydrocarbyls, due to their coordinative unsaturation are not kinetically stable and this origins several facile pathways for their decomposition and strong reactivity. These paths can be classified as; (1) migration of a substituent (generally hydrogen) from a σ–bonded hydrocarbyl to the metal, (2) intermolecular reductive elimination and (3) homolytic fission of M-C bond.

1. **Migration of a substituent from a σ–bonded hydrocarbyl to the metal**: It occurs via 3 types of mechanism:

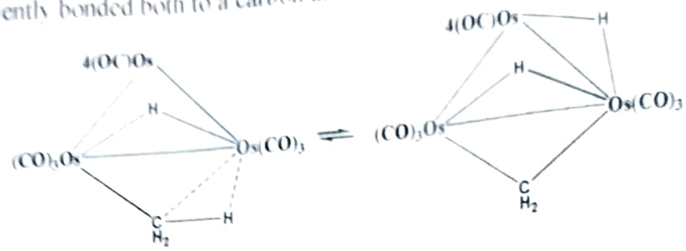
i. **β–elimination:** The most facile route for decomposition, preferred by transition metal alkyls is through the so called hydride transfer accompanied with alkene elimination. This type of reaction involves transfer of one hydrogen atom from the second or β–carbon atom of the alkyl chain to the metal, increasing its coordination number. Resulting intermediate hydrido-alkene complex tends to lose alkene upon formation of metal-hydride, which in some cases may decompose to metal and hydrogen too.



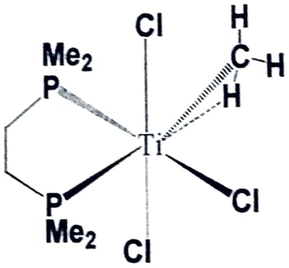
ii. **α–elimination:** α-Elimination pathways are much less observed for transition metal hydrocarbyls and main examples involve metal-methyls. However, these are of considerable synthetic utility in main group hydrocarbyls and involve the transfer of a substituent 'R' from the α–carbon atom to the metal. Binary permethyls, example: $TaMe_5$, WMe_6 and $ReMe_6$ are unstable and decompose explosively with the formation of methane via four-centred transition state. This plays a key role towards synthesis of alkylidene complexes. Several metal 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.

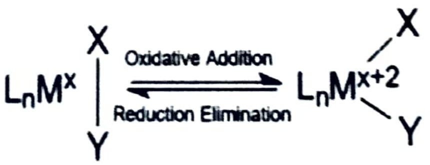


Crystallographic analysis shows that, when a methyl group is attached to a d°-metal centre, having less than 18-electron environment, one of the C-H bonds of that methyl group gets distorted to the extent that it gets into the bonding distance with the metal. Such strong interactions between metal and 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: $AuMe(PPh_3) \rightarrow Au(PPh_3) + C_2H_6$

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

$Au(CH_2SiMe_3)(PPh_3) + MeI \rightarrow AuIMe(CH_2SiMe_3)(PPh_3) \rightarrow AuI(PPh_3) + SiEtMe_3$

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.

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

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:

$Ti\,Me_4 + 4\,MeCOOH \xrightarrow{ROR} Ti\,(O_2CMe)_4 + 4CH_4$

$Zr\,(CH_2\,Si\,Me_3)_4 + 4\;2,6\text{-}C_6\,H_5\,Pr_2OH \rightarrow Zr\,(2,6\text{-}Pr_2\,C_6H_5O)_4 + 4\,Si\,Me_4$

$Cr\,Ph_3\,(THF)_n + \text{Acetyl Acetone} \rightarrow Cr\,(Acac)_3 + 3\,C_6H_6 + n\,THF$

$\text{Cis-}[PtCl_2(PEt_3)_2] \xleftarrow[-2CH_4]{2HCl} \text{Cis-}Pt\,Me_2\,(PEt_3)_2 \xrightarrow[-CH_4]{HCl} \text{Cis-}[Pt\,Cl\,(Me)(PEt)_2]$

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

$Ti\,Me_4 + 4I_2 \rightarrow 4\,MeI + Ti\,I_4$

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

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

$Pt\,Cl\,(CH_2\,CH_3)\,(PEt_3)_2 \rightarrow Pt\,H\,Cl\,(PEt_3)_2 + C_2H_4$

$Cu(CH_2CH_2CH_2CH_3)(PBu^n_3) \rightarrow C_2H_5\,CH = CH_2 + Cu\,H\,(PBu^n_3)$

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

3. **Replacement reactions**:

$[Pd\,Me_2\,(bipy] + 2\,C_3H_7\,I \rightarrow [Pd\,(C_3H_7)_2\,(bipy)] + 2\,CH_3\,I$

$M\,(CH_2Ph)_4 + 2\,EtOH \rightarrow M\,(CH_2\,Ph)_2\,(OEt)_2 + 2PhCH_3\,(M = Ti \text{ or } Zr)$

$Zr\,Me_2\,(\eta^5\text{-}C_5H_5)_2 + MeOH \rightarrow Zr\,Me\,(OMe)\,(\eta^5\text{-}C_5H_5)_2 + CH_4$

4. **Adduct Formation**:

$[Mn\,R_2]_n + TMEDA \rightarrow MnR_2(TMEDA)\;\; R = CH_2CMe_3, CH_2Si\,Me_3 \text{ or } CH_2(Me_2\,Ph)$

$Ti\,Me_2 + dmpe \rightarrow Ti\,Me_2\,(dmpe)_2$

$Ta\,Me_5 + dme \rightarrow Ta\,Me_5\,(dme)$

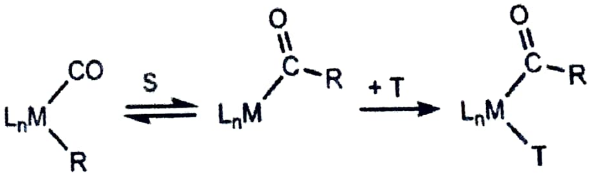
$[Mn\,(CH_2\,Si\,Me_3)_2] + 2\,Li\,CH_2\,Si\,Me_3 \rightarrow Li_2\,[Mn\,(CH_2\,Si\,Me_3)_4]$

5. **Redistribution**:

$\text{Cis-}Pt\,Me_2\,(PEt_3)_2 + \text{Cis }Pt\,Cl_2(PEt_3)_2 \rightarrow 2\;\text{Cis-}Pt\,Cl\,(Me)\,(PEt_3)_2$

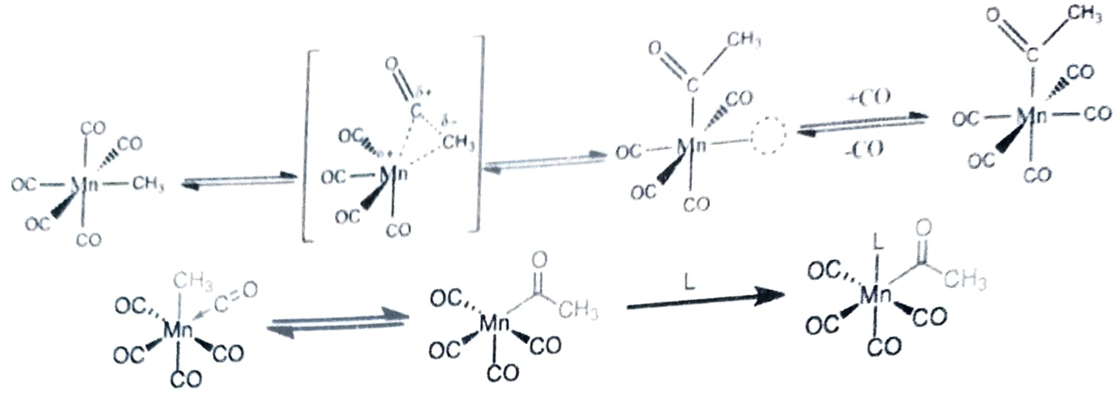
6. **Insertion Reactions**: Unsaturated ligands insert itself into M-C bond giving new products.

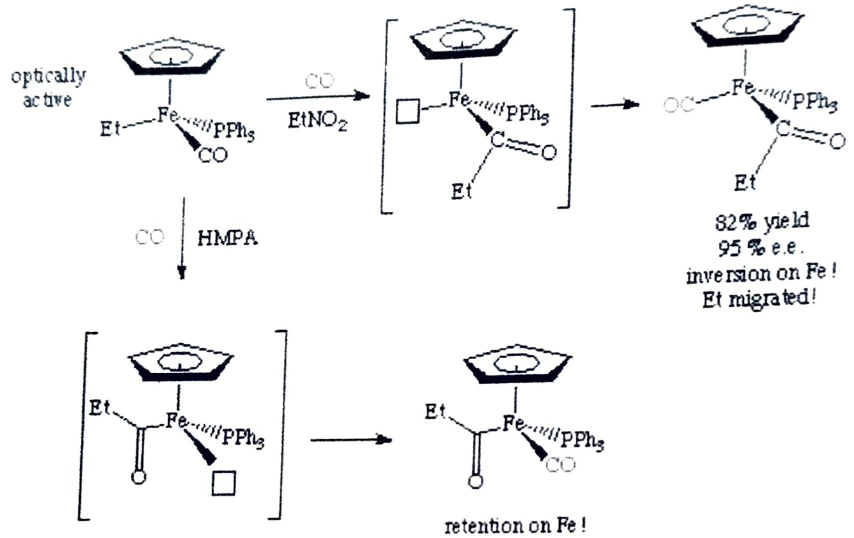
i. **CO insertion**:



AK.P

Transition Metal - Alkyl and Aryl Complexes

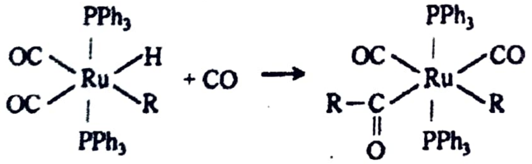


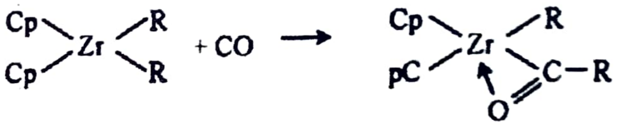


optically active

82% yield
95% e.e.
inversion on Fe!
Et migrated!

retention on Fe!
CO migrated!





ii. **CO_2, SO_2 or CS_2 insertion:**

$$\mathrm{Cu\,Me(PPh_3)_3} \xrightarrow{CO_2} \mathrm{Cu\,(O_2C\,Me)(PPh_3)_3}$$

$$\mathrm{Cu\,Me\,(Et_2O)\,(PPh_3)_2} \xrightarrow{CO_2} \mathrm{Cu(O_2C\,Me)(Et_2O)(PPh_3)_2}$$

$$\mathrm{Au\,Me\,(PMe_3)_3} \xrightarrow{SO_2} \mathrm{Au(SO_2\,Me)(PMe_3)_3}$$

$$\mathrm{Au\,Me_3\,(PMe_3)} \xrightarrow{SO_2} \mathrm{Cis\text{-}Au\,Me_2\,(SO_2Me)\,(PMe_3)}$$

$$\mathrm{Ti\,Me_2(\eta^5\text{-}C_5H_5)_2} \xrightarrow[-78^\circ C]{2SO_2} \mathrm{Ti\,(\eta^1\text{-}O_2\,SMe)_2\,(\eta^5\text{-}C_5H_5)_2}$$

Organo-Copper in Organic Synthesis: Most important organocopper reagent is lithium dimethyl cuprate, $Li[Cu(CH_3)_2]$, prepared by the action of methyl lithium with cuprous iodide:

$$4\,LiCH_3 + Cu_2I_2 \rightarrow 2\,Li[Cu(CH_3)_2] + 2\,LiI$$

Transition Metal - Alkyl and Aryl Complexes .

Typical characteristics of lithium dimethyl cuprate, $Li[Cu(CH_3)_2]$ are:

1. Strong nucleophilicity towards carbon atom and very high affinity for reaction at alkene or halide sites compared to carbonyl groups.
2. Inertness towards groups like cyano- or ester- etc.
3. In, α,β– unsaturated carbonyl systems, it selectively attaches with β– Carbon atom.
4. It has special ability to replace various types of halogen atoms by methyl groups.
5. It reacts with allylic acetates by SN^2 mechanism.
6. Reacts with epoxides to form open ring alkylated alcohols.
7. It adds to acetylene-esters.

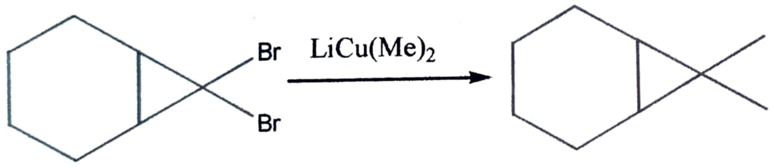
In addition, there are examples of similar reactions involving branched alkyl, phenyl and vinyl copper reagents.

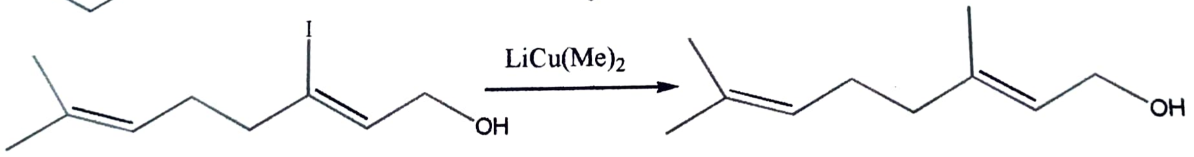
- **Halogen Substitution**:

  Trans-$PhCH{=}CHBr + LiCuMe_2 \rightarrow$ *Trans*-$PhCH{=}CHMe$

  $C_6H_5I + LiCuMe_2 \rightarrow C_6H_5Me$

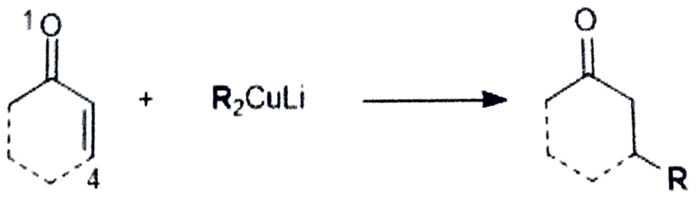
  $C_5H_{11}Br + Li[Cu^tBu2] \rightarrow {}^tBu(CH_2)_4CH_3$



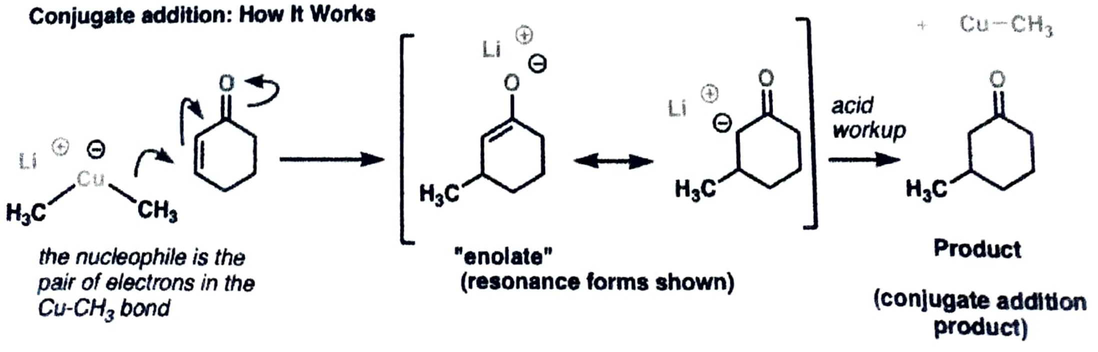


- **Conjugated Additions**:

1,4-addition of α,β-unsaturated carbonyl compounds



Conjugate addition: How It Works



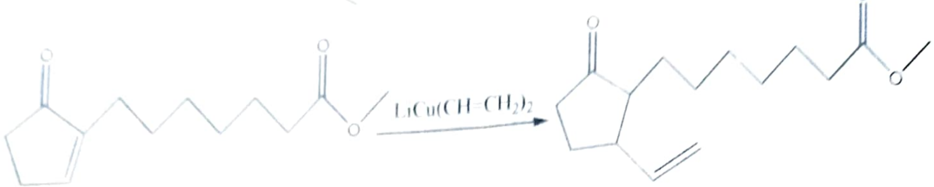
the nucleophile is the pair of electrons in the Cu-CH₃ bond

"enolate" (resonance forms shown)

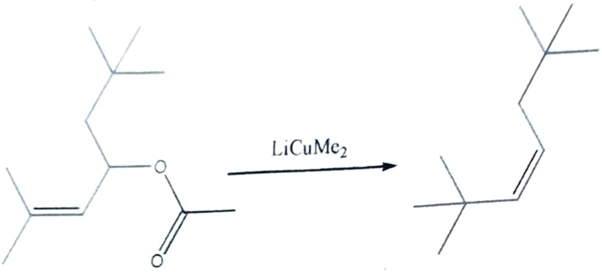
Product

(conjugate addition product)

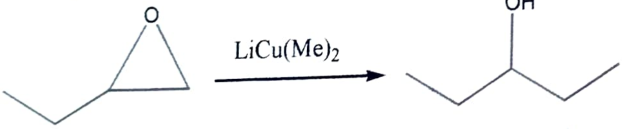
Transition Metal - Alkyl & Aryl Complexes.

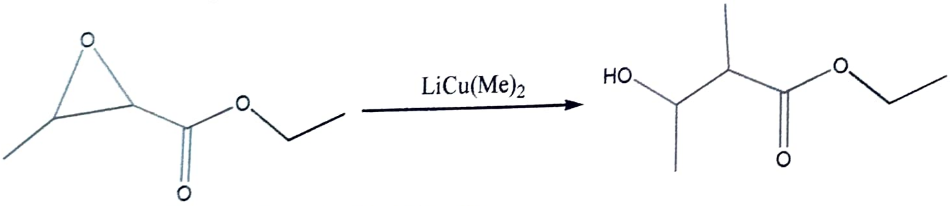


○ **Alkylation of Allyl Acetate:**

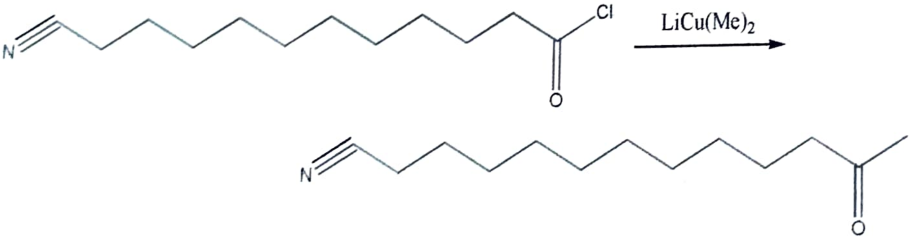


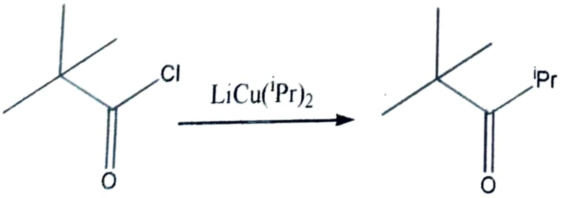
○ **Alkylation of Epoxides:**





○ **Formation Ketone from Acid- Chloride:**





The end.

A.K.P