

P.G. SEMESTER-IV

ELECTIVE COURSE-1a

INORGANIC CHEMISTRY SPECIAL

**UNIT-I[A]: ALKYL AND ARYL TRANSITION
METALS**

**TOPIC- TYPES OF ALKYL AND ARYL
TRANSITION METALS**

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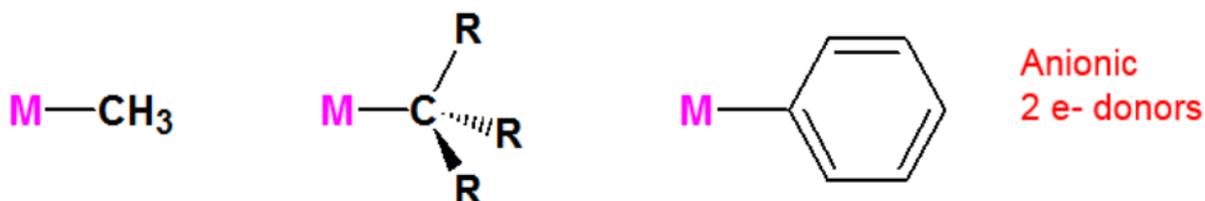
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METAL ALKYL AND ARYL COMPLEXES

Compounds of metal with alkyl radical are called metal alkyls while those with aryl are called metal aryls. It contains direct M-C bond.



Where C comes from alkyl or aryl radical and it acts as ligand. It may be generally sigma donor. It may be

- homoleptic (if ligands are same) or
- heteroleptic (if ligands are different)

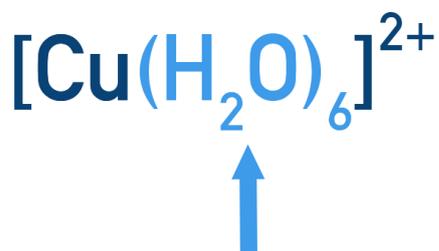
It may be -

- symmetrical (when ligands are same) or
- asymmetrical (when ligands are different)

Similarly it may be –

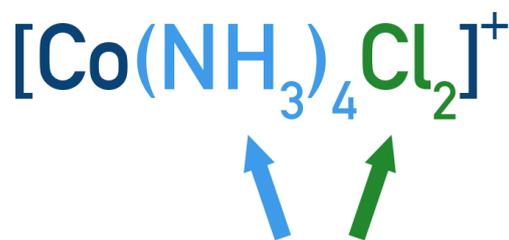
- mono nuclear or
- poly nuclear.

Homoleptic Complex Ion



only one type
of ligand

Heteroleptic Complex Ion



two types
of ligand

Homoleptic Complexes

In these complexes, the metal ion is bonded to identical donor groups. In these complexes, the metal ion is bonded to identical donor groups.

Examples-

Titanium Complexes: Tetramethyltitanium ($\text{Ti}(\text{CH}_3)_4$) is highly unstable, but stabilized by ligands. Neopentyl titanium ($\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$) is relatively stable because it lacks β -hydrogens.

Zirconium Complexes: Tetrabenzylzirconium ($\text{Zr}(\text{CH}_2\text{Ph})_4$) is a commonly cited, stable homoleptic aryl complex.

Chromium Complexes: Triphenylchromium (CrPh_3) and its THF-solvated forms are examples, although they are challenging to prepare.

Anionic Alkyl/Aryl Species: $\text{Li}_2[\text{Cu}(\text{CH}_3)_2]$ (Gilman reagent) and $\text{Li}_4[\text{Cr}_2(\text{CH}_3)_8]$ are anionic species where the metal is coordinated only to alkyl groups.

Rare-Earth Metals: Homoleptic tris(alkyl) complexes of lanthanides can be formed using bulky ligands.

Heteroleptic Complexes

In these complexes, the central metal is bound to more than one type of ligand.

Examples-

- **Organolanthanide Bimetallic "Ate" Complexes:** These often feature, for example, a Lanthanide (Y, Lu, Sm, Nd) bonded to bis(trimethylsilyl)methyl (alkyl) ligands and bridging chloride ligands, often paired with lithium, e.g., $\text{LiLu}(n\text{-Bu})_3\text{Cl}(\text{tmeda})_2$ or $\text{Sc}[\text{CH}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{thf})_3$.
- **Early Transition Metal Complexes:**
 - **Titanium:** Cp_2TiClMe (cyclopentadienyl titanium chloride methyl).
 - **Tantalum:** $\text{Ta}(\text{CH}_3)_3\text{Cl}_2$ (trimethyltantalum dichloride).
- **Late Transition Metal Complexes:**
 - **Platinum(II):** $\text{PtPh}(\text{Me})(\text{PPh}_3)_2$ (phenyl methyl bis(triphenylphosphine)platinum), which contains both an aryl (phenyl) and alkyl (methyl) group.
 - **Copper(I):** $\text{LiCu}(\text{CH}_3)_2$ (lithium dimethylcuprate).
 - **Nickel/Palladium:** Aryl-nickel-halide or Alkyl-palladium-phosphine complexes utilized in catalysis (e.g., Suzuki or Negishi coupling intermediates).
- **Lanthanide Amide/Bromide Complexes:** A specific example is $[\text{Nd}\{(\eta^5\text{-C}_{13}\text{H}_8)\text{C}_2\text{H}_4\text{N}(\kappa\text{-C})\text{C}_2\text{H}_2\text{N}(\text{Me})\}(\mu\text{-Br})\{\text{N}(\text{SiMe}_3)_2\}]_2$

.....TO BE CONTINUED

