

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 (PART 2)**

Dr. JASMINE SINGH

ASSISTANT PROFESSOR

DEPARTMENT OF CHEMISTRY

M.B.R.R.V.PD. SINGH COLLEGE, ARA

(MAHARAJA COLLEGE)

Symmetric Transition Metal Alkyl/Aryl Complexes

Symmetric complexes often feature identical alkyl or aryl ligands surrounding the metal, or the complex possesses a high degree of symmetry (C_2 , D_{3h} , etc.) in its structure.  Bhupendra Narayan Mandal University +2

- **Hexamethyltungsten(VI) [$W(CH_3)_6$]:** A classic example of a homoleptic alkyl complex, which exhibits a trigonal prismatic structure.
- **Tetranorbornylcobalt(IV) [$Co(Nor)_4$]:** A stable, homoleptic complex where the lack of β -hydrogens on the norbornyl ligand prevents decomposition, giving it a symmetric, tetrahedral-like structure.
- **Dimethylzinc [$Zn(CH_3)_2$]:** A linear, symmetric alkyl complex.
- **Diphenylzinc [$Zn(Ph)_2$]:** A symmetric aryl complex with two identical phenyl ligands.
- **Tetramethyltitanium [$Ti(CH_3)_4$]:** A symmetrical, though highly reactive, homoleptic alkyl complex.
- **Hexa-substituted aryl complexes:** For instance, $Cr(C_6F_5)_4^-$ (when stabilized).  Wikipedia +2

Asymmetric Transition Metal Alkyl/Aryl Complexes

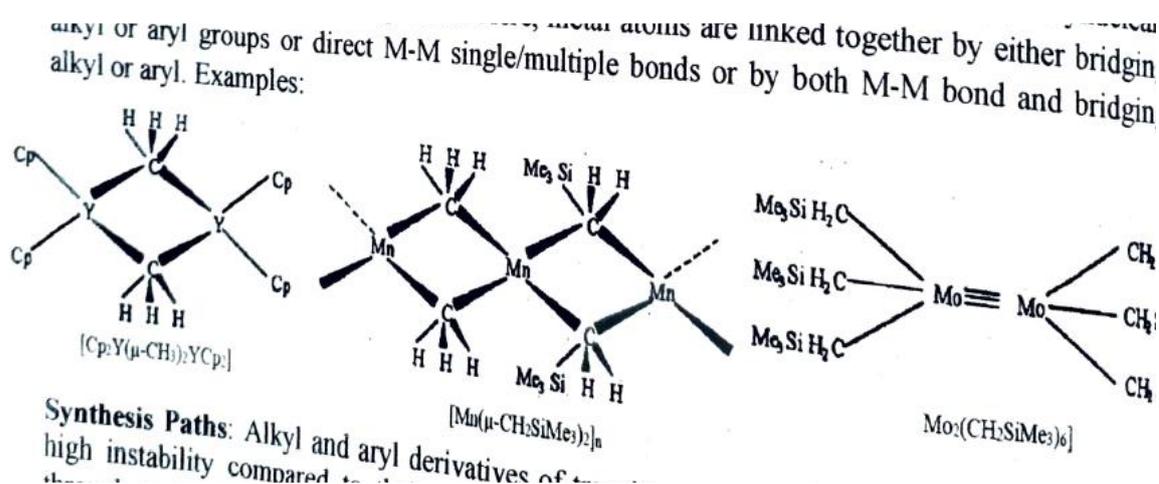
Asymmetric complexes (often referred to as heteroleptic) have different types of ligands attached to the metal, or they possess chiral ligands that create an asymmetric (chiral) environment around the metal center.  YouTube +1

- **Methyl(cyclopentadienyl)iron dicarbonyl [$CpFe(CO)_2CH_3$]:** A classic asymmetric alkyl complex where the methyl group is surrounded by different ligands: cyclopentadienyl (Cp) and carbonyl (CO) groups.
- **Vaska's Complex derivative [$IrCl(CO)(PPh_3)_2(CH_3)(I)$]:** Formed by the oxidative addition of methyl iodide to Vaska's complex, resulting in a square pyramidal or octahedral structure with different ligands.
- **Mes-Pd(II) complexes:** Asymmetric square planar palladium complexes, such as *trans* – [$Pd(Mes)_2(PR_3)_2$] (where Mes = Mesityl), which are kinetically stabilized.
- **Methylrhenium trioxide [CH_3ReO_3] (MTO):** A very stable, asymmetric, and versatile catalyst where a methyl group is attached to rhenium alongside three oxo ligands.
- **Chiral NHC-Pd complexes:** Palladium complexes with C_1 -symmetric or chiral N -heterocyclic carbenes (e.g., 1-phenylethyl or 1-naphthylethyl substituted NHCs), used in asymmetric catalysis.
- **Benzylzirconium complexes:** $Zr(CH_2Ph)_4$ or $ZrCl(CH_2Ph)_3$.  Wikipedia +4

1. Mononuclear Complexes

These contain a **single metal center** coordinated to one or more alkyl (e.g., methyl, ethyl) or aryl (e.g., phenyl) ligands. [Maharaja College, Ara +1](#)

- **Bonding:** The alkyl/aryl group acts as a strong anionic σ -donor.
- **Stability:** Often unstable due to pathways like **β -hydrogen elimination**, where a hydrogen atom on the β -carbon transfers to the metal. Stability is increased using ligands without β -hydrogens (e.g., $-\text{CH}_2\text{SiMe}_3$) or through steric hindrance.
- **Examples:** $W(\text{CH}_3)_6$ (hexamethyltungsten) and $[\text{Ti}(\text{C}_6\text{H}_5)_4]$ (tetraphenyltitanium). [Bhupendra Narayan Mandal University +4](#)



2. Polynuclear Complexes

These contain **two or more metal centers** within a single coordination sphere. [Britannica](#)

- **Structure:** Metal atoms are held together by:
 - **Direct Metal-Metal (M-M) bonds.**
 - **Bridging ligands (μ -ligands):** Alkyl or aryl groups can bridge two or more metals (e.g., $\mu - \text{CH}_3$).
- **Subtypes:**
 - **Low Nuclearity:** Small clusters like dimers or trimers.
 - **High Nuclearity:** Larger clusters with many metal atoms.
- **Example:** $[\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4]$, which features bridging alkyl groups. [YouTube +4](#)