

P.G. SEMESTER-IV

Elective Course-1a

Inorganic Chemistry Special

Unit -1 (a) Alkyl and Aryl Transition Metal Complexes

Topic: Routes of Synthesis of Alkyl and Aryl Transition Metal Complexes Part-1

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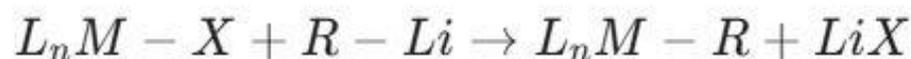
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1. Metathesis (Nucleophilic Displacement)

This is the most common laboratory method. It involves the reaction of a metal halide with an organometallic reagent of a more electropositive metal (typically Li, Mg, or Al).

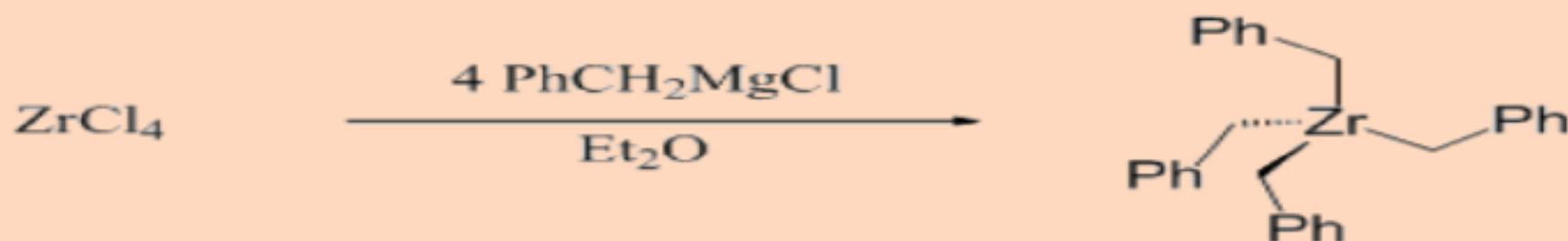
- **Process:** A metal halide ($L_nM - X$) reacts with an organolithium or Grignard reagent ($R - Li$ or $R - MgX$).
- **General Reaction:**



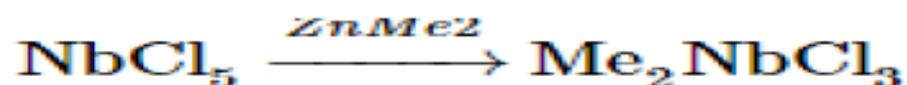
- **Examples:**
 - Synthesis of $W(CH_3)_6$ from WCl_6 and $LiCH_3$.
 - Synthesis of $Ti(CH_2Ph)_4$ using benzyl magnesium chloride.
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Metathesis

This involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents.



Of the different organoalkyl compounds listed above, the organolithium and organomagnesium compounds are strongly carbanionic while the remaining main group organometallics like the organoalkyl, organozinc and organotin reagents are relatively less carbanionic in nature. Thus, the main group organometallic reagents have attenuated alkylating power, that can be productively used in partial exchange of halide ligands.



2. Oxidative Addition

This method is central to catalytic cycles. A neutral metal complex reacts with an alkyl or aryl halide, increasing both the oxidation state and the coordination number of the metal by two.

- **Mechanism:** The metal must be coordinatively unsaturated and in a relatively low oxidation state.
- **Aryl vs. Alkyl:** Aryl halides are particularly good substrates for this because they lack β -hydrogens, making the resulting complex more stable.
- **General Reaction:**

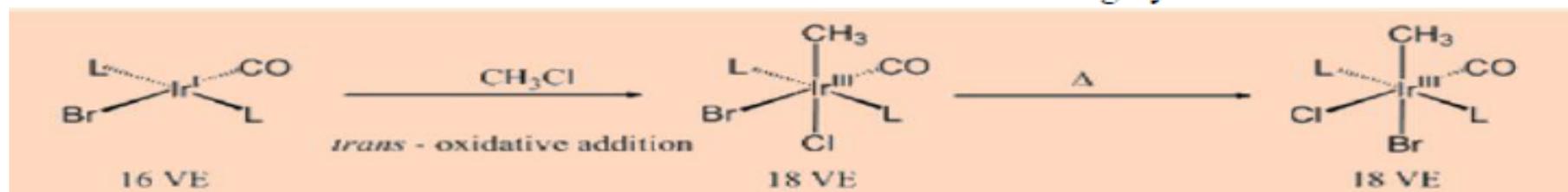


- **Example:**
 - Vaska's complex reacting with methyl iodide:



Oxidative addition reaction

Many unsaturated 16 VE transition metal complexes having d^8 or d^{10} configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.



3. Insertion Reactions (Migratory Insertion)

In this route, an unsaturated organic molecule inserts into an existing metal-hydride or metal-alkyl bond.

- **1,2-Insertion:** Typical for alkenes and alkynes.



- **1,1-Insertion:** Common for Carbon Monoxide (CO), forming acyl complexes.



- **Significance:** This is the key step in industrial processes like the Ziegler-Natta polymerization of ethylene.

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