

HYDRIDE AND ALKYL MIGRATORY INSERTIONS

Migratory insertion is a term to describe the transfer of a ligand from a metal to a carbon monoxide that is also bound to the metal. It is a special case of a 1,1-insertion. In a 1,1-insertion, a group is transferred from a metal to an atom attached to the same metal. A general 1,1-insertion is shown in figure MI2.1.



Figure MI2.1. A general 1,1-insertion. Formal charges would vary according to the specific groups X, Y and Z.

Carbonyl groups in organic compounds are electrophilic. The polar carbon-oxygen double bond places positive charge on the carbon, so the carbon atom attracts nucleophiles. One of the nucleophiles that can react with a carbonyl is a complex hydride, such as a borohydride ion or an aluminum hydride ion. Sometimes, these complex hydrides are anionic, making them more nucleophilic. An example is sodium borohydride, NaBH_4 . Sometimes, the hydride compound is neutral, as in BH_3 . However, the hydride is still nucleophilic even if the compound is not negatively charged, because of the electronegativity difference between the hydrogen and the boron (or the aluminum). A hydride ion is donated as a nucleophile to the electrophilic carbonyl. Transition metal hydrides, like boron and aluminum hydrides, are frequently nucleophilic. They can donate hydrides to electrophiles.

- A hydrogen attached to a metal atom frequently acts like a hydride.
- A nucleophilic hydride can donate to a carbonyl carbon.



Figure MI2.2. CO binding to a metal ion.

"Inorganic carbonyls", or metal-bound CO compounds, behave in many ways like organic carbonyl compounds. In one sense, the bound CO can be thought of as having a positive formal charge on the oxygen, so it is easy to imagine it as an electrophile. It looks like an "activated" organic carbonyl (for example, a ketone that has been protonated, and has a positively charged oxygen). If a metal has a hydride attached to it (a nucleophile) as well as a CO (an electrophile), then a reaction can

occur between them. The hydride can add to the carbonyl. This is one of the most useful things about transition metal chemistry: by binding different, reactive ligands, metals can organize reactants so that they react together.

- This reaction can occur intramolecularly; i.e. from a hydride to a carbonyl on the same metal.
- This event is called a migratory insertion.

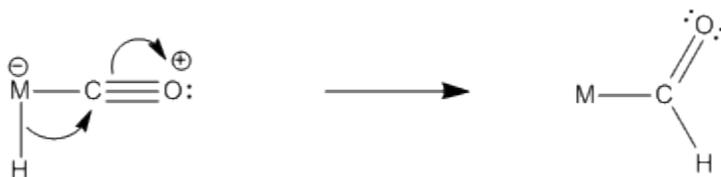


Figure MI2.3. A metal hydride reacting with a carbonyl bound to the same metal.

Note that the metal does not have to be anionic for the hydride to act as a nucleophile. The electronegativities of transition metals vary from about 1.0 to 1.75, but the electronegativity of hydrogen is about 2.2. Hydrogen is more electronegative than the transition metals, and so a hydrogen attached to a transition metal is usually nucleophilic.

This reaction, migratory insertion of a hydride to a carbonyl, forms a metal "formyl" compound. The "formyl" is the CH=O group attached to the metal. Migratory insertions can also take place with metal alkyls. Metal alkyls are also nucleophilic, just like metal hydrides. The alkyl carbon is usually more electronegative than the attached transition metal, so it has a partial negative charge.

- Nucleophilic alkyl groups can also undergo migratory insertion reactions.



Figure MI2.4. A migratory insertion reaction, this time forming an acyl compound.