BASIC CONCEPTS:

In this chapter we discuss some of the basic concepts of organometallic chemistry and reaction kinetics that are of special relevance to homogeneous catalysis. The catalytic activity of a metal complex is influenced by the characteristics of the central metal ions and the attached ligands. We first discuss the relevant properties of the metal ion and then the properties of a few typical ligands.

THE METAL

Insofar as the catalytic potential of a metal complex is concerned, the formal charge on the metal atom and its ability to form a bond of optimum strength with the incoming substrate are obviously important. We first discuss a way of assessing the charge and the electronic environment around the metal ion. The latter is gauged by the "electron count" of the valence shell of the metal ion.

Oxidation State and Electron Count

The formal charge assigned to a metal atom in a metal complex is its oxidation state. The sign of the charge for metal is usually positive, but not always. It is assigned and justified on the basis of relative electronegativities of the central metal atom and the surrounding ligands. The important point to note is that a fully ionic model is implicit, and to that extent the formal oxidation state may not correspond to the real situation. It does not take into account the contribution from covalency, that is, electrons being shared between the metal atom and the ligand, rather than being localized either on the ligand or on the metal. A few examples of special relevance to homogeneous catalytic systems are given in Fig. along with total electron counts. The rationales behind the schemes that are used to arrive at the electron counts are described in the following. Electron counting could be done either after assignment of an oxidation state to the metal (i.e., assuming ionic character in the bonds) or without assigning any oxidation state (i.e., assuming full covalency and zero oxidation state of the metal). In the latter case, the counting is very similar to the procedure of counting electrons in CH_4, NH_3, etc. to arrive at the octet rule. Both ways of counting electrons are illustrated.

RhCl(PPh3)3: The chlorine radical (Cl) accepts an electron from rhodium metal (electronic configuration $4d$ 7,5s 2) to give Cl and Rh. The chloride ion then donates two electrons to the rhodium ion to form a dative or a coordinate
bond. Each PPh3 donates a lone pair of electrons on the phosphorus atom to the rhodium ion. The total number of electrons around rhodium is therefore 8 2 3 2 = 16, and the oxidation state of rhodium is obviously 1. The other way of counting is to take the nine electrons of rhodium and add one electron for the chlorine radical and six for the three neutral phosphine ligands. This also gives the same electron count of 16.

	Oxidation State	Electron count
(Cl, Rh, PPh₃ structure)	1+	16
(H, Rh, CO, PPh₃ structure)	1+	18
(Cp₂Zr(CH₃)(O) cation structure)	4+	16
(Co(CO)₄ anion structure)	1-	18

Figure 1 Formal oxidation states and valence electron counts of metal ions in some homogeneous catalysts

Similarly, for RhH(CO)(PPh3)3 the rhodium oxidation state is 1 because the hydrogen atom is assumed to carry, with some justification, a formal negative charge. The five ligands, H, CO, and three PPh3, each donate two electrons, and the electron count therefore is 8 5 2 = 18. With the covalent model the hydrogen ligand is treated as a radical, rhodium is considered to be in a zero oxidation state, and the electron count is 9 1 4 2 = 18.

[Cp2Zr(CH3)(THF)]: The zirconium oxidation state is 4 and each Cp ligand donates six electrons. The ligand donates two electrons. The solvent CH 3 molecule, THF, also donates two electrons, and the total electron count is 12
 0 2 2 = 16. With the covalent model zirconium is in the zero oxidation state and has four electrons (4d 2,5s 2) in the valence shell. Both Cp and CH3 are considered as radicals and therefore donate five and one electron, respectively. The valence electron count is therefore 4 2 5 1 2 1 = 16. Notice that because of the positive charge, we subtract one electron.

Co(CO) : 4 Since there is a net negative charge and CO is a neutral ligand, the formal oxidation state of cobalt is 1. The electron count is therefore 10 4 2 = 18. According to the covalent model, the electron count is also 9 4 2 1 = 18, but cobalt is assumed to be in a zero oxidation state, and one electron is added for the negative charge.

IMPORTANT PROPERTIES OF LIGANDS

A very large number of different types of ligands can coordinate to transition metal ions. Once coordinated the reactivity of the ligands may dramatically change. Here we first discuss some of the ligands that are often involved in homogeneous catalytic reactions.

CO, R₂CCR₂, PR₃, and H as Ligands

The traditional definition of a coordinate or a dative bond is the donation and sharing of electrons, usually a lone pair, by the ligand onto and with the metal. In other words, all ligands behave as Lewis bases, and the metal ion acts as a Lewis acid. The ligands listed are no exception insofar as the electron donation part is concerned. Both CO and PPh3 donate lone pairs on the carbon and the phosphorus atoms, respectively. With alkenes, since there are no lone pairs, it is the electrons that are donated and shared. Similarly, a gain of one electron from the metal by the hydrogen atom produces a hydride ligand, which then donates and shares the

electron pair with the metal ion. The first three of these ligands, and there are a few others, such as N_2, NO, etc., differ from H_2O, NH_3, etc. in that they also accept electron density from the metal; that is, they act as Lewis acids. The electron density is often accepted in an orbital of π^*, symmetry and in such cases the ligands are called acid ligands. The donation of electron density by the metal atom to the ligand is also referred to as back-donation. While H does not act as a Lewis acid, dihydrogen does. In fact, such an interaction is responsible for the formation of stable metal–dihydrogen complexes. In the extreme case where two electrons are formally transferred back to dihydrogen from the metal, the H–H bond breaks, and two H ligands are formed. For this reason we consider H along with π acid ligands. Fig. 2.3 shows the Lewis acid–like behavior of CO, C_2H_4, and H_2 in terms of overlaps between empty ligand and filled metal orbitals of compatible symmetry. Back-donation is a bonding interaction between the metal atom and the ligand because the signs of the donating metal d orbitals and the ligand π^* (σ^* for H_2) acceptor orbitals match. The π ligands play important roles in a large number of homogeneous catalytic processes. Alkene polymerization and a variety of other reactions involve alkene coordination. As the name suggests, CO is the main ligand in carbonylation reactions. All four ligands: CO, alkene, H, and PR_3, play important parts in hydroformylation reactions.
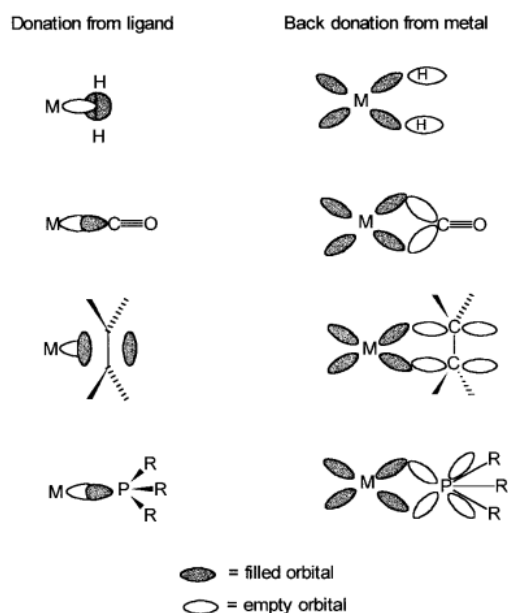

Figure. Schematic presentation of orbital overlaps for metal–ligand bond formations.

IMPORTANT REACTION TYPES

A relatively limited collection of common reactions include almost all homogeneous catalytic processes. We've seen some of these in the previous parts before. We'll address them in more depth here and add a few others.

Oxidative Addition and Reductive Elimination

Oxidative Addition is a reaction in which the metal undergoes formal oxidation, adding atoms, atom groups, or molecules to the metal centre. Reductive elimination is the exact opposite of oxidative addition-with the reduction of ligands, the metal ion is formally reduced. Some
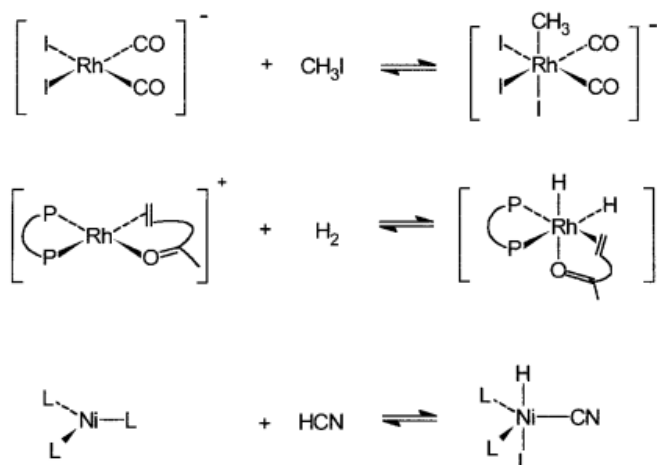
examples are mentioned in Fig. The forward reactions in all these examples are oxidative add-on (2 increase in oxidation states) and reduction of the reverse reactions (2 decrease in oxidation states). All the forward reactions in commercial homogeneous catalytic processes are essential steps. Reaction 2.2 is a step in methanol carbonylation (see Chapter 4), while reaction 2.3 is a step in the hydrogenation of an alkene with an acetamido functional group.

Alkyl   Alkylidene or carbene   Allyl

Figure. Typical examples of alkyl, alkylidene (carbene), and allyl complexes.

Formation of metal alkyl by addition of RX   Kinetic instability of metal alkyl. β-hydride elimination

α-hydride elimination   Agostic interaction

R = H or alkyl
olefin insertion into metal - hydrogen
or metal-alkyl bonds   Metallocycle formation

Figure. Some important reactions and interactions of metal–alkyl and metal– alkylidene complexes.

Figure. Representative examples of oxidative addition and reductive elimination reactions

Insertion Reactions

In homogeneous catalytic reactions, old bonds are usually broken by oxidative addition reactions and new bonds are formed by reductive elimination and insertion reactions. A few representative examples that are of relevance to catalysis are shown . The following points deserve attention. Reactions are crucial steps in hydrogenation, polymerization, and CO-involving catalytic reactions. This reaction is also called a "hydride attack" or "hydride transfer" reaction.
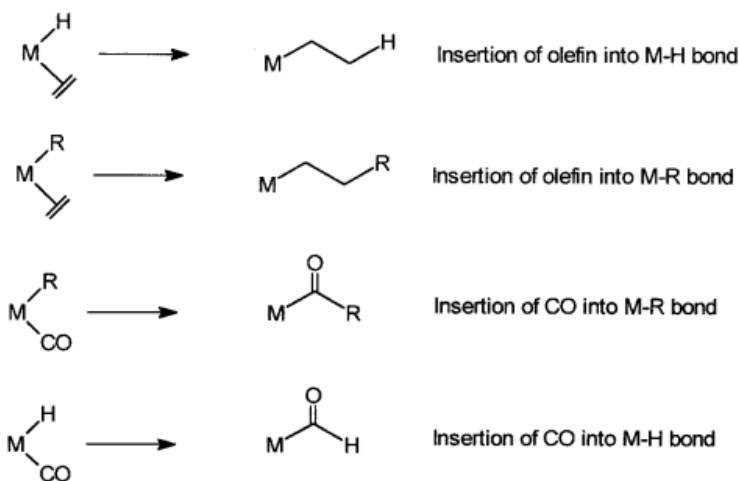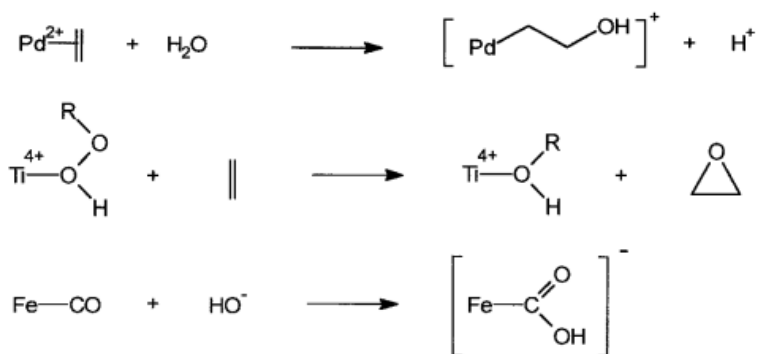

β-Hydride Elimination

We have already seen in Section 2.2.2 that metal–alkyl compounds are prone to undergo β-hydride elimination or, in short, β-elimination reactions (see Fig. 2.5). In fact, hydride abstraction can occur from carbon atoms in other positions also, but elimination from the β-carbon is more common. As seen earlier, insertion of an alkene into a metal–hydrogen bond and a β-elimination reaction have a reversible relationship. This is obvious in Reaction 2.8. For certain metal complexes it has been possible to study this reversible equilibrium by NMR spectroscopy. A hydrido–ethylene complex of rhodium, as shown in Fig. is an example. In metal-catalyzed alkene polymerization

Insertion

β-elimination

$L = PPr_3^i$

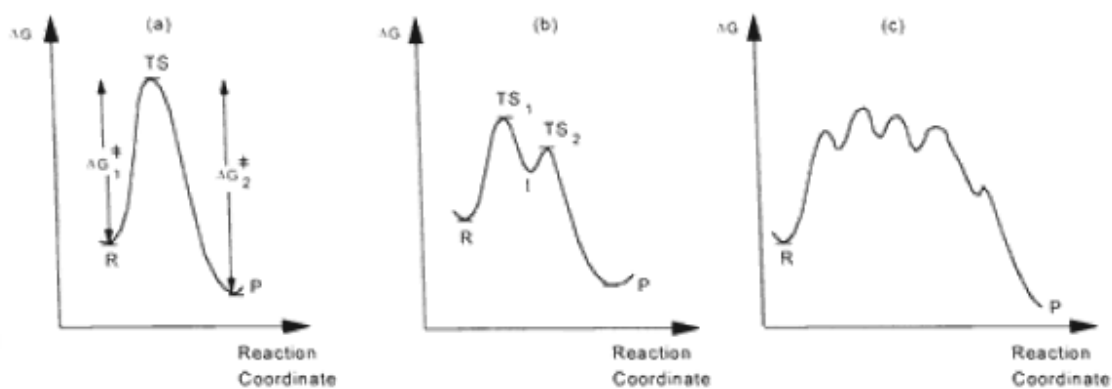Polymer chain termination by β-elimination
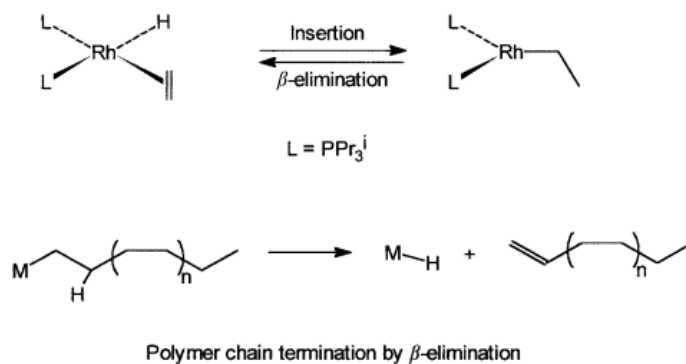
Nucleophilic Attack on a Coordinated Ligand

The ligand's electronic environment naturally undergoes a transition upon alignment to a metal base. The ligand can become susceptible to electrophilic or nucleophilic effects depending on the degree and nature of this shift. This is the enhanced electrophilicity or propensity that is often seen in homogeneous catalytic processes to undergo nucleophilic attack. Reactions include a few examples
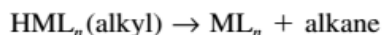
$$Pd^{2+}\| \;+\; H_2O \;\longrightarrow\; [Pd\text{-}CH_2CH_2\text{-}OH]^+ \;+\; H^+$$

$$Ti^{4+}\text{-}O(\!\!\begin{smallmatrix}R\\H\end{smallmatrix}) \;+\; \| \;\longrightarrow\; Ti^{4+}\text{-}O(\!\!\begin{smallmatrix}R\\H\end{smallmatrix}) \;+\; \triangle O$$

$$Fe\text{-}CO \;+\; HO^- \;\longrightarrow\; [Fe\text{-}C(\!\!\begin{smallmatrix}O\\OH\end{smallmatrix})]^-$$
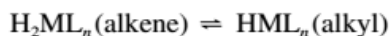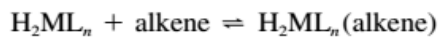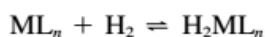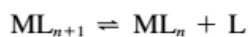
CATALYTIC CYCLE AND INTERMEDIATES

Consider a hypothetical metal complex that serves as a catalyst for the hydrogenation of an alkene ML_{n+1} (M = metal, L = ligand, n = 1 = number of ligands). Note also the list of reactions below

TS = Transition state   R = Reactant

I = Intermediate   P = Product

$$ML_{n+1} \rightleftharpoons ML_n + L$$

$$ML_n + H_2 \rightleftharpoons H_2ML_n$$

$$H_2ML_n + \text{alkene} \rightleftharpoons H_2ML_n(\text{alkene})$$

$$H_2ML_n(\text{alkene}) \rightleftharpoons HML_n(\text{alkyl})$$

$$HML_n(\text{alkyl}) \rightarrow ML_n + \text{alkane}$$

If all these reactions are added except the first one, we can obtain the net stoichiometric reaction alkene alkene alkane alkane alkane alkane. In the first step, the metal complex MLn reacts with dihydrogen, undergoes a series of reactions in the steps below, and is regenerated in the final step. As shown in Fig. 2.10, all these reactions are conveniently presented as a catalytic cycle. The following points are worth noting about the sequence of reaction presented in this cyclical manner. The stable metal complex added to the reaction.
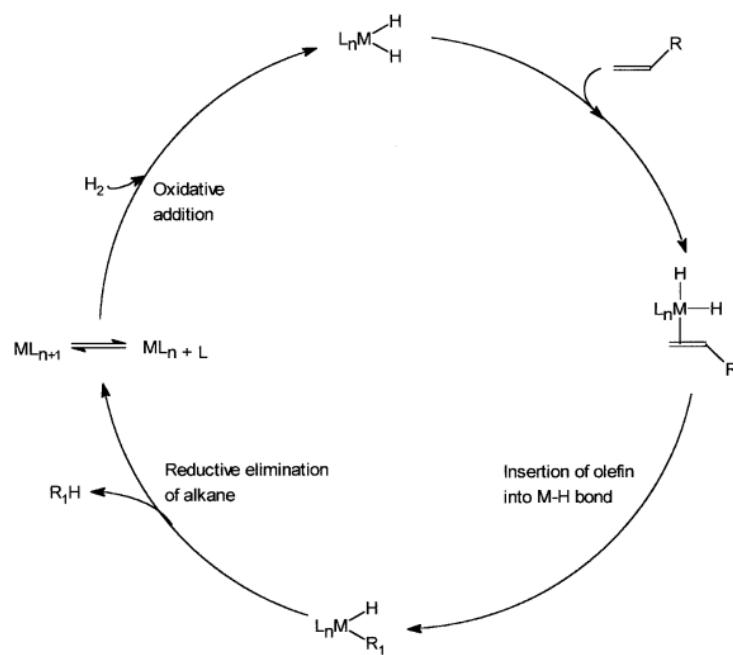
Figure. A hypothetical catalytic cycle with the precatalyst ML*n*1 and four catalytic intermediates.