1
Introductory Guide to Organonickel Chemistry

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Most organic chemists may be embarrassed and intrigued when they encounter
the type of reaction described in Eq. (1.1). In organic chemistry, most C–C bonds
are formed or cleaved by making use of, more or less, polarized functional groups,
for example, C=O, C–O, and C–halogens. Ethylene is lacking in these ordinary
functionalities and has only the double bond as a reactive group. Consequently,
these chemists may ask themselves: “What is happening here? Does the process
proceed via a radical reaction or a [2+2]cycloaddition followed by ring opening?”

\[
\text{H}_2\text{C} = \text{CH}_2 \xrightarrow{\text{cat Ni, AlR}_3} \text{H}_2\text{C} = \text{CH}_2
\]

This reaction, which marks the cornerstone for the flourishing development of
transition metal-catalyzed reactions and their use in industry, was discovered by
chance – as with many other great discoveries – by Ziegler (who was awarded the
Nobel Prize for chemistry in 1963), Wilke, and their coworkers while investigating
the production of polyethylene and ethylene oligomers (C₆–C₈) promoted by orga-
nolithiums and organoaluminums [1]. These investigators found that 1-butene was
obtained exclusively instead of the expected ethylene oligomers, but also noted that
contaminants such as nickel and acetylene changed the course of the reaction
(today these are referred to as “nickel effects”; see Section 1.6.3 and Schemes 1.26
and 1.27). At the same time, these researchers realized the uncovered potential of
transition metal catalysis in organic transformations and, after conducting many
tests with a wide range of transition metals, they established the protocol of low-
pressure polyethylene production based on the titanium-alkylaluminum catalytic
system.

The aim of this chapter is to outline the basic concepts in the coordination
chemistry as well as the elementary processes and basic reaction patterns in
nickel-catalyzed synthetic reactions. Together, these may help the reader to under-
stand the content of the following chapters, which describe much more sophisti-
cated reactions than that shown in Eq. (1.1).
1.1 The Crystal Field

If one imagines a nickel atom or its ions isolated in space, it has the five degenerated \( d \) orbitals (\( dx^2-y^2 \), \( dz^2 \), \( dxz \), \( dyz \), and \( dxy \)), all lying at the same energy level. As six ligands (represented here with L, such as \( \text{Cl}^- \), \( \text{NH}_3 \), and \( \text{H}_2\text{O} \)) approach the nickel from the \( x \), \( y \), and \( z \) directions to form an octahedron, the \( d \) orbitals split into two groups, \( d_\sigma \) and \( d_\pi \) (Fig. 1.1(a)). The orbitals of \( d_\sigma \) group (\( dx^2-y^2 \), \( dz^2 \), the orbitals with the \( \sigma \) bonding character) that point toward the L groups are greatly destabilized by electrostatic repulsion and move to a higher energy position. The \( d_\pi \) group orbitals (\( dxy \), \( dyz \), \( dxz \), the orbitals with the \( \pi \) bonding character), on the other hand, are less destabilized because these orbitals point away from L. The magnitude of the energy difference (designated by \( \Delta \) and called the “crystal field splitting” or the “ligand field splitting”) between the \( d_\sigma \) and \( d_\pi \) groups depend on the charges on Ni and L and the distance between them.

If the two Ls move away along the \( z \) axis, the other four Ls on the \( \pm x, \pm y \) axes will move closer to the central Ni, and this results in a square planar complex. The expected energy change of the \( d \) orbitals is shown in Figure 1.1(b), where the orbitals that possess the \( x \) and \( y \) components (\( dxy, dx^2-y^2 \)) rise, while those possessing the \( z \) component (\( dz^2, dxz \)) fall. The energy diagram of a tetrahedral complex is...
shown in Figure 1.1(c), where those orbitals $d\sigma(dz^2, dx^2-y^2)$ that spread along x, y, and z axes are apparently away from L and stabilize, whereas $d\pi$ are all in touch with L and destabilize. The relative energy levels of $d\sigma$ and $d\pi$ orbitals are reversed between the octahedral and tetrahedral complexes.

The energy levels in Figure 1.1 are drawn deliberately for all the octahedral, square planar and tetrahedral complexes to have the identical energy to that of the isolated Ni(0), the orbitals of which are fully occupied with 10e. For $d^8$ Ni(II), a square planar complex is likely most favored, as the 8e occupy from the most stable $d_{xz}$ up to the $d_{xy}$ orbitals, leaving the most unstable $dx^2-y^2$ orbital unoccupied. This is in accord with the structures that many Ni(II) complexes display (e.g., Me$_2$Ni(PR$_3$)$_2$, [Ni(CN)$_4$]$^{2-}$).

1.2 Nickel has Wings: The Mond Method

In the industrial process of Na$_2$CO$_3$ production (the Solvay soda process, 1865), erosion of the nickel bulb of CO$_2$ lines in an unduly short time period was a serious problem. Mond, in 1890, discovered that metallic nickel, although being a very hard solid with a high melting point (1455 °C), reacted with CO (a small contaminant of CO$_2$ in the above process) to form gaseous Ni(CO)$_4$ (b.p. 43 °C, extremely poisonous) at ambient temperature. He also found that Ni(CO)$_4$ decomposed at over 180 °C, depositing Ni metal. This unique reaction of Ni and CO has been utilized even today as the industrial refining method of metallic nickel (the Mond method). In fact, nickel is the only metal that reacts with CO at room temperature and at atmospheric pressure of gaseous CO [2]. Having been greatly impressed by the demonstration of the above transformations, one of Mond’s contemporaries noted, philosophically, that “Mond gave wings to a metal” [3].

1.3 The Ligand Field

Why does nickel react with CO so easily? Why is Ni(CO)$_4$ formed selectively, and not Ni(CO)$_3$ or Ni(CO)$_5$? To address this question, the idea of the ligand field is useful. The model makes up matching pairs between the nine atomic orbitals of Ni (the five $3d$, the one $4s$, and the three $4p$ atomic orbitals) and the molecular orbitals of CO. The most straightforward – but somewhat approximate – explanation is as follows. The C and O atoms of CO hybridize to make two sp-orbitals. One electron each of C and O atoms is then used to make a sp-$\sigma$ bond, and the two sets of lone pair electrons of C and O reside on their sp-hybridized orbitals. The one electron on each of the 2p orbitals of C and O forms a $\pi$ bond, and the two 2p electrons on O interact with the empty 2p orbital of C to form a charged $\pi$ bond (Fig. 1.2(a)). On the other hand, the one 4s and the three 4p orbitals of an Ni mix to make up the four empty $sp^3$-hybridized orbitals. The combination of the four empty $sp^3$ orbitals
of the Ni and the four sets of the \( sp \) lone pair electrons on the C of four CO provides the four bonding and the four anti-bonding molecular orbitals of the Ni–CO bond (\( \sigma \) and \( \sigma^* \) orbitals; Fig. 1.3). This process is similar to producing tetrahedral methane \((CH_4)\) from the \( sp^3 \)-hybridized C and the 1s orbitals of four hydrogen atoms. The difference between these reactions is that in the case of methane, the carbon bears four valence electrons and each hydrogen one valence electron, and these form the four covalent bonds. In contrast, in the case of Ni(CO)\(_4\) the nickel bears no valence electrons in the \( sp^3 \) orbitals: the two electrons of the Ni–CO \( \sigma \)-bond are donated from the C; hence the \( \sigma \)-bond should be ionic in nature (Ni–C) as depicted in Figure 1.2(b).

In addition to the \( \sigma \)-bonding, there operates another bonding mechanism, so-called “back bonding” or “back donation”. As is illustrated in Figure 1.2(c), the \( \pi^* \) orbital of the CO has a proper symmetry with the \( dx \) atomic orbital of the Ni, and these two interact to each other to make up a new \( \pi \)-bonding orbital, lower in energy than the \( dx \) atomic orbital (and at the same time, a \( \pi^* \)-anti-bonding orbitals higher in energy). In the case of Ni(CO)\(_4\), the three \( \pi \)-bonding and the three \( \pi^* \)-anti-bonding molecular orbitals form (Fig. 1.3). Owing to mismatch of symmetry, the \( dx \) orbitals cannot interact with the \( px^* \) orbital of CO and so remain at the same energy level. The \( \pi^* \) orbital of the CO is empty and the \( dx \) orbital of an Ni is filled, so the \( d \) electrons of the Ni flow into the \( \pi^* \) orbital of CO (back donation). This mechanism operates so effectively that CO is sometimes called a “\( \pi \)-acid ligand”. In all, the donation of 2e from the C atom (\( \sigma \)-bonding) and the back donation of 2e from the Ni (\( \pi \)-bonding) result in the formation of a formal Ni–C double bond (Fig. 1.2(d)). The reader should note that each CO possesses two \( \pi^* \) orbitals, which makes CO as a strong \( \pi \)-acid ligand. For clarity, only one of the two \( \pi^* \) orbitals is depicted in Figure 1.2(c).

The back donation significantly perturbs the electronic structure of CO, filling electrons in the anti-bonding \( \pi^* \) orbital and rendering the bond long and weak.

Fig. 1.2. The \( \sigma \) (a and b) and \( \pi \)-bonding interaction (c and d) between an Ni and CO.
this way, in general, the ligands coordinating to metals can be polarized and elongated, and therefore activated toward chemical reactions, the $\sigma$ and $\pi$ bonds in the ligands can be weakened or broken, and chemical bonds can be made or broken within and between different ligands. This rich pattern of the activation of ligands is a characteristic feature of organometallic chemistry.

Figure 1.3 illustrates how the whole system, composed of an Ni (left) and four CO (right), is energetically stabilized by forming tetrahedral Ni(CO)$_4$. That is, all the four sets of lone pair electrons on the C of CO are accommodated in the low-lying $sp^3$ $\sigma$-bonding orbitals, and the 6e of 10 $d$ electrons of an Ni are in the low-lying $\pi$-bonding orbitals. The other sets of hybridization of the one 4$s$ and the three 4$p$ of an Ni, for example, $(sp^3 + p)$ forming 3 $sp^2$ and 1$p$ atomic orbitals, are apparently more unfavorable than the $sp^3$ hybridization, because a $\sigma$-bond makes a stronger bond and is more stable in energy than a $\pi$-bond – that is, the more the number of $\sigma$-bonds the more stable the complexes. This is the reason why Ni(CO)$_4$ is formed selectively, and not Ni($\sigma$-CO)$_3$ or Ni($\sigma$-CO)$_3$($\pi$-CO). Then why is Ni(CO)$_5$ not formed? This is simply because an Ni is already saturated and no atomic orbitals are available to interact with the fifth CO.
1.4 The Formal Oxidation Number

It is sometimes very useful to assign a formal oxidation number to carbon and some heteroatoms that are frequently outside the octet rule, such as N, P, and S in organic molecules. For this, we impose an ionic model on the compound by artificially disconnecting it into an ion pair. In doing this, each electron pair in any bond is assigned to the most electronegative of the two atoms that constitute the bond. Some examples are shown in Scheme 1.1. The oxidation number of carbon ranges from 4− (e.g., methane) to 4+ (e.g., carbon dioxide). All the reactions in which the oxidation number is increased (making bond with oxygen or electronegative elements or losing hydrogen) are oxidations. The reverse processes are reductions. So, as shown in the Eq. (a) of Scheme 1.1, each of all the steps from carbon dioxide to methane is 2e reduction, and each of the reverse processes from methane to carbon dioxide is 2e oxidation.

![Scheme 1.1](image)

In organometallic chemistry, a confusing matter arises because most metal elements are less electronegative (or more electropositive) than H (Table 1.1). Hence, as shown in Eqs. (b) and (c) of Scheme 1.1, in contrast to the formation of methylcarbene and methane from atomic C and 2H and 4H are 2e and 4e reduction, respectively, the formation of BH₃ from an atomic B and 3H is 3e oxidation, as we disconnect BH₃ as one B³⁺ and three H⁻, that is, bond formation with H is reduction for an C, but it is oxidation for an B. The dotted trigonal line of B₂H₆ in Eq. (c) of Scheme 1.1 indicates that the three atoms, B, H, and B, form a three-center-two electron bond.

The idea of oxidation number provides a convenient way to determine the stoichiometric amounts of the reagents required in a variety of oxidation and reduction reactions. For example, as is shown in Eq. (a) of Scheme 1.2, for the oxidation of an alcohol with chromium(VI) reagents, balancing the formal oxidation number of the starting materials and the products shows that 2/3 mol of Cr(VI) are necessary to oxidize 1 mol of an alcohol to an aldehyde or a ketone. For the reduction of nitrobenzene to azobenzene with zinc dust under alkaline conditions, the amount of
Zn dust is very crucial (Eq. (b) in Scheme 1.2). Loading of the excess amount of Zn can cause over-reduction of azobenzene to $N\equiv N_0$-diphenylhydrozine. One mole of nitrobenzene produces 0.5 mol azobenzene; hence the total formal oxidation number of azobenzene should be divided by 2. Balancing the oxidation numbers of the starting material side and the product side indicates that 2 mol of Zn dust is the exact amount required to perform the reaction successfully.

For the hydride reduction, however, special care is needed, since – as is apparent

\[
3 \text{CH}_3\text{OH} \quad 2 \text{Cr}^{(IV)} \quad \text{PhNO}_2 \quad 2 \text{Zn}(0) \\
2\cdot \quad 6^+ \quad 0^3+ \quad 3^+ \quad 3^+ \quad 0^3+ \\
(-2)x3 + 6x2 = 6 \quad 0x3 + 3x2 = 6 \\
\text{ (a)}
\]

\[
\text{BH}_3 + 3 \text{CH}_3\text{O} \quad \text{B(OCH}_3)_3 \quad \text{NiH}_2 + \text{CH}_2=\text{CH}_2 \quad \text{Ni} + \text{CH}_3\text{CH}_3 \\
3^+ 1- \quad 0 \quad 3^+ 2- \quad 2^+ 1- \quad 0^3- 3^-
\]

\[
3 + (-1)x3 + 0x3 = 0 \quad 3 + (-2)x3 + 0x3 = -3 \quad 2 + (-1)x2 - 2 - 2 = -4 \quad 0 - 3 - 3 = -6
\]

\[
3 + (-1)x3 + 0x3 = 0 \quad 2 + (-2)x2 - 2 - 2 = -6
\]

\[
\text{ (c)} \quad \text{ (d)}
\]

Scheme 1.2. Balancing of the formal oxidation number in oxidation and reduction reactions. Special care is needed when balancing formal oxidation numbers for hydride reduction reactions.
from Eqs. (c) and (d) – the formal oxidation number of the hydrogen on C and metals is counted in a different way: \( \text{H}^- \) to metals (e.g., \( \text{BH}_3 \)) and \( \text{H}^+ \) to C. Accordingly, simple summation of the oxidation numbers results in a higher oxidation number being given to the reactant side by the number of hydrogens (Scheme 1.2(b)). For the hydride reduction, we should regard a hydride as a 2e donor, since \( \text{H}^- \) changes to \( \text{H}^+ \) in the reaction. The borohydride reduction (Eq. (c)) is not accompanied by the change of the oxidation number of the metal. On the other hand, the reduction with nickel hydride is accompanied by the change of the oxidation number of the metal (Eq. (d)). Even for such cases, the same idea applied to Eq. (c) holds.

1.5

The 16- and 18-Electron Rule

As the octet rule is a useful guide in organic chemistry (filling all the atomic orbitals of carbon with electrons: \( 2s^22p^2 \)), the 16- or 18-electron rule is useful in organonickel chemistry (filling all the atomic orbitals of an Ni with electrons: \( 3d^{10}4s^24p^6 \)). The tendency of transition metals to form complexes in which the metal has an effective atomic number corresponding to the next higher inert gas has long been recognized. The number of valence electrons (VE) consists of the valence electrons of the metal itself and the electrons donated or shared by the ligands, and would be 18 for an inert-gas configuration. If one restricts attention to Ni complexes, essentially all of the well-characterized compounds have 16 or 18 VE.

With regard to Ni complexes and Ni intermediates, Tolman’s proposal may be expressed as follows [4]:

1. Ni complexes may exist in a significant concentration at moderate temperatures only if the valence shell of an Ni contains 16 or 18 electrons. A significant concentration is one that may be detected spectroscopically or kinetically and may be in the gaseous, liquid, or solid state.

2. Organonickel reactions, including catalytic ones, proceed through elementary steps involving only intermediates with 16 or 18 VE.

For example, \( \text{Ni(CO)}_4 \) (VE 18) is dissociated into \( \text{Ni(CO)}_3 \) (VE 16) and CO in solution. \( \text{Ni(CO)}_4 \) is coordinatively saturated and no longer has any ability to interact with other molecules. By contrast, \( \text{Ni(CO)}_3 \) is coordinatively unsaturated and can accept 2e ligands. Usually, the equilibrium lies heavily to the \( \text{Ni(CO)}_4 \) side. The same holds for the saturated \( \text{Ni(cod)}_2 \) (VE 18) and the unsaturated \( \text{Ni(cod)} \) (VE 14) + COD.

Some of the common ligands and their ligand types and electron counts are summarized in Table 1.2. The symbol L signifies a neutral 2e ligand, which can be a lone pair donor, such as \( \text{PPh}_3 \), CO, a \( s \)-bond donor, such as ethylene, acetylene, and a \( s \)-bond donor such as \( \text{H}_2 \) and C–C. The symbol X refers to 2e ligands
bearing an anionic charge, such as Cl\(^-\), H\(^+\), and Me\(^-\). The symbol \(\eta\) (eta) \{(a Greek letter \(\eta\), hapticity, haptic from Gr. \(\kappaappa\)ticos, able to grasp or perceive\} indicates the number of ligand atoms bound to the metal. So, benzene, when coordinated to a metal in type \(L_3\), is indicated as \(\eta^6\)-benzene, and the cyclopentadienyl group in type \(L_2\) as \(\eta^5\)-Cp. Sometimes \(\eta\) is used without a superscript, such as \(\eta\)-benzene and \(\eta\)-Cp, when the number of ligand atoms is obvious. Allyl groups can exist in two forms, \(\eta^1\)-allyl (type \(X\)) and \(\eta^3\)-allyl (type \(LX\)). The double bond of \(\eta^1\)-allylnickel 1.1 does not interact with any nickel atomic orbitals, but conjugates with the C-M orbital, are bestowed a certain characteristic reactivity which is different from other \(\eta^1\)-alkyl complexes. The allyl group of \(\eta^1\)-allylnickel can be considered as a combination of an alkyl and a C\(-\)C group. The two resonance structures 1.2a and 1.2b show how all the three carbons are bound to an Ni as LX. This is also expressed as 1.3. \(\eta^1\)-Allylnickel chloride 1.4 is an air-stable, square planar 16-electron complex (8e from Ni, 4e from allyl and 4e from Cl\(_2\)), with chloride ions bridging in a dimeric structure. The bridging group is represented in formulas by using the Greek letter \(\mu\) (mu) as \([(\mu-Cl)_{2}(\eta^1\text{-CH}_{2}\text{-CHCH}_{2}\text{Ni})_2]((\eta^1\text{-allyl})\text{nickel chloride dimer})\). The Greek letter \(\kappa\) (kappa) is used instead of \(\eta\) in those cases that ligands bind to metals via heteroatoms, such as \(\kappa^2\)-acetylacetonate (\(\kappa^2\)-acac).

\[\begin{align*}
\text{Ni} & \quad \text{Ni} \\
\text{1.1} & \quad \text{1.2a} & \quad \text{1.2b} & \quad \text{1.3} & \quad \text{1.4}
\end{align*}\]

Cyclobutadiene is a compound that is extremely unstable not only because of its strain but an anti-aromatic electronic character (cyclic 4\(\pi\) electron anti-Hückel compound) and was a target from synthetic and physical organic points of view. Only under special conditions (e.g., a solid argon matrix), it has a life-time long enough to be spectroscopically detectable [5]. The two double bonds, however, locate nicely to serve as an \(L_2\) 4e donor to transition metals and the stabilization of cyclobutadiene by the coordination to transition metals was suggested theoretically [6]. In fact, cyclobutadiene forms some stable complexes with nickel, e.g., 1.5 and 1.6, and some other transition metals [7].
The molecular orbital diagram of a square planar cyclobutadiene (in fact, it has a rectangular structure), as illustrated in Figure 1.4(a), tells us that the 2e of the totally 4π electrons occupy bonding $\psi_1$ orbital and the other 2e occupy two degenerated non-bonding $\psi_2$ and $\psi_3$ orbitals one each (the Hund rule). Figure 1.4(b) shows how $\psi_1 \sim \psi_4$ molecular orbitals interact with the atomic orbitals of an Ni. These interactions of four molecular orbitals of cyclobutadiene and nine atomic

![Diagram](image_url)

**Scheme 1.3.** Formation of stable cyclobutadiene Ni complexes: \[([\mu-\text{Cl}]_2(p^4\text{-cyclobutadiene})\text{Ni(II)})_2\text{Cl}_2\ (1.5)\] and \[\text{bis}(p^6\text{-cyclobutadiene})\text{Ni(0)}\ (1.6).\]
orbits of an Ni make up 13 molecular orbitals; six bonding, one non-bonding, and six anti-bonding orbitals. The six bonding molecular orbitals are filled with 12e. The reader should note that the three Ni Cl bonding orbitals accommodate 6e, hence the complex 1.5 has a stable $d^8$ 18e electronic configuration. The complex 1.6 is another example which demonstrates that cyclobutadiene owes its stability to the coordination interaction with an Ni.

1.6 The Structure, Reactivity, and Electronic Configuration of Nickel-Complexes

Ferrocene, Cp$_2$Fe(II), is the monumental organometallic compound that serves as a milestone for the explosive developments in organometallic chemistry [8]. Ferrocene is a stable orange crystalline material, and has an ideally stable electronic configuration, $d^8$18e, 6e from an Fe and 12e from 2Cp; as is shown in Figure 1.5(a), all the 6d electrons are accommodated in the three low-lying orbitals. The nickel analog, nickelocene (1.7) has 20 VE (8e from an Ni and 12e from 2Cp) and is outside of the 18e rule. The extra 2e are indulged to occupy the high-lying degenerate orbitals, one each (Hund’s rule; Fig. 1.5(b)). Hence the complex is paramagnetic and extremely sensitive to oxidation, causing instantaneous decomposition in air. In contrast, the CpNi complexes with 18 VE, e.g., 1.8 [acetylenebis($\eta^5$-cyclopentadienyl)nickel(II)] and 1.8’ [dicarbonylbis($\eta^5$-cyclopentadienyl)nickel(II)], are rather stable [17]. The electron count of 1.8 and 1.8’ is as follows: 1.8, 6e (Cp) + 2e (acetylene) + 8e (Ni) + 2e (adjacent Ni); and 1.8’, 6e (Cp) + 2e (CO) + 8e (Ni) + 2e (adjacent Ni).

Figure 1.6 shows some organonickel complexes of chemical and structural interest, all the structures of which are determined using X-ray crystallographic analysis [9–16]. As is observed in the complexes 1.9–1.15, for the $d^{10}$ Ni complexes, the five d orbitals are fully occupied, so, in general, there is no preference for specific geometries (c.f., Fig. 1.1). Probably owing to avoiding steric repulsion between ligands, nickel(0) generally forms tetrahedral (with four ligands) or trigonal planar com-
plexes (with three ligands). Complex 1.13 is the famous Wilke’s complex, isolated as a reactive intermediate for the trimerization of butadiene. Thus, CDT, the ligand of 1.13 offers the seats for CDT of the next generation. In other words, as is shown in Eq. (1.2), CDT on an Ni is handed down from generation to generation.

\[
3 \quad \quad 3 \quad \quad 1.13 \quad 1.11 \quad 1.12
\]

All the three trans-double bonds of 1.13 adopt a propeller-like arrangement around the Ni atom, hence 1.13 is chiral. In fact, the enantiomer shown in 1.13

Fig. 1.6. Some organonickel complexes of chemical and structural interests. All the structures have been determined by X-ray analyses. Figures indicate bond distances (Å).
has been resolved (by use of a chiral phosphine ligand) and its specific rotation is determined to be \( \pi = +104^\circ \) [12].

The complex 1.10 is an interesting example which shows that the \( \pi \)-coordinated double bonds of ethylene and formaldehyde intersect perpendicularly to each other [10]. This unique spatial arrangement of ethylene and formaldehyde impels us to imagine a through-space orbital interaction between the ligands - a LUMO (C=O)-HOMO (C=C) interaction. The butterfly-like complex 1.11, despite the presence of a good chelating phosphine ligand, is coordinatively unsaturated and forms a trigonal planar \( d^{10}16e \) complex [11]. Note the difference of the spatial arrangements of the two \( \pi \)-ligands between 1.10 and 1.11. In 1.11, a P, Ni, and all the Cs of two ethylene molecules lie in a plane. The complex 1.11 is highly reactive towards acetylene, and forms the \( \eta^6 \)-arene complex 1.12 even at a temperature as low as \(-50^\circ C\). In the dinuclear complex 1.14, the originally aromatic and hexagonal benzene ring is distorted and forms the structure of cyclohexatriene with alternating single and double bonds [13]. The bond distances of the double bonds coordinating to an Ni are significantly longer than that of a standard double bond (1.34 Å). The bond length of the uncoordinated double bond of 1.14 is within a standard value. The lengthening of the coordinated double bond is due to \( dx-p\pi^* \) back donation, filling the anti-bonding \( p\pi^* \) orbital with the \( dx \) electrons, hence rendering the double bond long and weak. The \( dx-p\pi^* \) back donation is illustrated in Figure 1.7. Similar bond lengthening is reported for the complex 1.15, which is considered to be an intermediate leading to the oxidative addition product 1.16.

As is expected from the crystal field splitting (Fig. 1.1), the \( \Delta^\delta \) nickel complexes 1.16–1.18 show a strong tendency to form a square planar structure, leaving the most unstable \( dx^2-y^2 \) orbital empty. Ni(II) complexes also have a strong tendency to adopt the \( dx^2 \) configuration. The complex 1.17 is one of rare examples adopting \( dx^2 \)-18e electronic configuration. The benzene ring of the complex 1.17 is labile and is readily replaced by other aromatic molecules (e.g., toluene, anisole) or by alkenes. Replacement with norbornadiene (NBD) forms a rather stable complex 1.18.

For nickel complexes, 0 and 2+ are the oxidation states observed most frequently. The oxidation states of 1+ and 3+ are supposed to be the active forms in the redox system of some enzymes (e.g., nickel hydrogenase) [18]. The oxidation state of 4+ is very rare. The complex 1.19 is one such example, and is stable in crystalline form for several days in air, but readily decomposes in solution [16]. The stability of the complex can be attributed to the strong \( \sigma \)-bond electron-donor capabilities of the 1-norbornyl group and bromide anion, which provide the neces-
sary electron density for stabilizing the formal 4+ oxidation state. Both the crystal field and the ligand field require the complex 1.19 to be paramagnetic, with unpaired 2e in the $d\pi$ orbitals. In fact, 1.19 is diamagnetic; this is due to distortion, lowering the symmetry from $T_d$ to $C_3v$ (e.g., $T_d$ for methane, $C_3v$ for bromomethane), which splits the energy levels of the $d\pi$ orbitals and produces one orbital of lower energy that accommodates the 2e in pairs. The formal oxidation state of Ni(4+) has been claimed (speculated) sporadically to rationalize reaction schemes [19].

Figure 1.8 shows some inorganic Ni(II) complexes of structural and chemical interests. In contrast to organic Ni(II) complexes, which show a tendency towards having a square planar configuration, inorganic Ni(II) complexes can have a variety of configurations. For example, $[\text{NiCl}_4]^{2-}$ can not have a square planar configuration owing to the strong electrostatic repulsion between the neighboring chloride ions, and hence the complex adopts a tetrahedral arrangement, where the electrostatic repulsion becomes minimal. In contrast, $[\text{Ni(CN)}_4]^{2-}$ is square planar because of the lack in such a strong electronic and steric repulsion between the ligands. The tetradentate ligand, $N(CH_2CH_2NMe_2)_3$, topologically forces the Ni complex to accept the trigonal bipyramidal structure (Fig. 1.8(c)).

The hexahydrate complex of Ni(II) (e.g., Ni(SO$_4$)$_6$H$_2$O) is a green solid and is stable in solution (Fig. 1.8(d)). However, this aqua complex is outside of the 18e rule, $d^8$ 20e. This phenomenon is observed for many other transition metals. Pale red Co$^{2+}$(H$_2$O)$_6$ is, for example, a 19-electron complex, and blue Cu$^{2+}$(H$_2$O)$_6$ is a 21-electron complex. This is due to a small $\Delta$ splitting (Fig. 1.1). The six H$_2$O's make the relatively weak $\sigma$-bonds and hence render the $d\sigma$ orbitals weakly antibonding. Accordingly, the $d\sigma$ orbitals can accommodate extra electrons. In a sense, the water molecules may be regarded as a solvent to stabilize the positive charge of metals. In other words, the solvation stabilization overrides the electronic configuration rational destabilization.

The propensity of Ni$^{2+}$ to form octahedral complexes with weak-field ligands is utilized for the asymmetric Diels–Alder reaction (Scheme 1.4) [20]. The si-face of the acrylamide C–C bond forms a $\pi$-$\pi$ stack with the 4-phenyl group of the chiral oxazolidine ligand, and only the re-face is open to the cycloaddition toward cyclopentadiene. The central Ni(II) serves as a Lewis acid and activates the acrylic double bond toward the Diels–Alder reaction by lowering its LUMO. In fact, the
cycloaddition reaction even proceeds at \(-40^\circ C\) and provides the cycloaddition product with a high enantiomeric excess (ee).

The reaction shows an interesting chiral amplification – that is, a slight ee of the \(RR\) ligand is good enough to assure a high ee in the product. The \(RR\)-\(SS\) combination forms a strain-free \(meso\) complex 1.20, while the homo-chiral pair \(RR\)-\(RR\) does not form because of the steric repulsion between the 4-phenyl groups of the oxazolidine rings. The steric repulsion that the \(RR\)-\(RR\) complex experiences is readily understood by imagining an inversion the stereocenters bearing the phenyl groups of the ligand of 1.20 (shown in gray). This means that almost all of the \(SS\) ligand portion is engaged in forming the \(RR\)-\(SS\) complex. The remaining portion of the \(RR\) ligand forms the Ni\(^{2+}\) complex, which is coordinatively unsaturated and is able to activate the acrylamide through coordination.

1.7 The Elementary Reactions

Nickel-catalyzed or -promoted reactions usually proceed via the following six elementary processes: 1) oxidative addition; 2) insertion (or addition); 3) transmetallation; 4) reductive elimination; 5) \(\beta\)-hydrogen elimination (or dehydrometallation); and 6) \(\beta\)-carbon elimination, of which the “insertion” and the “transmetallation” have, more or less, the common ground in organic chemistry [21].

1.7.1 Oxidative Addition

As discussed previously in Section 1.3, the addition of \(H_2\) to an \(C\) is regarded as reduction of the carbon atom – that is, the addition of one and two molecules of \(H_2\) forms carbene (\(C^2^-\)) and methane (\(C^4^-\)) from \(C^0\), respectively. On the other hand, addition of \(H_2\) to an \(Ni\) is regarded as oxidation of the \(Ni\); \(Ni^0\) to \(Ni^{2+}\). This
is simply a matter of formalism. In organic chemistry, the oxidation number of H is assigned $1^+$ (a proton), while in organometallic chemistry, the oxidation number of H is $1^-$ (a hydride). In organic chemistry, the events transforming an C to CH$_2$ and CH$_4$ are rather imaginative, but in organometallic chemistry, this type of reaction is in all likelihood. As depicted in Scheme 1.5, an Ni(0) interacts with H$_2$ through the $\sigma$-$\sigma^*$ bonding and the $\sigma^*$-$\pi$ back bonding, both of which cooperate to cleave the H–H bond and make the two Ni–H bonds. In this process, an Ni(0) offers 2e to create two Ni–H bonds and the oxidation number changes from 0 to $2^+$. In organometallic chemistry, the formal oxidation number of a metal is equal to the number of the $\sigma$-type ligands (X) attached to the metal.

The process of generating Grignard reagents is a type of oxidative addition, where Mg(0) is changed to Mg(II) via oxidative addition of the Mg(0) upon the R–Cl bond. As shown in Eq. (a) of Scheme 1.6, this example is appealing because as Mg loses 2e, the previously positively charged R group changes to the negatively charged R group ("umpolung" = changing the polarity).

In contrast to Mg(0), Ni(0) is capable of undergoing oxidative addition towards a wide variety of compounds with C–heteroatom $\sigma$-bonds. Aryl, alkenyl, and allyl halides (and triflate, CF$_3$SO$_3^-$) are good substrates, where coordination of these unsaturated compounds through the double bonds helps to facilitate this process (cf., 1.15). The rate of addition decreases in the order: C–I > C–Br > C–Cl > C–F. The
C–F bond is so strong that it is very difficult to cleave. Some of the Ni(0) species—
and especially those coordinated by electron-donating σ-ligands, such as [alkyl]₂P
and H⁺, are capable of undergoing oxidative addition to the Csp²–F and even the
Csp¹–F bonds (cf., 1.16). Raney nickel is a typical example capable of undergoing
oxidative addition to the C–S bond, and reductively cleaves the C–S bond. The acyl
C–O bonds of aryl esters (Eq. (e)) [22], as well as the C–O bonds of epoxides (Eq.
(f)) [23], are also subject to the oxidative addition of an Ni(0).

As with the oxidative addition of an Ni(0) to σ-bonds, the oxidative addition of an
Ni(0) to π-bonds also takes place, breaking the π-bond and making new two
σ-bonds. Scheme 1.7 illustrates how the π-σσ (donation) and π'-σπ (back donation)
orbital interactions function to form nickellacyclopropane.

As shown in Scheme 1.8, a similar oxidative addition takes place across two or
more π-ligands of a wide variety of combinations of the ligands. The first example
is an intermediate supposed for the production of cyclooctatetraene by tetrameriza-
tion of acetylene (the Reppe reaction; Eq. (a)) [24]. Alkynes and dienes react with
carbon monoxide, carbon dioxide, and even with aldehydes and ketones in ways
shown in Eqs. (b)–(d) (Scheme 1.8) [25–27]. All of these transformations are ac-
companied by the oxidation of an Ni(0) and cyclization, and hence are commonly
referred to as oxidative cyclization.

Among nickellacycles, the Wilke complexes 1.21–1.24, formed by the oxidative
addition of an Ni(0) to two molecules of butadiene, and are the most famous and

\[
\begin{align*}
\text{Scheme 1.7.} & \quad \text{Schematic presentation of oxidative addition of} \\
& \text{an Ni(0) upon a double bond. The π-σσ (donation) and π'-σπ (back donation)} \\
& \text{interactions function to form nickellacyclopropane.}
\end{align*}
\]
cost-effective in chemistry (Scheme 1.9). All of the intermediates equilibrate one to another, and can exist in a variety of forms. Some of these are shown in Scheme 1.9 (see also 1.9 and 1.13 in Fig. 1.6). In the absence of ligands, the \( \eta^1,\eta^1 \)-complexes \( 1.24 \) may be most abundant, because these have a self-saturated \( \text{L}_2\text{X}_2 \text{d}^8\text{16e} \) electronic configuration. All the others are unsaturated, being either \( \text{X}_2 \text{d}^8\text{12e} \), e.g., \( 1.21 \), \( 1.22 \) or \( \text{LX}_2 \text{d}^8\text{14e} \), e.g., \( 1.23 \). The population of the \( \text{X}_2 \)-complexes may increase in the presence of bidentate ligands, such as DPPE [1,2-bis(diphenylphosphino)ethane] and that of the \( \text{LX}_2 \) by monodentate ligands, such as \( \text{PPh}_3 \).

The \( \eta^1,\eta^1 \)-complex \( 1.21 \) is all cisoid with respect to the allylnickel moieties, while the complex \( 1.21' \) is all transoid. The \( \eta^3 \)-nickel complexes (or \( \eta^3 \)-allylnickel complexes) are defined as follows. In the \( \eta^3 \)-three carbon skeleton, those having substituents on the terminal carbon \( \text{C}_1 \) and/or \( \text{C}_3 \) cis to the substituents on the central carbon \( \text{C}_2 \) (an H atom !, in this particular case) are syn, and those of opposite are anti. That is, the cisoid \( \eta^3 \)-complex \( 1.21 \) is transformed to the syn-\( \eta^1,\eta^1 \)-complex \( 1.24 \) without changing the olefinic geometries and the transoid \( \eta^1,\eta^1 \)-complex \( 1.21' \) to the anti-\( \eta^1,\eta^1 \)-complex \( 1.24' \).

1.7.2

**Insertion**

The nickel hydride \( \text{Ni–H} \) and the hydrides of main group elements – for example, \( \text{B–H} \) of diborane \( \text{B}_2\text{H}_6 \) – show similar reaction patterns, with respect to regio- and
stereoselectivity, towards polar double bonds as well as to non-polar double and triple bonds (Scheme 1.10) [28]. In organic chemistry, these reactions are referred to as either the hydride reduction of carbonyls, hydrogenation of alkenes and alkynes, or addition of B–H to alkenes and alkynes (or hydroboration), as in organic chemistry the change of functional groups of organic molecules is the main concern. On the other hand, in organometallic chemistry, where the change of the metallic species is the main concern, these reactions are simply regarded as the insertion of C=O, C=C and C≡C into the B–H or Ni–H bond. These reactions proceed, more or less, via a four-membered cyclic transition state (syn addition).

As is apparent from Scheme 1.11, the situation changes dramatically when it comes to the reactivities of the Ni–R and B–R species. The B–R species never react with ethylene (Eq. (a)), while the Ni–R species engages in the reaction with ethylene (Eq. (b)). In fact, even under room temperature, the insertion of ethylene into the Ni–R bond is repeated almost infinitely, and polyethylene forms (Eq. (b)). The B–R species reacts with carbon monoxide in a similar way with aldehydes and ketones. The BR3 species repeats the same process two more times finally to provide a tertiary alcohol (Eq. (c)). The Ni–R species, on the other hand, reacts with
CO in a quite different way, and never reacts in the way shown in Eq. (d). Formally, CO inserts into the Ni–R bond at the C atom and forms an acylnickel species, as shown in Eq. (e) in Scheme 1.11.

Mechanistically, the CO insertion proceeds by the migration of the alkyl group from an Ni (accompanied by the Ni–R σ-bond breaking) to the carbon of CO (accompanied by the Ni–CO σ-bond strengthening) (Scheme 1.12). This process is referred to as either 1,2-migration of the R (from the Ni to the C of CO), 1,1-insertion of the Ni–R (to the same C of CO), or, by putting together these two, migratory insertion of CO upon the Ni–R bond. For the migratory insertion to proceed, the R and the C=O groups must be cis to each other. The trans-isomer is topologically unable to undergo the 1,2-migration (Scheme 1.12. The symbol □ denotes a vacant site on Ni).

Sequential insertion of different molecules (or functionalities) diversifies the insertion reactions. Scheme 1.13 shows that the diene inserts to the Ni–H bond regioselectively, providing an internal $\eta^3$-allylnickel species. Then, the formyl group undergoes insertion into the thus-formed $\eta^3$-allylnickel bond [29]. The latter process is regarded as the nucleophilic addition of $\eta^3$-allylnickel to an aldehyde, and is a unique reactivity which is associated specifically with the $\eta^3$-allylnickel species among the Group 10 $\eta^3$-allylmetal species; neither $\eta^3$-allylpalladiums nor $\eta^3$-allylplatinums undergo nucleophilic addition to carbonyl compounds. It should be noted that in all the insertion processes discussed above, the formal oxidation number of the nickel does not change but remains at 2+.

1.7.3 Transmetallation

Grignard reagents (RMgX), which were first prepared in 1900, have been among the most popular and useful organometallic reagents, as they react with a wide variety of carbonyl compounds to produce C–C bonds: these include CO$_2$, aldehydes,
ketones, esters, and carbonates. The reagent, however, is usually not reactive toward alkyl halides (Scheme 1.14(b)). This is fortunate for the Grignard reagents, because if that reaction could proceed, their preparation would become a very difficult task!

The change in reactivity of Grignard reagents in the presence of a catalytic amount of transition metal salts has long been recognized. A cobalt salt helps the Grignard reagents to undergo a coupling reaction with alkyl halides (the Kharash reaction), while a cuprous salt guides the Grignard reagents selectively to undergo 1,4-addition to conjugated enones, instead of 1,2-addition to the C=O. The newly gained reactivity is apparently ascribed to a new metallic species RM, generated by exchanging X and R between MX and the R of RMgX (Scheme 1.15). This equilibrium process is termed “transmetallation”. In order for the equilibrium to go to the right, M must be less electropositive than Mg. Fortunately, almost all transition metals are less electropositive than Mg (see Table 1.1), and transmetallation works in favor of the formation of RM. However, this condition is not always necessary; an all-important point is that the species RM formed by transmetallation is, irrespective of the population in the equilibrium, more reactive than RMgX toward the given target reaction.

In addition to the “Wilke nickel effect” (see Section 1.1), there is another “nickel effect” that is closely associated with transmetallation. The Grignard-type vinylation of aldehydes with vinylchromium(III) is now known as the NHK reaction (Nozaki–Hiyama–Kishi reaction; Eq. (a) in Scheme 1.16) [30]. The reaction proved indispensable for the total synthesis of palitoxin (a marine natural product), but the original authors (Nozaki and Hiyama) and Kishi soon realized independently that the reaction was not reproducible and that its success depended on the source and batch of the Cr(II) and Cr(III) salts. After prolonged investigation and careful scrutiny, both groups concluded that a trace amount of nickel in the Cr(II) or Cr(III) species was essential in order to promote the reaction. Initially, palladium salts were thought to be an effective catalyst, but again it transpired that a trace amount of nickel in the palladium salt was the true active species. The reaction is mediated
by a facile oxidative addition of an Ni(0) upon vinyl iodide (Scheme 1.16(b)). Transmetallation between vinylnickel(II) iodide and CrX₃ produces vinylchromium(III), which undergoes nucleophilic addition to aldehydes. The Ni(0) species is produced by the reduction of 1 mol of Ni(II) with 2 mol of Cr(II), and enters a catalytic cycle (Eq. (c) in Scheme 1.16).

The NHK reaction shows a wide compatibility with functional groups, chemoselectivity (aldehydes > ketones), and a low basicity; hence the reaction has been widely used for the total synthesis of many natural products of structural complexity. Examples include a brefeldin series by Schreiber [31], allopumiliotoxin 339A by Kibayashi [32], and brevetoxin B by Nicolaou [33]. One of these examples is shown in Scheme 1.17, and illustrates how well the reaction works [33]. In this particular case, the aldehyde possesses no enolizable α-proton with respect to aldehyde. The low basicity of the NHK reagent allows one to perform the vinylation of chiral aldehydes bearing enolizable protons, without racemization.
1.7.4

Reductive Elimination

Reductive elimination is the reverse of oxidative addition. As shown in Eq. (1.3), the formation of nickella-3-cyclopentene from butadiene and Ni(0) is oxidative addition, whilst the reverse to produce a mixture of butadiene and an Ni(0) is reductive elimination. As mentioned in Section 1.7.1, oxidative addition is accompanied by an increase in the formal oxidation number of Ni by 2 units; conversely, in reductive elimination the formal oxidation number is decreased by 2 units. This is why the process is termed reductive elimination. This type of microscopic reverse is seen very clearly in organic transition metal chemistry. The reaction of Eq. (1.3)

\[
\text{Ni}(0)L_4 + \text{oxidative addition} \rightarrow \text{Ni}(II)L_2 + L_2
\]

is by itself not productive, but the insertion of another molecule (e.g., of butadiene) renders the chemistry productive (Scheme 1.18). Reductive elimination of an Ni(0) from 1.21', 1.23', and 1.22' provides cis-1,2-divinylcyclobutane, 4-vinylcyclohexene, and 1,5-cyclooctadiene, respectively. In the most cases this reductive elimination is rate-determining, though the selective formation of one of these is clearly dependent upon the reaction conditions.

![Scheme 1.18. Various types of reductive eliminations of (butadiene)_2Ni^{II} complexes.](image)

It is now well recognized that, in most cases, reductive elimination is accelerated by the coordination of the fifth electron-deficient ligand (associative activation). In this regard, it is fortunate for organonickel chemistry that most Ni(II) complexes have unsaturated \(d^816e\) configuration and still have one vacant coordination site for coordination of the fifth ligand. A. Yamamoto remains among the outstanding pioneers in this field, and showed that dialkyl(bpy)Ni(II) complexes 1.25 are thermally stable and activated in the presence of some electron-deficient alkenes (e.g., acrylonitrile, maleic anhydride) to undergo reductive elimination to provide the coupling product R–R and (alkene)_n(bpy)Ni(0) (n = 1 or 2) in quantitative yields (Scheme 1.19). Yamamoto also succeeded in detecting the five-coordinated complexes using both infra-red and ultra-violet spectroscopy [34].

T. Yamamoto (a former coworker of A. Yamamoto) has shown that the rate of reductive elimination of diethyl(bpy)Ni(II) 1.25, \(R = \text{Et}\) is expressed as \(k\)\(|\text{Et}_2\text{Ni}(\text{bpy})|\)\([\text{aromatic compound}]\), and a plot of a log \(k\) value against a \(\Sigma\alpha\) value
(\(\sigma\)) is the Hammett \(\sigma\) value of the substituents on aromatic compound) affords a linear correlation with \(\rho\)-value of +1.4. Furthermore, as is illustrated in Scheme 1.20, when hexafluorobenzene is used as an aromatic compound, reductive elimination is coupled with oxidative addition of an Ni(0) upon the C–F bond [35].

These observations are suggestive of why the Kumada–Tamao coupling reaction proceeds so smoothly when using unreactive (in terms of organotransition-metal chemistry) aryl chlorides as substrates [36]. In palladium chemistry, the oxidative addition of Pd(0) on the aryl–Cl bond has long been regarded as almost impractical, but a recent breakthrough led to the palladium-catalyzed transformation of chloroarenes to aromatic derivatives, and this remains among the most topical subjects currently under investigation [37].

The Kumada–Tamao (or the Corriu–Kumada–Tamao) reaction proceeds according to Eq. (b) in Scheme 1.21 – that is, oxidative addition of an Ni(0) upon an aryl chloride, transmetallation between the thus-formed arylnickel(II) chloride and a Grignard reagent, followed by reductive elimination [38]. The idea of an associative elimination (Scheme 1.21(a)) that achieves both reductive elimination to give a cross-coupling product and oxidative addition to feed arylnickel(II) chloride simultaneously, may be worth further examination.

In general, the higher the electronegativity of the ligand \(R\), the easier and more rapid the reductive elimination. Accordingly, ary(Csp\(^2\))-ary(Csp\(^2\)) coupling proceeds quantitatively in most cases, and the success of the ary(Csp\(^2\))-alkyl(Csp\(^2\)) coupling subtly depends on the reaction conditions, especially the type of organometallic. All types of organometallics (e.g., RMgX, R\(_n\)ZnX\(_{2-n}\), R\(_n\)AlX\(_{6-n}\), R\(_n\)BX\(_{3-n}\),...
etc.) display characteristic reactivities, with alkyl-alkyl coupling being most difficult and having been developed only recently. For example, Knochel has succeeded in the coupling reaction shown in Eq. (1.4) [39], but this is successful only in the presence of 20 mol% p-fluorostyrene, which may serve as the fifth ligand to facilitate reductive elimination. Remarkably, the reaction is tolerant to the acidic amide NH bond and the carbamate CO, the characteristic behavior associated with organozinc reagents.

$$\text{R} + \text{Ni} \rightarrow \text{Ar}$$

In order for reductive elimination to proceed, the organic ligands to be coupled must be cis to each other. The trans-isomers never undergo reductive coupling, and must isomerize to the cis-isomers prior to undergoing reductive elimination. To help the reductive elimination, bidentate ligands – especially those having a large bite angle ($\theta$) – have been shown to be effective, as they topologically force the organic ligands cis and closer to each other [40].
1.7.5  
\(\beta\)-Hydrogen Elimination

The instability of nickel alkyl complexes, or in general, of transition metal-alkyl complexes, had long prohibited their isolation until the mid-1950s. The main reason for this instability was attributed to the weakness of the metal-alkyl bonds (thermodynamic instability). However, this was not the case; rather, the transition metal-alkyl bond strengths are comparable to those of typical elemental metal-alkyl bonds. There are two kinetic pathways that facilitate the decomposition of transition metal-alkyl complexes: one is \(\beta\)-hydrogen elimination, which was first proposed by Wilkinson; and the other is reductive elimination (see Section 1.7.4). The thermal instability of some dimethyl- and di(neopentyl)metal complexes that do not have \(\beta\)-hydrogen and are unable to undergo \(\beta\)-hydrogen elimination is mostly attributed to the ease of reductive elimination.

\(\beta\)-hydrogen elimination is the reverse of migratory insertion of an alkene into an Ni–H bond (Scheme 1.10(b)). As shown in Scheme 1.22, \(\beta\)-hydrogen elimination is thought to proceed via a concerted mechanism – that is, via a single transition state, where both the alkyl and \(\beta\)-hydrogen remain on the Ni, and hence the coordination number increases by one unit. Accordingly, for this process to proceed smoothly, a preceding dissociation of one L is necessary.

The unusual stability of dialkyl(bpy)Ni(II) complexes (1.25, Scheme 1.19) may be attributed to the bidentate bipyridyl ligand, which is not only a good \(s\)-donor, but also a good \(\pi\)-acceptor. Moreover, it binds tightly to an Ni and always keeps the Ni(II) saturated.

In contrast, the diimine complex 1.26, which is of close structural similarity to 1.25 but of different electronic nature and steric requirement for the ligand, is rather unstable. Although 1.26 is stable in the solid state for an indefinite period at temperatures below \(-15^\circ\text{C}\) and under inert atmosphere, it is thermally sensitive when in solution, and liberates the reductive elimination product, hexane, in CD\(_2\)Cl\(_2\) above \(-20^\circ\text{C}\) [41]. The cationic diimine complex 1.27, generated by protonation with 1 equiv. of Et\(_2\)O\(^+\)HBAr\(_4^–\) and liberation of 1 mol of propane at low temperature, is formulated as the \(d^914e\) \([L_2X\text{Ni(II)}]^+\) cationic complex. These types of coordinatively unsaturated cationic metallic species tend to show a \(\beta\)-hydrogen agostic structure, a structural equivalent to the transition state supposed for \(\beta\)-hydrogen elimination (Scheme 1.22) [42]. The structure of i-1.27 has been well
characterized using low-temperature \(^1\)H NMR. For example, at \(-130\) °C in CDCl\(_2\), the agostic hydrogen is observed at \(-12.5\) ppm (t, \(J = 19\) Hz). The other two geminal hydrogens on the agostic methyl group are chemically inequivalent and appear at 0.26 and 0.11 ppm (multiplet). The methyne proton appears as a complex multiplet, which becomes a septet above \(-80\) °C. Dynamic NMR analysis has revealed that the exchange of agostic and nonagostic protons occurs with a \(\Delta G^0\) of 8.0 Kcal mol\(^{-1}\) at \(-99\) °C, and the barrier for the exchange of agostic and nonagostic methyl groups is slightly higher, 9.0 Kcal mol\(^{-1}\) at \(-77\) °C.

It should be realized that there is a crucial difference between the agostic structures in Schemes 1.22 and 1.23. In the equilibrium in Scheme 1.22, the agostic complex is a transition state structure for \(\beta\)-hydrogen elimination (towards the right) or for migratory insertion of an alkene into the Ni–H (towards the left). On the other hand, in the equilibrium initiated from cationic unsaturated complexes \(1.27'\) (d\(^{14}\)e) (Scheme 1.23), the agostic complexes \(i\)-1.27 and \(n\)-1.27 are intermediates and lower in energy than the alkene–NiH complexes shown in square brackets in Scheme 1.23. \(n\)-1.27 serves as a very efficient catalyst for the polymerization of ethylene. As shown in Scheme 1.24, the polymerization of ethylene even proceeds at \(-100\) °C.

Scheme 1.23. Generation of a coordinatively unsaturated alkynickel(II) cationic complex 1.27' and its isomerization to \(\beta\)-hydrogen agostic complexes \(n\)-1.27 and \(i\)-1.27. The figures indicate chemical shifts (in ppm) in \(^1\)H NMR.

Scheme 1.24. Polymerization of ethylene catalyzed by an \(\eta^1\)-(diimine)alkynickel(II) cationic complex.
The Ni(II)- and Pd(II)-a-diimine complexes, such as 1.26, which were developed recently by Brookhart and others, exhibit high reactivity for the polymerization of ethylene (Scheme 1.24), the copolymerization of ethylene and functionalized alkenes, the oligomerization of ethylene and a-olefins, and the homo-polymerization of cyclic and internal acyclic olefins [43].

1.7.6 a- and \( \beta \)-Carbon Elimination (C–C Bond Cleavage)

By using nickellacycles as the probes, Grubbs has demonstrated that all of the competitive reactions, namely \( \beta \)-hydrogen elimination (Scheme 1.25(a)), reductive elimination (Eq. (b)), and reductive ring opening (Eq. (c)) (the reverse of oxidative cyclization), are subject to the number of phosphine ligands in the complexes [44]. The \( \beta \)-hydrogen elimination proceeds cleanly when Cp\( \text{P} \) is used as the ligand. The ligand has a large cone angle, and hence blocks the coordination of another ligand to the Ni(II) center, keeping the fourth coordination site vacant. With DPPE, reductive elimination giving rise to cyclobutane takes place selectively. The reductive ring opening (Eq. (c)) accompanies cleavage of the C–C bond and is closely related to the \( \beta \)-hydrogen elimination, the cleavage of the C–H bond. However, examples of this type of C–C bond cleavage reaction are very scare, most likely because, for this reaction to proceed the Ni–C and C–C bonds must be syn to each other, and this conformation is only possible for nickellacycloalkanes. For most alkynickel(II) species, the alkyl chains take on an extended zigzag conformation and only the C–H bonds take a conformation syn to the Ni–C bonds. In fact, \((\text{PPh}_3)\text{Pt}^{2+}(n-\text{Bu})_2\) undergoes \( \beta \)-hydrogen elimination approximately \(10^4\) times faster than \((\text{PPh}_3)\text{Pt}^{2+}(\text{CH}_2)_2\) (cf. Scheme 1.25(a), Pt\( ^{2+}\) in place of Ni\( ^{2+}\)) [45]. The catalytic version of C–C bond cleavage has been developed recently (Scheme 1.25(d)) [46]. Again in this case, a five-membered ring is a common structural motif. Equation (e) in Scheme 1.25 demonstrates a novel C–elimination, providing a carbene complex which serves as the catalyst for the olefin metathesis [47].

---

![Scheme 1.25](image-url)
reaction was reported by Grubbs as early as 1978, at which time the catalyst performance was modest, though this is in fact a protocol of the ruthenium-based Grubbs olefin metathesis catalysts which is currently undergoing investigation [48].

1.8 Catalytic Reactions

Catalytic reactions usually start with oxidative addition and end up with either reductive elimination or $\beta$-hydrogen elimination with regeneration of a catalytically active nickel species. During these two events, the insertion of a variety of unsaturated molecules, transmetallation with organometallics, and skeletal rearrangement take place. First, we should consider the Wilke 1-butene formation, the dimerization of ethylene (Eq. (1.1)), elementary steps of which are shown in Scheme 1.26. The reaction starts with transmetallation between a catalytic amount of a
Ni(II) salt and Et₃Al, which produces the key reactive intermediate, EtNi(II) species with one vacant coordination site (Eq. (a)). The EtNi(II) species then reacts with ethylene to form (η²-ethylene)ethylnickel(II) (Eq. (b)). The insertion of ethylene into the Ni-ethyl bond yields the BuNi(II) species (Eq. (c)), which is coordinatively unsaturated and undergoes β-hydrogen elimination to give (η²-1-butene)nickel(II)-hydride (Eq. (d)). Ligand exchange between 1-butene and ethylene (Eq. (e)), followed by insertion of ethylene into the Ni–H bond regenerates the coordinatively unsaturated EtNi(II) species (Eq. (f)).

The summation of Eqs. (b) to (f) in Scheme 1.26 leaves 2 mol ethylene as the starting material and 1 mol 1-butene as the product. All of the processes (b) to (f) are microscopic reverse, and hence the driving force of this reaction is partly ascribed to its large exothermic property ($\Delta H^0 = -21.9$ Kcal mol⁻¹). Provided that the β-hydrogen elimination step (Eq. (d)) was very slow, then the reactions (b) and (c) would be repeated infinitely and provide polyethylene. The number of times that the cycle of Eqs. (b) and (c) repeat depends on the reaction conditions (temperature, pressure, etc.) and the types of ligands. Under Wilke’s original conditions, 1-butene was produced almost exclusively [1, 49]. The Shell higher olefin process (SHOP), which was started in 1977, typically produces a mixture of 1-butene, 1-hexene, and 1-octene in varying ratios, these being controlled by market demands [3, 50].

The means of expression in Scheme 1.26 is both intricate and time-consuming in drawing. Hence, catalytic reactions are frequently presented as shown in Scheme 1.27, where the catalytic species are placed on a circle and the reactants and products are placed outside the circle, with the curved arrows directing inwards and outwards, respectively. As is apparent from Scheme 1.27, the ligand L and an anionic species do not change all through the reaction, and in this sense
these are regarded as a *spectator ligand* and a *spectator anion*, respectively; indeed, for clarity they are sometimes omitted from the schemes.

\[
\text{Br} + \text{Ni(CO)}_4 \rightarrow \text{Br} + \text{Ni(CO)}_4
\]  

Equation (1.5) illustrates the carbonylation of allyl bromide catalyzed by Ni(CO)\(_4\) under an atmosphere of CO. The reaction provides 3-butenoyl bromide and, as illustrated in Scheme 1.28, proceeds in order of: 1) oxidative addition of Ni(CO)\(_3\) into the C–Br bond of allyl bromide, giving 1.28, 2) migratory insertion of CO into the Ni–allyl bond, forming an acynickel species 1.29; and 3) reductive elimination to yield 3-butenoyl bromide with regeneration of Ni(CO)\(_3\). For most organic chemists, this reaction may be easier to access than that of Eq. (1.1), because it possesses many familiar functionalities and has a reaction pattern similar to that of the Grignard reaction. However, when looked at in detail, this reaction is more complicated than it appears. For example, in Scheme 1.28 Ni(CO)\(_3\) is proposed as an intermediate, but the question remains as to whether this is reasonable. The dissociation of Ni(CO)\(_4\) to Ni(CO)\(_3\) and CO is highly endothermic, and Ni(CO)\(_3\) must be present in a minute concentrations, especially under the carbonylation conditions (an atmosphere of CO).

\[
\text{Ni(CO)}_4 \rightarrow \text{Ni(CO)}_3 + \text{CO} \quad \Delta H^\circ = +22\text{~}23 \text{ Kcal mol}^{-1}
\]

The initial oxidative addition can proceed either through coordination of the C–C double bond of allyl bromide to Ni(CO)\(_3\) or through the coordination of bromide to Ni(CO)\(_3\), which provide the \(\eta^1\)-allyl complex (\(\eta^1\)-1.28) or the \(\eta^1\)-allyl

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**Scheme 1.28.** Catalytic cycle for the nickel-catalyzed carbonylation of allyl bromide under an atmosphere of CO.
complex ($\eta^1$-1.28), respectively. The migratory insertion of CO of $\eta^1$-1.28 provides the $d^816e$ acyl complex (1.29), whereas the reaction of $\eta^3$-1.28 leads to the coordinatively unsaturated $d^814e$ acyl complex (1.29'). Two additional questions here are: 1) Is the latter process realistic? and 2) How does the allyl group migrate – does CO move toward the allyl C–Ni bond, or does the allyl group move and ride on the C of CO?

Calculation methods at high levels are very helpful in addressing these questions, especially with regard to the transition state structures and the activation energies for each of the elementary steps. The results obtained at the DFT (B3LYP) level are sketched out in Schemes 1.28 and 1.29 [51].

With regard to the problem of which of Ni(CO)$_4$ or Ni(CO)$_3$ is a real species, the calculations conclude that both are equally probable; the reaction of Ni(CO)$_3$ with allyl bromide – irrespective of the formation of the $\eta^1$-bound complex $\eta^2$-1.30 or the $\eta^1$-bound complexes $\eta^1$-1.30 – is exothermic and barrier free. On the other hand, the formation of $\eta^2$-1.30 and $\eta^1$-1.30 by displacement of CO from Ni(CO)$_4$ is endothermic, and the activation energy is the same (19 Kcal mol$^{-1}$) for both pathways (Eqs. (a) and (b) in Scheme 1.29). The following oxidative addition process is rate-determining, and the reaction giving rise to $\eta^1$-1.28 proceeds as shown in Eq. (a) in Scheme 1.29, where formation of the Ni–C and Ni–Br bonds and loosening of the Ni–CO bond ant to the C–Br bond proceed in concert. For the formation of $\eta^1$-1.28, two routes are conceivable (Eq. (b)); one route involves migration of
the allyl fragment from the halogen to the metal, and is less probable owing to its large activation energy (31 Kcal mol$^{-1}$). The other route involves a slide of the allyl fragment along a direction parallel to the Ni–Br bond, where the carbon originally bound to bromine becomes the terminal methylene carbon in the final product. $\eta^1$- and $\eta^3$-1.28 isomerize to each other either by losing ($\eta^1 \rightarrow \eta^3$) or gaining CO ($\eta^3 \rightarrow \eta^1$) and by overcoming a barrier of less than 10 Kcal mol$^{-1}$.

As for the migratory insertion of CO, $\eta^1$-1.28 is more reactive than $\eta^3$-1.28 and forms the square-planar acynickel complex 1.29 (Eq. (c), Scheme 1.29), during which the allyl group migrates to the carbon of one of the two cis-coordinated CO and, simultaneously, the Ni–CO bond becomes shorter. The same acynickel complex 1.29 can be derived from $\eta^3$-1.28, although this route is apparently unfavorable owing to the inherent instability of the coordinatively unsaturated $d^814e$ complex, 1.29$^\prime$ ($\Delta H^\prime_{1.29} = 11$ Kcal mol$^{-1}$).

Once the acynickel complex 1.29 is formed, the following few steps are all barrier-free, exothermic, and proceed spontaneously (Scheme 1.30). The coordination of CO facilitates reductive elimination (associative mechanism, see Section 1.7.4) to yield first the Ni(0)-$\eta^1$-acyl bromide complex and then the acyl bromide, the final product.

![Scheme 1.30. Microscopic views of reductive elimination of 1.29 giving rise to the final product. All the steps are exothermic and barrier free, and the reactions proceed spontaneously.](image)

The example shown in Scheme 1.31 emphasizes the importance of the electronic and steric effects of the ligands. Because of the stability (to air) and the ease of handling (solid and odorless), PPh$_3$ has been used most widely as the ligand of catalytic reactions. PPh$_3$ is not only an appropriate electron donor to an Ni, but also an electron acceptor from the Ni (back donation or back bonding, vide infra). The molecular size allows it to coordinate to an Ni by four molecules, forming Ni(PPh$_3$)$_4$, which is a flammable solid and usually prepared in situ, for example:

$$\text{NiX}_2 + \text{DIBAL (or Zn-dust, Et}_2\text{Zn, a reducing agent)} + 4 \text{ PPh}_3 \text{ or}$$

$$\text{Ni(cod)}_2 + 4 \text{ PPh}_3.$$

However, as shown in Scheme 1.31 (and also in the subsequent chapters), the success (course) of reactions depends markedly on the electronic and steric effects.
of the ligands. In order to promote the particular reaction shown in Scheme 1.31, the use of sterically bulky and highly basic ligand, PCy₃ (Cy = cyclohexyl), is essential. This ligand is so bulky that the maximum number which can coordinate to an Ni is limited to two. In solution, Ni(PCy₃)₂ equilibrates with Ni(PCy₃)⁺PCy₃. The thus-generated NiPCy₃ complex is coordinatively unsaturated and shows a strong propensity to fill the vacant sites with ligands of a small size. In this particular case, NiPCy₃ reacts with acrylamide, a bidentate ligand, to provide 2-azanickellacyclopentane 1.30 [52]. Acrylic acid forms the 2-oxa-analogue of 1.30 [53].

The intermediate 1.30 may be formed either via initial oxidative addition of an Ni(0) upon the N–H bond followed by endo-hydrometallation (Scheme 1.32(a)), or via oxidative addition across acrylamide, either stepwise (Eq. (c)) or in concert (Eq. (d)). Owing to its unsaturated 14e configuration, the intermediate 1.30 is still labile and is subject to β-hydrogen elimination. Exo-hydrometallation – a process which

![Scheme 1.31. Catalytic cycle for the Ni-catalyzed hydrovinylation of acrylamide with ethylene.](image)

Scheme 1.31. Formation of nickellalactam 1.30 via endo-hydrometallation (Eq. (a)) or oxidative cyclization (stepwise Eq. (c) or concertedly Eq. (d)) and its isomerization to 1.31 via β-hydrogen elimination and exo-hydrometallation (Eq. (b)).
is preferred to endo-hydrometallation – leads however to a strained 2-azacyclobutane intermediate 1.31 (Scheme 1.32[b]). Compound 1.31 acquires a higher reactivity towards the insertion of ethylene to give a six-membered 2-aza-metallalactam 1.32; this occurs not only because of its strain, but also because of the stability of the product 1.32. β-Hydrogen elimination of 1.32 and reductive elimination of the thus-formed N–Ni–H intermediate provides the final product with regeneration of NiPCy₃. Clearly, the reductive elimination is competitive to endo-hydrometallation (regenerating 1.32) or to exo-hydrometallation (giving the 4,5-dimethyl derivative of 1.30).

One might propose a more straightforward mechanism, namely the direct formation of 1.31 (Scheme 1.32[b]), but this is not the case. The formation of 1.30 has been demonstrated spectroscopically; in fact, X-ray structure analysis has shown that the PEt₃ derivative of 1.30 forms a cyclic tetramer, where the Ni(II) centers have a square planar structure (d⁸e) with the coordination of the amide oxygen of the adjacent 1.30 unit [54].

It is worth noting that all of the intermediates 1.30–1.32 have the same electronic configuration; they differ only in the ring size, and this difference bestows each of them with unique roles in the catalytic cycle. For example, 1.32 is thermodynamically the most stable and plays a decisive role in liberating the final product, whilst 1.30 and 1.31 are configurational isomers and equilibrate to each other in favor of 1.30 (Eqs. (a) and (b) in Scheme 1.32). The major component 1.30 is not productive; rather, only the minor isomer 1.31 is productive and undergoes insertion of ethylene. An interesting point here is that in organometallic chemistry the Curtin–Hammett principle applies to configurational isomers, because organometallic configurational isomers can change one to another with activation energies within a few Kcal mol⁻¹, in the same way that conformational isomers do in organic molecules [55]. Here, the principle tells us that the ratio of products formed from conformational isomers is not determined by the conformation population ratio.

Although the two reactions shown in Eq. (1.1) and in Scheme 1.31 appear to be somewhat different in appearance, they are closely related to each other in terms of reaction type; the former is hydrovinylation of ethylene and the latter hydrovinylation of an alkene.

Tolman has quantified the electronic effect of various phosphine ligands on the basis of the ν(CO) (the A₂ carbonyl stretching frequencies) of a series of complexes of Ni(CO)₃L (L = P ligand), based on the assumption that the more electron-donating the ligand L, the lower the frequency of ν(CO) of the complexes, and vice versa [56]. One extreme is that of the trialkylphosphine complexes, which show ν(CO) values as low as 2055 cm⁻¹. The other extreme is the PF₃ complex, which shows ν(CO) values as high as 2110 cm⁻¹. The latter type of ligands are sometimes referred to as π-acid ligands, because the σ⁺ orbital of, for example the P–F bond, is low in energy and able to serve as an electron pool from the Ni dσ orbitals (Scheme 1.33(a)). This back donation compensates for the weak donative Ni–P σ-bonding that stems from the weak basicity associated with PF₃. Ph₃P is inferior to R₃P as a donative ligand but is superior as a π-acid ligand, because Ph₃P has the σ⁺(P-CₛP) lying lower than the σ⁺(P-CₛP) of R₃P.
Scheme 3.33. The $d\pi$-$\sigma^*$ back donation interaction (a) and the cone angle (b).

Fig. 1.10. Plots of the Tolman scales of electronic ($\nu$CO, in cm$^{-1}$) and the steric effects ($\Theta$, in degrees) of phosphine ligands. Reproduced from Ref. [56] with permission of the American Chemical Society.
Tolman has also evaluated the steric effects of phosphine ligands with a cone angle $\theta$ (Scheme 1.33(b)) [56]. This is determined by measuring the angle of the cone that will just contain all of the ligand molecule (space-filling model), setting the apex of the cone at an Ni.

In practice, Figure 1.10 can be used to identify the electronic and steric natures of phosphine ligands. By examining Figure 1.10 vertically, it is possible to find many phosphine ligands with different electronic natures, without changing the steric requirement of the ligand. Then, by examining the figure horizontally, alternative ligands can be found with different sizes, but without changing their electronic nature.

References

2 Mond succeeded in preparing many other transition metal carbonyls at high temperature and pressure of CO: Co₂(CO)₈ (30–250 atm of CO at 150–220 °C), Co(CO)₅, Fe(CO)₅ (150–200 atm of CO at 180–220 °C), Mo(CO)₆ (150 atm of CO at 200 °C).
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46 (a) Y. Tamaru, M. Kimura, M. Mori, Y. Takahashi, to be published; (b) For corresponding Pd-catalyzed reaction: H. Harayama, T. Kuboki,
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