

Modern Organonickel Chemistry

Edited by Yoshinao Tamaru



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Editor

Professor Dr. Yoshinao Tamaru

Department of Applied Chemistry
Faculty of Engineering
Nagasaki University
1-14 Bunkyo-machi
Nagasaki 852-8521
Japan

Cover Picture

The front cover is showing a Kabuki actor dressed like a devil, drawn by Sharaku. Nickel was first isolated in 1751 from an ore referred to as “devil Nick copper”. Miners named the ore in that way because it resembled copper ore, but did not yield their objective copper. (Old Nick, informal the devil; Satan, from Webster’s Unabridged Dictionary). Nickel was named after its accursed nickname. Reproduced with permission of the Tokyo National Museum.

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Preface

The monographs, *The Organic Chemistry of Nickel, Volume 1* (1974) and *Volume 2* (1975), which were written by P. W. Jolly and G. Wilke, have long been the “Bible” for organonickel chemists. Unfortunately, however, during the past three decades no books have been published specializing in organonickel [1], whilst in sharp contrast there has been a flood of monographs focusing on organopalladium [2]. As a measure of academic activity, Figure 1 compares the number of publications in journals and letters relating to Ni, Pd, and Pt during the past four decades (SciFinder, searched on 5th March, 2004). Within the last decades, although academic interest in organonickel has clearly fallen, it is still comparable to that in organopalladium. By contrast, during the last three years in industry, all of the group 10 transition metals have vied one with another, as demonstrated by the number of patents relating to Ni, Pd, and Pt (1139, 1173, and 1251, respectively in 2001; 1319, 1320, and 1469, respectively in 2002; and 1268, 1208, and 1481, respectively in 2003).

Nickel and palladium were born under diametrically opposite stars – nickel was

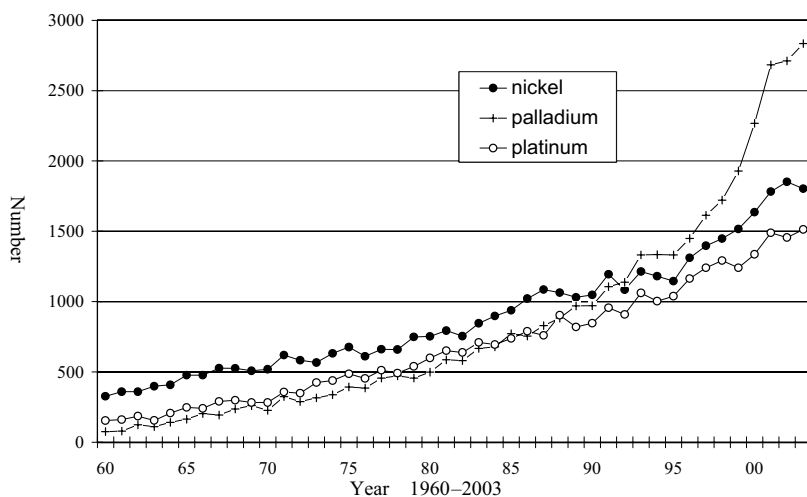


Fig. 1. The number of publications in journals and letters (SciFinder, 5, March, 2004).



Fig. 2. (a) A Kabuki actor dressed like a devil, drawn by Sharaku (front cover). Reproduced with permission of Tokyo National Museum. (b) One of wooden images of Buddhist saints



(a *Bosatsu* who is a Buddhistic goddess of wisdom) decollating the wall of Byodo-in, Uji, Japan. Reproduced with permission of ©平等院, 1999.

born poor, and palladium to wealth. Nickel was first isolated in 1751 by a Swedish mineralogist, A. F. Cronstedt (1722–1765), from an ore referred to as “devil Nick copper”. Miners named the ore in that way because it resembled copper ore, but did not yield their objective copper. (Old Nick, *informal* the devil; Satan, from *Webster’s Unabridged Dictionary*). Nickel was named after its accursed nickname (Fig. 2(a)), whereas palladium was discovered in 1803 in South African crude platinum ore. Palladium was named after *Pallas*, a name associated with Greek mythology, the goddess of wisdom (Fig. 2(b)). Nickel has transmigrated repeatedly, and today – as a result of many studies and discoveries – has been re-incarnated in the shape of the goddess of wisdom.

The advantage of using Ni as a catalyst is its low cost, which is about one-tenth to one-fiftieth that of Pd and Pt (see Table 1). However, certain disadvantages of Ni and its derivatives (e.g., $\text{Ni}(\text{CO})_4$ [3], Ni_3S_2) are associated with toxicity, human carcinogenesis, and skin allergies.

I feel that a book dealing with recent developments in organonickel chemistry would be beneficial to both organometallic chemists and synthetic organic chemists, alike. This book covers many discoveries which have been made during the past three decades, and I am very pleased to have received authoritative reviews of all chapters from experts working at the forefront of organonickel chemistry. These colleagues are also active researchers in the field of organopalladium chemistry, and recognize that these two transition metals show many similarities – and indeed many dissimilarities; for example, Ni forms $\text{Ni}(\text{CO})_4$, while Pd never forms

Tab. 1. Price comparison of Ni, Pd, and Pt and their dichlorides (Aldrich Catalog, 2004).

	<i>Ni slug (99.995)^{a,b}</i>	<i>Pd slug (99.95)^{a,b}</i>	<i>Pt slug (99.99)^{a,b}</i>
EU g ⁻¹	5.4	62.9 [11.6]	83.1 [15.4]
EU mol ⁻¹	317	6693 [21.1]	16 212 [51.1]
	<i>NiCl₂ (99.99)</i>	<i>PdCl₂ (99.999)</i>	<i>PtCl₂ (99.99)</i>
EU g ⁻¹	26.0	120.0 [4.6]	250.8 [9.6]
EU mol ⁻¹	3370	21 277 [6.3]	66 713 [19.8]

1 euro (EU) = 130 Yen.

^a Figures in parenthesis refer to the purity in %.

^b Figures in square brackets refer to price rates relative to nickel compounds.

Pd(CO)₄; and η^3 -allylnickel is nucleophilic, while η^3 -allylpalladium is electrophilic, and so on. Consequently, comparisons made sporadically in this book between Ni and Pd may help the reader to understand more deeply the characteristics of these metals.

Finally, I would like to acknowledge the assistance of those reviewers who checked the content of each chapter to minimize errors and enhance the book's academic value. The project of publishing this book in its present form began with an invitation from Wiley-VCH, and I would like also to acknowledge the initiative of Dr. Elke Maase and the cooperation of Carola Schmidt in bringing the book to fruition. My acknowledgments are also extended to my wife, Keiko, to my secretary, Kiyomi Nishina, and also to my colleagues, Dr. Shuji Tanaka and Dr. Masanari Kimura for their help.

Yoshinao Tamaru
December 2004

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List of Contributors

Tamio Hayashi

Kyoto University
Graduate School of Science
Kitashirakawa Oiwake-cho
Sakyo-ku, Kyoto, 606-8502
Japan

Shin-ichi Ikeda

Graduate School of Pharmaceutical
Sciences
Nagoya City University
Tanabe-dori, Mizuho-ku
Nagoya 467-8603
Japan

Ken-ichiro Kanno

Catalysis Research Center and Graduate
School of Pharmaceutical Science
Hokkaido University
Kita 21, Nishi 10, Sapporo 001-0021
Japan

Masanari Kimura

Graduate School of Science and Technology
Nagasaki University
852-8521 Nagasaki
Japan

Yuichi Kobayashi

Department of Biomolecular Engineering
Tokyo Institute of Technology
4259 Nagatsuta-cho
Midori-ku, Yokohama 226-8501
Japan

Miwako Mori

Graduate School of Pharmaceutical Sciences
Hokkaido University
Sapporo 060-0812
Japan

Tsutomu Osawa

Faculty of Science
Toyama University
Gofuku Toyama 930-8555
Japan

Shin-ichi Saito

Department of Chemistry
Faculty of Science
Tokyo University of Science
Kagurazaka, Shinjuku-ku
Tokyo 162-8601
Japan

Ryo Shintani

Kyoto University
Graduate School of Science
Kitashirakawa Oiwake-cho
Sakyo-ku, Kyoto, 606-8502
Japan

Tamotsu Takahashi

Catalysis Research Center and Graduate
School of Pharmaceutical Science
Hokkaido University
Kita 21, Nishi 10, Sapporo 001-0021
Japan

Masanori Takimoto

Graduate School of Pharmaceutical Sciences
Hokkaido University
Sapporo 060-0812
Japan

Yoshinao Tamaru

Department of Applied Chemistry
Faculty of Engineering
Nagasaki University
1-14 Bunkyo-machi
Nagasaki 852-8521
Japan

Abbreviations

→→	Multi-step reactions
□	Vacant site on transition metal
1°, 2°, 3°	Primary, secondary, tertiary
AcO ⁻	Acetate ion
acac	Acetylacetonate
AO	Atomic orbital
aq	Aqueous
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
bpy	2,2'-Bipyridyl
Bu	<i>n</i> -Butyl
Bz	Benzoyl; PhCO
Bzl	Benzyl; PhCH ₂
CAN	Ceric ammonium nitrate
cat	Catalyst
cat M	Catalytic reaction with respect to the Metal (over reaction arrows)
CN	Coordination number
CHD	Cyclohexadiene
COD (cod)	1,5-Cyclooctadiene (when used as a ligand)
COT (cot)	1,3,5,7-Cyclooctatetraene (when used as a ligand)
CDT (cdt)	1,5,9-Cyclododecatriene (when used as a ligand)
Cp*	Pentamethylcyclopentadienyl; C ₅ Me ₅
Cp	Cyclopentadienyl; C ₅ H ₅
Cy (<i>c</i> -Hex)	Cyclohexyl
Δ	Crystal field splitting
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAL	Diisobutylaluminum hydride
δ ⁺ , δ ⁻	Partial positive, negative charge
diglyme	Diethylene glycol dimethyl ether (MeOCH ₂ CH ₂ OCH ₂ CH ₂ OMe)
DMA	<i>N,N</i> -Dimethylacetamide
DMAD	Dimethyl acetylenedicarboxylate
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide

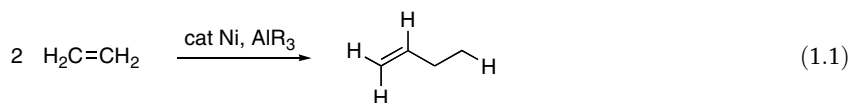
DMG	Dimethyl glyoxime
DMI	1,3-Dimethylimidazolidinone
DMPE (dmpe)	1,2-Bis(dimethylphosphino)ethane (when used as a ligand)
DMSO	Dimethyl sulfoxide
d^n	Electron number in d orbital
DPPB (dppb)	1,4-Bis(diphenylphosphino)butane (when used as a ligand)
DPPE (dppe)	1,2-Bis(diphenylphosphino)ethane (when used as a ligand)
DPPEN	cis-1,2-Bis(diphenylphosphino)ethylene
DPPF (dppf)	1,1'-Bis(diphenylphosphino)ferrocene (when used as a ligand)
DPPP (dppp)	1,3-Bis(diphenylphosphino)propane (when used as a ligand)
d_σ, d_π	d Orbital with σ, π symmetry
e	Electron (as in 18e rule)
ee	Enantiomeric excess
en	Ethylenediamine; $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
Eq.	Equation
equiv.	Equivalent
Et	Ethyl
η	Hapticity in π -bonding ligands
HBpz ₃	Tris (pyrazolyl)borate
HOMO	Highest occupied molecular orbital
HMPA	Hexamethylphosphoric triamide
<i>c</i> -Hex	Cyclohexyl
Hex	<i>n</i> -Hexyl
<i>i</i> -Bu	<i>iso</i> -Butyl
<i>i</i> -Pr	<i>iso</i> -Propyl
IR	Infrared
κ	Hapticity in σ -bonding ligands
KHDMS	Hexamethyldisilazane potassium salt ($\text{KN}(\text{SiMe}_3)_2$)
L	Generalized ligand a 2e neutral ligand (e.g., PPh_3 , pyridine)
LUMO	Lowest unoccupied molecular orbital
μ	Descriptor for bridging
<i>m</i> -	Meta
Me	Methyl
MAO	Methylaluminoxane: $-\text{[Al(Me)O]}_n-$
ML_n	Generalized metal fragment with n ligands (L)
MO	Molecular orbital
MS	Molecular sieves
Ms	Methanesulfonyl: CH_3SO_2^-
NBD (nbd)	Norbornadiene (when used as a ligand)
NMP	<i>N</i> -Methylpyrrolidone
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
Np	Neopentyl
Nu	Nucleophiles
OAc ⁻	Acetate anion

<i>o</i> -Tol	<i>o</i> -Tolyl: 2-methylphenyl
Ph	Phenyl
phen	1,10-Phenanthroline
pin	Pinacolate: O ₂ CMe ₂ CMe ₂ O
PFS	<i>p</i> -Fluorostyrene
PMB	<i>p</i> -Methoxybenzyl: 4-CH ₃ OC ₆ H ₄ CH ₂ -
PPTS	Pyridinium <i>p</i> -toluenesulfonate
Pr	Propyl
<i>i</i> -Pr	<i>iso</i> -Propyl
<i>pro-R</i> , or <i>-S</i>	Stereochemical descriptor
Py (py)	Pyridine (when used as a ligand)
R	Alkyl group
RCM	Ring-closing metathesis
ROMP	Ring-opening metathesis polymerization
Sia	Siamyl: 1,2-dimethylpropyl
<i>sec</i> -Bu	secondary Butyl
TASF	Tris(diethylamino)sulfonium fluoride
TBAF	Tetrabutylammonium fluoride
TBDMS	<i>tert</i> -Butyl(dimethyl)silyl
TBDPS	<i>tert</i> -Butyldiphenylsilyl
<i>t</i> -Bu	tertiary Butyl
TDMPP	Tri(2,6-dimethoxyphenyl)phosphine
Tf	Trifluoromethanesulfonyl
TFP (tfp)	Tri(2-furyl)phosphine (when used as a ligand)
THF	Tetrahydrofuran
THP	Tetrahydropyran
TIPS	Tri(isopropyl)silyl
TMEDA (tmeda)	<i>N,N,N,N</i> -Tetramethyl-1,2-diaminoethane (when used as a ligand)
TMM	Trimethylenemethane
TMP	2,2,6,6-Tetramethylpiperidine
TMS	Trimethylsilyl
Ts	Tosyl; <i>p</i> -toluenesulfonyl; <i>p</i> -CH ₃ C ₆ H ₄ SO ₂
TsOH	<i>p</i> -Toluenesulfonic acid; <i>p</i> -CH ₃ C ₆ H ₄ SO ₃ H
X	Generalized a 2e anionic ligand (e.g., Cl ⁻)

1

Introductory Guide to Organonickel Chemistry*Yoshinao Tamaru*

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?”



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 organolithiums 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 understand the content of the following chapters, which describe much more sophisticated reactions than that shown in Eq. (1.1).

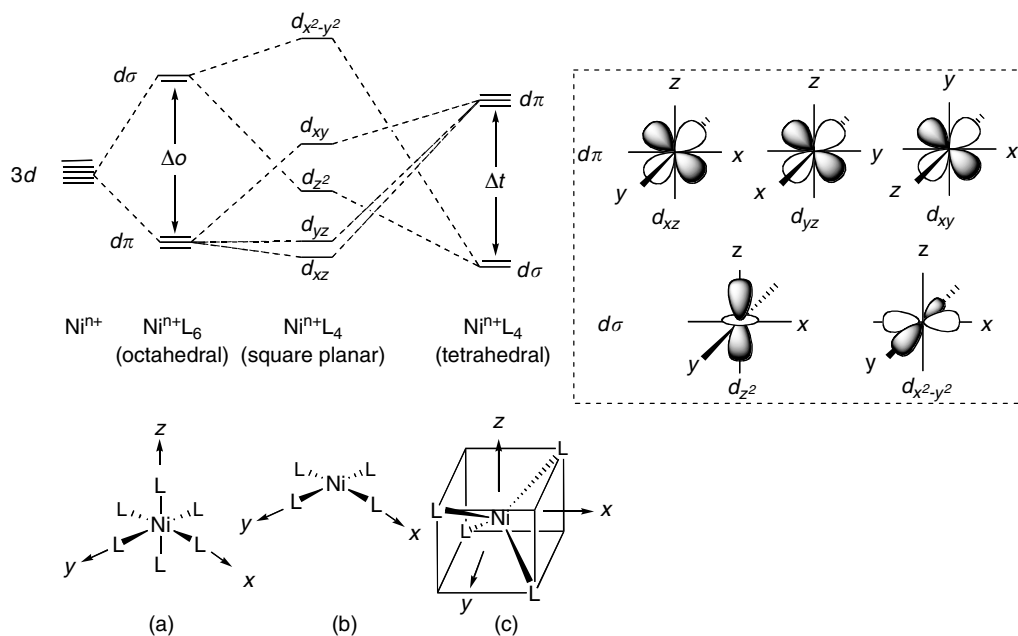


Fig. 1.1. Schematic presentation of the d orbital splitting in the crystal fields of an octahedral (a), a square planar (b), or a tetrahedral (c) environment.

1.1

The Crystal Field

If one imagines a nickel atom or its ions isolated in space, it has the five degenerated d orbitals (d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2}), all lying at the same energy level. As six ligands (represented here with L, such as Cl^- , NH_3 , and H_2O) approach the nickel from the $\pm x$, $\pm y$, and $\pm z$ 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 ($d_{x^2-y^2}$, d_{z^2} , the orbitals with the σ 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 (d_{xy} , d_{yz} , d_{xz} , the orbitals with the π bonding character), on the other hand, are less destabilized because these orbitals point away from L. The magnitude of the energy difference (designated by Δ 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 (d_{xy} , $d_{x^2-y^2}$) rise, while those possessing the z component (d_{z^2} , d_{xz}) 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., $\text{Me}_2\text{Ni}(\text{PR}_3)_2$, $[\text{Ni}(\text{CN})_4]^{2-}$).

1.2

Nickel has Wings: The Mond Method

In the industrial process of Na_2CO_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 $\text{Ni}(\text{CO})_4$ (b.p. 43 °C, extremely poisonous) at ambient temperature. He also found that $\text{Ni}(\text{CO})_4$ 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 $\text{Ni}(\text{CO})_4$ formed selectively, and not $\text{Ni}(\text{CO})_3$ or $\text{Ni}(\text{CO})_5$? 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 - σ 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 π bond, and the two $2p$ electrons on O interact with the empty $2p$ orbital of C to form a charged π 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

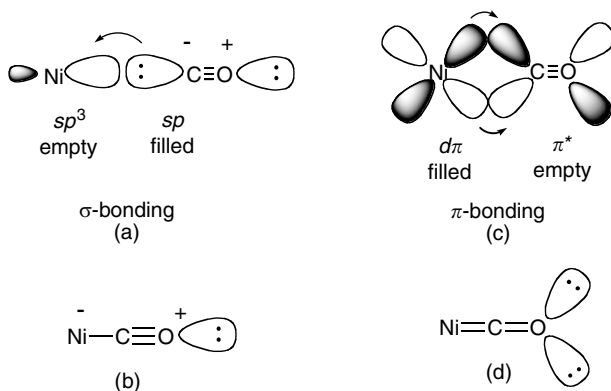


Fig. 1.2. The σ (a and b) and π -bonding interaction (c and d) between an Ni and CO.

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 (σ and σ^* 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 $\text{Ni}(\text{CO})_4$ the nickel bears no valence electrons in the sp^3 orbitals: the two electrons of the Ni–CO σ -bond are donated from the C; hence the σ -bond should be ionic in nature (Ni^- –C) as depicted in Figure 1.2(b).

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

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

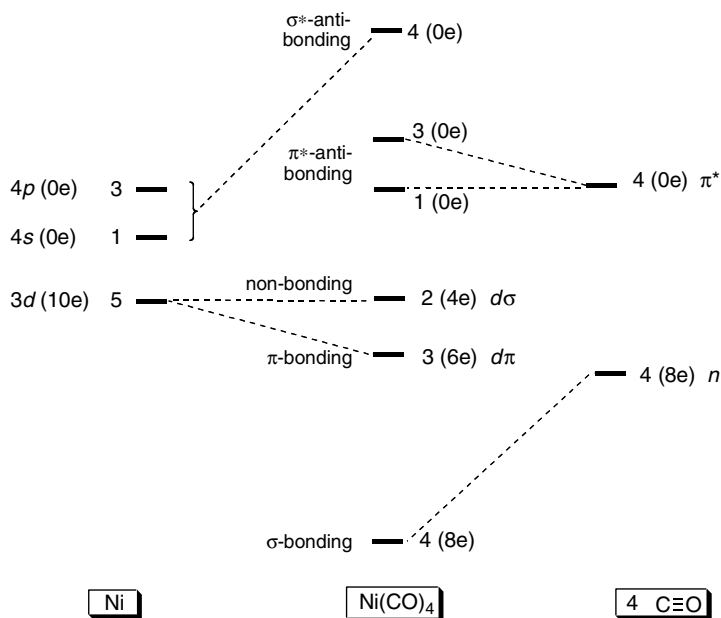


Fig. 1.3. Orbital interaction between an Ni(0) and four CO that forms 4σ bonding (8e), 3π bonding (6e) and two non-bonding (4e) molecular orbitals. All anti-bonding orbitals are empty. Values indicated beside the energy levels refer to the number of the orbitals.

this way, in general, the ligands coordinating to metals can be polarized and elongated, and therefore activated toward chemical reactions, the σ and π 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.

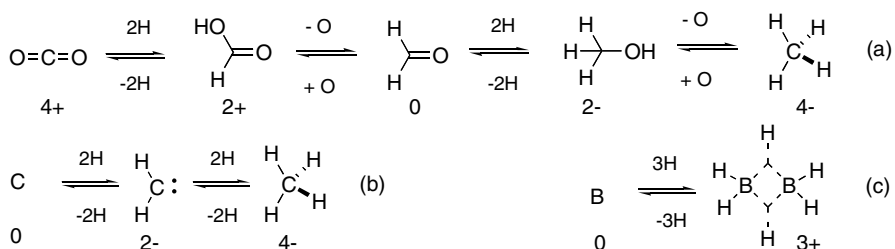
Figure 1.3 illustrates how the whole system, composed of an Ni (left) and four CO (right), is energetically stabilized by forming tetrahedral Ni(CO)₄. That is, all the four sets of lone pair electrons on the C of CO are accommodated in the low-lying sp^3 σ -bonding orbitals, and the 6e of 10d electrons of an Ni are in the low-lying π -bonding orbitals.

The other sets of hybridization of the one 4s and the three 4p of an Ni, for example, ($sp^2 + p$) forming 3 sp^2 and 1p atomic orbitals, are apparently more unfavorable than the sp^3 hybridization, because a σ -bond makes a stronger bond and is more stable in energy than a π -bond – that is, the more the number of σ -bonds the more stable the complexes. This is the reason why Ni(CO)₄ is formed selectively, and not Ni(σ -CO)₃ or Ni(σ -CO)₃(π -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. The count of the formal oxidation number.

Figures indicate the formal oxidation number of carbon (Eqs.

(a) and (b)) and boron (Eq. (c)).

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.

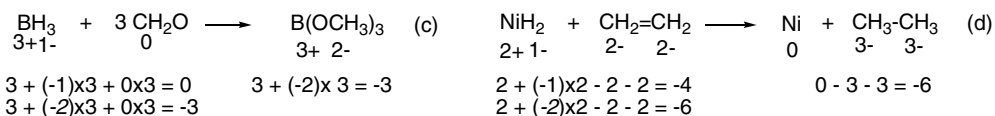
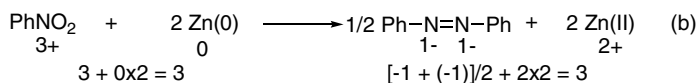
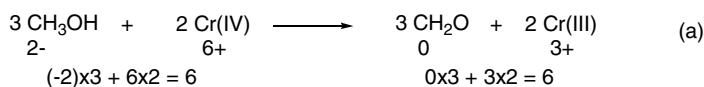
The idea of oxidation number provides a convenient way to determine the stoichiometric amounts of the reagents required in a variety of oxidation and reduction reactions. For example, as is shown in Eq. (a) of Scheme 1.2, for the oxidation of an alcohol with chromium(VI) reagents, balancing the formal 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

Tab. 1.1. Physical properties of Group 8, 9, and 10 transition metal elements.

55.845 6, 3, 2, 0, -2 1.8 26 Fe $[\text{Ar}]3d^64s^2$	58.933 3, 2, 0, -1 1.9 27 Co $[\text{Ar}]3d^74s^2$	58.693 4, 3, 2, 1, 0, -1 1.8 28 Ni $[\text{Ar}]3d^84s^2$
101.07 8, 6, 4, 3, 2, 0, -2 - 44 Ru $[\text{Kr}]4d^75s^1$	102.906 5, 4, 3, 2, 1, 0 2.3 45 Rh $[\text{Kr}]4d^85s^1$	106.42 4, 2, 1, 0 2.2 46 Pd $[\text{Kr}]4d^{10}$
190.23 8, 6, 4, 3, 2, 0, -1 - 76 Os $[\text{Xe}]5d^66s^2$	192.217 6, 4, 3, 2, 1, 0, -1 2.2 77 Ir $[\text{Xe}]5d^76s^2$	195.078 4, 2, 0 2.3 78 Pt $[\text{Xe}]5d^96s^1$
relative atomic mass oxidation state electronegativity atomic number electron configuration	Electronegativity: H (2.2), Li (1.0), B (2.0), C (2.6), N (3.0), O (3.4), F (4.0), Na (0.9), Mg (1.3), Al (1.6), Si (1.9), P (2.2), S (2.6).	

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,N'*-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



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: H^- to metals (e.g., BH_3) and 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 H^- changes to 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: $2s^2 2p^6$), the 16- or 18-electron rule is useful in organonickel chemistry (filling all the atomic orbitals of an Ni with electrons: $3d^{10} 4s^2 4p^6$). 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, $\text{Ni}(\text{CO})_4$ (VE 18) is dissociated into $\text{Ni}(\text{CO})_3$ (VE 16) and CO in solution. $\text{Ni}(\text{CO})_4$ is coordinatively saturated and no longer has any ability to interact with other molecules. By contrast, $\text{Ni}(\text{CO})_3$ is coordinatively unsaturated and can accept 2e ligands. Usually, the equilibrium lies heavily to the $\text{Ni}(\text{CO})_4$ side. The same holds for the saturated $\text{Ni}(\text{cod})_2$ (VE 18) and the unsaturated $\text{Ni}(\text{cod})$ (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 PPh_3 , CO, a π -bond donor, such as ethylene, acetylene, and a σ -bond donor such as H_2 and C–C. The symbol X refers to 2e ligands