Proceedings of ICEGEE 2026 Symposium: AI-Based Medicine and Biological Data Analysis
DOI: 10.54254/2753-8818/2026.AU32306

Principle of Organometallic Catalyst and Sustainable Building Strategy

Shengze Cui

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Tokyo, Japan
a23.66s4@g.chuo-u.ac.jp

Abstract. Catalysts are designed to enhance reaction rates for target product. Among various catalysts, organometallic catalysts play a crucial role in improving the reaction efficiency, selectivity and economic efficiency of chemical transformations to material manufacture. This article outlines the development of organometallic catalysts, fundamental principles of organometallic catalysts focusing on carbon-metal bonding and electron counting of d-block metals, key steps in the catalytic circle, particular reactions involved in the catalytic circle, and strategies to improve catalyst durability and main product selectivity by selecting the proper ligand and metal center under milder conditions. Furthermore, integrating organometallic catalysts into sustainable production processes enables the reduction of reaction waste and supports environmental benignity, for example, contributing to the goal of carbon neutrality for green chemistry purpose. However, considering the distinction between homogeneous and heterogeneous catalyst, it shows different application methods for industry.

Keywords: Organometallic Catalysts, Carbon-Metal Bonding, Catalytic Cycle, Sustainable Catalysis

1. Introduction

Although the current application of organometallic catalyst has advanced to a high level, their historical development is relatively brief. Dating back to the earlier 19th, when William Christopher Zeise acted as the assistant to H. C. Orsted at the University of Copenhagen, he reported the discovery of a new compound between 1825-1830, which was the first organometallic compound written as Pt(C2H4)Cl2 and its salt KPt(C2H4)Cl3 by bubbling ethylene(CH2=CH2 ethene)in an aqueous solution of K2[PtCl4] [1]. Each compound contains ethylene, now considered as the olefin-complexes; KPt(C2H4)Cl3 is now known as Zeise's salt. This discovery established the existence of stable metal-carbon bonds and laid the foundation for organometallic chemistry.

Later, in 1849, Edward Frankland, while investigating organozinc compounds (Table 1) [2], found that decomposition of these compounds yielded zinc and methane. Direct analysis confirmed that each contained one equivalent of methyl and one equivalent of zinc. Frankland thus named this species zinc methyl. Such result reminded Frankland to review the reaction of iodide of ethyl with

© 2026 The Authors. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).

DOI: 10.54254/2753-8818/2026.AU32306

zinc which gave the product as zinc ethyl. The discovery provides the evidence that metal could stable organic group(e.g. methyl, ethyl) [3].

Table 1. Frankland's table of known(*)and predicted alkyl species relative to the parent hydrides [2]

Hydrogen series.	Methyl series.	Ethyl series.	Butyl series.	Valyl series.	Amyl series.	Phenyl series.
Zn H	Zn C_2H_5*	Zn C_4H_5*	Zn C_6H_7	Zn C_8H_9	Zn $C_{10}H_{11}$	Zn $C_{12}H_{13}$
As H_2*	As $(C_2H_5)_2$*	As $(C_4H_5)_2$	As $(C_6H_7)_2$	As $(C_8H_9)_2$	As $(C_{10}H_{11})_2$	As $(C_{12}H_{13})_2$
Sb H_3*	Sb $(C_2H)_3$	Sb $(C_4H_5)_3$	Sb $(CH_7)_3$	Sb $(CH_9)_3$	Sb $(C_{10}H_{11})_3$	Sb $(C_{12}H_{13})_3$
P H_3*	P $(C_2H_5)_3$*	P $(C_4H_5)_3$	P $(C_6H_7)_3$	P $(C_8H_9)_3$	P $(C_{10}H_{11})_3$	P $(C_{12}H_{13})_3$

In 1900, the French chemist Victor Gringard discovered that treating an alkyl halide with magnesium in dry diethyl ether yield a turbid solution containing organomagnesium compound:

$$RX + Mg \rightarrow RMgX\,(X = Cl,\ Br,\ I) \tag{1}$$

These substances further react with aldehydes and ketones to form secondary and tertiary alcohols. This discovery established a method to generate carbon-carbon bond [4]. This article summarizes the discoveries from different researchers and illustrates the possibility of multiple catalyst' utilization and sustainable building strategies based on discovered research.

2. Organometallic catalytic principle

2.1. Chemical bond

When comparing the electronegativity() of the d block elements against carbon(2.55), the difference between them is within $0.5<\Delta\chi<1.5$. According to the van Arkel-Ketelaar triangle [5], this indicates that M-C bonds are predominantly covalent, conferring a remarkable reactivity to the carbanion(ligand). Consequently, carbanions exhibit unique nucleophilicity compared to elements in the main group, which typically act as stronger nucleophiles.

2.2. Metal-ligand bonding and ligand type

2.2.1. M-L bonding

The simplest M-L bond is considered as the interaction between the metal center's d orbit and the ligand's lone pair forming the σ bond. This type of bond between the ligand and metal center is considered the most typical. With only one atom of the ligand group connected to the metal center, it gives the denticity of 1 in organic chemistry. For instance, 1,2-diaminoethane is a bidentate ligand which binds to a metal center with its two nitrogen atoms. Denticity is denoted using the Greek letter κ 2. The number 2 is superscribed on the Greek letter. In the compound of Zeise's salt KPt(C2H4)Cl3, the π electrons of ethene are donated to the Pt(II) forming the Pt-C bonds. Since 2 carbon atoms in the ethene ligand coordinate to a metal center Pt(II), the hapticity is 2 which could denote with the Greek letter η2. This bond can be categorized by π-complex between an olefin and a metal center. When olefins bind to a metal center, the donation of electron density of a πC=C to the metal center occurred. This bond is intensified with the backdonation of electron density from the

DOI: 10.54254/2753-8818/2026.AU32306

occupied d orbital metal center. With the interaction between olefins(ethene) and metal center(Pt), the η2 olefin-metal bond formed. Ligands such as olefins may have two carbon atoms bridge to the metal center; for example, Zeise's salt KPt(C2H4)Cl3 features a two-electron, three-center interaction (C1, C2, Pt). However, when ligands act as a bridge to connect two or more metal center, for example, one ligand CO bridging two Fe(0) centers, this ligand CO is denoted with the Greek letter μ-CO. Since there're one 2 electrons on the carbon of CO, it cannot coordinate to 2 Fe center. In this situation, 2 electrons are shared among Fe-C-Fe, which is 2 electron, 3 center interaction. Since this type of bond cannot be described as a normal chemical bond by Lewis mode, the 2 electrons, 3 centers bond are introduced [6].

2.2.2. The 18-electron rule

The 18-electron rule acts as a tool for checking the stability of certain structure. Considering the d block elements, the total electron count can reach 18, as s, p, d orbital are available.

$$2\,(s)+2\times 3\,(p)+2\times 5\,(d)=18 \tag{2}$$

Thus, the octet rule is invalid, as the limited number of electrons is 8(s orbital + p orbital). With total 18 electrons shared in the compound between the ligands and metal center, the structure is considered more stable since its electron configuration is similar to rare gas. Two electron-counting methods are employed: the covalent model and the ionic model. In the Covalent mode, for example, Pt(C2H4)Cl2, contains C2H4 and Cl. C2H4 and Cl each donates 2 and 1 electron; the neutral Pt center contributes 10 electrons, resulting in a total electron count of 14, indicating an unstable configuration In the Ionic mode, the metal center Pt(II) has 2 fewer elections due to 2 Cl ions. Since, C2H4 and Cl both offer 2 electrons. The total electrons are

$$8\left(Pt^{2+}\right)+2\left(C_2H_4\right)+2\times 2\left(Cl^{-}\right)=14 \tag{3}$$

14e which is the same as Covalent mode. Although the 18e rule is considered as a more detailed model for evaluating structural stability, it is not a universal law. This is exemplified by ML_6 complexes (six ligands coordinated to a metal center). According to the MO Theory(Molecular Orbital), electron counts can flexibly range from 12 to 18, as electrons populate nonbonding orbitals [7].

3. Key mechanistic steps in catalytic cycles

According to IUPAC, the catalyst is defined as a substance that increases the reaction velocity without changing the standard Gibbs energy in the reaction system. A Homogeneous catalyst operates in a single phase. By contrast, a heterogeneous catalyst operates across multiple phases. Considering the d block elements' ability to modify the organic ligand's reactivity, industry use homogeneous catalysts incorporating organometallic species in catalytic circle. Below is a discussion of nickel(II)-catalyzed olefin hydrocyanation for nitrile production. Hydrocyanation is a homogeneous catalyzed reaction in which olefins are converted into nitriles via a Ni-circle. The addition of hydrogen cyanide to unactivated carbon-carbon double bond using di-cobalt octa

DOI: 10.54254/2753-8818/2026.AU32306

carbonyl was described by P. Arthur Jr. in 1954. This reaction is effective at temperature 70-160C, with optimal conversion achieved at approximately 130C. Since dicobalt octacarbonyl is not recoverable from the hydrocyanation reaction systems, according to P. Arthur Jr. [8], nickel complexes coordinated by phosphorous ligands are generally utilized as catalyst nowadays [9].

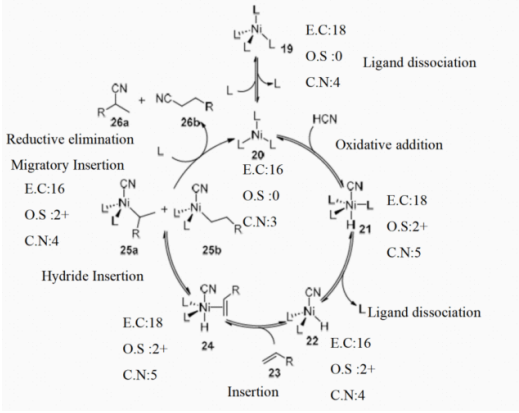


Figure 1. Nickel-based catalytic circle in hydrocyanation [9]. (E.C: electron counts; O.S: oxidation state; C.N: coordination number)

In industry, linear products(26b) in the Figure 1 exhibit higher market demand than their branched counterparts(26a), the linear: branched ratio is a crucial reaction indicator. The utility of Nickel catalysts with large bite angle of bidentate phosphite ligands, for example, DPEPhos and Lewis acid such as AlCl3 improved the linear products' selectivity from(< 1 : 99) to (23 : 77).

3.1. Ligand dissociation

In the initial phase, reversible ligand dissociation yields the catalytically active species 20, which is electronically and coordinatively unsaturated compared to the species 19.

3.2. Oxidative addition

As the unsaturated species 20 formed, with the electron count of 16 and a coordination number of 3, it allows species 20 to accept a ligand which is hydrogen cyanide HCN molecule. The coordination causes the molecule to cleavage into H and CN ligands hence increase the coordination number from 3 to 5 and the oxidation stage' s increasement from 0 to 2+ forming species 21 as showed in the Figure 2.

3.3. Ligand dissociation*

Similar to the preceding ligand dissociation step, this process serves the same purpose: enhancing the catalytic activity of species 21 to form species 22, enabling interaction with olefins (Figure 2). This dissociation reduces the electron count and coordination number by 1.

3.4. Insertion of olefin

The dissociation of the ligand creates a vacant site in species 22 which allows the coordination of olefin 23 giving the electronically and coordinatively saturated species 24.

DOI: 10.54254/2753-8818/2026.AU32306

3.5. Insertion of hydride

In the coordination sphere of Ni(II), hydride insertion converts the olefin molecule to olefin ligand which indicated by the conversion 24→25a / 25b in Figure 2. This reaction can be classified by 1,2-insertion of hydride or 2,1-insertion of hydride since metal center bond with carbon atom at position 1 while hydride bond with carbon atom at position 2. By contrast, 2-1 insertion involves the metal center binding to C2 and the hydride to C1.

3.6. β-elimination

Both 1,2-insetion and 2,1-insertion of hydride are reversable reactions constituting the β-elimination which is a key process in isomerization and oligomerization. In β-elimination, an interaction between hydride and metal center forms an agostic hydrogen. β-elimination represents a major route of organometallics decomposition, it releases olefin and complicates the isolation of organometallic compounds.

3.7. Migratory insertion

The bond between metal center and alkyl creates the polarization which makes the C-end of alkyl ligand nucleophilic(more electron density). This would cause the migratory insertion of CN ligand adjacent to the alkyl ligand. Consistent with the selectivity of hydride insertion, 1,2-insertion of hydride gives a linear product and 2,1-insertion gives the branched. Migratory insertion of CN generates a vacant site on the metal center Ni(II) with no change in oxidation state but a reduction in electron count by 2.

3.8. Reductive elimination

In the final step of the catalytic circle, coordination of an additional ligand increases the coordination number from 4 to 5. The irreversible reaction releases primary nitrile products (26a 26b) and recreate the catalytic reactive species 20 hence complete the catalytic circle. The coordination number would decrease from 5 to 3 accompanied with decrease of oxidation state from +2 to 0. Since reductive elimination decreases the oxidation state and coordination number of metal center Ni, it is essential to utilize the ligand with large steric hinderance that promote the reductive elimination and accelerate the entire reaction circle. Additionally, π accepter ligands(phosphite ligand e.g. DPEPhos) stabilize low oxidation states [6,9].

4. Representative catalytic circle and catalyst design strategies

4.1. Hydroformylation of aldehyde (oxo process)

Hydroformylation involves the addition of syngas, a mixture of carbon monoxide and hydrogen, to olefins with the utility of cobalt-based catalyst discovered accidently by Otto Roelen in 1938. High acidity is hypothesized to promote both alkene addition and hydrogenolysis of transient metal-acyl complexes in the late stages of the catalytic cycle. Thus HCo(CO)4 is considered a more suitable catalyst. However, this compound exhibits low stability at process temperature of 110-180C, requiring extremely high pressure of syngas (20-35 MPa). These high pressures reduce reaction rate and induce reduction of olefins. To address this issue, the replacement of one CO with phosphine ligand was proposed. Phosphine ligands with large steric hinderance on the metal center would favor

DOI: 10.54254/2753-8818/2026.AU32306

1,2-insetion of hydride and hence obtain more linear product which increase the selectivity from 80% to 88%. Additionally, the whole process pressure decreased about 5-10 MPa compared to the use of HCo(CO)4. Another solution for the problem is using more reactive metal center, such as rhodium with phosphine ligand. However, rhodium, a rare metal, is 1000 times more expensive than cobalt. This necessitates the development of alternative strategies for sustainable industrial production [6,10].

4.2. Wacker reaction

Wacker reaction was discovery in the late 1950s by Smith et al. and later applied at industrial scale by the Wacker Chemie company.

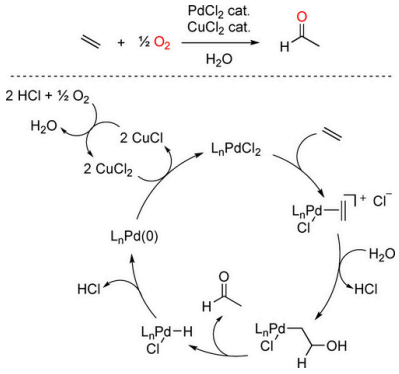


Figure 2. Wacker reaction [11]

From Figure 2, the reaction circle shown above involves the oxidation of olefins to obtain both ketones and aldehyde and typically use the expensive palladium(II)-based catalyst with copper(II)-based co-catalyst under extreme conditions (e.g. high pressure of air and high temperatures). Since it has industrial purpose, the process that avoid the use of Pd catalysts and the utility of milder condition for sustainable development are necessary in green chemistry.

4.3. Homogeneous catalyst and heterogeneous catalyst

Homogeneous catalyst operates in the same phase as reagent and are typically organometallic complexes. In hydrocyanation, ligands control the selectivity of target product and influence catalyst species' stability. Ligand which are strong -donor such as CN increase the electron density of metal center could promote the irreversible formation of catalytically inactive species including LNi(CN)2. A potential solution is the use of bidentate phosphite ligands (e.g., DPEPhos) instead of monodentate ligands (e.g., PPh_3).

Heterogeneous catalyst exists in different phase (solid, gas, liquid). The main goal for this is to control the density of active sites. For example, zeolite presents up to 1000 m2/g, facilitating efficient reaction occurrence [12].

5. Conclusion

This article explained the fundamental principles of catalytic circle and hence their significance in sustainable manufacturing process. Review the history of organometallic compound, the first appearance of Zeise's salt, Frankland's organozinc compound and later Grignard reagent, those developments have showed the rapid pace that science technologies are developing among 200

DOI: 10.54254/2753-8818/2026.AU32306

years. By summarizing the discoveries of organometallic circles' utilizations, the existing problems for instance, the formation of inactive species in the catalytic circle, severe react conditions for example, extreme high pressure and temperature, and products' selectivity need solutions for both industrial and environmental purposes. The application of organometallic catalysts relies on fundamental reaction steps, including insertion, oxidative addition, and reductive elimination. A thorough understanding of these basic processes is essential for catalyst design and optimization. The 18e rule are used for determining the stability of d block compound's structure. The Nickel-based hydrocyanation, cobalt/rhodium-based hydroformylation(oxo reaction), Wacker reaction proved that how the metal and ligand selection could have the effect on total cost, reaction activity, product selectivity, catalyst durability. The comparison between homogeneous and heterogeneous catalyst illustrates their distinct industrial applications. Homogenous catalyst systems offer high selectivity of product while heterogeneous catalyst system such as zeolite provides recyclability. Combining the advantages of both systems could enable more efficient, low-waste, and environmentally benign processes in green chemistry. For example, photoredox heterobimetallic dual catalysis which combines visible-light photoredox catalysis with d block metal catalysis. This system contains two different metal centers(Ir3+ and Ni2+) that operate cooperatively in the catalytic cycles could be possible considering green chemistry [13].

References

[1] Prof. Dr. Curt Wentrup (2019), Zeise, Liebig, Jensen, Hückel, Dewar, and the Olefin π-Complex Bonds. Angewandte Chemie International Edition. Volume 59. Issue 22. 8332-8342

[2] E. Frankland (1852), On a New Serious of Organic Bodies Containing Metals, Philos. Trans. R. Soc. London, 142, 417-444

[3] Seth C. Rasmussen (2024), EDWARD FRANKLAND AND THE BIRTH OF ORGANOMETALLICS (1). Bulletin for the History of Chemistry. Volume 49. Issue 2. 111-121

[4] Dietmar Seyferth (2009), The Grignard Reagents, Organometallics, 28, 1598-1605

[5] Mark, W., Tina, O., Jonathan, R., Fraser, A. (2016), INORGANIC CHEMISTRY, Tokyo Kagaku Dozin, Japan, 69

[6] Robert H. Crabtree (2014), The Organometallic Chemistry of the Transition Metals, 6th Edition, Wiley, Chapter 1

[7] Seth C. Rasmussen (2015), The 18-electron rule and electron counting in transition metal compound : theory and application, ChemTexts, Volume 1, article number 10

[8] P. Arthur Jr., D. C. England, B. C. Pratt, G. M. Whitman (1954), Addition of Hydrogen Cyanide to Unsaturated Compound, Volume 76

[9] M. Sc. Till Köhler (2024), Optimizing Nickel-based Hydrocyanation Catalysts

[10] Zhang, B. Fuentes, D.P. Börner, A (2021) Hydroformylation. ChemTexts, Volume 8

[11] Rajeshwaran, P. Trouvé, J. Youssef, K. Dr. Rafael Gramage-Doria (2022) Sustainable Wacker-Type Oxidations. Angewandte Chemie, International Edition. Volume 61. Issue 50. e202211016

[12] Prof. Dr. Jens Hagen (2005), Industrial Catalyst : A Practical Approach

[13] López-Magano, A. Ortín-Rubio, B. Imaz, I. Maspoch, D. Alemán, J. Mas-Ballesté, R(2021) Photoredox Heterobimetallic Dual Catalysis Using Engineered Covalent Organic Frameworks. Acs Catalysis. Volume 11. Issue 19