Applications of Cyclometalation Five-Membered Ring Products and Intermediates as Catalytic Agents

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Abstract

The five-membered ring products and intermediates of cyclometalation reactions are very easily synthesized via donation from a hetero atom to a metal atom, which leads to the very high functionality of the product. This functionality is caused by the donation of the hetero atom and various types of metal atoms, halogen atom and other ligands such as alkanes, alkenes, alkynes, Cp, Cp*, aryl groups and heterocyclic compounds. These products have three types of catalytic applications: cyclometalation five-membered ring products as catalysts, cyclometalation five-membered ring intermediates as catalyst agents and cyclometalation five-membered ring intermediates with unconventional substrates and as catalyst actions. Because of the high functionality of these products, the applications of them have been increasing not only as the metathesis in the first and second generations of Hoveyda-Grubbs catalysts but also as in chiral reactions, cross-coupling reactions and polymerization reactions. The above cyclometalation products have been utilized for the production in many industrial fields such as pharmaceuticals, OLEDs, carbon dioxide utilizations, dye-sensitizer solar cells and sensors. We expect that these products would be used for the development of further new industrial products.

Keywords

Cyclometalation, Catalyst, Five-Membered Ring, Chiral Reaction, Metathesis Reaction, Cross-Coupling Reaction
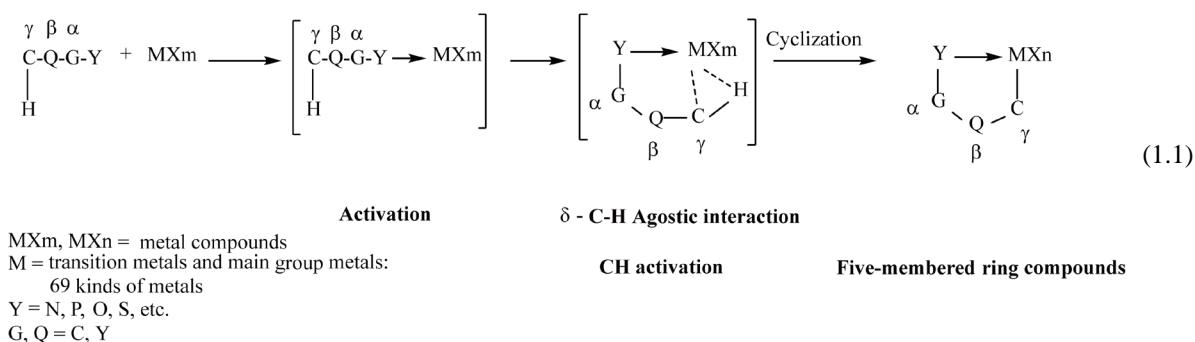
1. Introduction

When cyclometalation reactions are performed using metal compounds with substrates that contain heteroatoms

with a strong donor ability, such as amines, phosphines, alcohols and sulfur compounds, the reactions show high reactivity of the substrate to the metal compounds because the compounds with these heteroatoms are usually used as catalysts. Therefore, various articles, many reviews [1]-[49] and books [50]-[55] on this subject have been published since the 1960s, and cyclometalation reactions are considered representative reactions in organic synthesis.

Commonly, cyclometalation reactions with conventional substrates that have a γ carbon atom as the heteroatom proceed very easily via agnostic interactions with CH activation, as shown in Equation (1.1) [45]. Then, the metal atom is coordinated by the heteroatom and becomes the active center in the five-membered ring products. Many compounds easily afford their derivatives from reactions such as alkylation, alkenylation, alkynylation, carbonylation, isocyanation, halogenation, chiral reactions with amino acids, enantioselective rearrangement, asymmetric Diels-Alder reactions and dehydrogenation [41] [43] [55].

Cyclometalation Reactions

(1.1)

Activation

δ - **C-H Agostic interaction**

MXm, MXn = metal compounds
M = transition metals and main group metals:
    69 kinds of metals
Y = N, P, O, S, etc.
G, Q = C, Y

CH activation   **Five-membered ring compounds**

Ligands in cyclometalation reactions include atoms such as N, P, As, O and S. and groups such as alkenyl, allyl, alkynyl, aryl, cyclopentadienyl (Cp) and pentacyclopentadienyl (CP*). In the chelate compounds, five-membered ring compounds are well known to be more stable than the comparable four- and six-membered ring compounds [56]. The ring products are coordinated with one of the above-mentioned ligand atoms in cyclometalation reactions are also generally known to be stable in organic ring compounds.
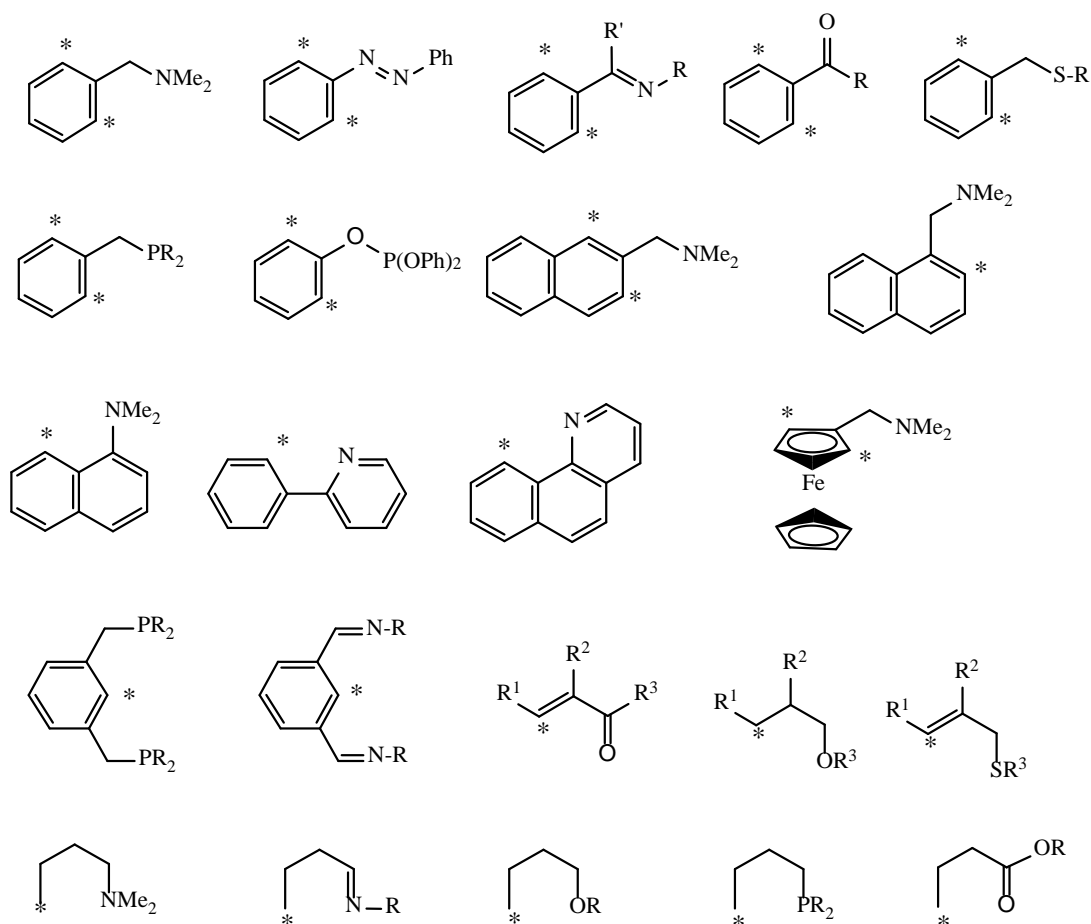
The products of the cyclometalation reactions are mainly four- to six-membered ring products. In particular, five-membered ring products are mostly synthesized in the cyclometalation reactions because five-membered ring compounds are the most stable type of rings [40] [41] [43] [55], and these products are very easily synthesized.

A monograph [55] was published to explain why organometallic intramolecular-coordination five-membered ring products are extremely easily synthesized through cyclometalation reactions, and three reasons were listed. First, activation of the metal is caused by coordination of a lone electron pair of a heteroatom to the metal atom. Second, the chelate effect is caused by the formation of a five-membered ring. Third, the metal is activated by ligands such as heteroatom-containing groups (e.g., bipyridnes, phosphines and carboxylates), unsaturated groups (e.g., aryl, allyl, Cp and Cp*), carbonyl groups and halogen atoms (F, Cl, Br and Cl), which bond to a central metal atom. Many articles have been published with title words such as C-H activation, C-X activation, C-H functionalization and chelation-assisted reactions which are related to the aforementioned metal activation and chelate effect in cyclometalation reactions [11] [13] [25] [26] [28] [30] [45] [55].

Among the other types of cyclometalation reaction, reactions with ligand groups [57]-[60] are compared with those with ligand atoms. However, there are few publications on this subject, and this article does not describe them.

In these cyclometalation reactions, the substrates and metal compounds are as follows:

1) Substrates with heteroatoms such as N [7] [15] [21] [32] [36], P [16]-[18] [20] [35], As [20] [37], O [12] [31] [34] [38] [44] and S [33].

2) Conventional substrates with a γ carbon atom as the heteroatom to form five-membered ring products, as shown in **Figure 1**.

3) Unconventional base substrates such as 2-amino-3-picolines and anilines and auxiliary substrates such as alkynes and aldehydes [47].

Figure 1. Representative conventional substrates to synthesize five-membered ring compounds in cyclometalation reactions [55]. Asterisks (*) indicate the reaction sites of the metal compounds. There are generally at the γ-position to a coordinating atom such as N, P, O or S.

4) Ancillary ligands such as 2,2'-bipyridines, terpyridines and 1,10-phenanthroline in some cyclometalation reactions, which chelate with metal compounds.

5) Transition metal and main group metals in general. In total, of 69 types of metal atoms are used [44] [55].

6) Various types of metal compounds.

Accordingly, various five-membered products of cyclometalation reactions are synthesized with all types of combinations of substrates with heteroatoms, conventional substrates, unconventional substrates, ancillary ligands, metal atoms and metal compounds.

Therefore, many articles on the five-membered ring products of cyclometalation reactions have been published. These metal compounds, which are coordinated by a heteroatom and many ligand groups are used as catalysts [41] [43] [55] and in the fields of OLED [48], pharmaceuticals [46], CO_2 utilization [49], dye-sensitizer solar cells [55], sensors, etc. [55].

This article describes three types of catalytic actions of the five-membered ring products of cyclometalation reactions [41] [43] [47] [55].

1) Use of stable five-membered ring products of cyclometalation reactions as catalysts [41] [43] [55].

2) Use of the catalytic action of the reactive five-membered ring intermediates of cyclometalation reactions. Conventional substrates are used [41] [43] [55].

3) Use of the catalytic action of the reactive five-membered ring intermediates of cyclometalation reactions. However, unconventional substrates of the base substrates and auxiliary substrates are used [47].

Furthermore, recent articles on the first and second types of catalytic actions of the five-membered ring products of cyclometalation reactions are also described.

2. Three Types of Applications of Cyclometalation Five-Membered Ring Products and Intermediates as Catalytic Agents

2.1. Introduction

Many five-membered ring products of cyclometalation reactions have been synthesized because the reactions proceed very easily with many types of metal compounds, substrates and ancillary ligands. The five-membered ring products have many functions: they can be used as catalytic agents and in the fields of OLED, pharmaceuticals, CO_2 utilization compounds, dye-sensitized solar cells and sensors, as previously described.

This article describes three types of catalytic agents from the five-membered ring products of cyclometalation reactions.

1) Use of the five-membered ring products of cyclometalation reactions as catalysts because of their catalytic activity and high stability.

2) Use of the catalytic agents of the reactive five-membered ring intermediates of cyclometalation reactions as catalytic agents. In general, the final reaction products are the derivatives of the conventional substrates, which have a γ-carbon atom as the heteroatom in the substrates.

3) Use of the catalytic action of the reactive five-membered ring intermediates in cyclometalation reactions. These substrates are unconventional base substrates and auxiliary substrates [47].

2.2. Applications of Cyclometalation Five-Membered Ring Products as Catalysts

Several catalytic reactions that involve the five-membered ring products of cyclometalation reactions as catalysts have been reported in reviews [41] [43] and a monograph [55].

Recently three Nobel prizes in synthetic organic reactions were awarded for chiral reactions in 2001, metathesis reactions in 2005 and cross-coupling reactions in 2010. This chapter briefly describes these chiral, metathesis, cross-coupling reactions and other reactions such as polymerizations, reductions and dehydrogenations.

In chiral reactions with the five-membered ring products of cyclometalation reactions, the metal atoms in the metal compounds act as the catalysts, and the Pd atom is mainly used as the catalyst. Many reviews report that palladium compounds serve as chiral catalysts [61]-[67]. The other metal atoms are Pt, Rh and Ru. Other articles have been published on other catalytic metal compounds such as Fe, Au, Ir, Sc, Y and Lu [68]-[71].

For the heteroatoms, a stronger donor N atom is mainly used, and other heteroatoms include P, O and S.

Some examples of palladium catalysts for chiral reactions are shown in **Figure 2** [61] [62] [72] [73].

In 1980, Noyori *et al*. [72] reported the synthesis of BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphtyl), which shows high enantioselectivity and catalytic activity as a super-chiral ligand of a chiral N,N-dimethylamine palladium compound **2.2**, as shown in **Scheme 1**.
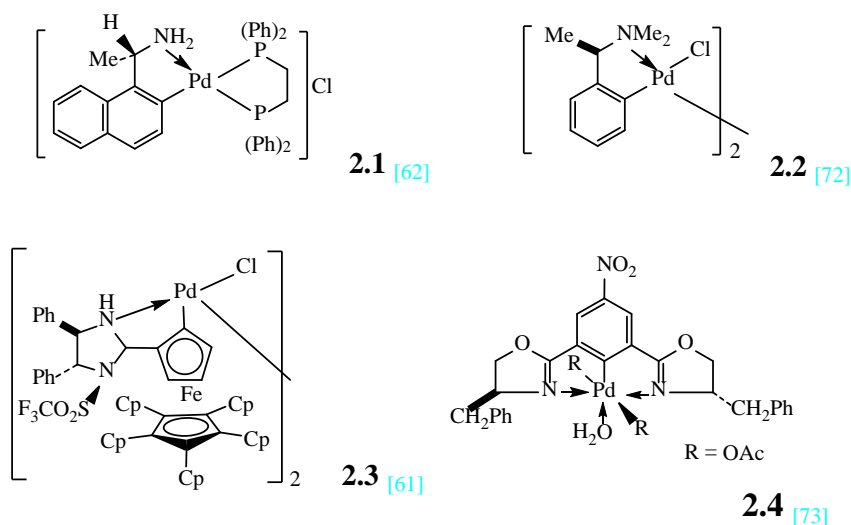

Figure 2. Examples of five-membered ring palladium compounds **2.1 - 2.4** as catalysts for chiral reactions.

(BINAP : Binaphthyldiphosphine Ligand)
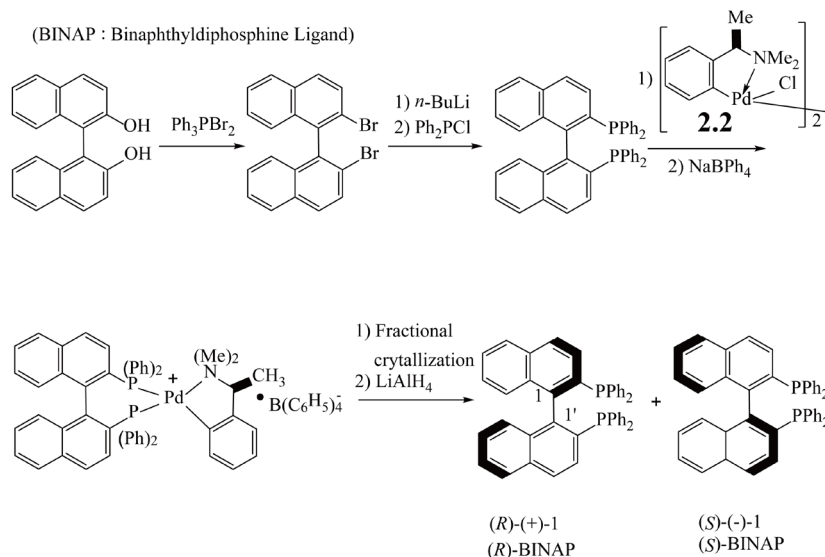
Scheme 1. Preparation of BINAP [72].

For chiral reactions, two examples of five-membered ring products of cyclometalation reactions for rearrangements and Michael addition reactions are shown in Equations (2.2.1) and (2.2.2).

Moreover, with a cyclopalladate (η^4-tetraphenylcyclobutadiene)cobalt oxazoline propyl chloro-bridged compound **2.5** as a catalyst, the rearrangements of *N*-(4-methoxyphenyl)trifluoroacetimidate **2.6** [74], to the corresponding amides **2.7** proceed with high yields and high enantiomeric purities without using a silver salt as an activator, as shown in Equation (2.2.1).

$$(2.2.1)$$

Yield 99%
96% ee (*R*)

Cat =

2.5
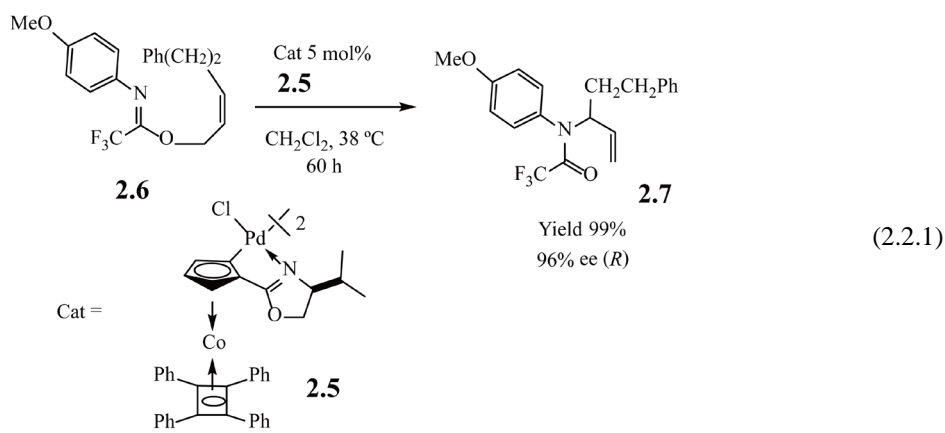
Pincer metal compounds such as those with tin [75], rhodium [76], palladium [77] and platinum [78], are used as catalysts for Michael addition reactions. For example, the addition of an α-cyanopropionate to acrolein under mild, neutral conditions in the presence of a bis(oxazolinyl)phenylstannane-derived rhodium complex **2.8** enantioselectively proceeds with high yield and high TON, as shown in Equation (2.2.2) [76].

$$(2.2.2)$$

Yield 91%
81% ee
TNO : 10,920

Cat. =

2.8
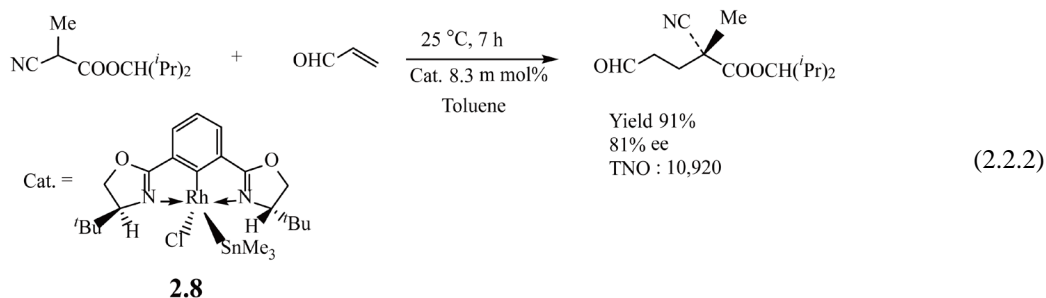
Metathesis reactions were reported in some reviews [79]-[84] and a handbook [85]. There are notably fewer types of metal atoms in metathesis reactions than in chiral reactions. Mainly Mo, W, Ta and Ru are used for this types of reactions.

The ruthenium-carbene complex **2.9** is an excellent commercially available example of Grubbs' catalyst. However, cyclometalation five-membered ring products 1_{st}- and 2_{nd}-generation Hoveyda-Grubbs catalysts **2.10 - 2.12** which are activated by coordination with an ether oxygen atom, are much more active with respect to electron-deficient olefins and stable with respect to air as shown in **Figure 3** [55] [81] [82] [86].
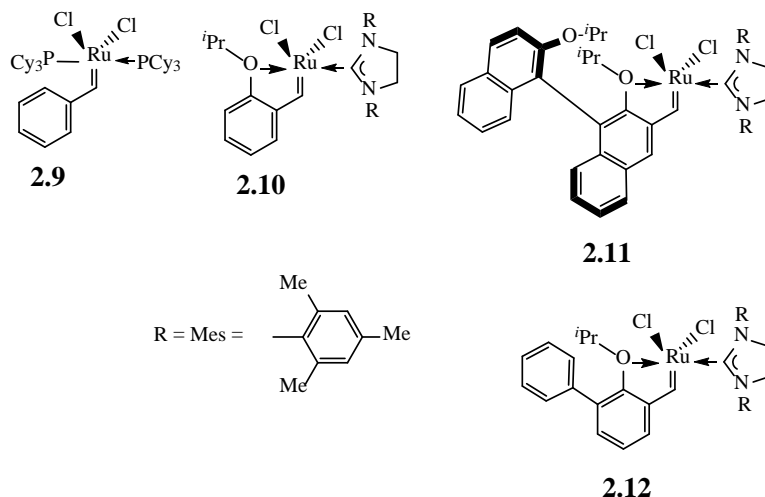
Figure 3. Representative metathesis reaction catalysts.

Many ruthenium carbene five-membered ring compounds have recently been reported to show good activities for metathesis. Many types of reactions proceed with the help of these catalysts, such as ring-closing metathesis, ring-opening metathesis, cross metathesis, enyne metathesis and diyne metathesis [55] [81].

For example, the ring-closing metathesis of an acyclic diene easily proceeds at room temperature with a high yield in the presence of the 1,3-dimesityl-4,5-dihydroimidazole-2-ylidene ruthenium catalyst **2.10**, as shown in Equation (2.2.3) [86] [87].

$$\text{(2.2.3)}$$

Ts = tosyl, *p*-toluenesulfonyl
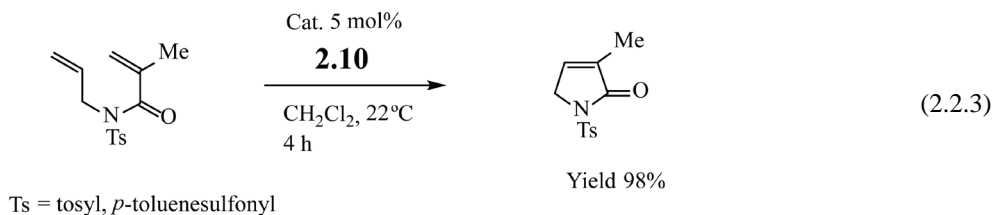
Many cross-coupling reactions have been reported since 1967, as shown in **Figure 4** [88].

These reactions include Heck reactions, Mizoroki-Heck reactions, Negishi reactions and Suzuki-Miyaura reactions.
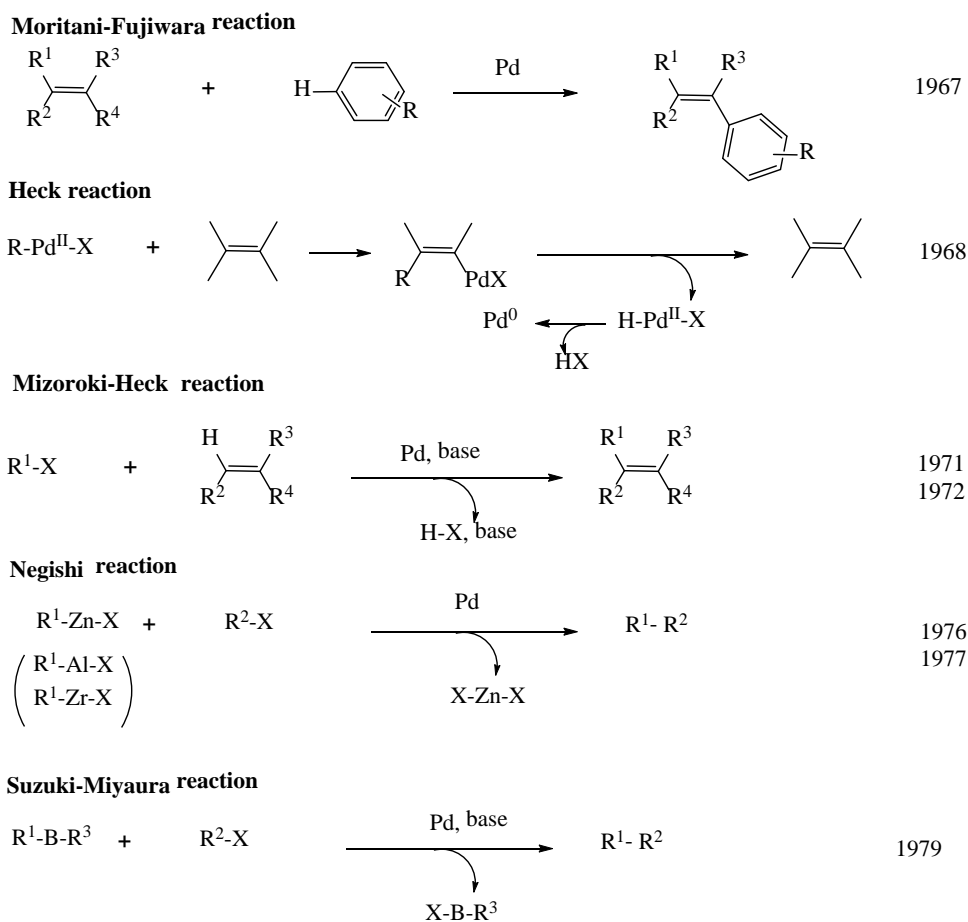
Among these reactions, three were recognized with a Nobel Prize in Chemistry in 2010. The Nobel Prize was awarded based on practical use in the industrial sector. Heck reactions were used to synthesize of more than 100 types of natural products and physiologically active substances, Negishi reactions were used to synthesize Pumi-liotoxins A (PTXs) and Hennoxazole A. Suzuki-Miyaura reactions were used to synthesize Dynemicin A and Dragmacidine F [88].

Various articles and many reports [89]-[94] have been published on cross-coupling reactions using the five-membered ring compounds of cyclometalation reactions as catalysts:

Palladium compounds are mainly used as catalysts, but Ni, Ir, Ru and Pt compounds are also used.

In particular, many Heck and Suzuki-Miyaura reactions have been reported for the five-membered ring products of cyclometalation reactions.

Some examples are shown bellow:

Moritani-Fujiwara reaction

1967

Heck reaction

1968

Mizoroki-Heck reaction

1971
1972

Negishi reaction

1976
1977

Suzuki-Miyaura reaction

R^1-B-R^3 + R^2-X $\xrightarrow{\text{Pd, base}}$ R^1- R^2

X-B-R^3

1979

Figure 4. Cross-coupling reactions [88].

In 2005, Heck reactions with phospha-palldacycles [95] or *N*-heterocyclic carbene phospha-palladacycles [96] were reported to show highly catalytic activities, as evidenced by their TONs of up to 300,000 and 533,000, respectively.

Among the Suzuki reactions, palladacycle catalysts exhibit very high TONs. Most notably, phosphite palladacycles **2.13** show the highest TON of 10^6 [97]-[100].

2.13
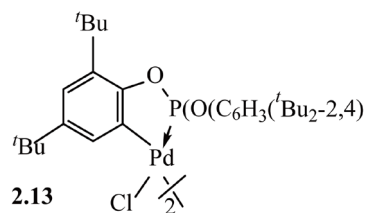
For other reactions, this section shows two examples of polymerizations and reductions.

Among the polymerization catalysts, Ziegler catalysts (Et_3Al and $TiCl_4$), Natta catalysts (Et_3Al and $TiCl_3$), and metallocene catalysts (Cp_2M(M = Ti, Zr, Hf, Fe)) and -(O-Al(R))$_n$- (R = Me, Et)) are used as vinyl polymerization catalysts. Ca, Hg, Zn and Cd compounds and Ti, Ge, Sn, Pb and Sb compounds are used for ester exchange and their polyester polymerization catalysts, respectively.

However, organometallic intramolecular-coordination five-membered ring compounds have also recently been used as polymerization catalysts.
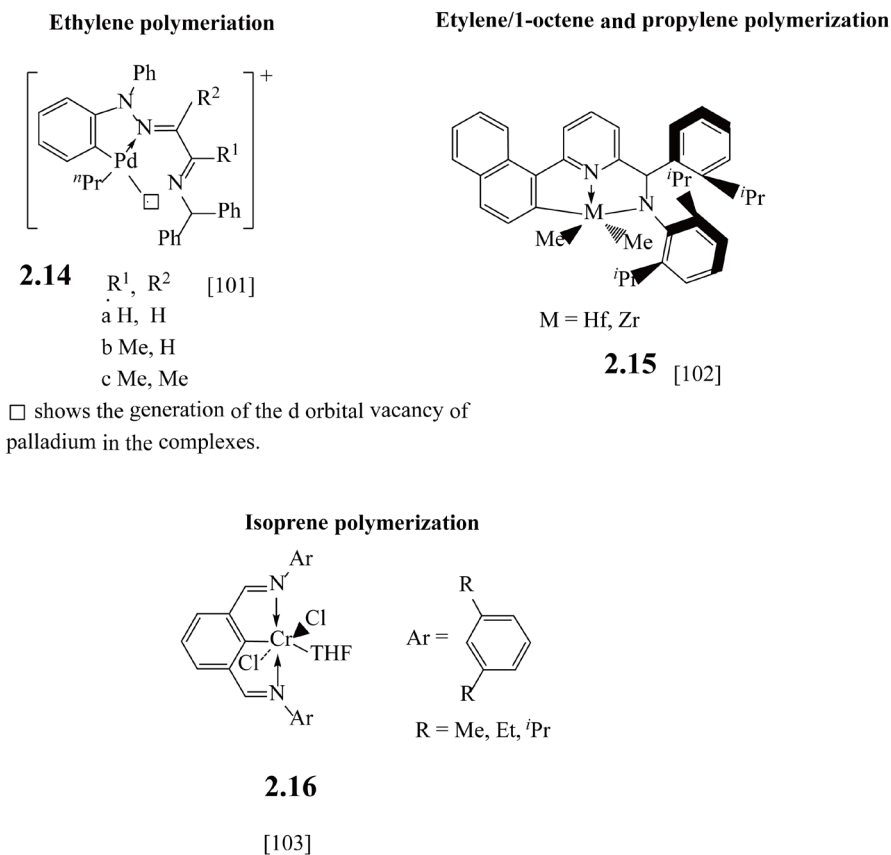
The polymerization reactions of compounds such as ethylene polymerization, ethylene/1-octene and propylene polymerization and isoprene polymerization reactions and their catalysts of cyclomelated products are

shown in **Figure 5** [101]-[103].

For example emine-type cyclopalladated products **2.14** have good activity for ethylene polymerization [101]. The molecular weight and molecular weight distribution of the obtained polymers correspond to single-site catalysts, and the polymers have narrow molecular weight distribution, as shown in **Table 1**.

Pincer organometallic compounds are reported mainly with regard to two types of compounds, NCN and PCP transition-metal complexes [63] [91]. However, ruthenium pincer CNN compounds have also been applied to the hydrogen-transfer reductions of ketones.

For example, 6-(4'-methylphenyl)-2-pyridylmethylamine ruthenium pincer compound **2.17** is a highly efficient catalysts in transfer hydrogenation, which involves 2-propanol, quantitatively reduce ketone with notably low loading in a short time, as shown in Equation (2.2.4) [104].

Ethylene polymeriation

Etylene/1-octene and propylene polymerization

2.14   R^1, R^2 [101]
a H, H
b Me, H
c Me, Me

□ shows the generation of the d orbital vacancy of palladium in the complexes.

M = Hf, Zr

2.15 [102]

Isoprene polymerization

Ar =

R = Me, Et, ^{i}Pr

2.16

[103]

Figure 5. Polymerization reactions and their catalysts with cyclometalated products.

82 °C
Cat. 0.005 mol%

NaOH (2 mol%),
2-propanal

Coversion 99%

TOF: 2.5 × 10^6 h^{-1}

(2.2.4)

Cat. =

2.17
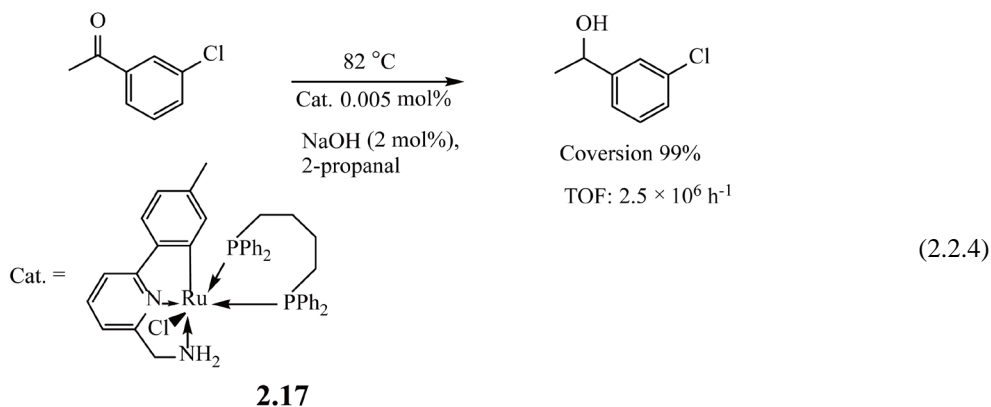
Table 1. Molecular weight, molecular weight distribution and melting temperature (Tm) of polyethylene obtained using the imine cyclometalated palladium catalysts **2.14b** and **2.14c** [101].

| Catalyst	Reaction temp. (˚C)	Tm (˚C)	Mw	Mw/Mn
2.14b	80	136	74,000	1.7
2.14c	40	137	245,000	2.1

2.3. Applications of Cyclometalation Five-Membered Ring Intermediates as Catalytic Agents

The second type of catalytic agent has weak coordination to the metal compounds and the catalysts are highly reactive intermediates of the five-membered ring cyclometalation reactions [105]. In particular, Murai *et al.* have published reports on such catalytic actions with ruthenium compounds since 1993 [106]-[116]. In this type of catalytic agents, the ligands mainly use the relatively weak donation of the oxygen atoms of ketone carbonyl, ester carbonyl, aldehyde carbonyl and amide carbonyl groups and the nitrogen atoms of oxazole, amide, imine and azo groups, whereas Ru, Rh, Co, Zr and Pd compounds are mainly used as the metal compounds.

For example, the alkenylation reaction with a phenyl ester as a substrate proceeds via cyclometalation with intermediate **2.18** to produce an alkenyl derivative in high yield, as shown in Equation (2.3.1) [117].
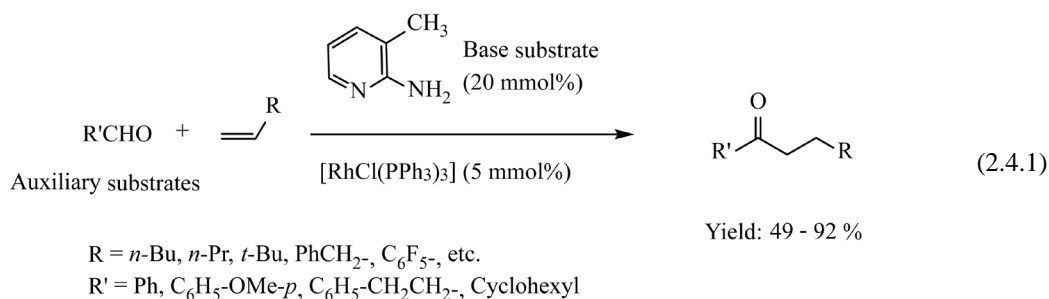

(2.3.1)
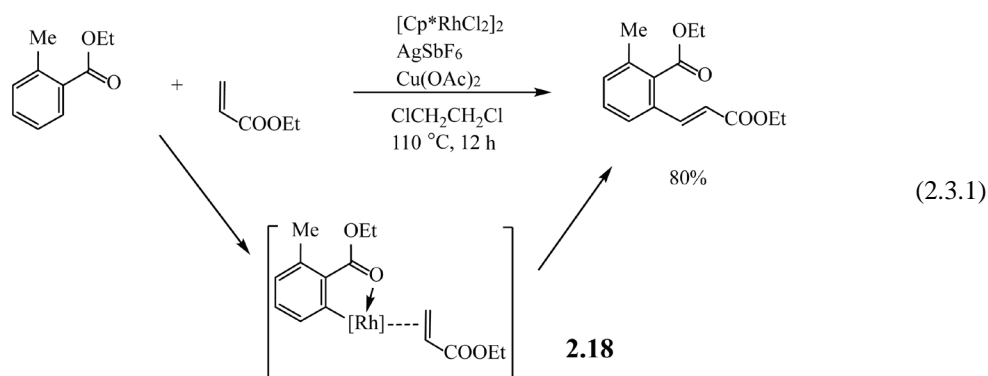
Cyclopalladated *t*-butylimine compounds react with styrene and are consequently treated with trifluoroacetic acid to produce *o*-formylstilbenes in high yield. Their *N*-methylimine derivatives are converted to other heterocyclic compounds (3-aryl-*N*-methyl-isoquinolones **2.19**) by oxidation with mercuric acetate, as shown in Equation (2.3.2) [118].

(2.3.2)

R = H, 5-Cl, 3-MeO, 4-MeO, 5-MeO, 4,5-(MeO)₂

2.19
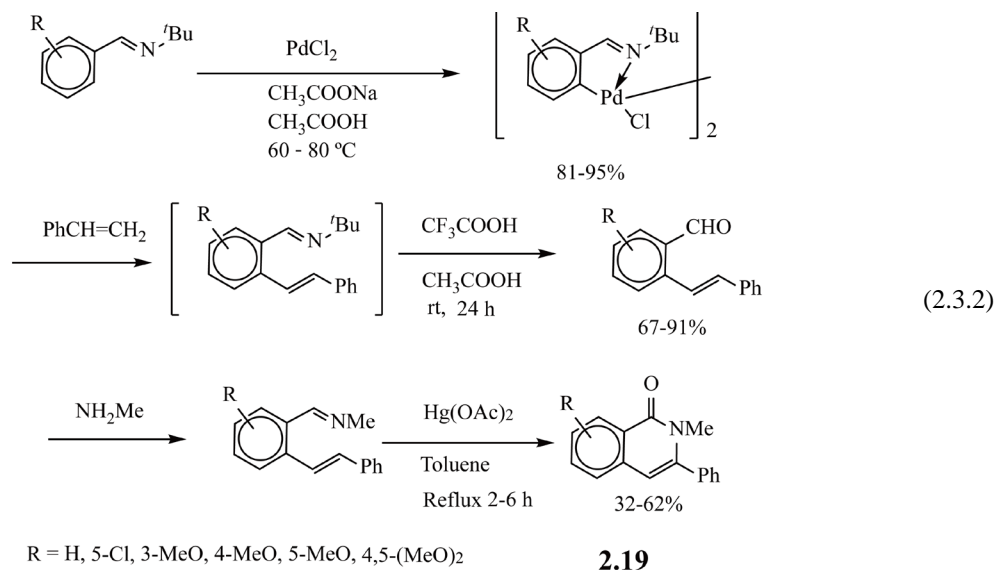
Other reactions such as alkylation, alkynylation, arylation, carbonylation, hydroacylation, ring-expansion reaction, carbocyclization, cross-coupling reaction, reductive elimination, carbonylation and hydroacyclation have also been reported [41] [43] [55].

2.4. Applications of Cyclometalation Five-Membered Ring Intermediates with Unconventional Substrates as Catalytic Agents

The third type includes reactions that using base substrates such as 2-amino-3-picoline and anilines which do not have a γ-carbon atom as the hetero atom, and auxiliary substrates such as aldehydes and alkynes. This reaction produces conventional substrates, and the reactions with metal compounds produced the reactive five-membered ring intermediates from cyclometalation reactions. Finally, the derivatives of the reactive five-membered ring intermediates are formed as shown in Equation (2.4.1) and **Scheme 2** [119].

$$R'CHO \ + \ =\!\!/^R \xrightarrow[\text{[RhCl(PPh}_3)_3]\text{ (5 mmol%)}]{\text{Base substrate (20 mmol%)}} R' \overset{O}{\underset{}{\frown}} R \qquad (2.4.1)$$

Yield: 49 - 92 %

R = *n*-Bu, *n*-Pr, *t*-Bu, PhCH$_2$-, C$_6$F$_5$-, etc.
R' = Ph, C$_6$H$_5$-OMe-*p*, C$_6$H$_5$-CH$_2$CH$_2$-, Cyclohexyl

In metal compounds, such as Mn, Pd, Rh and Ir compounds, the cyclization reactions of unsaturated compounds, such as alkynes, alkenes and phenyl compounds proceed via cyclocarbonylation based on the following four characteristics [47].

1) Carbon-carbon π-electrons in these unsaturated compounds easily form π-coordination bonds to the metal atom.

2) In the metal carbonyl compounds, hydrogen or an organic group easily migrates to a carbonyl.

3) The coupling reactions between a carbonyl carbon in the metal carbonyl compounds and a carbon atom in
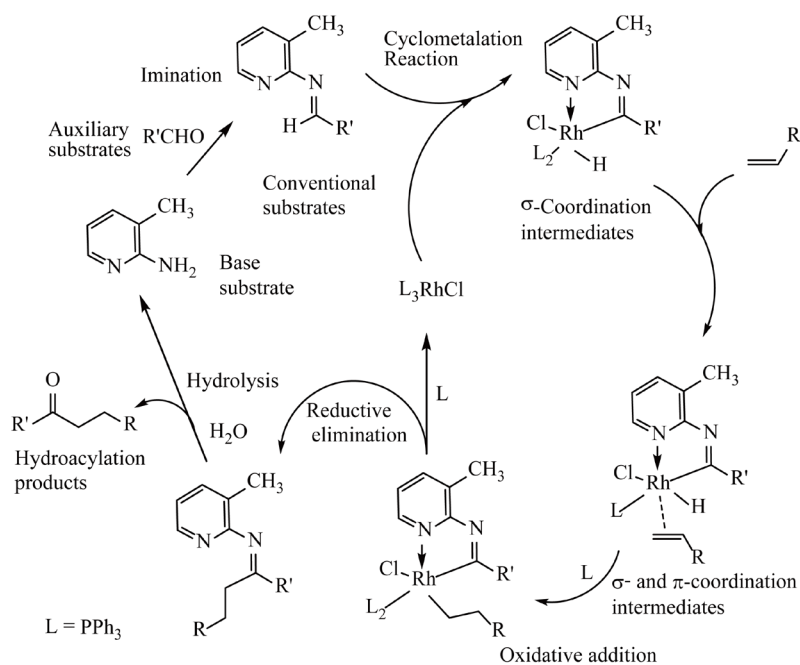
Scheme 2. Proposed mechanism for hydroacylation via cyclometalation reactions [119].
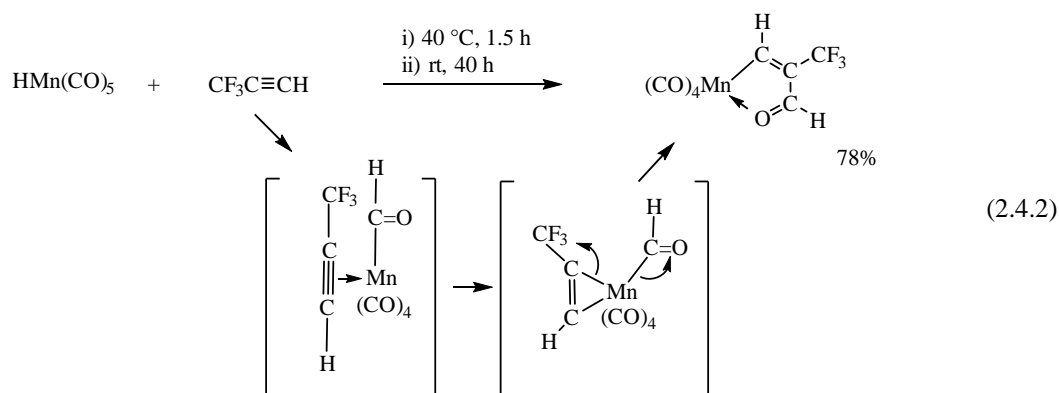
the unsaturated π-coordination bonds easily proceed.

4) Five-membered ring compounds are easily formed by the σ-coordination of the carbonyl oxygen atom to the metal atom.

These characteristics of metal carbonyl compounds and unsaturated hydrocarbons enable the cyclometalation reactions of these compounds to easily proceed without using conventional substrates.

For example, Stone *et al*. [120] reported the unconventional cyclometalation reaction of a manganese carbonyl with an alkyne as shown in Equation (2.4.2).

First, the unsaturated π-electrons of the alkyne coordinate to the manganese atom with the concomitant migration of a hydrogen atom from the manganese to a carbonyl group.

The coupling reaction between a carbonyl carbon atom and hydrogen occurs via the migration reaction, where the alkyne carbon atom bonds with an electron attractive trifluoromethyl group. Finally, cyclization reactions occur in the form of cyclocarbonylation, which is caused by the coordination of the carbonyl oxygen atom to the manganese atom.

$$\text{HMn(CO)}_5 \quad + \quad \text{CF}_3\text{C}{\equiv}\text{CH} \quad \xrightarrow[\text{ii) rt, 40 h}]{\text{i) 40 °C, 1.5 h}} \quad (2.4.2)$$

78%

Alkynes or alkenes react with alkylmanganese carbonyl compounds at high pressures (2 - 10 kbar) to provide the five-membered ring products **2.20** and **2.21** via the coupling reactions of the organyl migration carbonyl moiety with alkynyl or alkenyl groups in good yields. These cyclometalated products are used as intermediates to prepare organic compounds [121].

For example, alkyne cyclometalated intermediates **2.20** afford *E*-enones **2.23** under acidic conditions by demetalation. Alternatively, the intermediates **2.20** afford butenolides **2.24** via an intramolecular Reppe reaction by hydride reduction. Finally, alkene cyclometalated intermediates **2.21** afford ketones **2.25** by photochemical demetalation as shown in **Scheme 3** [121].
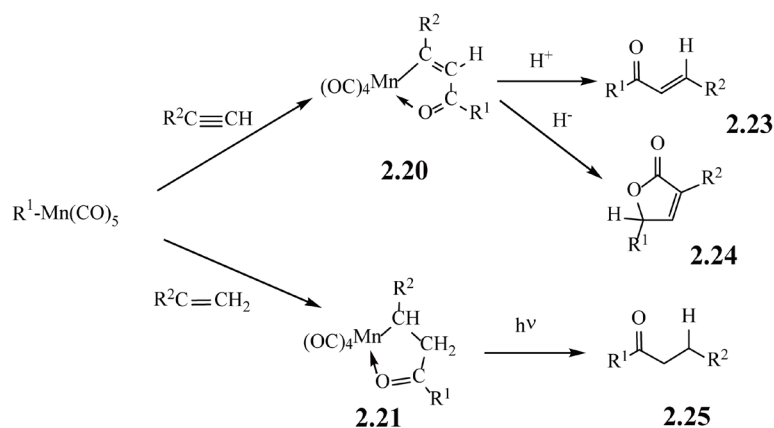
Scheme 3. A variety of alkylmanganese pentacarbonyl compounds regioselectively react with structurally diverse alkynes or alkenes to produce their cyclometalated intermediates [121].

3. Recent Applications of Cyclometalation Five-Membered Ring Products and Intermediates as Catalytic Agents

3.1. Introduction

The author has published a review article on the applications of cyclometalation five-membered ring (intermediate) products with catalytic actions [41] [43] [55]. Thus, this chapter only describes very recent cyclometalation five-membered ring products as catalysts and cyclometalation five-membered ring intermediates with catalytic actions.

3.2. Recent Applications of Cyclometalation Five-Membered Ring Products as Catalysts

Recently, the main metal compounds of the five-membered ring products of cyclometalation reactions, which are used as catalysts in the chiral reactions, are Pd compounds, and the other metal compounds are Pt, Ir, Rh, Ru and Fe compounds [122]-[130].
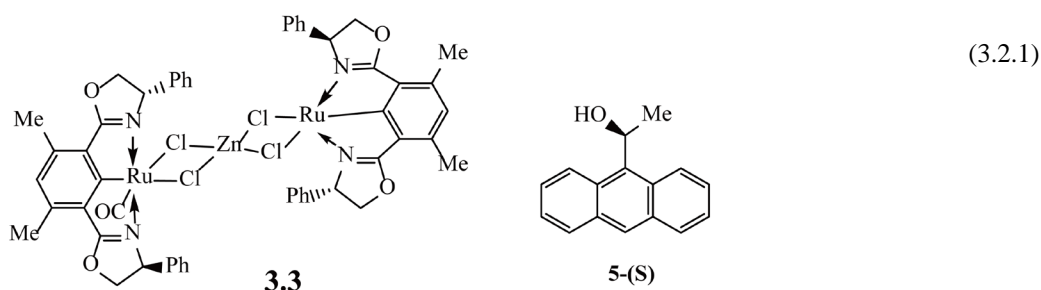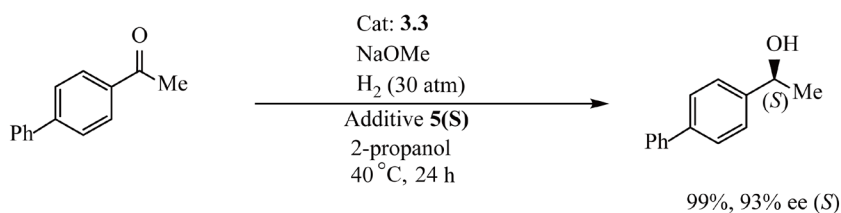
For examples, the asymmetric hydroarsination reaction [131], hydrogenation [132] and asymmetric aza-Michael reaction are cited [133].

An asymmetric hydroarsination reaction between diphenylarsine and 3-diphenylphosphanyl-but-3-en-1-ol has been achieved using *ortho*-metalated (*R*)-[1-dimethylamino)ethenylnaphthalene as the chiral reaction template **3.1** with high stereoselectivity under mild reaction conditions, as shown in **Scheme 4** [131]. The hydroarsination of 3-diphenylphosphanyl-but-3-en-1-ol with diphenylarsine produces only one stereoisomer as a five-membered As-P bidentate chelate on the chiral naphthylamine palladium template **3.2**. The naphthylamine auxiliary can be chemoselectively removed by treatment with concentrated hydrochloric acid. The absolute configuration of the final hydroarsination product has been established using single crystal X-ray analysis.
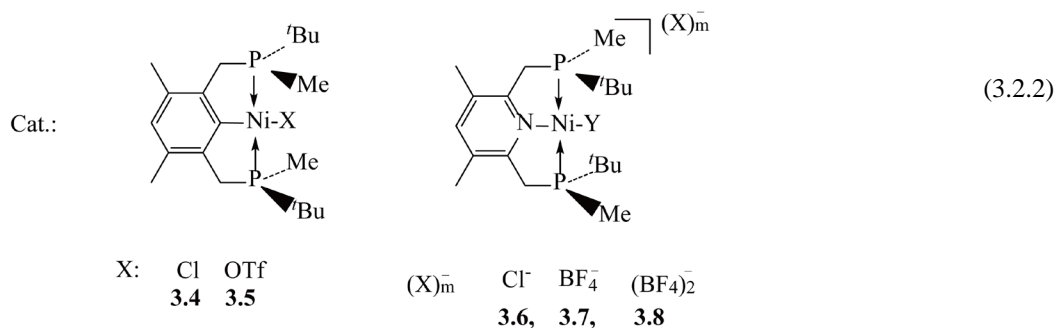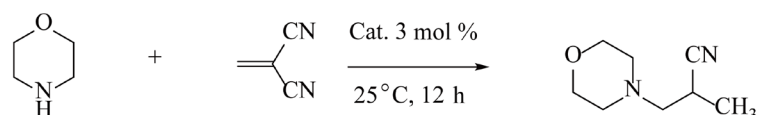
The following chiral reactions of phenyl alkyl ketone were reported for hydrogenation in the presence of bis(oxazolinyl)phenyl metal compounds **3.3**, as shown in Equation (3.2.1) [132]. Furthermore, for the latter bis(oxazolinyl)phenyl ruthenium catalyst **3.3**, Ito, J., Teshima, T. and Nishiyama, H. [132] reported, a significant increase in enantioselectivity with a zinc-chloride-bridged ruthenium compound.
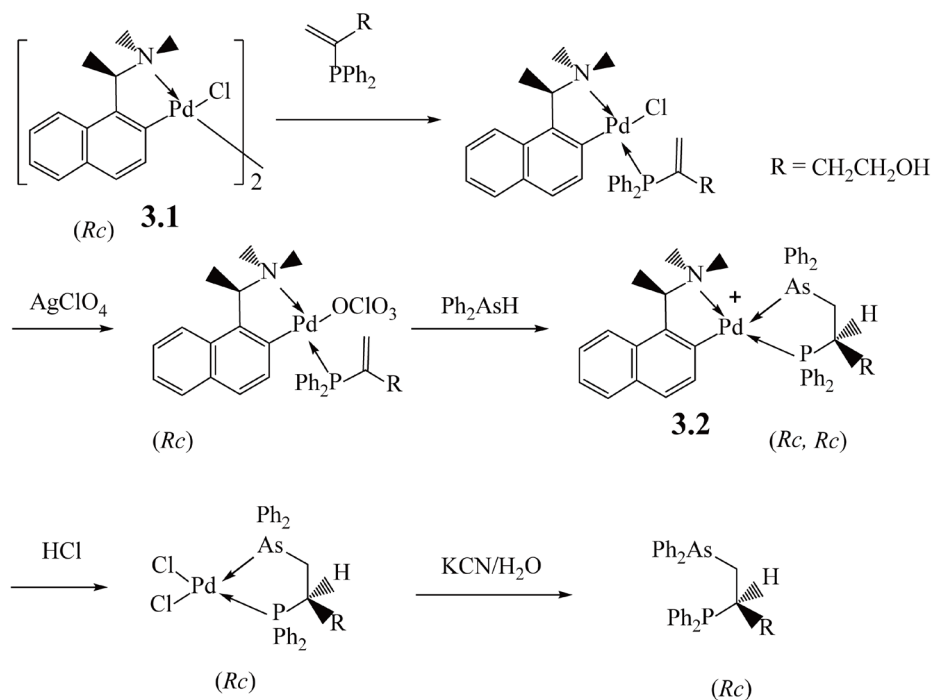
Scheme 4. Asymmetric hydroarsination reaction between diphenylarsine and 3-diphenlphosphanyl-bu-3-en-1-ol with *ortho*-metalated (*R*)-[1-dimethylamino]ethenylnaphthalene as the chiral reaction template [131].

Cat: **3.3**
NaOMe
H$_2$ (30 atm)
Additive **5(S)**
2-propanol
40 °C, 24 h

99%, 93% ee (*S*)

3.3

5-(S)

(3.2.1)

W. Zhang *et al*. [133] attempted the asymmetric aza-Michael addition of α,β-unsaturated nitriles using the P-stereogenic Ni compounds of common five-membered ring **3.4** and **3.5** (Ni PCP) compounds and chelate type **3.6**, **3.7** and **3.8** (Ni PNP) compounds. The reactions with the common Ni PCP pincer **3.4** and **3.5** compounds show much higher yields and higher ee% than the reactions with the chelate type **3.6 - 3.8** Ni PNP pincer compounds as shown in Equation (3.2.2) and **Table 2**.

Cat. 3 mol %
25 °C, 12 h

(3.2.2)

Cat.:

X: Cl   OTf
    3.4   3.5

$(X)_{\overline{m}}$ Cl⁻   BF$_4^-$ (BF$_4$)$_2$
   **3.6,   3.7,   3.8**

In Chapter 2, many metathesis reactions are shown with a Hoveyda-Grubbs metathesis catalyst, which has an oxygen donor atom as shown in **Figure 3**.

Recently, other catalysts have used nitrogen atoms as the heteroatoms:

Table 2. Reaction conditions of aza-Michael addition.

| Cat	Additive	Yield (%)	ee (%)
3.4	AgOTf	83	35
3.5		85	28
3.6	AgOTf	nd	
3.7	AgOTf	9	8
3.8	AgOTf	11	11

The reaction of the Grubbs' 3rd-generation complex (1,3-bis(2,6-diisopropylimidazolin)-2-ylidene complex) with 2-ethenyl-N-methylaniline forms complex **3.9**. Compared to the conventional *O*-Grubbs-Hoveyda complex (such as **2.9 -2.12** in **Figure 3**), the new complexes are characterized by fast catalyst activation, which translates into fast and efficient ring-closing metathesis reactivity. Catalyst loadings of 15 - 150 ppm (0.0015 - 0.015 mol%) are sufficient to convert a wide range of diolefinic substrates into the respective ring-closing metathesis products after 15 min at 50°C in toluene as shown in Equation (3.2.3). The use of complex **3.9** in ring-closing metathesis reactions enables the formation of N-protected 2,5-hydropyrroles with turnover numbers (TONs) of up to 58,000 and turnover frequencies (TOFs) of up to 232,000 h^{-1} [134].

Ring-closing metathesis

TON   78,000
TOF   232,000 h^{-1}

(3.2.3)
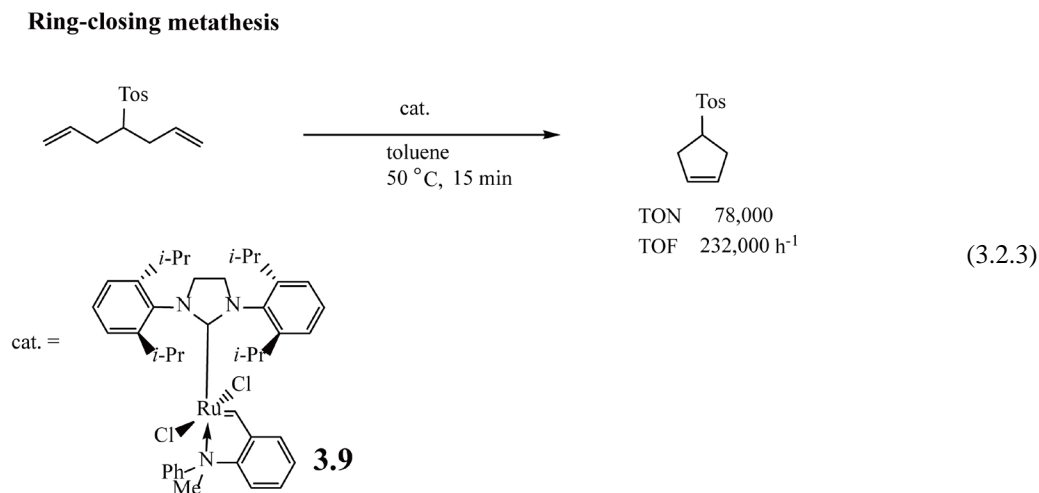
Recently, many cross-coupling reactions using cyclometalation reaction five-membered ring products as catalysts for Heck-type, Mizoroki-Heck and Suzuki cross-coupling reactions were reported, as shown in **Figure 6**.

Recently, the five-membered ring products of cyclometalation reactions for polymerization catalysts were reported as shown in **Figure 7**.

Heck-type reactions
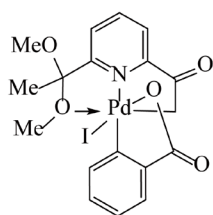
Mizoroki-Heck reactions

3.10 [135]

X = Br, NCH$_3$
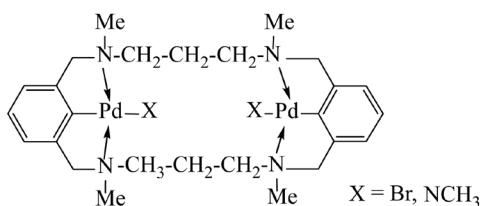
3.11 [136]

Suzuki cross-coupling reactions
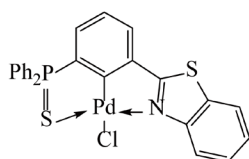
Suzuki cross-coupling reactions

3.12 [137]

3.13 [138]

Figure 6. Recent cross-coupling reactions with cyclometalated five-membered products as catalysts for Heck type, Mizoroki-Heck, and Suzuki cross-coupling reactions.

Ethylene polymeriation

**Olefin polymeriation
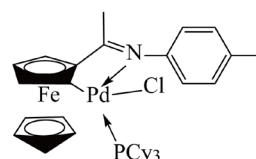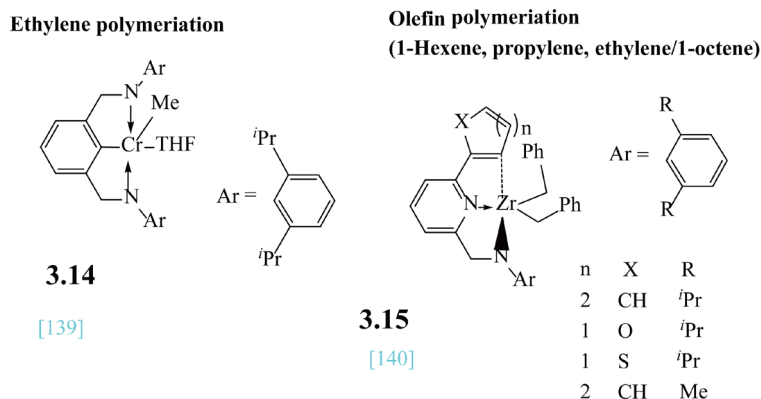(1-Hexene, propylene, ethylene/1-octene)**

3.14

[139]

3.15

[140]

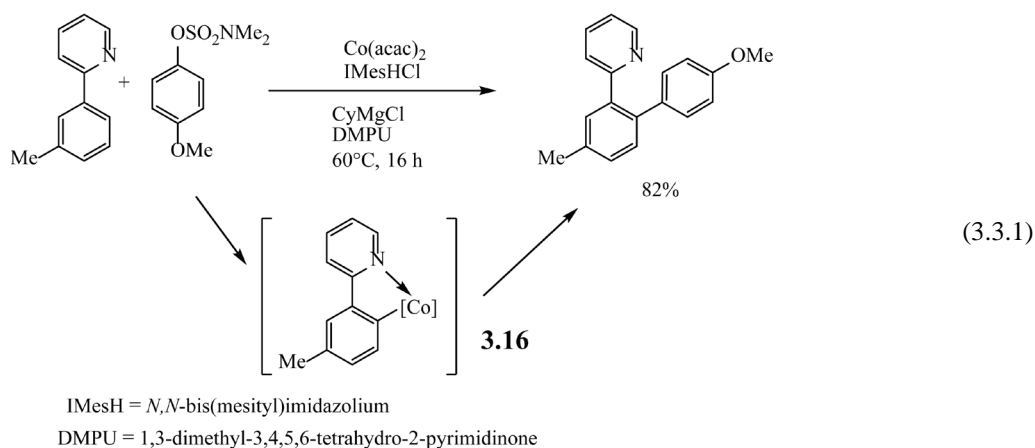| n	X	R
2	CH	^{i}Pr
1	O	^{i}Pr
1	S	^{i}Pr
2	CH	Me

Figure 7. Recent polymerization reactions of ethylene polymerization and olefin polymerization (1-Hexene, propylene, and ethylene/1-octene).

Other reactions have also been repoted, such as acceptorless cyclooctane dehydrogenation and aldehyde decarbonylation [141], transfer hydrogenation of ketones and Oppenauer-type oxidation of alcohols [142], *otho*-benzoxylation of 2-arylpyridines [143], etc. using cyclometalation compounds as their catalysts.

3.3. Recent Applications of Cyclometalation Five-Membered Ring Intermediates as Catalytic Agents

Many articles on arylations have reported the synthetic applications of cyclometalation reactions, in particular. For example, Song and Ackermann [144] have reported that the cobalt acac complex reacts with 2-phenylpyridine first to produce a cobalt intermediate, which is bonded with the γ-carbon atom **3.16**, and the intermediate subsequently reacts with an aryl sulfamate to produce the final substitution product in high yield, as shown in Equation (3.3.1).

(3.3.1)

IMesH = *N,N*-bis(mesityl)imidazolium

DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone

With 2-phenyloxazolines [145] and phenyltriazenes [146] as the substrates, their alkenylations also proceed in the presence of rhodium compounds, as shown in Equations (3.3.2) - (3.3.3).

(3.3.2)

[145]

55%

(3.3.3)

[146]

75%
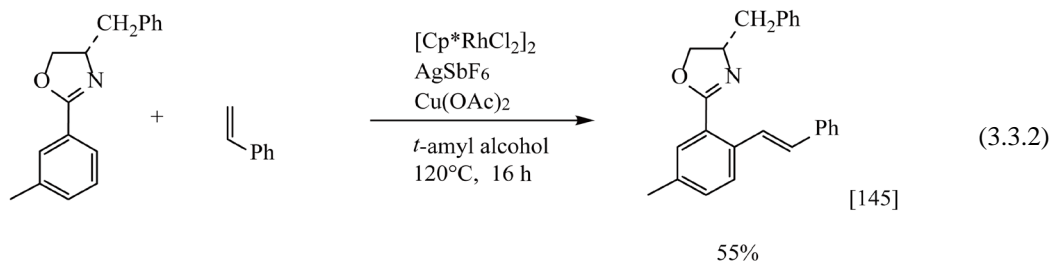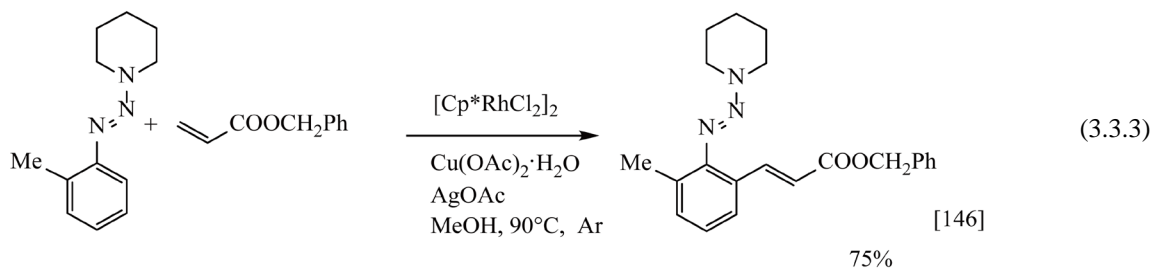
Alkynylations have been shown as reactions of cyclometalation reaction products with alkynes.

For example, a phenyimine as an arylimine reacts with an alkyne in the presence of a renium compound to give the cyclization product aminoindane **3.18** via a cyclometalation intermediate **3.17**, which is coordinated by an alkyne, as shown in Equation (3.3.4) [147].

(3.3.4)
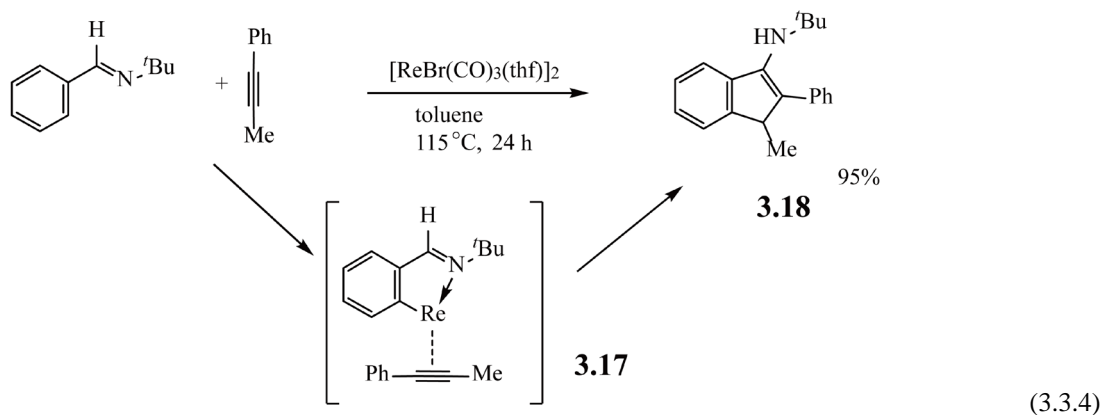
Other reactions are acylation [148], amination [149], halogenation [150] and silylation [151], as shown in Equations (3.3.5)-(3.3.8), respectively.

Acylation

DMEDA = *N,N'*-dimethylenediamine

(3.3.5)

[148]

83 %

Amination

(3.3.6)

[149]

97%

Halogenation

$$\tag{3.3.7}$$

99%

PivOH = Me$_3$CCH$_2$OH

Silylation

$$\tag{3.3.8}$$

92%
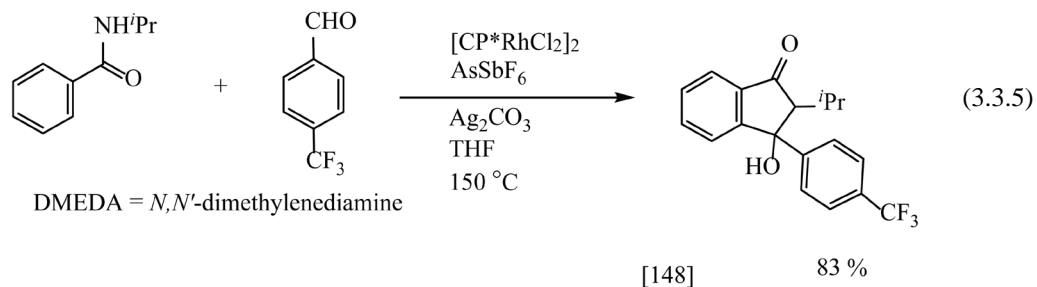
4. Concluding Remarks

The five-membered ring products and intermediates of cyclometalation reactions are synthesized with various types of substrates, metal compounds (69 types of meal atoms), and ancillary ligands. In particularly, we noticed the substrates such as carbenes, pincers, heterocyclic compounds and dendrimers, and on the metal compounds such as common metals and rare earth metals.

As to the carbenes, for example, first and second generation Hoveyda-Grubbs metathesis catalysts have been used as very highly active catalysts. Recently, new third Hoveyda-Grubbs catalysts (compounds **3.9**) a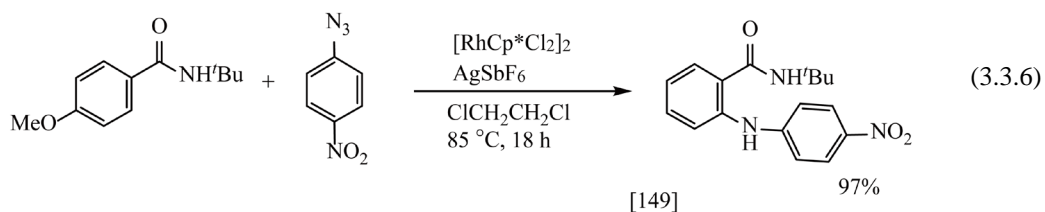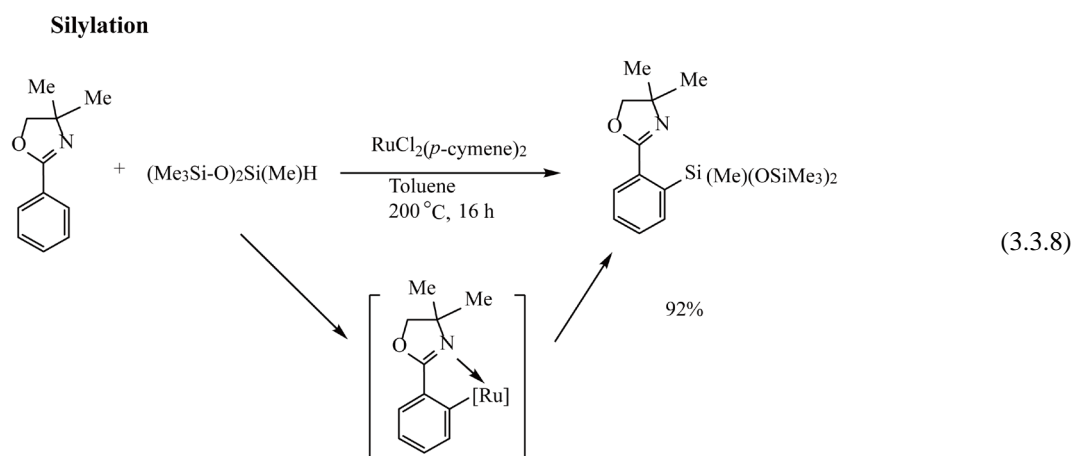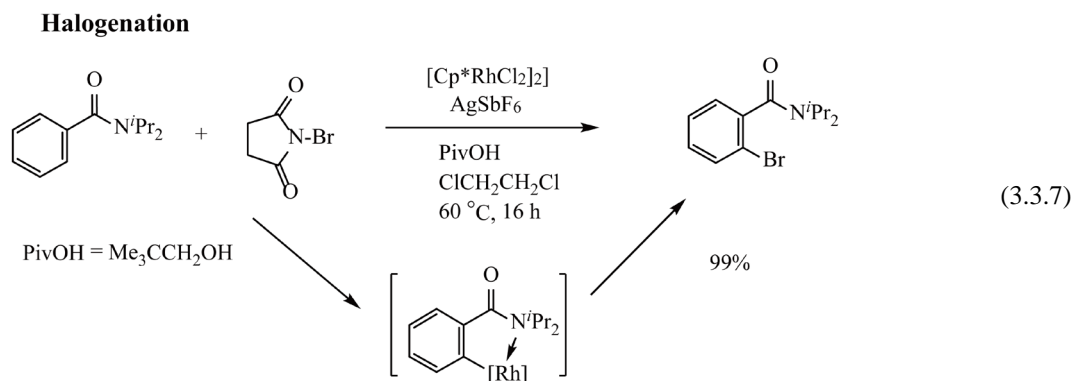s very highly active metathesis catalysts, exhibiting very high both TNOs and TOFs, are used with the simple changing of hetroatom from O to N atom.

The pincer compounds are tridentate substrates, they are very stable and having many functionality, for example, Michael addition reactions proceed at room temperature in high yields and high TNOs by using bisoxazolinylphenyl rhodium compound **2.8** as the catalysts.

The heterocyclic compounds, for example, oxazolinylphenyl compounds (compounds **2.4**, **2.8** and **3.3**), and the compounds in Equations (3.3.2) and (3.3.8)) are highly active catalysts.

The dendrimers are expected stable, high TNO and high functional catalysts [48].

These products are usually prepared by the reactions of noble metal compounds such as Pd, Pt, Ru and Rh metal compounds. Recently, articles concerning common metals such as Fe, Ni and Cu and main group metals such as Zn and Al, and rare earth metals such a Lu, Eu and Sm have been published. These metal compounds are expected to be used as inexpensive and special catalysts with various conventional substrates and other ligand compounds.

Finally, I believe firmly that these cyclometalation five-membered ring products and intermediates would be utilized for the development of further new industrial products in many fields such as pharmaceuticals, OLEDs, carbon dioxide utilizations, dye-sensitizer solar-cells, sensors and the other many field by utilizing their function such as catalytic activity, etc.

Acknowledgements

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