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Journal of Organometallic Chemistry 692 (2007) 2608–2632
Journal of Organometallic Chemistry
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Review

Three types of reactions with intramolecular five-membered ring compounds in organic synthesis

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Received 27 September 2006; received in revised form 14 February 2007; accepted 14 February 2007
Available online 2 March 2007

Abstract

There are three types of reactions with intramolecular five-membered ring compounds in organic syntheses: The first type is reactions involving intramolecular five-membered ring compounds which are utilized for the ease of synthesis of these compounds and the stability of the products. The second is reactions performed via intramolecular five-membered ring intermediates, because such intermediates are very reactive and labile compounds. The third is the metal-catalyzed reactions with the intramolecular five-membered ring compounds because these metal compounds have catalytic activities. The third type reactions involving intramolecular five-membered ring pincer compounds are also provided.

The first type reactions include carbonylations, alkenylations, alkynylations, acylations, isocyanations, Diels–Alder reactions, etc. The second type reactions include carbonylations, cross-coupling reactions, hydroacylations, ring expansion reactions, carbocyclizations, etc. The third type reactions include cross-coupling reactions, rearrangements, metatheses, reductions, Michael reactions, dehydrogenations, Diels–Alder reactions, etc.

Keywords: Organometallics; Intramolecular; Five-membered ring; Organic synthesis; Catalysts; Applications; *Cyclo*-metalation

Contents

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doi:10.1016/j.jorganchem.2007.02.036

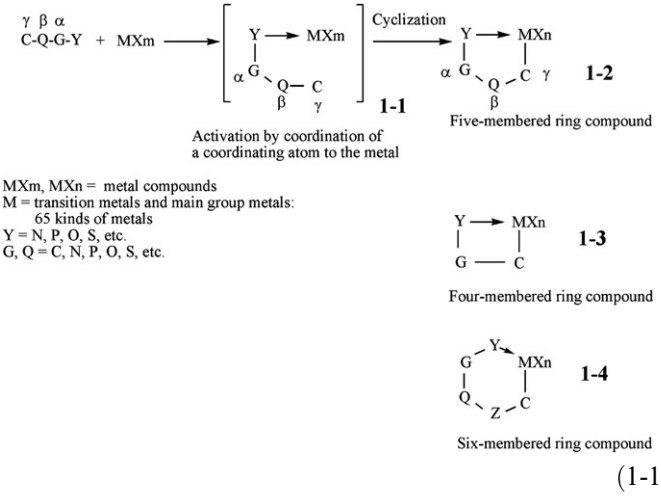
1. Introduction

In 1955, Bähr and Müller [1–3] first published a report regarding organometallic intramolecular-coordination compounds which tend to form five- or six-membered ring compounds. They could not verify their intramolecular coordination states with analytical instruments such as IR and NMR spectroscopies at that time. They estimated the intramolecular coordination state from the data of elemental analysis, molecular weight, decomposition products, and the reaction routes.

However, after about 10 years, in 1966, the intramolecular coordination bonds in the five-membered ring organotin compounds were verified with the IR and NMR spectroscopies [4]. These organotin compounds having a five-membered ring structure were found to be completely different from the other organotin compounds having a four- or six-membered ring. The organotin compounds having only one five-membered ring were easily isolated from these reaction solutions as the crystalline products [4–20]. From these reactions, it was understood that metalacyclic five-membered ring compounds having a coordinating atom such as oxygen or nitrogen show the extremely high stability of the ring.

Generally, the first article on the *cyclo*-metalation with a transition metal is considered to be a reaction between azobenzene and nickel compound in 1963 [21]. The publications of articles on the *cyclo*-metalation had gradually increased since in 1970's, and, after 1980's it had extraordinarily increased, especially, reactions between benzylamine ($PhCH_2NMe_2$) or azobenzene (Ph–N=N–Ph) with transition metal compounds. Many reviews [22–42] and two books [43,44] have also been published.

These *cyclo*-metalations are generally considered that, as their first step, the metal compounds are activated by coordination with a coordinating atom such as N, P, O and S, **1-1** [42–44]. In the second step, the metal element can easily bond with a carbon atom at the γ-position to a coordinating atom as shown in Eq. (1-1). The five-membered rings **1-2** have almost no strain as compared with the other membered rings such as four- **1-3** and six-membered ring **1-4**. These *cyclo*-metalations easily proceed with the metal compounds of many kinds of metals of both transition metals and main group metals. The number of the kinds of metals was 57 in the former review [42], however, it is reported that the total is 68 by adding eleven atoms of Cs, Ba, Hf, Nb, Pr, Eu, Gd, Dy, Ho, Tm and Th by an investigation with on a SciFinder Scholar database system on July 11, 2006 as shown in Table 1.



(1-1)

More than several thousand articles on the *cyclo*-metalation reactions have been published since 1955. The representative substances of intramolecular five-membered ring compounds used for the organic syntheses are shown in Table 2. Especially, surprisingly many articles regarding

Table 1
Kinds of metal elements of the intramolecular five-membered ring compounds

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 *H*																	2 *He*
2	3 **Li**	4 **Be**											5 **B**	6 *C*	7 *N*	8 *O*	9 *F*	10 *Ne*
3	11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 *P*	16 *S*	17 *Cl*	18 *Ar*
4	19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 *Br*	36 *Kr*
5	37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc** *	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 *I*	54 *Xe*
6	55 **Cs**	56 **Ba**	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi** *	84 *Po* *	85 *At* *	86 *Rn* *

Lanthanide series	58 **Ce**	59 **Pr**	60 **Nd**	61 *Pm* *	62 **Sm**	63 **Eu**	64 **Gd**	65 *Td*	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
Actinide series	90 **Th** *	91 *Pa* *	92 **U** *	93 *Np* *	94 *Pu* *	95 *Am* *	96 *Cm* *	97 *Bk* *	98 *Cf* *	99 *Es* *	100 *Fm* *	101 *Md* *	102 *No* *	103 *Lr* *

dimethylbenzylamine **1-5** or azobenzene **1-6** with transition metal compounds have been published. Therefore, the ease of the synthesis expedites its application, especially for the synthesis of aromatic derivatives since 1980's.

Many organic compounds are synthesized by using the intramolecular five-membered ring compounds because the reactions using these compounds have following three advantages: The first is that these *cyclo*-metalations very easily proceed because the activation of metal compounds by the coordination of a coordinating atom to the metal atom is very high as shown in Eq. (1-1). The second is that the production of these *cyclo*-metalation products regiospecifically proceeds because the reactions proceed at the γ-position to the coordinating atom. The third is that the application of many kinds of catalytic reactions is possible because the *cyclo*-metalation proceeds with many kinds of metal compounds as shown in Table 1.

There are the following three types of reactions in the application of these intramolecular five-membered ring compounds in organic syntheses. The first applications are to utilize the ease of synthesis of these compounds and the chelate ring stability. The second is to use only the very high ease of synthesis of these compounds; that is, the reactions proceed via the intermediates of the intramolecular five-membered ring compounds. The third is the metal-catalyzed reactions of the intramolecular five-membered ring compounds. The third reactions also proceed with the intramolecular pincer five-membered ring compounds.

This article shows the first, second and third applications in Sections 2–4, respectively, and the pincer metal-catalyzed reactions are shown in the Section 5.

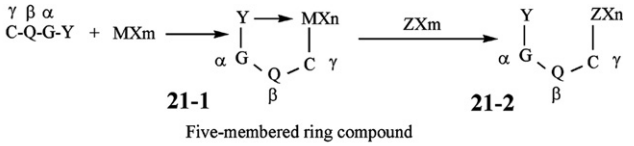
Recently, Vincente, Pfeffer, Djukic, Main and many researchers have published enourmously large number of articles regarding *cyclo*-metaltions and their applications. Therefore, this review is a select account only regarding their applications on the organic synthesis.

2. Reactions with intramolecular five-membered ring compounds

2.1. Introduction

The intramolecular five-membered ring compounds are easily synthesized by *cyclo*-metalation reactions with many kinds of metal compounds as shown in Eq. (1-1).

These *cyclo*-metalation products **21-1** are utilized for the synthesis of organic derivatives by many reactions such as insertion, substitution and rearrangement by using many kinds of compounds such as carbon monoxide, alkenes, alkynes and isonitriles as shown in Eq. (21-1).



21-1 **21-2**

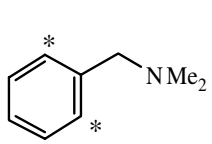
Five-membered ring compound

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

(21-1)

The most representative reactions in the *cyclo*-metalations are *ortho*-metalations. The *ortho*-derivatives of phenyl compounds are obtained by substitution reactions. For example, at first, the nitrogen atom of phenyloxazoline coordinates to a lithium metal **21-3**, and the lithium metal which is activated by the coordination, is able to bond with an *ortho*-carbon atom at a γ-position to the coordinating atom to form the five-membered ring compound **21-4**. These reactions of phenyl derivatives usually proceed at their *ortho*-position. Hence, these reactions are called *ortho*-lithiation, that is, *ortho*-metalation. These *ortho*-lithiation products are very reactive compounds. Therefore, these compounds easily react with electrophiles such as alkyl halides, iodine, deuterium oxide, isocyanates,

Table 2
Representative substrates for synthesis of intramolecular five-membered ring compounds



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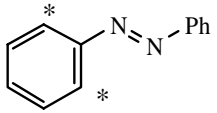

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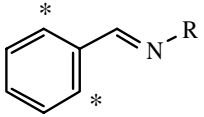

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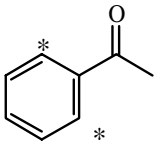

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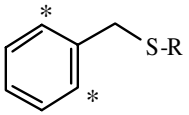

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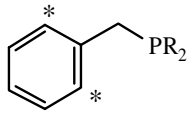

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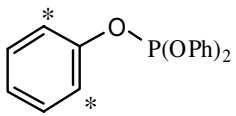

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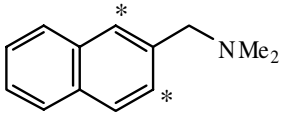

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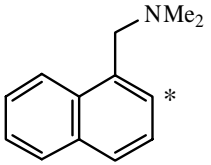

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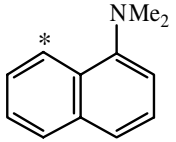

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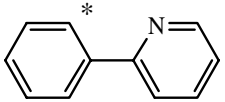

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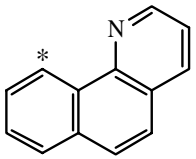

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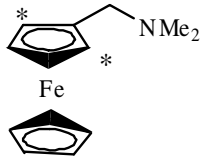

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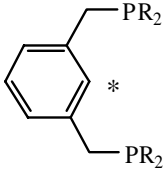

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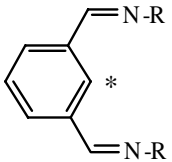

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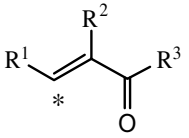

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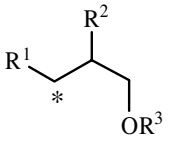

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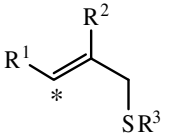
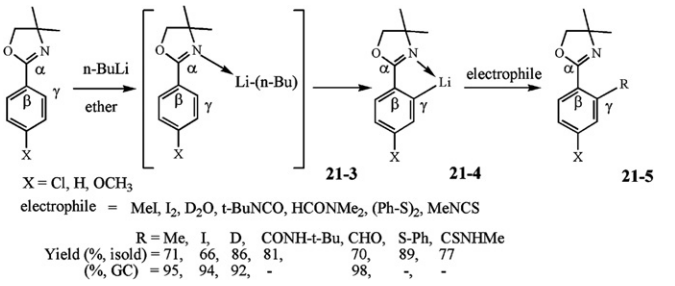


1-22

Symbol "∗" means the reaction site of the metal compounds.
It is generally at the γ-position to the coordinating atom such as N, P, O and S.

N,*N*-dimethylformamide, diphenyl disulfide and isothiocyanate, to give the derivatives of an alkyl, an iodide, deuterium, an isocyanate, a formyl, a phenylthio, and an isothiocyanate compound as shown in Eq. (21-2) [45,46].



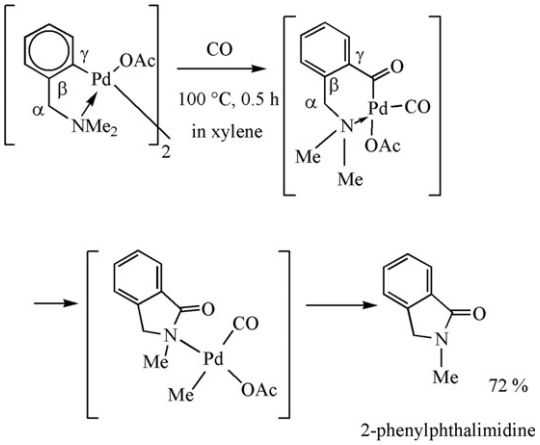
(21-2)

The other applications of the intramolecular five-membered ring compounds by these *cyclo*-metalation, are carbonylations, alkenylations, alkynylations, acylations, isocyanations, Diels–Alder reactions, etc.

2.2. Carbonylations

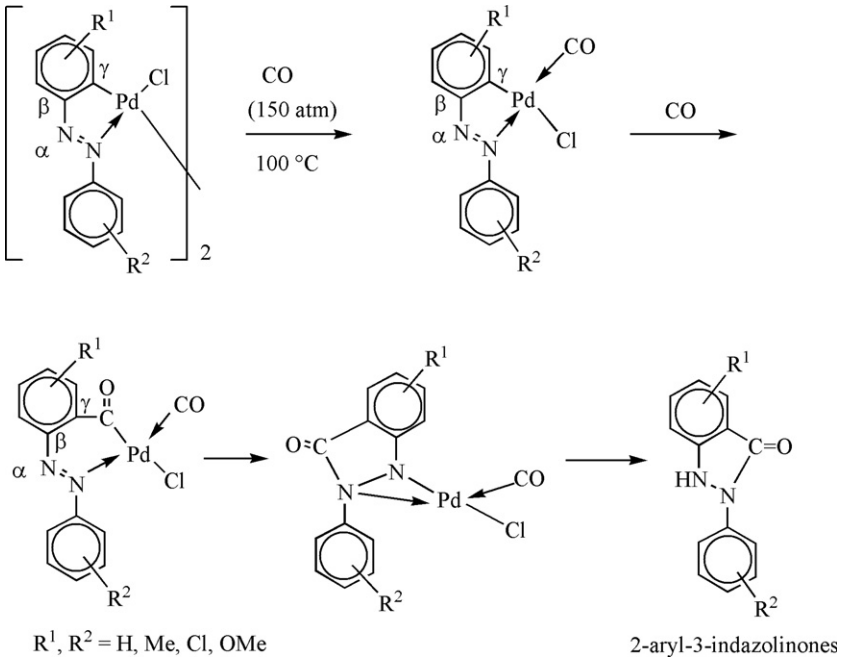
The carbonylation of the intramolecular five-membered ring compounds proceeds usually via the insertion of carbon monoxide between a metal and carbon atom at the γ-position to the coordinating atom. For example, 2-aryl-3-indazolinones are presumed to be prepared by via the insertion of carbon monoxide into a bond between palladium metal and the *ortho*-carbon atom in the diazobenzene and by the elimination of the palladium atom as shown in Scheme 1 [47].

The carbonylation of a dimethylbenzylamine *cyclo*-palladation product also gives the similar bicyclic phenylamino ketone, 2-phenylphthalimidine, as shown in Eq. (22-1) [48].

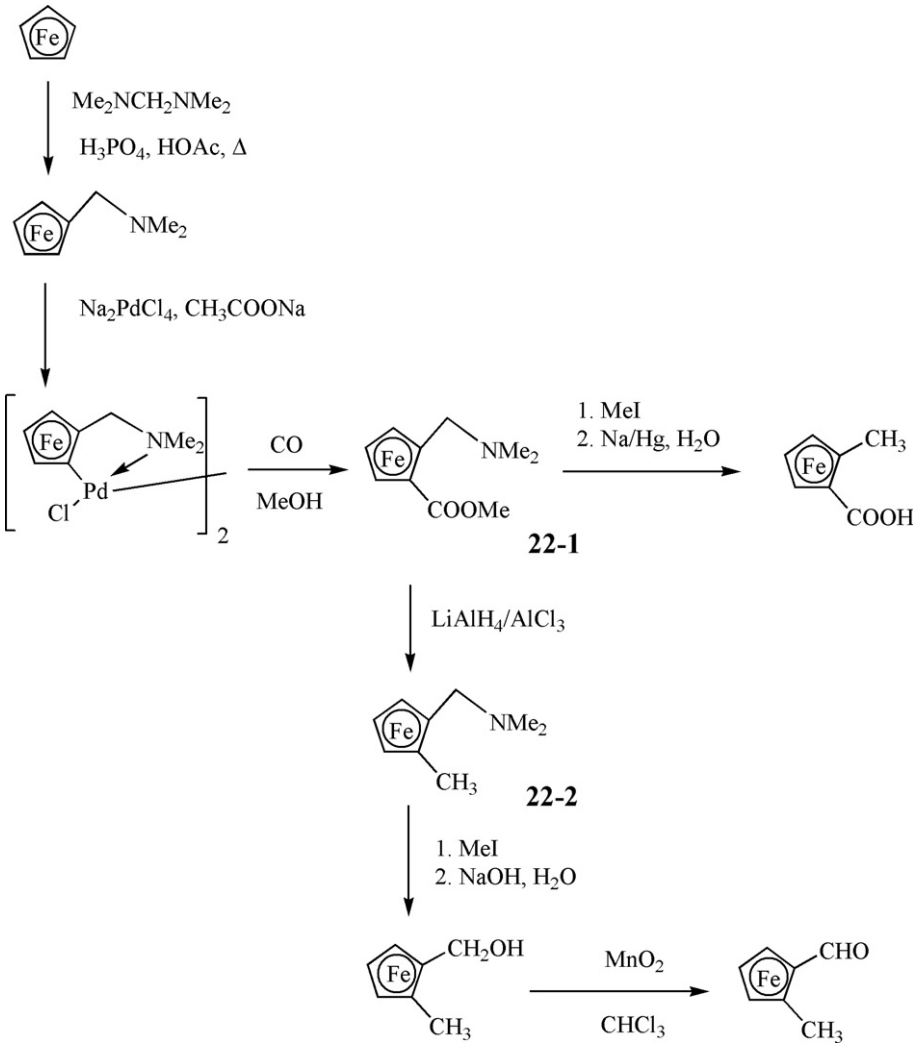


(22-1)

These carbonylations are easily applicable to the synthesis of carbonyl derivatives such as carboxylic acids and esters at the γ-position to the coordinating atom. The *N*,*N*-dimethylaminomethyl derivatives (**1-5**, **1-12**, **1-13**, **1-17**) are the first representative substrates of *cyclo*-metalation as shown in Table 2. For example, ferrocene provides to the *N*,*N*-dimethylaminomethylferrocene (**1-17**) by the reaction of ferrocene with bis(dimethylamino)-methane [49]. The *cyclo*-metalation of this *N*,*N*-dimethylaminomethylferrocene with palladium halides proceeds to give a halo-bridged *cyclo*-palladation dimer. Further, a carboxylic acid ester **22-1** and the methyl derivative **22-2**, etc. are easily prepared as shown in Scheme 2 [49,50]. Actually, the *cyclo*-palladation in the presence of optically pure amino acids such as *N*-acetyl(*L*)-valine, *N*-acetyl(*R*)-leucine, and *N*-acetyl(*S*)-leucine proceeds to



Scheme 1.

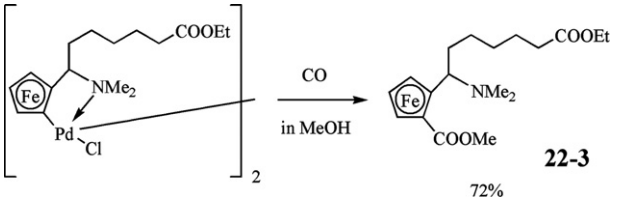


Scheme 2.

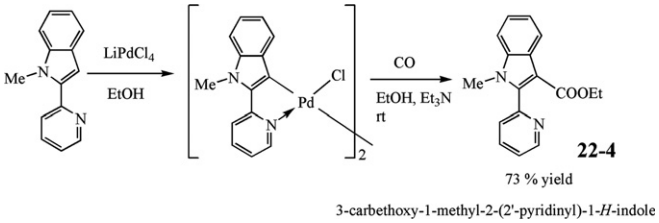
give the optically active chiral *cyclo*-palladation products. All of these derivatives forms the optically pure derivatives [50,51].

These reactions are utilized for the syntheses of pharmaceutical intermediates, e.g., diastereomeric 1,2-disubstituted ferrocene by using an enantiomeric ferrocene **22-3** as shown in Eq. (22-2) [52,53].

A chloro-bridged *cyclo*-palladated pyridine compound is also carbonylated by the reaction of carbon monoxide with bubbling through a reaction mixture at the room temperature in the presence of NEt_3 as a proton scavenger. Metallic palladium is separated out, while the ethyl ester **22-4** was recovered in 73% yield as shown in Eq. (22-3) [54].



(22-2)

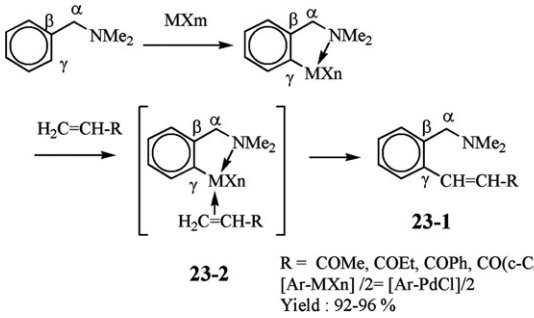


(22-3)

2.3. Alkenylations

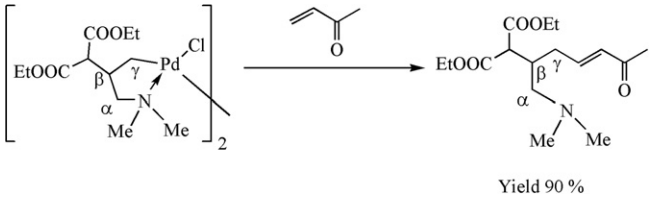
The intramolecular five-membered ring compounds react with alkenes and the alkenylation products **23-1** are easily obtained, via an intermediate metal complex **23-2** coordinated by vinyl bond, and by a C–C coupling between the terminal carbon in alkenes and a carbon atom, which is bonded with the metal element, at the γ-position to the coordinating atom, e.g., as shown in Eq. (23-1) [42,55]. The *N*,*N*-dimethylbenzylamines **1-5** (Eq. (23-1)), [42,55,56], *N*,*N*-dimethylbenzylamine derivatives [55,57–59], *N*,*N*-dimethylaminomethylnaphthalenes (**1-12**, **1-13**) [60], *N*,*N*-dimethylamino

methylruthenocene [61], *N*,*N*-dimethylaminomethylferrocenes (**1-17**) [62,63] and others [61,64,65], are used as the substrates for the vinylation with alkyl vinyl compounds, aryl vinyl compounds, vinyl ketones, vinyl esters, vinyl nitriles, etc.



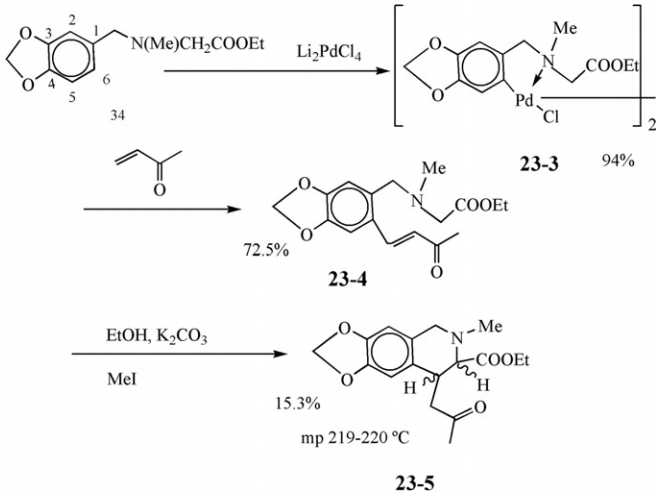
(23-1)

The alkenylation of an alkyl amine also forms a vinyl ketone derivative through the reaction at the γ-position to the coordinating atom in a high yield as shown in Eq. (23-2) [66,67].



(23-2)

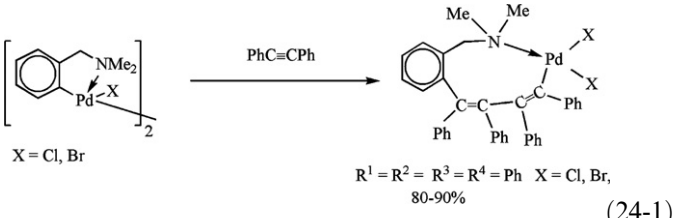
These vinylation products are easily utilized for the formation of heterocyclic compounds by the cyclization reactions. For example, ethyl *N*-methyl-*N*-(3,4-methylenedioxy)benzylglycinate is *cyclo*-palladated regio-specifically at C(6) when treated with Li_2PdCl_4. The product, di-μ-chloro-bis(*N*,*N*-dialkylbenzylamine-6-*C*,*N*)-dipalladium(II) complex **23-3**, undergoes a substitution reaction via the insertion of methyl vinyl ketone between the palladium metal and the phenyl carbon atom. The resultant β-aryl-α,β-unsaturated ketone **23-4** is cyclized using anhydrous potassium carbonate in ethanol to the corresponding ethyl *N*-methyl-1,2,3,4-tetraisoquinolium-3-carboxylate **23-5** as shown in Eq. (23-3) [52,59].



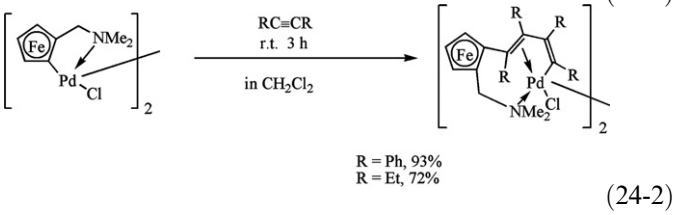
(23-3)

2.4. Alknylations

Alkynes insert into a bond between a metal and a carbon atom at the γ-position to the coordinating atom in the *cyclo*-metalated compounds. There are two types of insertions, i.e., mono- and di-insertions. In the *N*-dimethylbenzylamine or *N*-dimethylferrocenylamie halo-bridged *cyclo*-metalation products, di-insertions proceed as shown in Eqs. (24-1) and (24-2) [52,68–72].

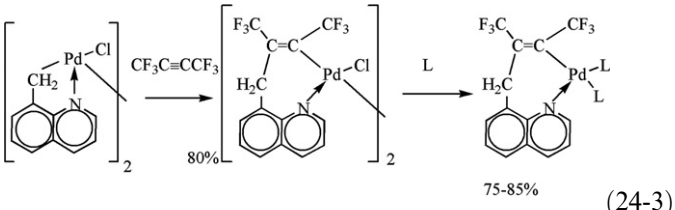


(24-1)

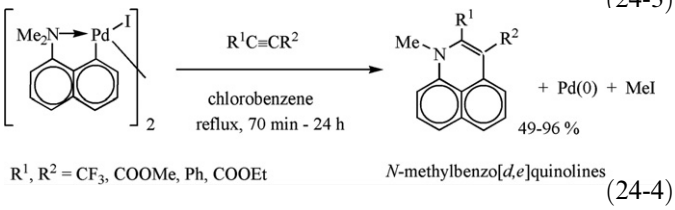


(24-2)

On the other hand, in the methylquinoline or *N*,*N*-dimethylaminonaphthalene *cyclo*-metalation products, mono-insertions proceed as shown in Eqs. (24-3) and (24-4) [52,68,70–76]. The latter reactions are applied to the syntheses of the *N*-methylbenzo[*d*,*e*]quinolines [70,72,75].



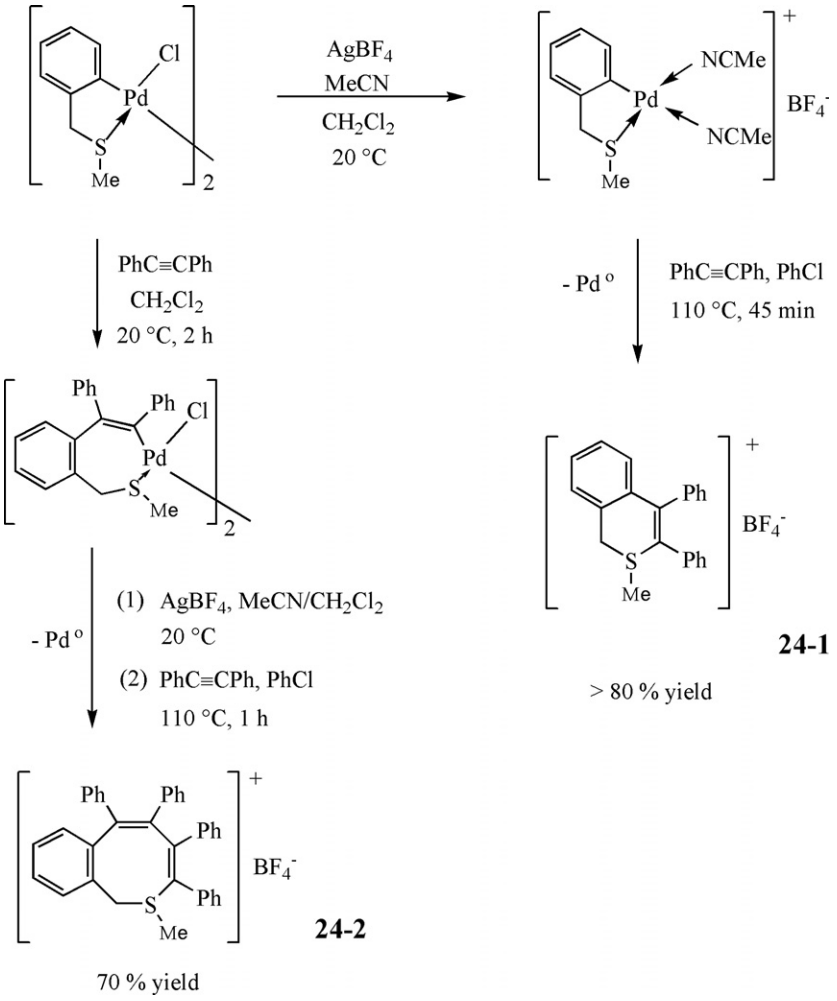
(24-3)



(24-4)

Dupont and Pfeffer reported the one-pot synthesis of heterocyclic compounds through two types of insertions of an alkyne into the metal–carbon bond of activated *cyclo*-metalated benzyl methyl sulfide. The reaction of the alkyne with the cationic *cyclo*-palladated compound gives a six-membered ring arising from the insertion of one alkyne molecule **24-1**. On the other hand, the reaction of the alkyne with the choloro-bridged *cyclo*-palladated compound gives an eight-membered thio cyclic ring compound **24-2**, arising from the insertion of two alkyne molecules as shown in Scheme 3 [77].

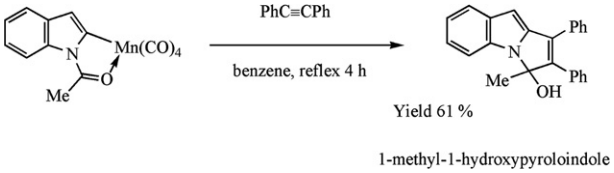
The alkynylation of *cyclo*-metalated compounds are utilized for the synthesis of indenols or indenones. The thermally promoted reactions of the alkynes with an *ortho*-manganated acetophenone **24-3** give 1*H*-indene-



Scheme 3.

1-ols **24-4** in a high yield. However, the reaction of the corresponding *ortho*-manganated derivatives of methyl 3,4,5-trimethoxybenzoate gives the indenone **24-5** in a high yield as shown in Scheme 4 [78].

Further, the alkynylation of *cyclo*-manganated acetylindole gives the former type thermally promoted mono inserted product, 1-methyl-1-hydroxypyroloindole, in a good yield as shown in Eq. (24-5) [79].

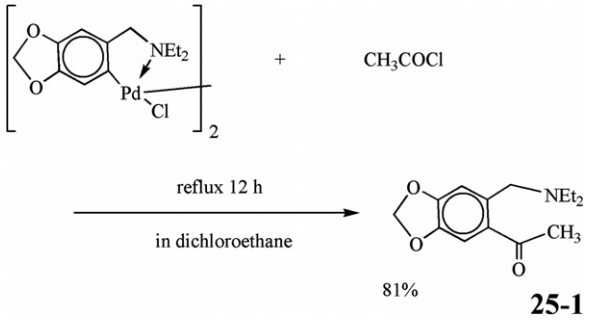


(24-5)

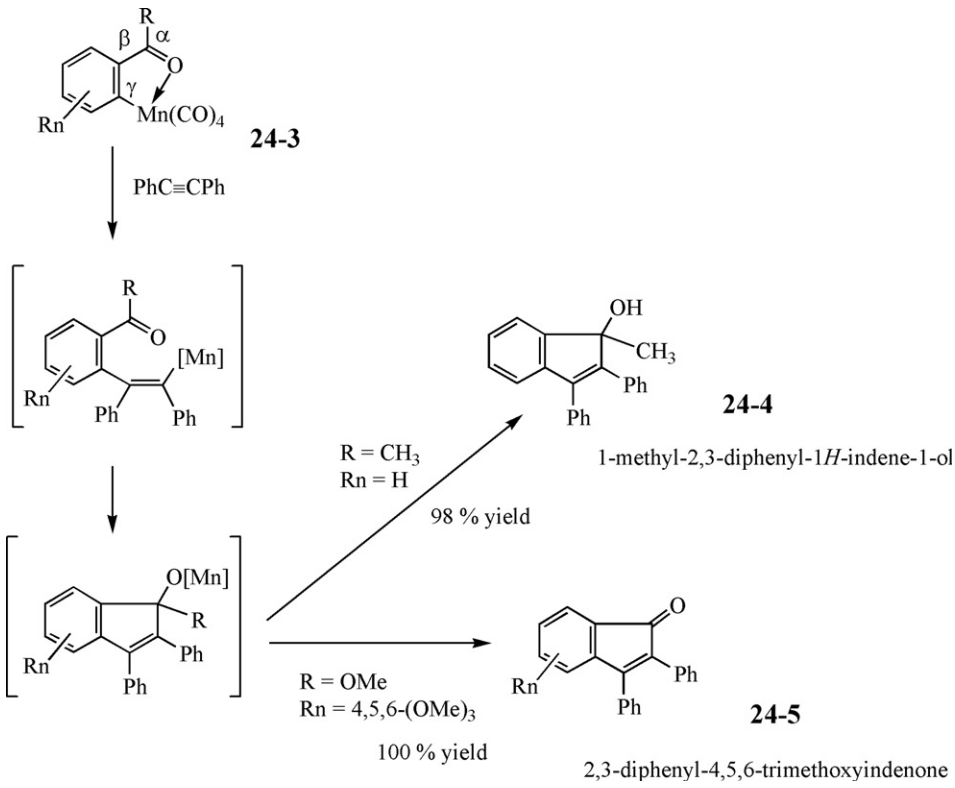
2.5. Acylations

The reaction of palladacycles with acyl halides regiospecifically proceeds to give a 2-acyl derivative **25-1** in a high yield as shown in Eq. (25-1) [80].

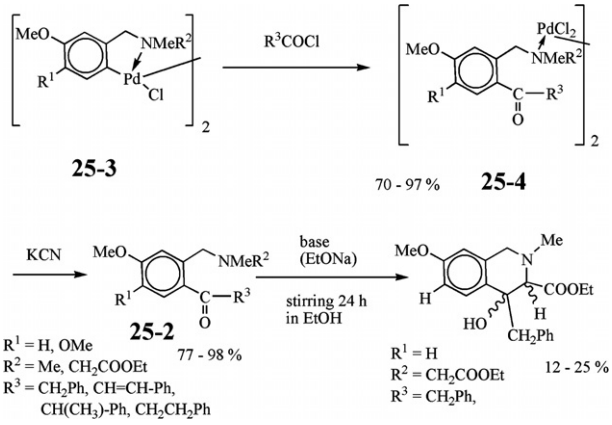
Cyclopalladated *N*,*N*-dimethylbenzylamine derivatives bearing methoxy-groups on the ring behave similarly with respect to acetyl and benzoyl chlorides to give the corresponding ketones **25-2** also in high yields as shown in Eq. (25-2). The presence of electron-withdrawing substituents appears to drastically decrease the rate; a complex di-μ-chlorobis[*N*,*N*-dimethyl-5-chlorobenzylamino-2*C*, *N*]dipalladium(II) **25-3** is recovered unchanged after three days under reflux under the same reaction conditions. These reactions are presumed to proceed through a two-step process: The first is the insertion of acyl halides. The second is the potassium cyanide-induced dissociation of these intermediates **25-4**. The heterocyclic compounds are also synthesized by stirring these acyl compounds with a base such as sodium ethoxide in dry ethanol solution [52,81].



(25-1)



Scheme 4.



(25-2)

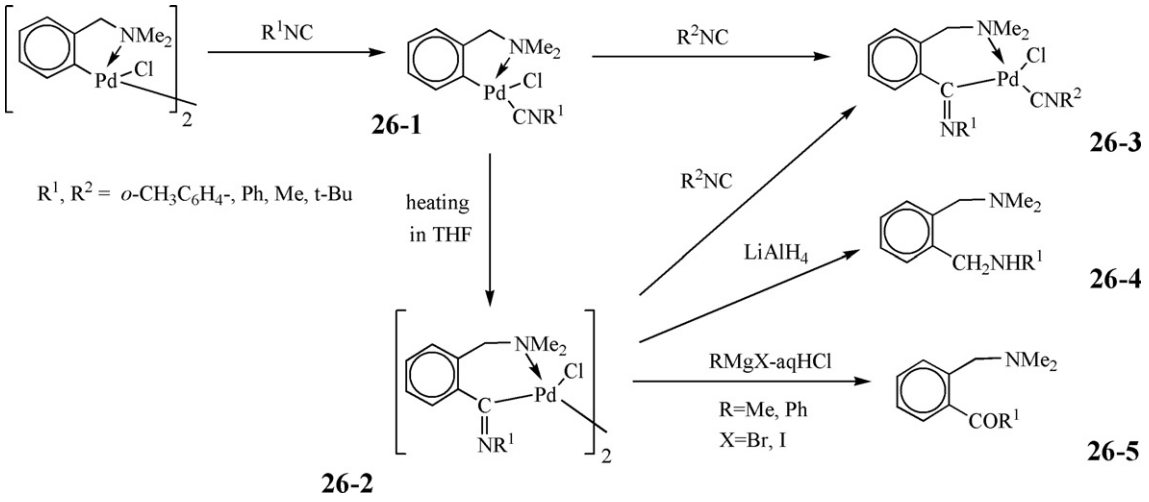
2.6. Isocyanations

The reactions of *N*,*N*-dimethylbenzylamine palladacycles with isocyanates lead to the cleavage of halide bridges to give monocyanate products **26-1**. On heating the monoisocyanates **26-1**, an intramolecular insertion takes place to give dimeric iminoacyl complexes **26-2**. The treatment of the monoisocyanates **26-1** and the dimeric iminoacyl products **26-2** with isocyanide produces diisocyanate products **26-3**. The reactions of the products **26-2** with $LiAlH_4$ or a Grignard reagent give diamines **26-4** or ketones **26-5**, respectively, as shown in Scheme 5 [82].

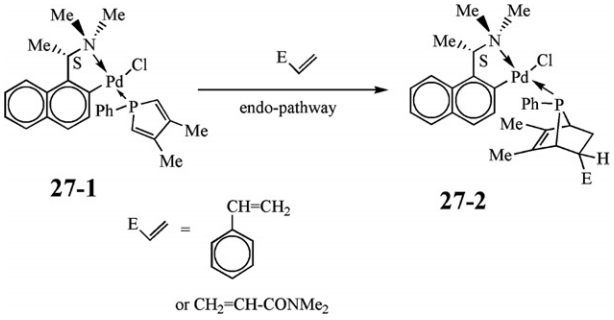
On the other hand, in the reactions of azobenzene *cyclo*-palladated products with isocyanides, the mono-insertion proceeds with the cleavage of the chloride bridges to yield very stable yellow orange complexes **26-6**. The thermal degradation of the cleaved products proceeds smoothly at 100–130 °C in toluene to give the heterocyclic compounds, 3-imino-2-phenylindazolines **26-7**, with the separation of metallic palladium [83]. This indazolines **26-7** may also be obtained from the reaction of the azobenzene *cyclo*-palladation products in toluene at 120 °C with isocyanides in a 1:2 molar ratio respectively as shown in Scheme 6 [83].

2.7. Diels–Alder reactions and other reactions

By using bulky chiral *cyclo*-metalated compounds, some asymmetric Diels–Alder reactions proceed at the metal [84–88]. For example, the organopalladium complex containing the (*S*)-form of *ortho*-palladated (1-(dimethylamino)ethyl)-naphthalene has been used successfully as a chiral template to promote asymmetric *cyclo*-addition reactions between coordinated 3,4-dimethyl-1-phenylphosphole **27-1** and a dienophile (*N*,*N*-dimethy lacrylamide or styrene) via an *endo* pathway, that proceed to give the compound **27-2** as shown in Eq. (27-1) [84].



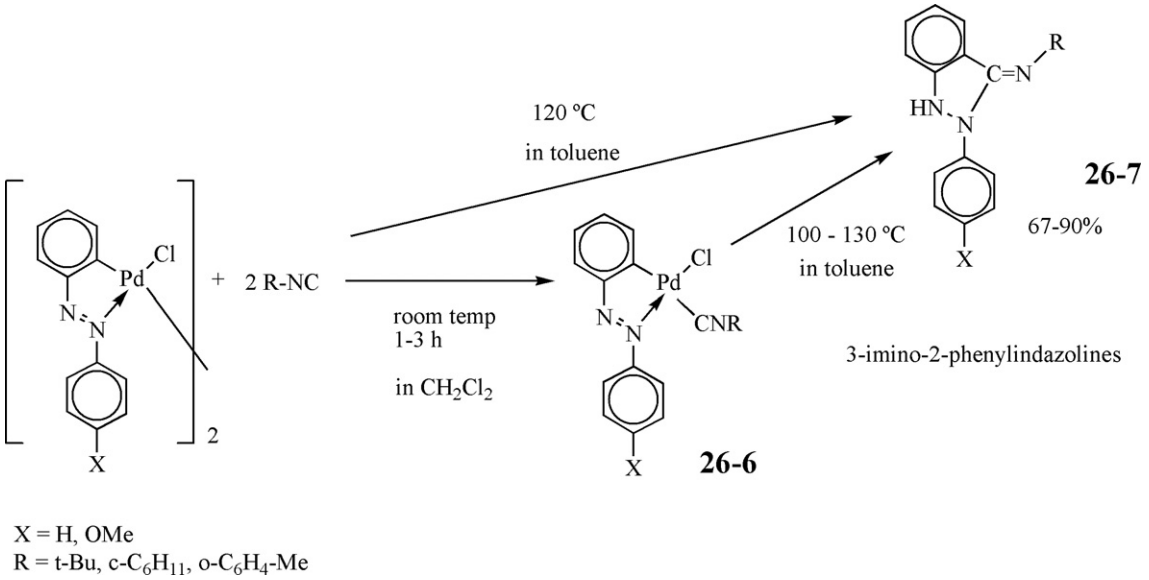
Scheme 5.



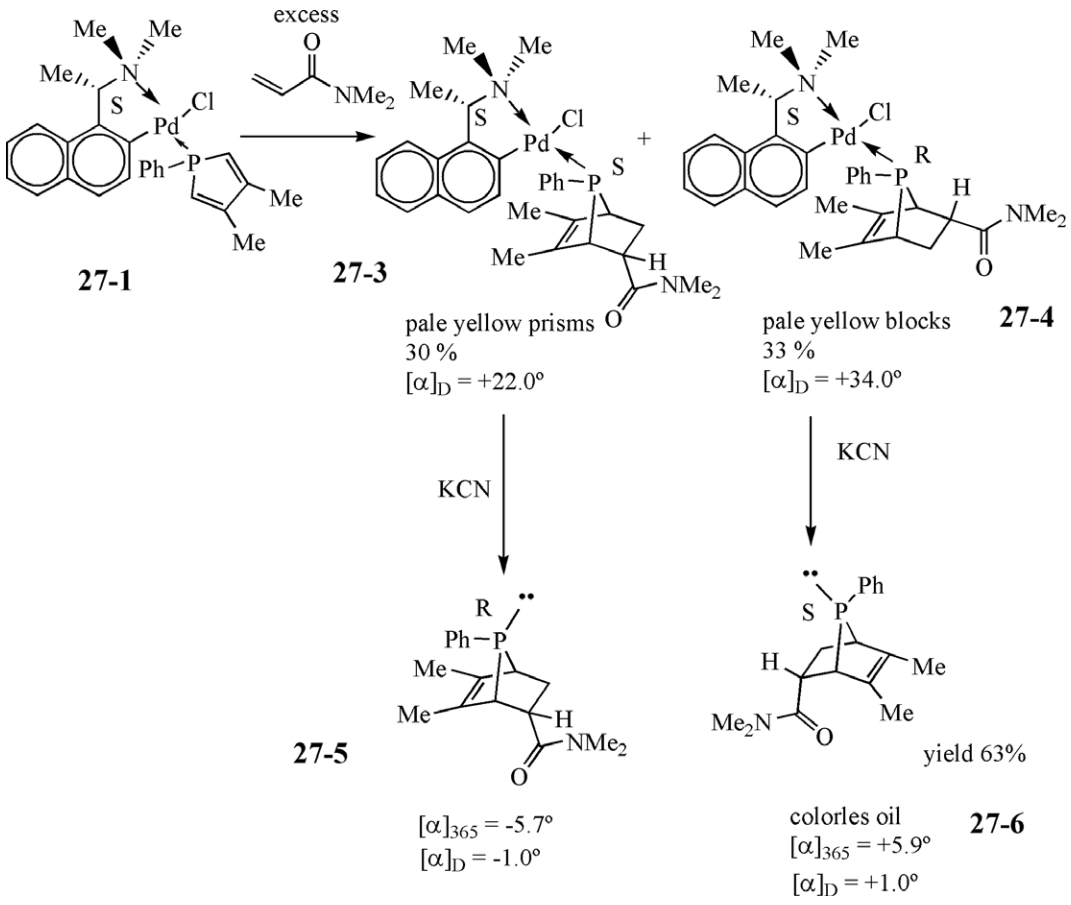
(27-1)

In the reactions with *N*,*N*-dimethylacrylamide, diastereomeric *cyclo*-adducts were separated as pale yellow prisms and pale yellow blocks by fractional crystallization with dichloromethane and diethyl ether. These molecular structures (compounds **27-3, 27-4**) were determined by X-ray structural analyses. Further, by treatment with aqueous potassium cyanide, the optically active phosphinoamides were isolated as both of pure R-*endo* **27-5** ($[\alpha]_{365} = -5.7$) and S-*endo* **27-6** ($[\alpha]_{365} = +5.9$) forms as shown in Scheme 7 [84].

As shown in Eq. (21-1), many kinds of organic compounds **21-2** are synthesized by the reaction of *cyclo*-metalated products **21-1** with many kinds of substrates **ZXm** by carbonylations, alkenylations, alkynylations, acylations, isocyanations and Diels–Alder Reactions described above. The other reactions such as transmetalations, deuterations [89], Ullmann type coupling reactions [90–92], C–C coupling reactions [93], halogenations[94], oxidations [95], resolutions [96–98], ring expansion reactions by insertion reactions of carbenes [99], the *ortho*-silylations of



Scheme 6.



Scheme 7.

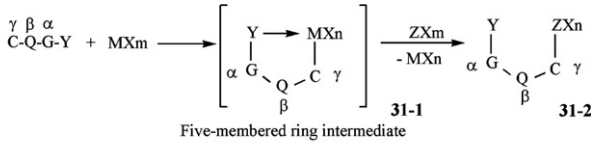
benzylidene amines with palladium or platinum catalysts [100,101], the asymmetric hydrogenations of dehydroamino acid derivatives [102], and asymmetric hydro phosphination reactions with chiral *N*,*N*-dimethyl-1-naphthylamine [103], are also actually utilized for many kinds of organic syntheses. In these reactions, the transmetalations, halogenations and deuterations, are already shown in Eq. (21-2) in Section 2.1.

3. Reactions with intramolecular five-membered ring intermediates

3.1. Introduction

In the *cyclo*-metalation reactions, if the *cyclo*-metalation products **31-1** are very labile, they easily react with the other substrates **ZXm** through intramolecular five-membered ring intermediates **31-1**, to give the substitution products **31-2** with a metal moiety **MXn** as shown in Eq. (31-1).

These reactions are the second type reactions of the intramolecular five-membered ring compounds in the organic syntheses. These reactions have been reported on carbonylations, cross-coupling reactions, hydroacylations, ring expansions, and carbocylization reactions, etc.

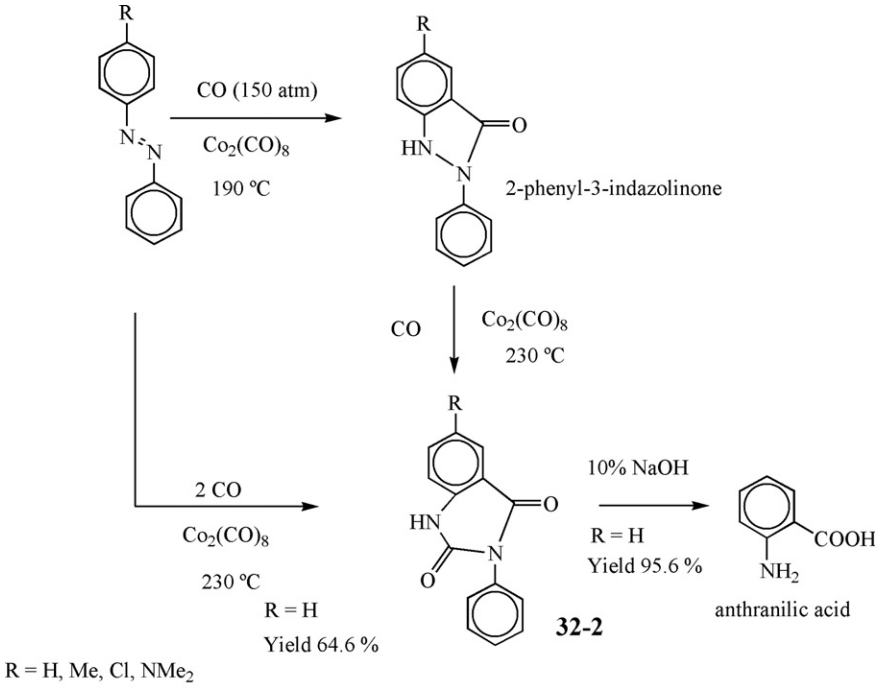


MXm, MXn = metal compounds
M = transition metals and main group metals, 65 kinds of metals
Y = N, P, O, S, etc.
G, Q = C, N, P, O, S, etc.
ZXm, ZXn = subtrates

(31-1)

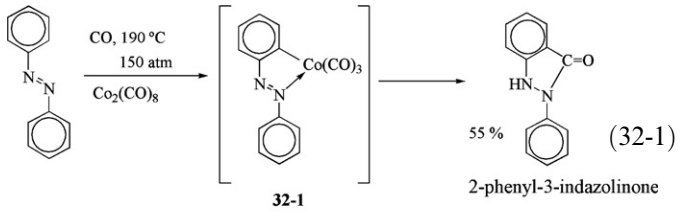
3.2. Carbonylations

In former chapter, the synthesis of 2-aryl-3-indazolines by the carbonylation of *cyclo*-palladation product of diazobenzene at 100 °C and under 150 atm of carbon monoxide was shown in Scheme 1 [47]. These reactions are the first type reactions of the intramolecular five-membered ring compounds in the organic syntheses. However, the 2-aryl-3-indazoline is also synthesized by the second type carbonylations. Because the 2-phenyl-3-indazoline is directly synthesized by the carbonylation of diazobenzene in the presence of $Co_2(CO)_8$ at a higher temperature (190 °C) and under the same high pressure of carbon monoxide as shown in Eq. (32-1) [104], and the reaction is presumed

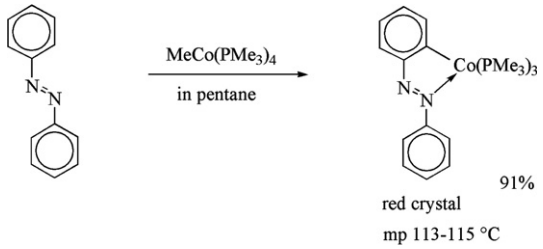


Scheme 8.

to proceed via the intramolecular five-membered ring intermediate **32-1**. Actually, similar *cyclo*-metalated organocobalt compound was prepared by the reaction of azobenzene with methyltetra(trimethylphosphine)cobalt as shown in Eq. (32-2) [105].



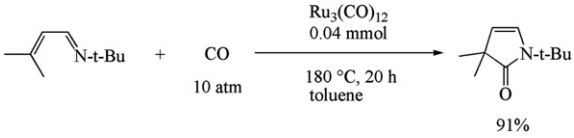
(32-1)



(32-2)

On the other hand, in the reaction at 230 °C, the 2-phenyl-3-indazolinone is further carbonylated to give 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline **32-2**. Anthranilic acid is easily prepared in a high yield by the hydrolysis of the quinazoline derivative **32-2**. Hence, the double carbonylation of diazobenzene at 230 °C is good method for the preparation of anthranilic acid as shown in Scheme 8 [104,106,107].

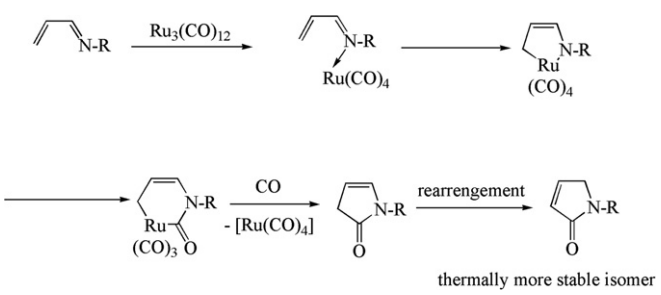
Catalytic carbonylative [4+1]*cyclo*-addtion is also considered to be one of carbonylation with ruthenium catalysts via the intramolecular five-membered ring structure. The substrates are α,β-unsaturated imines. A β,γ-unsaturated γ-lactam is prepared in a high yield by a reaction with carbon monoxide at 180 °C for 20 h in the presence of $Ru_3(CO)_{12}$ [108]. A representative reaction and its reaction mechanism are shown in Eq. (32-3) and Scheme 9, respectively [108].



(32-3)

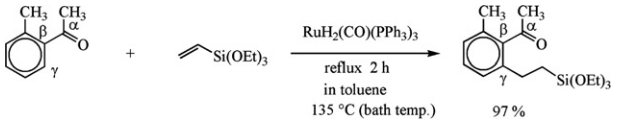
3.3. Cross-coupling reactions

Murai et al. [109–133] reported on many cross-coupling reactions regarding the representative substrates such as



Scheme 9.

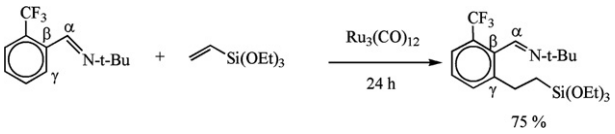
methyl phenyl ketone **1-8** and phenylimine **1-7** shown in Table 2 in the presence of metal catalysts such as ruthenium triphenylphosphines. A representative example of the C–H/olefin coupling reaction is given in Eq. (33-1) [115].



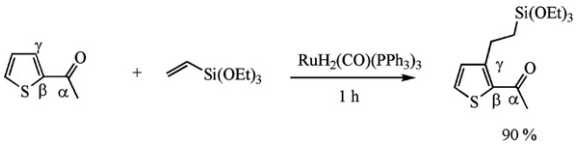
(33-1)

Ruthenium complexes having three triphenylphosphine ligands such as $RuH_2(CO)(PPh_3)_3$ or $Ru(CO)_2(PPh_3)_3$ are the best catalysts [115]. They presumed to act via the *ortho*-metalation of the triphenylphosphine ruthenium catalyst and the reductive elimination of its metal element via the five-membered ring structure of the ruthenium catalyst **33-1** is shown in Scheme 10 [115].

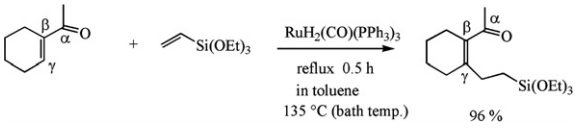
As shown in Scheme 10, these metal compounds act as the catalyst because these *cyclo*-metalation products are very reactive and they easily react with other reagents. The substrates of these reactions are not only aromatic compounds such as methyl phenyl ketone (Eq. (33-1)) [109–111,115] and phenylimine (Eq. (33-2)) [109,115] but also nonbenzonoid compounds such as thiophene methyl ketone (Eq. (33-3)) [109,111], and cyclohexene methyl ketone (Eq. (33-4)) [115], etc.



(33-2)

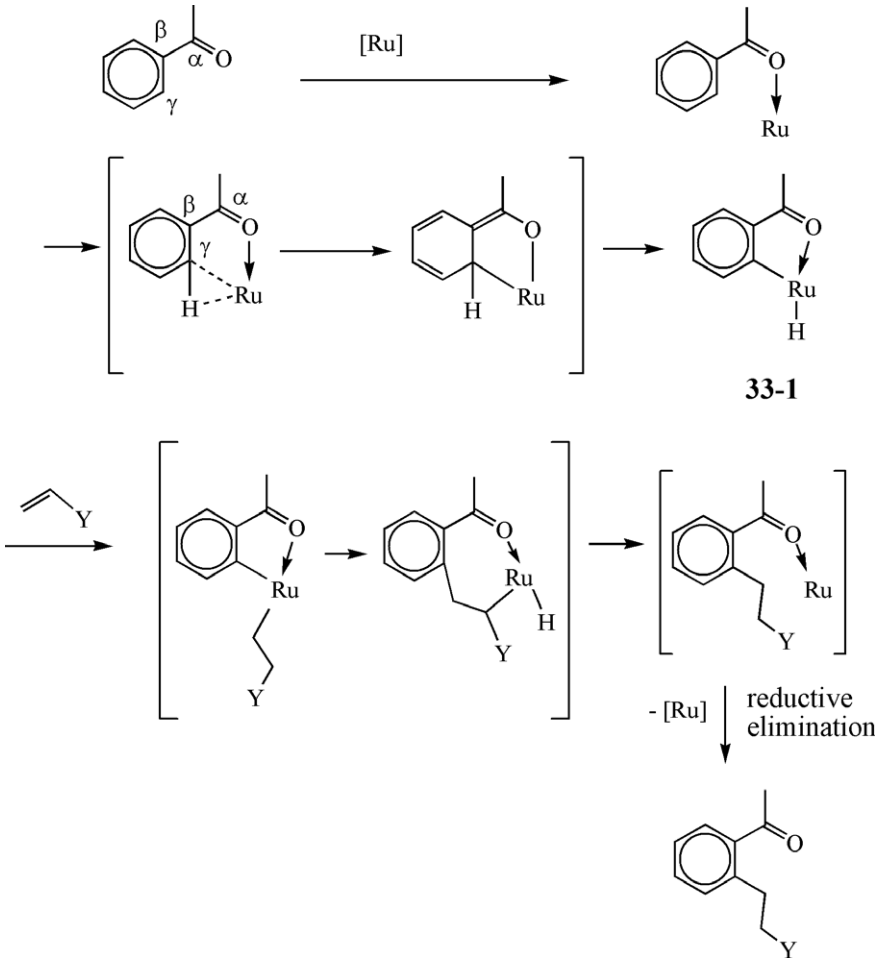


(33-3)



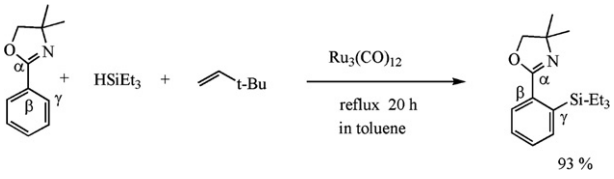
(33-4)

In these reactions of ketones or imines, which have a reaction site at the γ-position to the coordinating atom, with vinylsilanes in the presence of a ruthenium catalyst, the CH/olefin coupling reactions proceed as shown in Eqs. (33-1,33-2,33-3,33-4). However, as shown in



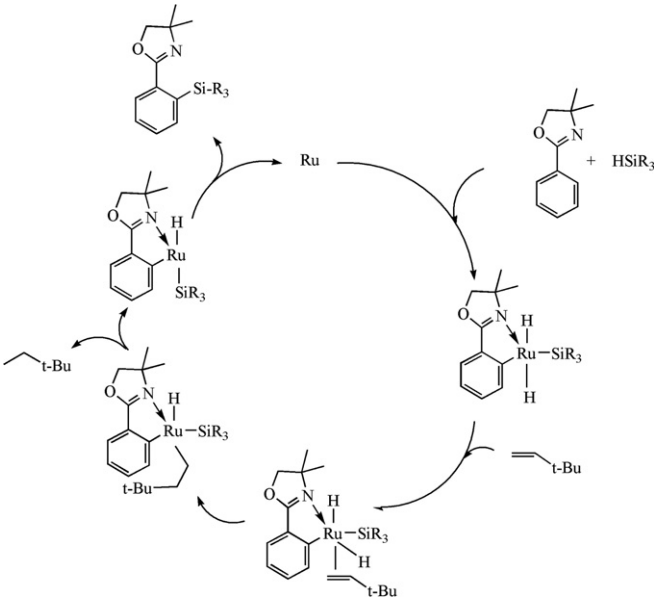
Scheme 10.

Eq. (33-5), the CH/SiR_3 coupling reactions proceed only in the presence of very reactive trialkylhydrosilanes. At first, the nitrogen atom of the oxazoline ring coordinates with the ruthenium atom, the activated ruthenium atom bonds with the *ortho*-carbon of phenylring (γ-position) and trialkylhydrosilanes. Then the olefins coordinate with Ru, and inserted into a Ru–H bond to give an alkyl derivative. After the reductive elimination of a corresponding alkane, the trialkylsilylruthenium compounds are formed. From this intermediate, its reductive elimination, produces a C-Si bond and leads to the corresponding silylation products, and active ruthenium(0) species is regenerated as shown in Scheme 11 [132].

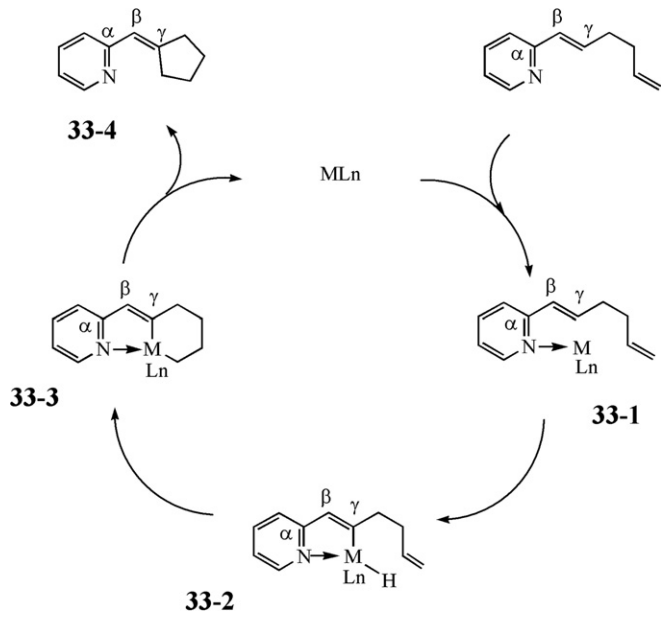


(33-5)

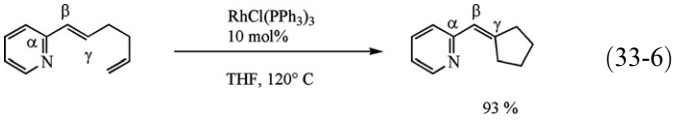
Intramolecular C–H/olefin coupling proceeds by the reaction of 1-(2-pyridyl)-1,5-dienyl compounds in the presence of rhodium compounds as shown in Eq. (33-6) [108,119,122]. At first, the metal (**33-1**) is activated by the coordinating atom, then the activated metal bonds with the γ-carbon atom by the insertion of vinylic C–H bond to form a five-membered ring and metal hydrogen bond (**33-2**). The intramolecular insertion of an olefin into the metal-hydrogen bond gives a tricylic intermediate (**33-3**), then the reductive elimination of metal atom forms a cyclic product (**33-4**) as shown in Scheme 12 [118].



Scheme 11.



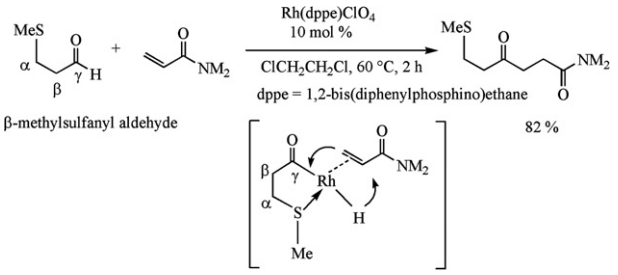
Scheme 12.



(33-6)

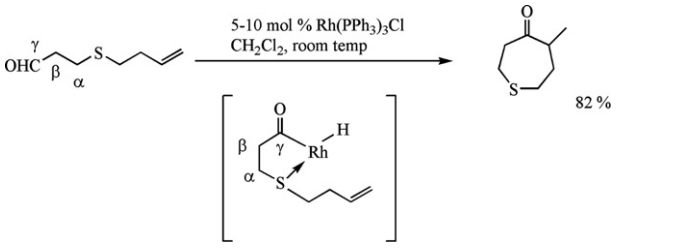
3.4. Hydroacylation

In the reactions of sulfanyl aldehydes with alkenes in the presence of a rhodium catalyst, hydroacylation proceeds via an intramolecular five-membered ring intermediate and by the insertion of an alkenyl moiety into between rhodium and carbonyl carbon at the γ-position to the coordinating atom (S) [134–136]. For example, β-methylsulfanyl aldehyde reacts with an amide alkene to give an intermolecular hydroacylation product by the insertion of an amide alkenyl moiety in a high yield as shown in Eq. (34-1) [134].

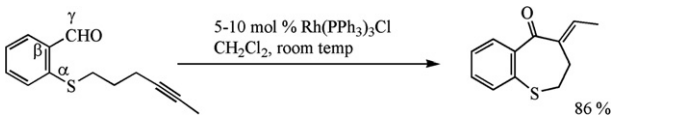


(34-1)

On the other hand, in the reaction of sulfanyl aldehydes having the a carbon–carbon double bond at the terminal position or a carbon–carbon triple bond, metal-catalyzed cyclizations by an intramolecular hydroacylation proceed via the intramolecular five-membered ring intermediate as shown in Eqs. (34-2) and (34-3), respectively [136].



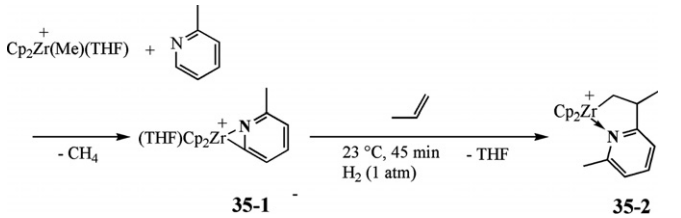
(34-2)



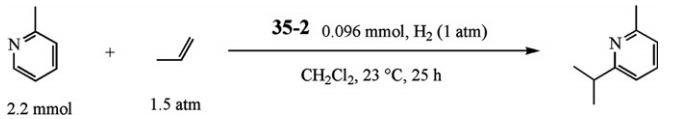
(34-3)

3.5. Ring expansion reactions

As three-membered ring compounds have generally ring strain, the ring expansion reactions often proceed via the intramolecular five-membered ring intermediates. For example, cationic Zr alkyl complexes react with 2-Me-pyridine (α-picoline) to give a zirconium pyridine three-membered ring compound **35-1**. The reaction with propene produces the ring expansion compound having a five-membered ring compound **35-2** as shown in Eq. (35-1) [137]. The coupling of propene and α-picoline is indeed catalyzed by the zirconium five-membered ring compound **35-2** in the presence of H_2 as shown in Eq. (35-2). This coupling reaction by the ring expansion with a zirconium compound and hydrogenolysis are considered as shown in Scheme 13 [137].



(35-1)

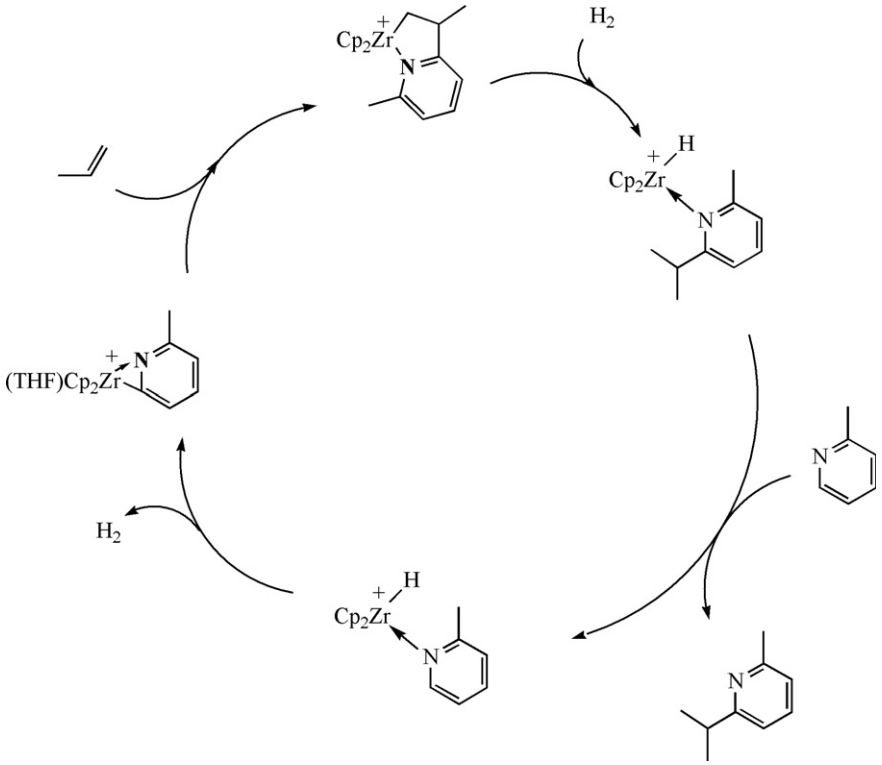


(35-2)

3.6. Carbocyclizations and other reactions

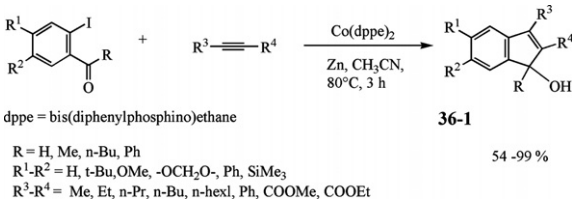
o-Iodophenyl ketones or aldehydes react with alkynes to give regioselectively carbocyclic compounds **36-1** in high yields in the presence of cobalt catalysts via the five-membered phenylcarbonyl compounds **1-8** in Table 2 as shown in Eq. (36-1) (see Compound 24-4 in Scheme 4) [138,139].

Its reaction mechanism is considered as follows: The reduction of Co(II) to Co(I) by zinc dust initiates the catalysis. The cobalt catalyst is activated by the coordination of the oxygen in the *o*-iodephenylaldehydes or the ketones and yield *cyclo*-metalated products **36-2** are produced. The five-membered ring compounds **36-2** undergo an insertion with an alkyne to produce a seven-membered cobaltacycle **36-3**. The intramolecular nucleophilic additin of the cobalt–carbon bond in **36-3** to the carbonyl group leads



Scheme 13.

to the formation of a cobalt alkoxide **36-4**. The reduction of the latter by zinc powder affords a Co(I) alkoxide **36-5**. The transmetalation of **36-5** with ZnI_2 gives an active Co(I) species and the corresponding zinc alkoxide **36-6**, which is converted to a final product after hydrolysis (see Scheme 14).



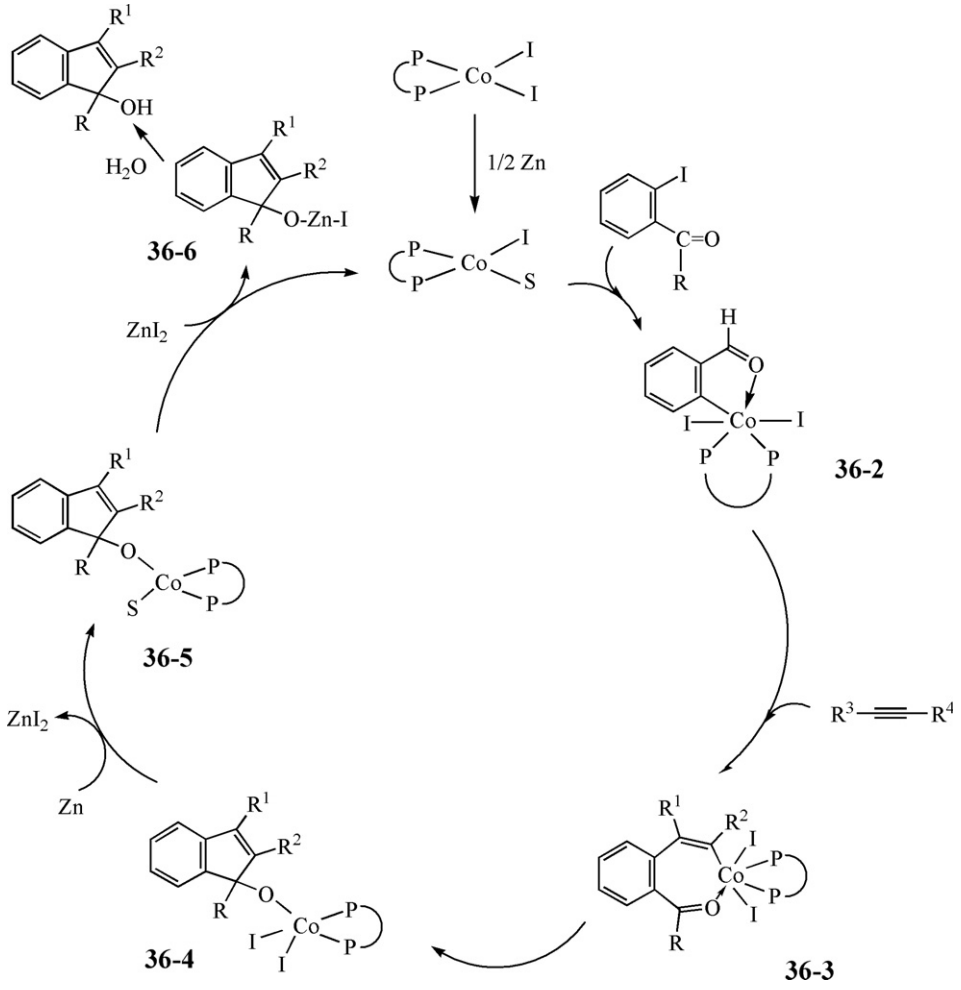
(36-1)

The other reactions via the intramolecular five-membered ring intermediates are decarbonylative cleavages with organoruthenium catalysts [140], asymmetric hydrogenations with rhodium catalysts [141], reductive eliminations with rhodium catalysts [142], the one-pot preparations of chiral homoallylic alcohol or amine derivatives by the reactions of vinylic copper reagents, bis(iodomethyl)zinc carbenoid and aldehyde or *N*-sulfonyl aldimines[143], CO/olefins copolymerizations [144–148], lactone formations [149], the hydrolysis of methyl parathion [150], and the acetoxylations of *O*-methyloxime with palladium catalysts [151].

4. Metal-catalyzed reactions with intramolecular five-membered ring compounds

4.1. Introduction

Many kinds of metal compounds are easily synthesized by *cyclo*-metalation regarding not only transition metal compounds but also main group metal compounds. Generally, these compounds are organometallic intramolecular five-membered ring compounds. These compounds show various kinds of catalytic activity. These are generally easily handled because these are relatively stable compounds by the chelating effect. Reactions with these compounds not only regeiospecifically but also stereospecifically proceed because they have one reaction site at the metal–carbon bond in the metallacycle five-membered ring, that is, the carbon at the γ-position to the coordinating atom and some of them have bulky groups in the ring systems.



Scheme 14.

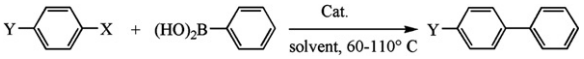
These reactions include cross-coupling reactions, rearrangements, metatheses, reductions and other reactions.

4.2. Cross-coupling reactions

Kharasch, Negishi, Stille, Suzuki, Sonogashira, and Heck reactions, are metal-catalyzed cross-coupling reactions. The first four reactions, that is, Kharasch, Negishi, Stille and Suzuki reactions are the coupling reactions of aryl halides with Grignard reagents, organozinc, organotin and organoboron, respectively. The fifth Sonogashira reactions are the reactions of terminal alkynes with aryl halides or alkyl halides in the presence of amines with palladium phosphine catalysts. The Heck reactions are the reactions of aryl halides with alkenes in the presence of palladium catalysts and are the most industrially utilized reactions [42,152–177].

In 1999, *cyclo*-palladated tolyl phosphine compounds were reported to show highly catalytic activities for not only the Heck reactions of which turnover numbers (TNO) is, e.g., up to 1,000,000, but also all the other metal-catalyzed cross-coupling reactions [152,156]. In 2005, the Heck reactions with naphthyl phosphines [166] or *N*-heterocyclic carbene phospha-palladacycles [172] were also reported to show highly catalytic activities, e.g. the TON of up to 300,000 and 10,800, respectively.

In the Suzuki reactions, palladacycle catalysts show very high TON's as shown in Eq. (42-1) and Table 3 [173–176]. Especially, phosphite palladacycles **42-2** shows the highest TON, 10^8 [174,175]. *N*-(2-(Diphenylphosphino)phenyl)-2,6-diidopropylanilinde palladacycles **42-3** do not have a metal–carbon bond, but, they also show high catalytic activities [176].

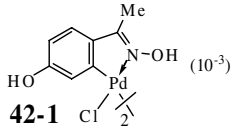
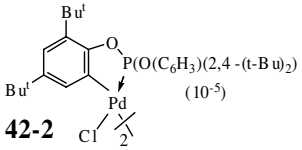
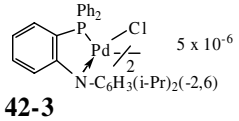
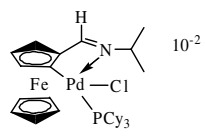


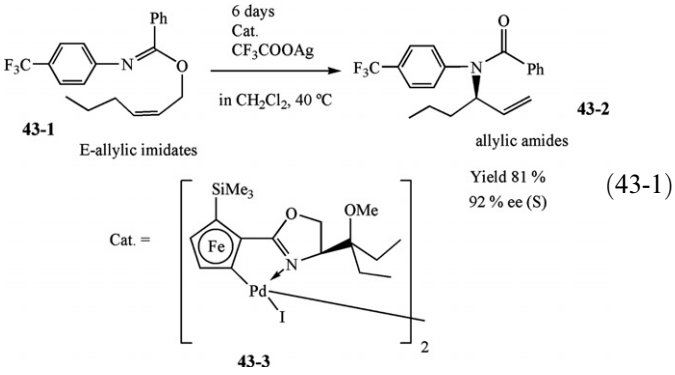
(42-1)

4.3. Rearrangements

With chiral *cyclo*-palladate ferrocenyl compounds, allylic imidates rearrange to allylic amides. By using the catalysts having planar chiral elements such as Pd, O, N, C and Si, their enantioselectivities were dramatically improved. For example, a *cyclo*-palladate ferrocenyl oxazoline 3-methoxy-3-pentyl derivative **43-3** was activated in CH_2Cl_2 by deiodination with CF_3COOAg to give the rearranged allylic amide **43-2** in a high yield and high enantioselectivity from *E*-allylic imidate **43-1** as shown in Eq. (43-1) [178].

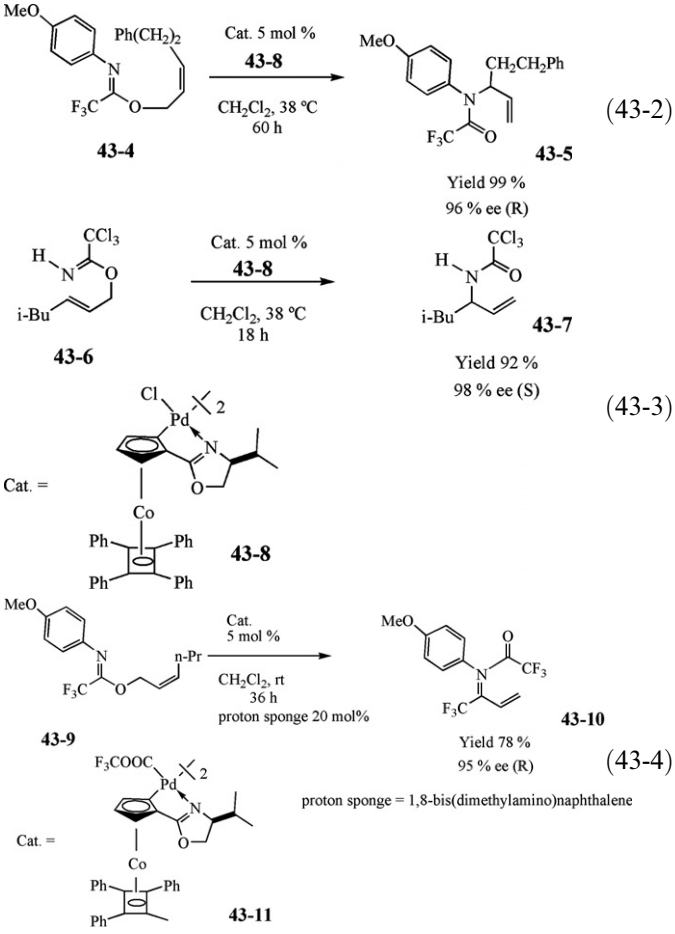
Table 3
Reaction conditions and catalyst studies on the Suzuki coupling of *p*-halobenzene derivaitives and phenylboric acid [173–177]

Catalyst (mol%)	Y(X)	Solvent	*T* (°C)	Time (h)	% Yield	TON	TOF (h^{-1})	Ref.
 **42-1**	$CH_3CO(Br)$	MeOH–H_2O (3/1)	60	2	100	100,000	50,000	173
 **42-2**	$CH_3CO(Br)$	toluene	110	18	q.y	100,000,000		174,175
 **42-3**	MeO(Br)	dioxane	110	12	100	10,000,000		176
 **42-4**	$CH_3CO(Cl)$	dioxane	100	10	98.7			177



(43-1)

Furthermore, with a *cyclo*-palladate (η^4-tetraphenylcyclobutadiene)cobalt oxazoline propyl chloro-bridged compound **43-8** and a trifluoroacetate-bridged compound **43-11** as the catalysts, the rearrangement of *N*-(4-methoxyphenyl)trifluoroacetimidate **43-4** [179], allylic trichloroacetimidate **43-6** [180], and *N*-(4-methoxyphenyl) tifluoroacetimidate **43-9** [181] to the correspond amides (**43-5**, **43-7**, **43-10**) proceeds in high yields and high enantiomeric purities without using a silver salt as an activator as shown in Eqs. 43-2,43-3,43-4, respectively.



(43-2)

(43-3)

(43-4)

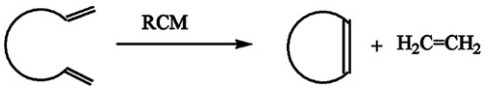
4.4. Metathesis

Metathesis means "change places". Metathesis reaction is an exchange reaction between mainly two olefins in which alkylidene groups are interchanged. The metathesis reactions use catalyst systems based on molybdenum, tungsten or ruthenium. Especially, molybdenum and ruthenium–carbene complexes have been a useful tools in synthetic organic chemistry since 1990. The 2005 Nobel prize for chemistry went to Y. Chauvin, who elucidated the reaction mechanism of the metathesis, R.H. Grubbs and R.R. Schrock, who found Grubbs' catalyst and Schrock catalyst, respectively.

The ruthenium–carbene complex **44-1** is a commercially available excellent catalyst as the Grubbs' catalyst. However, the intramolecular five-membered ring compounds **44-2**–**44-4**, which are activated by coordination with an ether oxygen atom, are much more active to electron-deficient olefins, and are stable to air (see Charts 1–4).

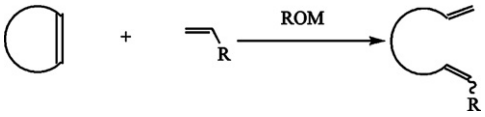
Recently, many ruthenium carbene five-membered ring compounds are reported to show good activities for the metathesis [182–203]. Many types of reactions such as ring-closing metathesis, ring-opening metathesis, cross metathesis, enyne metathesis and diyne metathesis proceed with these catalysts as shown in Eqs. 44-1,44-2,44-3,44-4,44-5 [189].

Ring- Closing Metathesis (RCM)



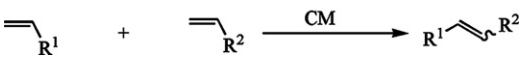
(44-1)

Ring-Opening Metathesis (ROM)



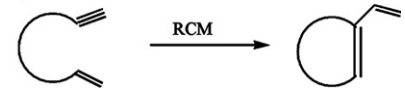
(44-2)

Cross Metathesis (CM)



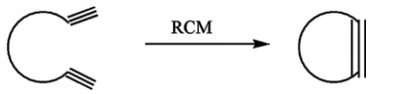
(44-3)

Enyne Metathesis



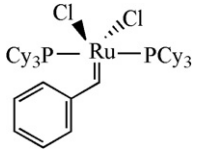
(44-4)

Diyne Metathesis



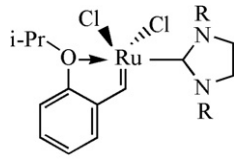
(44-5)

For example, the ring-closing metathesis (Eq. (44-1)) of an acyclic diene easily proceeds at a room temperature in a high yield in the presence of 1,3-dimesityl-4,5-dihydroimi-



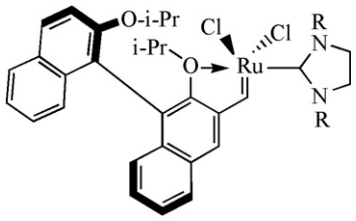
44-1

Chart 1.



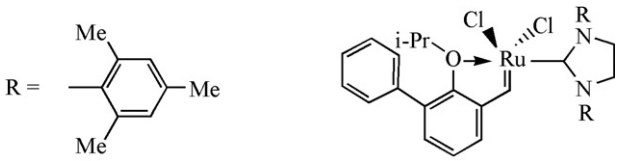
44-2

Chart 2.



44-3

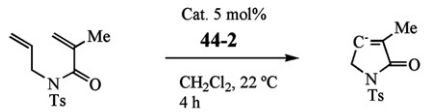
Chart 3.



44-4

Chart 4.

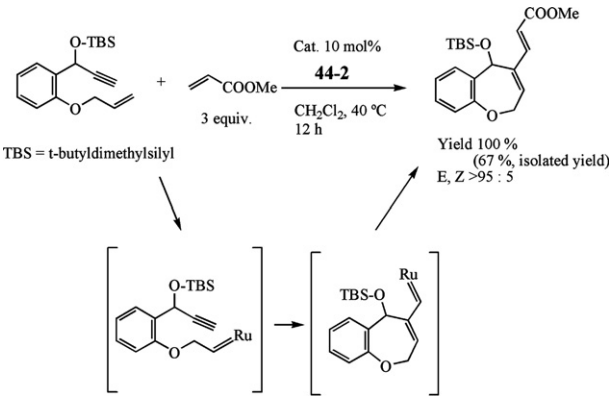
dazole-2-ylidene ruthenium catalyst **44-2** as shown in Eq. (44-6) [182–185].



(44-6)

Ts = tosyl, *p*-toluenesulfonyl

A tandem (domino) cross-metathesis reaction between an enyne and 3 equivalents of a conjugated alkene proceeds in dichloromethane at 40 °C for 12 h in a high yield in the presence of the same ruthenium carbene five-membered ring compound **44-2** as shown in Eq. (44-7) [185,186].

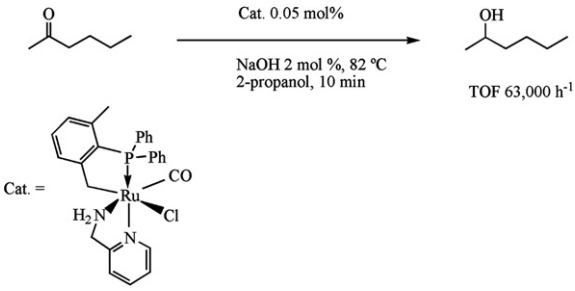


TBS = t-butyldimethylsilyl

(44-7)

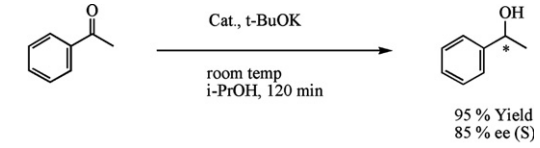
4.5. Reductions and other reactions

Dialkyl, alkyl aryl and diaryl ketones can be converted into corresponding alcohols quantitatively in the presence of an intramolecular five-membered ruthenium xylyl phosphine compound. For example, methyl butyl ketone is quantitatively converted into an alcohol within a few minutes at 82 °C in 2-propanol in the presence of ruthenium catalyst and sodium hydroxide. The turnover frequency at 50% conversion is 63,000 h^{-1} as shown in Eq. (45-1) [204].

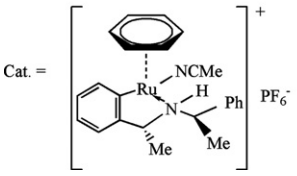


(45-1)

On the other hand, with an enantiopure aromatic secondary amine η^6-benzene ruthenacycle, the reduction of methyl phenyl ketone at a room temperature in the presence of *t*-BuOK proceeds in a high yield enantioselectively as shown in Eq. (45-2) [205].



(45-2)



The reactions with the intramolecular five-membered ring compounds as the catalysts, are cross-coupling reactions, rearrangements, metatheses and reductions as described above. The other reactions are intramolecular alkyne hydroalkoxylations and hydroaminations [206]. The catalysts are a *cyclo*-metalated ketone or an ester carbonyl oxygen-coordinated iridium diphosphine complex.

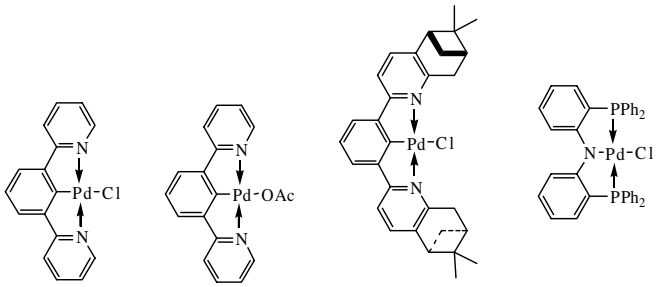
5. Pincer metal-catalyzed reactions

5.1. Introduction

Cyclo-metalated compounds are generally bidentate cyclic compounds. Recently, reports on many kinds of pincer cyclic compounds have been published. These compounds are tridentate cyclic compounds. The reactions with the tridentate pincer compounds are expected to show a higher catalytic stability than that of the bidentate compounds. These reactions with the pincer compounds

Table 4
Heck reactions of iode benzene and olefins in the presence of pincer palladium compounds [207,208,210]

Catalyst (mol%)		R	Solvent	T (°C)	Time (h)	% Yield	TON	TOF (h^{-1})	Refs.
52-1	0.001	COOMe	DMF	135	0.33	93	9.3×10^4	2.8×10^3	208
52-2	0.001	COOMe	DMF	110	14	99	10^5	7.1×10^3	208
52-3	0.24	Ph	DMF	110	14	97 (conversion)		400	210
52-4	0.000002	Ph	NMP	160	39	91	4.55×10^7		207

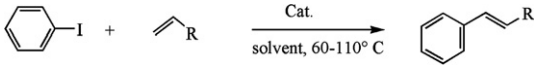


52-1 **52-2** **52-3** **52-4**

are expected to be stereospecific, because these are generally bulky compounds. These compounds show some similar catalytic reactions such as cross-coupling reactions and reductions to the catalytic reactions of bidentate *cyclo*-metalation compounds, and the other reactions are Michael addition, dehydrogenations, Diels–Alder reactions, etc.

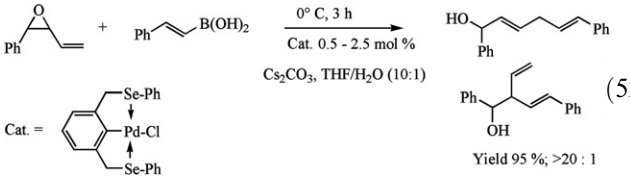
5.2. Cross-coupling reactions

Pincer compounds are also used as the catalysts of the metal-catalyzed cross-coupling reactions described in the Section 4.2 [207–213]. For example, the Heck reactions [207–210] with the pincer palladium compounds, proceed in high yields and high TON's as shown in Eq. (52-1). The [PNP]PdCl pincer compound **52-4** does not have a metal–carbon bond, that is, it is not an organometallic catalyst, but it also achieved a very high TON (4.55×10^7) [207] (see Table 4).

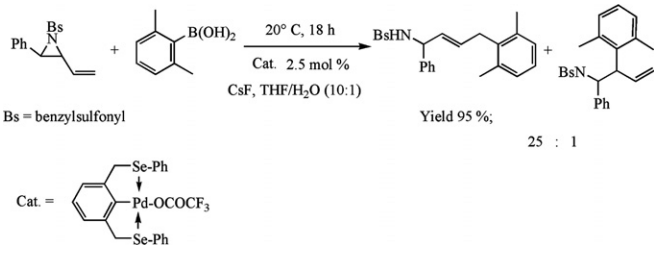


(52-1)

The cross-coupling reactions of vinyl epoxides or aziridines with organoboronic acids proceed in the presence of 0.5–2.5 mol% of the palladium pincer compounds as shown in Eqs. (52-2) and (52-3), respectively. These reactions proceed under mild reaction conditions, and afford allyl alcohols and amines with high regioselective values and in high yields [213].



(52-2)

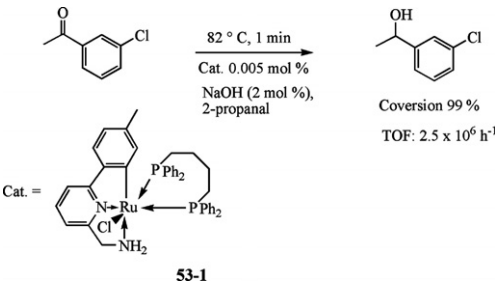


(52-3)

5.3. Reductions

Pincer organometallic compounds are reported regarding to largely two types of compounds, PCP and NCN transition-metal complexes [214,215]. However, the ruthenium pincer CNN compounds were also applied to the hydrogen-transfer reductions of ketones.

For example, 6-(4′-methylphenyl)-2-pyridylmethylamine ruthenium pincer compound **53-1** are a highly efficient catalyst in transfer hydrogenation involving 2-propanol to perform quantitatively the reduction of ketone with a very low loading and in a short time as shown in Eq. (53-1) [216].



53-1

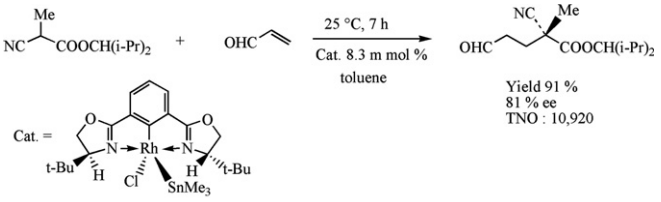
(53-1)

5.4. Michael addition reactions

Michael addition reaction is generally an addition of an active methylene such as a malonate and nitroalkane to

activated olefins such as α,β-unsaturated carbonyl compounds in the presence of a base.

Recently, pincer metal compounds such as those with rhodium [217], palladium [218,219] and platinum [220] are used for the Michael addition reactions as the catalysts. For example, the addition of an α-cyanopropionate to acrolein under mild and neutral conditions in the presence of a bis(oxazolinyl)phenylstannane-derived rhodium complex **54-1** proceeds enantioseletively in a high yield and high TON as shown in Eq. (54-1) [217].



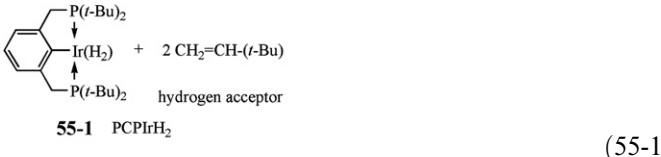
54-1

(54-1)

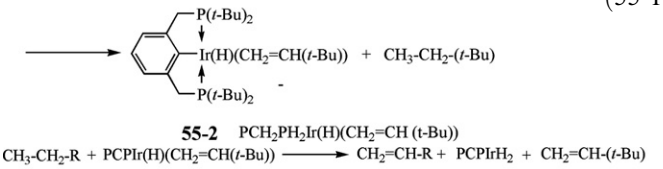
5.5. Dehydrogenations

A pincer complex ($PCPIrH_2$) ($PCP = 2,6\text{-}C_6H_3(CH_2P(t\text{-}Bu_2))_2$, **55-1**) is widely applied for the selective dehydrogenations of alkanes and alkyl groups [214,221–223]. In the dehydrogenations, *t*-butylethylene acts as a hydrogen acceptor for a substrate in the reaction system with the iridium pincer catalyst **55-1**. The two moles of the *t*-butylethylene convert the iridium monohydride to an active iridium catalyst **55-2**, and *t*-butylethane, and the active iridium catalyst **55-2** reacts with alkanes or alkyl groups to give the dehydrogenation products, *t*-butylethylene and the pincer catalyst **55-1** as shown in Eqs. (55-1) and (55-2), respectively.

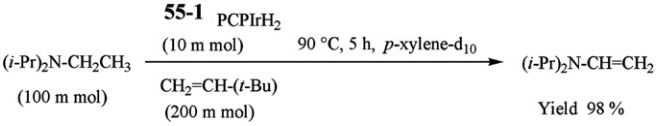
For example, by heating the solution of *N*,*N*-di(isopropyl)ethylamine, the iridium catalyst **55-1** and *t*-butylethylene (hydrogen acceptor), at 90 °C in *p*-xylene for 5 h yields vinyl *N*,*N*-dipropylamine in 98% yield as shown in Eq. (55-3) [223].



(55-1)



(55-2)

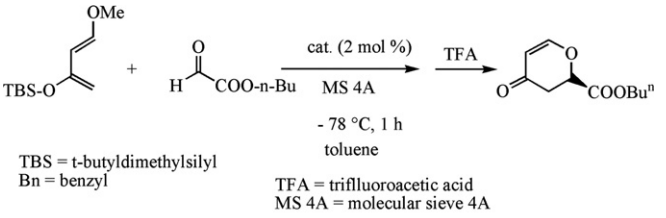


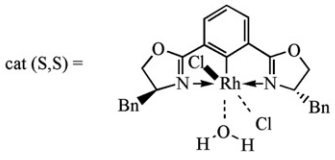
(55-3)

5.6. Diels–Alder reactions and other reactions

Tridentate bis(oxazolinyl)pyridinyl rhodium or ruthenium pincer complexes are useful for hydrosilylations, and *cyclo*-propanations as the catalysts. However, These NNN type inorganic pincer complexes are not so stable as phosphine or salen type pincer complexes are. But, an organometallic tridentate bis(oxazolinyl)phenyl NCN type is stable. This optically active pincer NCN type complexes act as efficient catalysts for the enantioselective hetero Diels–Alder reaction of Danishefsky's diene with glyoxylates [224].

For example, the asymmetric hetero Diels–Alder reaction of 1-methoxy-3-[(*t*-butyldimethylsilyl)oxy]-1,3-butadiene (Danishefsky's diene) with *n*-butyl glyoxylate is catalyzed highly enantioselectively with *cis*(*endo*)-diastereoselectivity by chiral bis(oxazolinyl)phenylrhodium aqua dichloride **56-1** as shown in Eq. (56-1) [225].





56-1

(56-1)

The other metal-catalyzed reactions with five-membered pincers are asymmetric aldol-type condensations [215, 224, 226,227], *cyclo*-propanations [229], enantioselective allylations [230], reductive eliminations [231], transfer hydrogenations [214,215,227,228], hydroaminations [215], polymerizations [215], etc. [224,232].

6. Concluding remarks

Intramolecular five-membered ring compounds are easily synthesized by *cyclo*-metalation with metal compounds. Many organic compounds are synthesized by the reactions of the intramolecular five-membered ring compounds with substrates. These synthetic reactions have following three advantages: The first is that these *cyclo*-metalations proceed very easily proceed by the strong activation of metal atoms caused by the coordination of a coordinating atom such as N, P, O and S. The second is that the reactions with these *cyclo*-metalation products regiospecifically proceed easily because the reactions proceed at the γ-position to the coordinating atom. The third is that many kinds of catalytic reactions proceed because almost all transition

metals and main group metals, in total of 68 kinds of metals are available for these application reactions.

There are three types of reactions with these intramolecular five-membered ring compounds in organic syntheses: The first type reactions are applications of the ease of the synthesis and the high stability of the five-membered chelate ring. Some of them are air-stable compounds or moisture-stable compounds though these are mainly transition metal compounds. However, they are very reactive with the substrates.

The second type reactions are reactions via intramolecular five-membered ring intermediates, because the intermediates are very reactive and labile. The third types of reactions are reactions as organometallic catalysts because there are many active organometallic compounds. Many kinds of organometallic pincer compounds are also used as the third applications.

The first reactions are carbonylations, alkenylations, alkynylations, acylations, isocyanations, asymmetric Diels–Alder reactions, etc. The second reactions are carbonylations, cross-coupling reactions, hydroacylations, ring expansion reactions, carbocyclizations, etc. The third reactions are cross-coupling reactions, rearrangements, metatheses and reductions, etc. The pincer metal-catalyzed reactions are cross-coupling reactions, reductions, Michael additions, dehydrogenations, Diels–Alder reactions, etc.

Recently, these many reactions are utilized for organic syntheses, especially for pharmaceuticals and fine chemicals.

Acknowledgment

I should like to express my sincere appreciation to Dr. Sumio Chubachi for reading the full manuscript which enhanced its accuracy and clarity, and for providing much valuable constructive criticism.

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