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Review

Intramolecular five-membered ring compounds and their applications

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Contents

Abstract

Bäller and Müller reported the first intramolecular five-membered ring with a main group element in 1955 when they synthesized an organoaluminium compound. These five-membered ring compounds are very easily and selectively synthesized when compared with other compounds containing four-, six- and seven-membered rings. Many such compounds, especially, organotransition metal compounds have been isolated by cyclometalation since the 1970s with a wide variety of metals. These organometallic compounds are highly reactive and are also used as high turn over catalysts in dehydrogenation and metal-catalyzed cross-coupling reactions. They are useful in organic syntheses

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doi:10.1016/j.ccr.2004.05.011

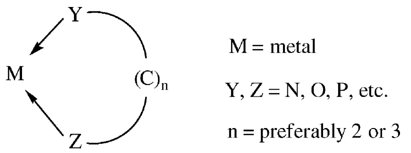
such as alkenylation, alkynylation, acylation, carbonylation, halogenation, reactions with isocyanates, thermal degradations, reactions of chiral compounds with amino acids, enantioselective rearrangements and asymmetric Diels–Alder reactions.

Keywords: Intramolecular compounds; Five-membered ring; Cyclometalation; Carbonylation; Metal-catalyzed cross-coupling

1. Introduction

Chelate compounds are generally known as stable inorganic ring compounds. In these chelate compounds, five-membered ring compounds are well known to be more stable than four- and six-membered ring compounds [1]. In the inorganic chelate compounds, central metals are generally coordinated with two coordinating atoms as shown in general formula **1**.

There are two types of organometallic intramolecular coordination compounds, i.e. σ-coordination compounds and π-coordination compounds, see formula **2** [2–5]. In the σ-coordination compounds, coordination is with atoms such as O, N, S, P, and As. The coordination in π-coordination compounds involves coordination groups such as cyclopentadienyl, an alkenyl, an allyl, an alkynyl, a dienyl and an aryl [4]. Since 1970, many reviews [2,3,6–21] and monographs [4,5] have been published dealing with organometallic intramolecular ring species.



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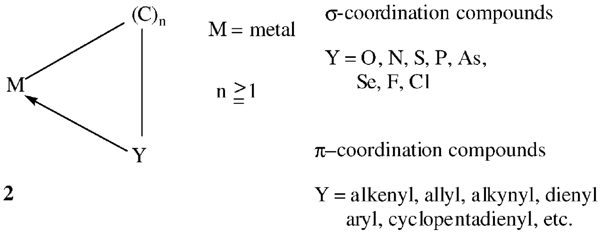

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Organometallic compounds are generally unstable compounds because they have an unstable metal–carbon bond. However, organometallic intramolecular compounds with organic rings that form chelates are comparatively stable [4]. In the σ-coordination compounds, those with five-membered ring compounds are more stable than those with four- and six-membered ring compounds.

The intramolecular five-membered ring compounds are very easily synthesized with almost every type of metal. Hence, they are utilized as intermediates for organic syntheses. They are especially used in regio-selective organic syntheses because generally, only the formation reactions of five-membered rings proceed easily. They also show high reactivity because of the presence of reactive metal–carbon bonds which makes them useful as excellent catalysts.

This article describes intramolecular five-membered ring compounds and their applications. This research was presented recently at the 10th International Symposium on Inorganic Ring Systems at Burlington, VT, USA [22].

2. Intramolecular five-membered ring compounds

2.1. High stability of intramolecular five-membered ring compounds

Ring compounds that are chelates are commonly more stable than non-cyclic similar compounds [23]. Ring sizes are usually five- or six-membered. In the book, "Coordination Chemistry", published in 1965, Basolo and Johnson [1] stated: "In general, it has been observed that for ligands that do not contain double bonds, those that form five-membered metal-chelate rings give the most stable products. Chelate rings that contain either four atoms or more than six atoms have been observed, but they are relatively unstable and uncommon".

The chelate effect occurs when a chain compound is stabilized by changing it to the ring compound [24–26]. For example, when Ni^{2+}(aq) reacts with NH_3 (aq) or ethylenediamine (en), the overall equilibrium constants ($\log \beta$) are as follows:

$[Ni(NH_3)_6]^{2+}$ (aq) (no ring) 8.61

$[Ni\,en_3]^{2+}$ (aq) (three rings) 18.28.

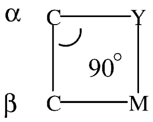
The system $[Ni\,en_3]^{2+}$ in which three chelate rings are formed, is nearly 10^{10} times more stable than when no ring is formed [24].

The chelate effect is partly attributable to the fact that the simultaneous rupture of both bonds holding the ligand to the metal is highly improbable, and if only one bond breaks, there is a high probability that the broken bond will be reformed before the second bond is ruptured. As the ligand chain length between one donor atom and the terminal carbon atom increases, the chance for reformation of the broken bond declines; thus, large rings usually show a decrease in stability [27].

In the cases of polydentates, the stability becomes higher because the probability of cutting at two or more points at the same time is less than a single bond [27,28]. Hence, the five-membered ring of two or more polydentates is more stable than a single five-membered ring. For example, bidentate pincer complexes are usually more stable than monodentate five-membered ring compounds as shown in Section 3.7.

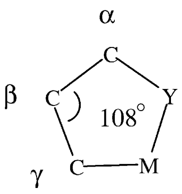
2.2. Comparison of five-membered ring compounds with four- and six-membered compounds

The interior angles of a regular tetragon, an equilateral pentagon and an equilateral hexagon, are 90, 108 and 120° as shown in formulae **3**, **4** and **5**, respectively. The sp^3 structure of a carbon-carbon single bond is a tetrahedral structure, and its bond angle is $109°28'$. Therefore, if all of the elements of a ring are carbon, the equilateral pentagon easily forms an almost planar stable structure without strain because the bond angles of the tetrahedral structure are almost the same as the interior angles of the equilateral pentagon.



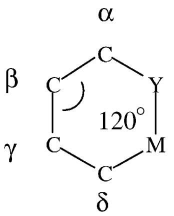
Four-membered Ring

3



Five-membered Ring

4



Six-membered Ring

5

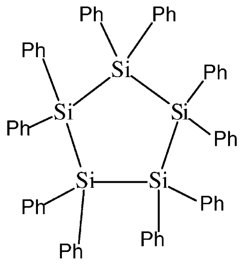
M = metal atom
Y = N, O, S, P, As

In the intramolecular five-membered ring compounds, if the metal and coordination atom have similar bond angles to that of carbon, the compound tends to easily form an almost planar structure as shown in formulae **4** of the equilateral pentagon.

Compounds having a cyclopentane ring are easily prepared and stable, as indicated by the 10,645 compounds (out of a total of 281,263 reported until 31 December 2002) reported in The Cambridge Structural Database Compounds having a cyclopentane type ring of carbon, silicon, germanium, tin and lead in Group 14 elements are actually almost planar, for example in the cases of carbon **6**, silicon **7** and germanium **8** [29–31].

The number and the ratio of articles, which are reported in the Cambridge Structural Database, on compounds **9**, **10** and **11** having four-, five- and six-membered rings, where the coordinating atoms are N, P, As, O and S, and the metal is Sn, are shown in Table 1.

The five-membered ring compounds predominate because the formation of other ring compounds is not so easy. For example, in the case of the five-membered tin carboxylic acid ester compounds, the tin compounds are easily formed, but the isolation of the four-membered ring compounds are difficult as shown below (Scheme 1). No crystal data for four-membered ring organotin carboxylic acid esters have yet been published. However, organotin four-membered rings containing a pyridine skeleton may be relatively stable since two of three above organotin four-membered ring compounds are pyridine type compounds. Few other four- and six-membered ring compounds are reported [4,5].



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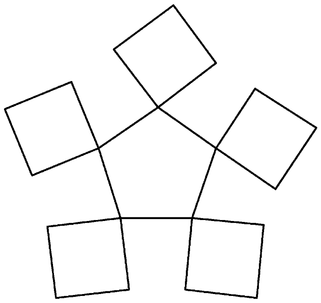

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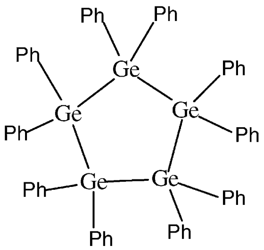

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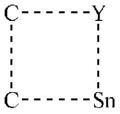
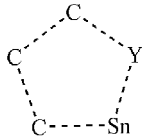
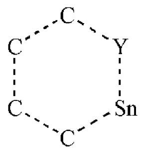
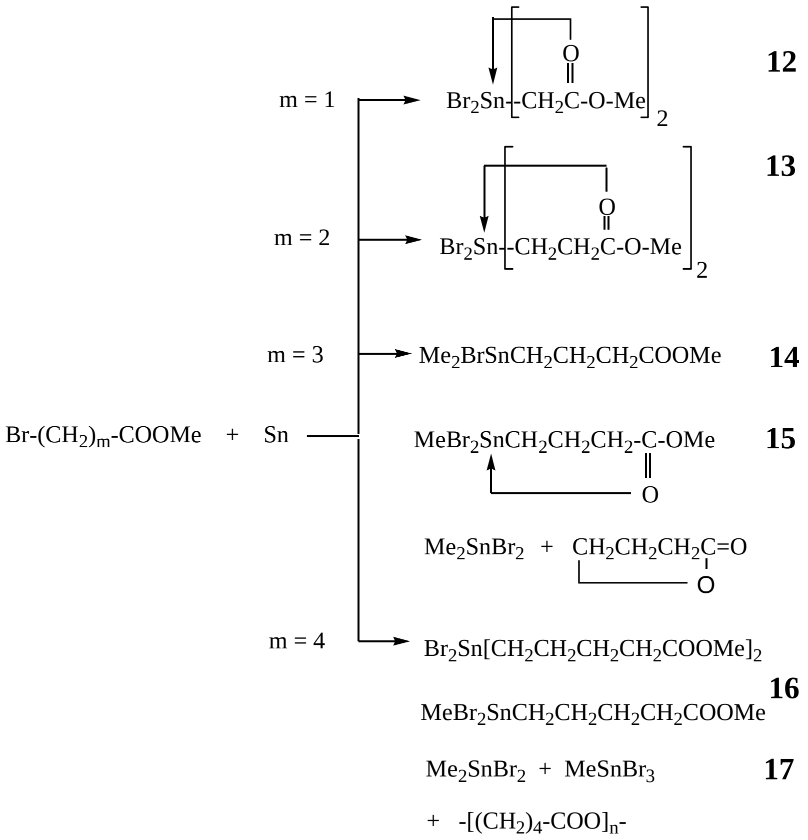
The ease of synthesis and the high stability of intramolecular five-membered ring compounds are understood by the following reactions shown in Scheme 1 [32]. The reactions of tin foil with ω-bromocarboxylic acid methyl esters are performed. An α-bromocarboxylic acid ester ($m = 1$) reacts with tin, but the product of the reaction decomposes immediately and cannot be isolated. However, β-bromocarboxylic acid ester ($m = 2$) reacts very smoothly with tin, and the product of the reaction having a five-membered ring **13** is easily isolated, purified, and quite stable in air. With γ-bromocarboxylic acid ester ($m = 3$), the reaction with tin gives mono- (**14**) and dibromides (**15**), in low yields, having a methoxycarbonyl group together with various decomposition products of the starting materials. The dibromide **15** has a six-membered ring structure. It is not as stable as the five-membered ring compound **13** because while the six-membered ring retains its structure in the solid state the ring is partly opened in benzene or tetrahydrofuran. Further-

Table 1
The number of articles which are reported on compounds having four-, five- and six-membered rings in The Cambridge Structural Database

		
21(10.9%)	165 (85.9%)	6(3.1%)
Four-membered Ring	Five-membered Ring	Six-membered Ring
9	**10**	**11**

Y = N, P, As, O, S

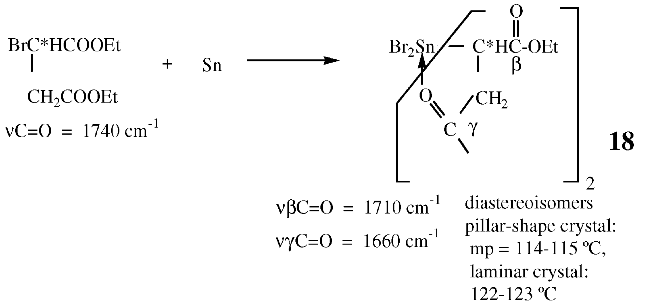


Scheme 1. [32].

more, the reaction of δ-bromocarboxylic acid ester ($m = 4$) no longer forms any ring compound (**16** and **17**) but linear compounds. Only the β-bromocarboxylic acid methyl ester ($m = 2$) reacts easily with metallic tin to yield the stable five-membered ring compound **13**. The other ω-carboxylic acids ($m = 1$, 3 or 4) do not produce any stable intramolecular coordination compounds [32].

In the 1960s our research group easily synthesized many organotin intramolecular five-membered ring compounds such as the carboxylic acid monoesters, carboxylic acid diesters, ketones, amides, and acid amides [32–52]. Almost no rings of other sizes were synthesized because these reactions did not proceed.

The ring structure of these intramolecular five-membered ring compounds was first proposed in 1965 based on the infrared spectra of organotin dicarboxylic acid esters (**18**) and published in 1966 in *Kogyo Kagaku Zasshi* (Chemical Industry (Japanese Journal)) [4,33]. These esters are easily prepared by the reaction of bromosuccinic acid ethyl ester and tin foil in the presence of magnesium metal and *n*-butyl alcohol as catalysts as shown in Eq. (1). The products were isolated by fractional crystallization with a mixed solvent as two diasteroisomers with different types of crystals having different melting points. In the infrared spectra of the starting material, only one strong C=O absorption at 1740 cm^{-1} was observed, but for the two crystalline species of product (**18**), two bands appeared at 1710 cm^{-1} and at about 1660 cm^{-1} in both the solid state and in organic solvents. The latter large shift in position is proposed to be due to coordination of the γ-carbonyl oxygen to the tin atom [4,5,33].



(1)

The crystal structures of these diasteroisomers were determined by X-ray diffraction in 1968 [34] and 1969 [35].

2.3. Types of metal ions incorporated in five-membered rings

Bähr and Müller [53,54] reported an aluminium five-membered ring complex in their first article in 1955.

Table 2
Kinds of metal elements of the intramolecular five-membered ring compounds [22]

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	*He*
Li	**Be**											**B**	*C*	*N*	*O*	*F*	*Ne*
Na	**Mg**											**Al**	**Si**	*P*	*S*	*Cl*	*Ar*
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	*Br*	*Kr*
Rb	**Sr**	**Y**	**Zr**	*Nb*	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	*I*	*Xe*
Cs	*Ba*		*Hf*	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	*Po*	*At*	*Rn*
Fr	*Ra*																
Lanthanoids			**La**	**Ce**	*Pr*	**Nd**	*Pm*	**Sm**	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	**Er**	*Tm*	**Yb**	**Lu**
Actinoids			*Ac*	*Th*	*Pa*	**U**	*Np*	*Pu*	*Am*	*Cm*	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*	*Lr*

In 1957, they used a second metal, beryllium also a main group element [55].

In 1963, Kleiman and Dubeck [56] reported on the cyclometallation of azobenzene with nickel, a transition metal. After their publication, the number of similar publications on cyclometallation rapidly increased. The metals used in the cyclometallation reactions were mostly transition metals. In 1977, in a review of cyclometalation by Bruce [6], 15 kinds of transition metals were shown to form five-membered ring compounds synthesized by cyclometalation.

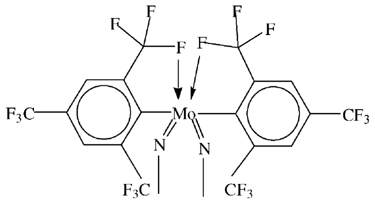
In 1986, a monograph [4] entitled "Organometallic Intramolecular-coordination Compounds" reported 31 main group and transition group elements forming five-membered ring compounds. In 1998, the Japanese Review Journal (*Kagaku Kogyo*) [57] reported 48 metals and also phosphorus being used as the central atoms of five-membered cyclic compounds.

Nine metals in intramolecular five-membered ring compounds were added to Chemical Abstracts and The Cambridge Structural Database, to lead to a total of 57 different metal ions found in intramolecular five-membered ring compounds. The elements are listed in Table 2 [22].

Indeed, almost all metal ions are found in the intramolecular five-membered ring compounds. The excluded elements are some radioactive elements such as Fr, Ra, Po and At, some lanthanoids and most of the actinides. Only four other elements, Cs, Ba, Hf and Nb, have never been found to form intramolecular five-membered ring compounds.

2.4. Kinds of coordinating atom

The coordinating atoms of the intramolecular five-membered ring compounds **2** are predominantly five elements, namely N, P and As of the 15th group, and O and S of the 16th group. However Se of 16th group and F and Cl of 17th group as shown in compounds **2** do form such compounds. These donor atoms have been reported in several examples of five-membered ring compounds shown as formulae **19–25** [58–63].



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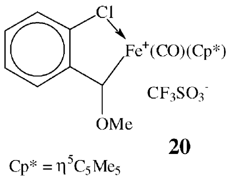

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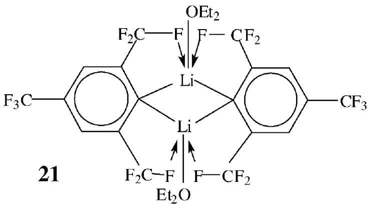

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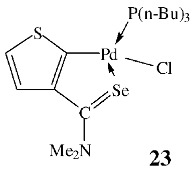

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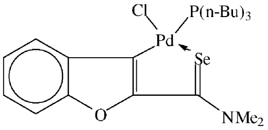

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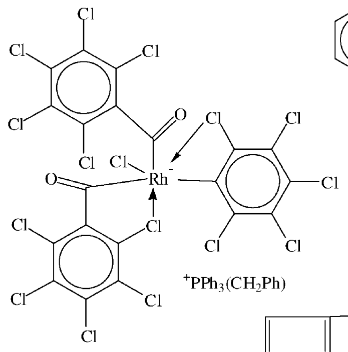

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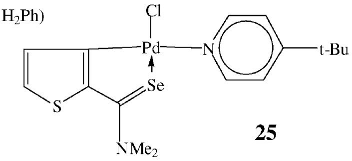

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2.5. Major types of compounds

The intramolecular five-membered ring compounds, at first, were reported on alkyl compounds of the main group elements in 1955, as described before. On the other hand, Kleiman and Dubeck [56] in 1963, reported on the cyclometalation of a phenyl compound with a transition metal. Therefore, afterward, many articles on the cyclometalation of aryl compounds with transition metals such as nickel, palladium, platinum and rhodium, have been reported.

The major types of aryl compounds are as follows: *N*,*N*-dimethylbenzylamines **26**, azobenzenes **27**, 1,3-bis (dimethylaminomethylbenzenes) (pincer complexes) **28**, alkyl(or aryl)phenylketones **29**, alkyl(or aryl)benzylethers **30**, *N*-benzylideneaminealkyl(or aryl) derivatives **31**, alkyl (or aryl)benzylthioethers **32**, *o*-methyldimethylanilines **33**, *N*,*N*-dimethylbenzylamine diakyl(or diaryl) derivatives **34**, 2-ethylpyridines **35**, dialkyl(or diaryl)benzylphosphines **36**, 8-dimethylaminonaphthalenes **37**, 1-dimethylaminomethylnaphthalenes **38**, 8-diakyl(or diaryl)methylquinolines **39**, benzo[*h*]quinolines **40** and 2-phenylpyridyl compounds **41** as shown in Table 3.

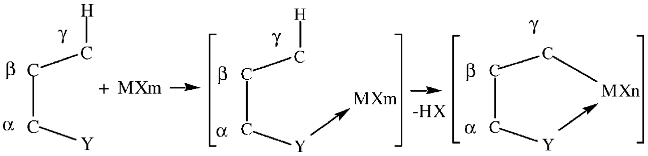
The other types of compounds are dimethylaminomethylferrocenes **42**, dimethylaminopropyl(or propenyl) compounds **43**, *N*-alkyl(or aryl)ethyl(or ethenyl)imines **44**, alkyl(or aryl)ethyl(or ethenyl)ketones **45**, alkyl(or aryl) propyl(or propenyl)ethers **46**, dialkyl(or diaryl)propyl(propenyl)phosphines **47**, alkyl(or aryl)propyl(or propenyl)thioethers 48 and alkyl(or aryl)propionic acid(propenoic acid) esters **49**, etc. are shown in Table 4.

The numbers attached to each of the compounds in Tables 3 and 4 are the number of articles published in The Cambridge Structural Database, which contain that particular intramolecular five-membered ring. These data show that, especially, dimethylaminomethylbenzenes compounds are the most popular, 350 being reported while there are 168 benzylmethyl derivatives (also see Section 3).

2.6. Formation mechanisms of intramolecular five-membered ring compounds

2.6.1. Two-step reaction mechanisms

The organometallic intramolecular coordination compounds are synthesized via many types of reactions. However, primary compounds are synthesized by cyclometalation. Cyclometalation was generally considered to proceed by the following two-step reaction mechanism as shown in Eq. (2) [4,6,7].



(2)

The first step is the coordination of a coordinating atom or coordinating group (Y) to a metal (M). In the case of the intramolecular five-membered ring compounds, Y is usually O, N, S, P and As which high electronegativities compared with those of the metal atom.

In the cyclometalation of aryl compounds with transition elements, the first step is the coordination of the coordinating atom to the atom of the transition element which is activated by coordination. The metal is located at a position close to one phenyl ring bond between the β-carbon atom and γ-carbon atom. The metal is π-coordinated by the phenyl ring bond, and the π-coordination bond changes to

Table 3
The major aryl type of intramolecular five-membered ring compounds and the number of the articles regarding to each of the compounds reported in The Cambridge Structural Database

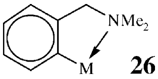
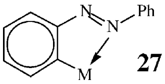
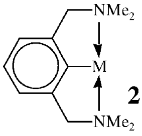
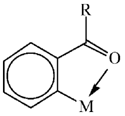
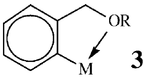
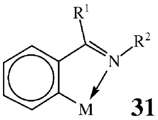
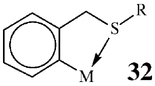
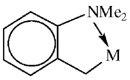
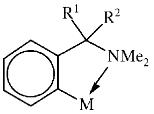
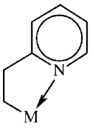
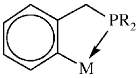
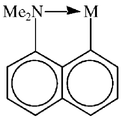
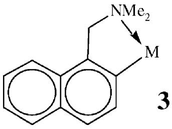
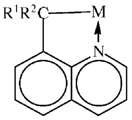
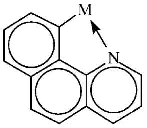
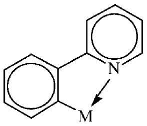
	Number of the articles reported in The Cambridge Structural Database
 **26**	350
 **27**	89
 **28**	100
 **29**	32
 **30**	45
 **31**	41
 **32**	52
 **33**	28
 **34**	168
 **35**	67
 **36**	73
 **37**	26
 **38**	64
 **39**	51

Table 3 (*Continued*)

	Number of the articles reported in The Cambridge Structural Database
 **40**	13
 **41**	135

the σ-bond upon bonding to the γ-carbon atom. Phenyl compounds such as *N*,*N*-dimethylbenzylamines form intramolecular five-membered ring compounds as shown in Scheme 2 [64].

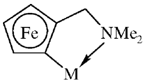
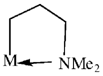
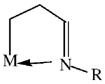
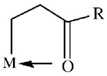
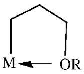
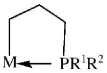
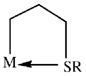
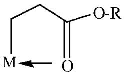
In 1967, Takahashi and Tsuji [65] reported the cyclopalladation of azobenzene derivatives. From the degradation products as shown in Scheme 3, it was concluded that σ-bond formation is an electrophilic substitution of palladium chloride on the benzene ring because the structure of the product shows that σ-bond formation with palladium took place mainly with the benzene ring having an electron-donating methyl group.

2.6.2. *Intermolecular C–H activation*

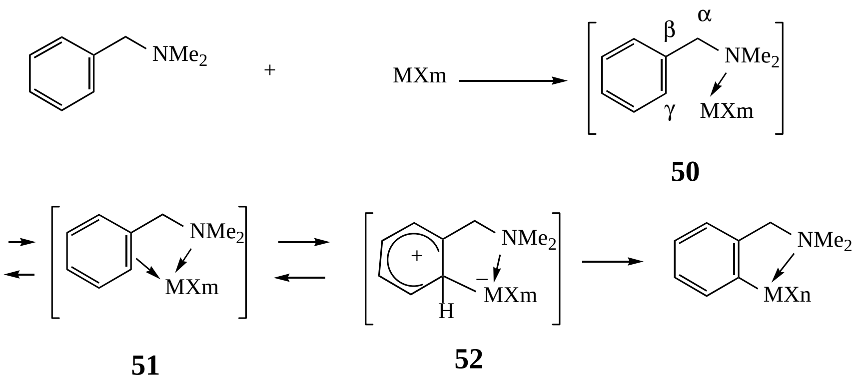
Reactions with a strong aromatic C–H bond (110 kcal/mol) were generally thought to be difficult as those with a weak alkane C–H bond (94–100 kcal/mol) [66]. However, reactions of aromatic compounds with transition metals are found easily to proceed as described above.

Recently, the bond length between the hydrogen atom and the other element was determined accurately by neutron diffraction studies, and many bond lengths between hydrogen and other elements have been reported. Since the 1980s, many reports on the agostic bond have been published. The agostic bond (M← H–C) is formed when a transition atom approaches a C–H bond. Many agostic compounds are highly fluxional and undergo rapid exchange of the agostic hydrogen with other hydrogen atoms, normally those attached to the same carbon atom as shown in Scheme 4. In the agostic bond, the M← H bond is usually longer than an ordinary M–H bond by ca. 10–20%, and the C–H bond is longer than an ordinary C–H bond by ca. 5–10%. The activation energy to change the fluxional structure is very little, only 8 kcal/mol or more [67,68].

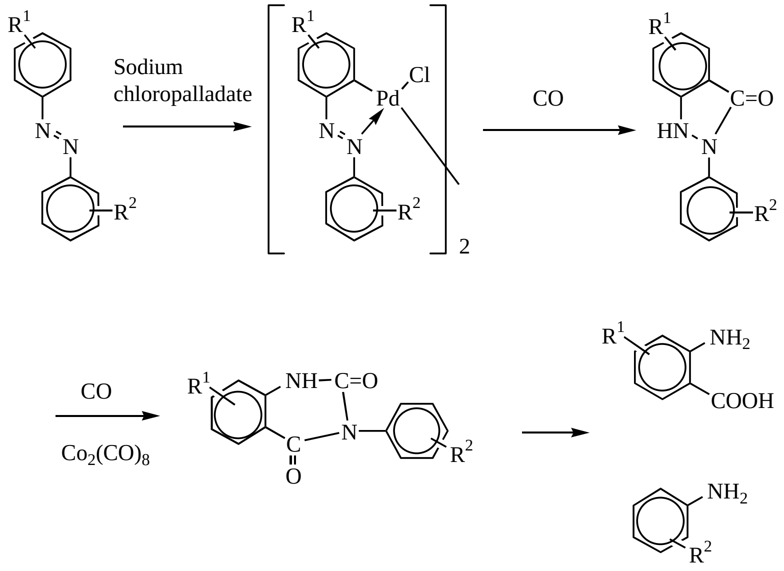
Table 4
The other types of intramolecular five-membered ring compounds and the number of article regarding to each of the compounds reported in The Cambridge Structural Database

	Number of the articles reported in The Cambridge Structural Database
 **42**	42
 **43**	159
 **44**	82
 **45**	108
 **46**	99
 **47**	206
 **48**	58
 **49**	164

If a metal is coordinated by a coordinating atom, the metal is located at a position close to the carbon atom as shown in Eq. (2). Then, the metal is able to form an agostic bond with the C–H bond at the γ-carbon atom. That is, most of the



Scheme 2. [64].



Scheme 3. [65].

cyclometalations proceed with a low energy via this agostic bond.

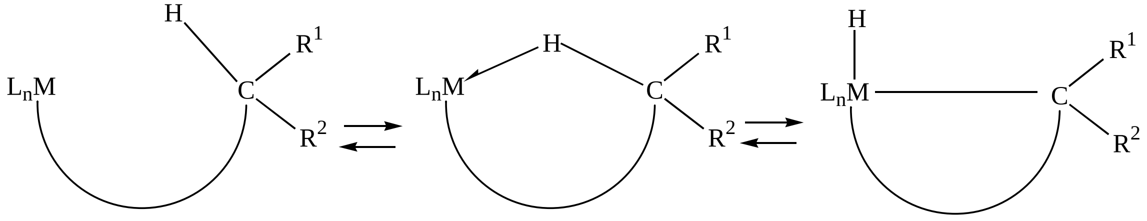
Crabtree et al. [69] compared the available structural parameters for a range of compounds containing M◄– H–C bonds. The data are represented in Fig. 1, which shows a trajectory, whereby as the C–H bond approaches the surface of the metal atom M, the C–H bond is pointing towards the metal with a M–H–C angle of 130°. As seen from Fig. 1, the C–H bond is not significantly lengthened until the C–H bond approaches very close to the metal. This implies a late transition state. The M–H–C angle at H, 130° when there is a big distance between the metal and the C–H bond, falls rapidly as the distance decreases [69,70].

3. Applications of intramolecular five-membered ring compounds

The intramolecular five-membered ring compounds have two important properties, high reactivity caused by reactive metal–carbon bond, and high regio-selectivity caused by formation reactions of the five-membered ring as described above. Hence, they are very useful for organic syntheses. Many cyclometalation reactions of benzylamine compounds with palladium complexes are especially conveniently utilized, their synthetic reactions being shown below, e.g. Eqs. (4), (5), (8), (10), (14), (19), (20), (22) and Scheme 11.

3.1. Reaction with alkenes, alkynes and acyl halides

Many aryl, ferrocenyl, alkyl and alkenyl compounds such as compounds **26**–**49**, easily form five-membered ring compounds by bonding, usually, at the γ-positions by the cyclometalation reaction with metal compounds as shown in Eq. (2). These five-membered ring compounds easily react with alkenes, alkynes and acyl halides by replacing their functional groups with the metal at the γ-position. Therefore, these reactions proceed regio-selectively at the γ-positions, usually yielding γ-derivatives.



53 **54** **55**

Scheme 4. [68].

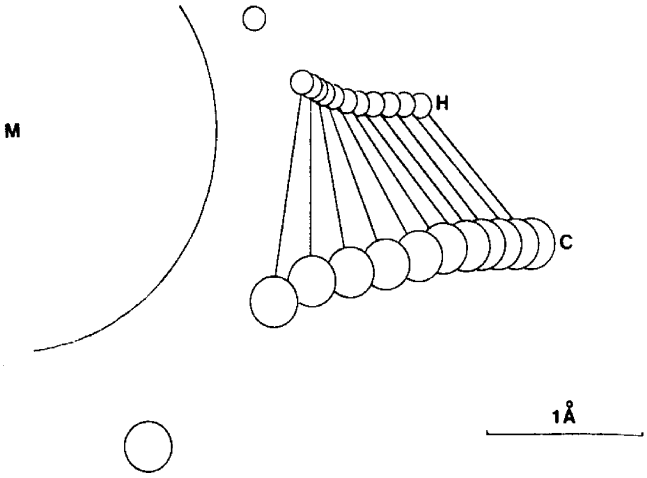
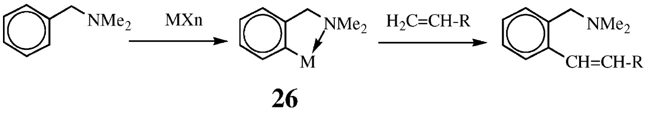


Fig. 1. Reaction trajectory for C–H + M → C–M–H [69,70]. d is the distance from the metal to this C–H bonding electron pair and r_M the covalent metal radius. The r is effectively the covalent radius of the C–H bonding electrons. r value: −0.4 to 0.5 Å, strong contact; −1.0 to 1.5 Å, weak agostic interactions; ≧1.9 Å, trivial van der Waals interactions. The isolated circles are the final positions of the carbon and hydrogen atoms expected for a *cis* alkyl hydride complex, assuming normal M–C and M–H distances and an angle of 90° for C–M–H.

3.1.1. Reactions with alkenes

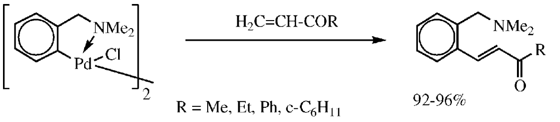
Representative intramolecular five-membered ring compounds **26** are prepared through the reaction of *N*,*N*-dimethylbenzylamines with metal compounds.

Vinylation reactions take place with these species as shown in Eq. (3).



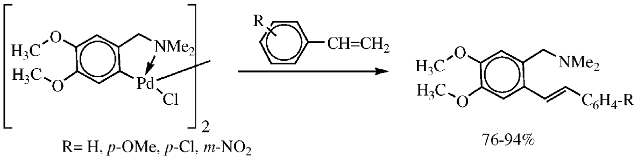
(3)

These vinylation reactions using five-membered ring compounds are widely used in synthetic organic chemistry. Reactions of alkyl or aryl vinyl ketones with a cyclometalated palladium compound are shown as an example of vinylation in Eq. (4) [71].

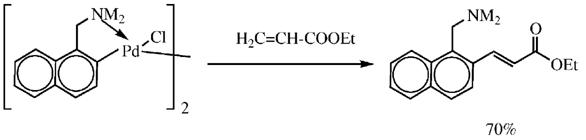


(4)

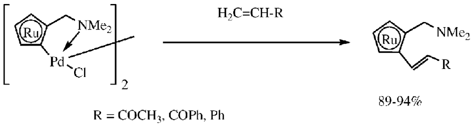
Other vinylations with dimethoxyphenyl, naphthyl and ruthenocenyl metal derivatives also proceed as shown in Eqs. (5)–(7), respectively [72–74]. Terminal olefins are used for these vinylation reactions because the reactivity of branched olefins is low [75].



(5)



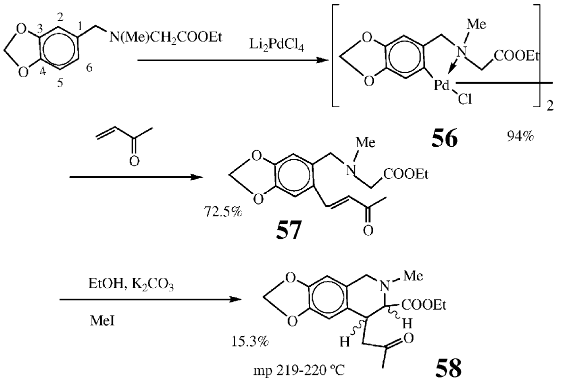
(6)



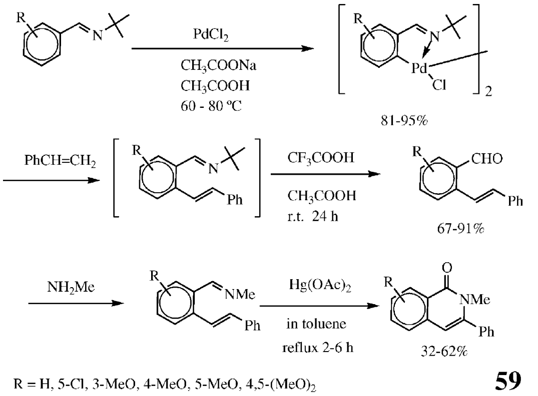
(7)

These vinylation products are easily utilized for the formation of heterocyclic compounds by cyclization reactions. For example, ethyl *N*-methyl-*N*-(3,4-methylenedioxy)benzylglycinate is cyclopalladated 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 **56**, undergoes a substitution reaction via an insertion of methyl vinyl ketone between the palladium metal and the phenyl carbon atom. The resultant β-aryl-α,β-unsaturated ketone **57** is cyclized using anhydrous potassium carbonate in ethanol to the corresponding ethyl *N*-methyl-1,2,3,4-tetrahydroisoquinolinium-3-carboxylate **58** as shown in Eq. (8) [75,76].

Cyclopalladated *t*-butylimine compounds reacted with styrene and are then treated with trifluoroacetic acid to give *o*-formylstilbenes in high yield. Their *N*-methylimine derivatives are converted to other heterocyclic compounds, 3-aryl-*N*-methyl-isoquinolones **59** by oxidation with mercuric acetate as shown in Eq. (9) [77].



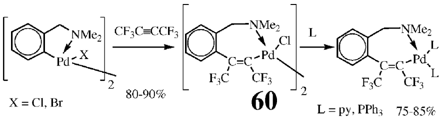
(8)



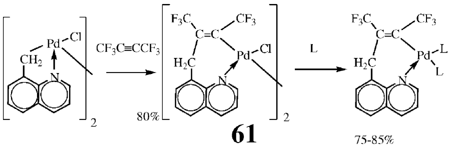
(9)

3.1.2. Reactions with alkynes

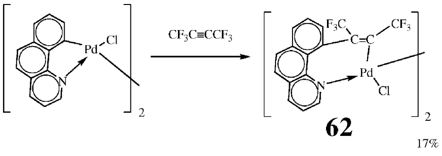
The reactions of hexafluorobut-2-yne with *N*,*N*-dimethylbenzylamine, 8-methylquinoline or benzo[*h*]quinoline palladium dimer, form halide-bridged binuclear products with insertion of one hexafluorobut-2-yne (**60**–**62**) to the Pd–C bond as shown in Eqs. (10)–(12). These benzyl and quinolinyl dimeric complexes easily afford monomeric derivatives in high yield by bridge-splitting reactions with pyridine or triphenylphosphine [78–80].



(10)

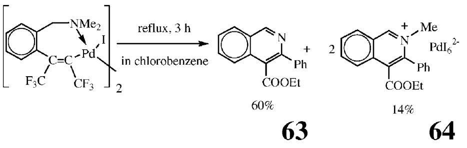


(11)



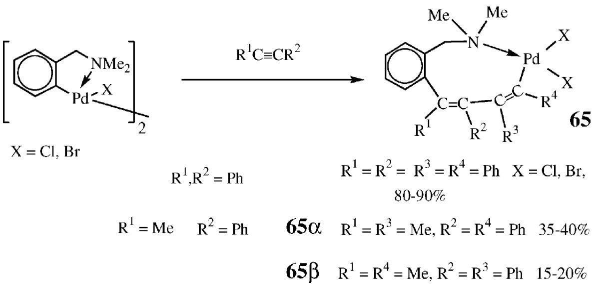
(12)

These inserted compounds (**60**–**62**) showed unexpected thermal stability so that any reaction performed to recover the modified palladium-free ligand did not lead to any clean products. However, the stability of these compounds is very much dependant upon the nature of the other ligands on the Pd atom. Thus, changing the chloride for an iodide, led to a dramatic decrease in the thermal stability of the cyclopalladated compounds [81–83]. In this latter reaction, the total or partial dealkylation of the NMe_2 group occurs to produce compound (**63**) or compound (**64**), respectively, as shown in Eq. (13). In a related reaction, it was possible to detect the presence of MeI together with an amount of CH_4 [81].



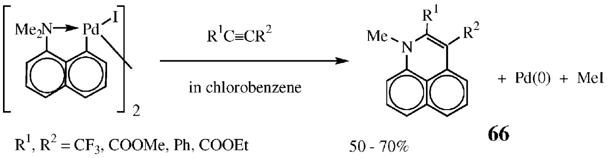
(13)

On the other hand, with diphenylacetylene or phenylmethylacetylene, cyclometalated compounds form nine-membered ring compounds (**65**) by a bis-insertion of the alkynes as shown in Eq. (14). When R's are dissymmetric (R^1, R^3 = Me, R^2, R^4 = Ph; R^1, R^3 = Ph, R^2, R^4 = Me), head-to-tail and tail-to-tail arrangement isomers (**65**α and **65**β) are isolated; X-ray diffraction studies were made on a bromo-derivative (**65**α) and chloro-derivative (**65**β) [78].

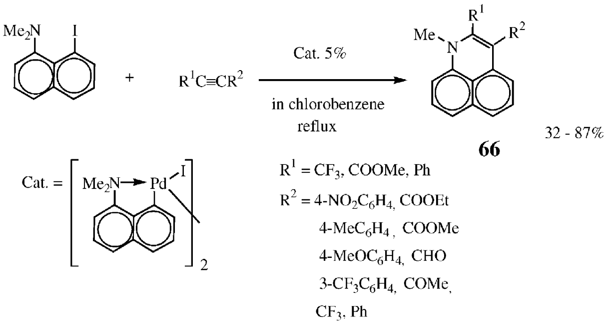


(14)

Insertion reactions of acetylene compounds with di-μ-iodo-bis(*N*,*N*-dimethyl-1-naphthylamine-*C*,*N*)-dipalladium, form substituted heterocyclic products (**66**) with formation of palladium metal and the loss of one *N*-methyl groups by refluxing in chlorobenzene (Eq. (15)) [78,81,83]. The heterocyclic compounds are synthesized directly by the reaction of iododimethylaminonaphthalenes with acetylenes in the presence of a catalytic amount of the 1-dimethylaminonaphthalene palladacycle as shown in Eq. (16) [83].

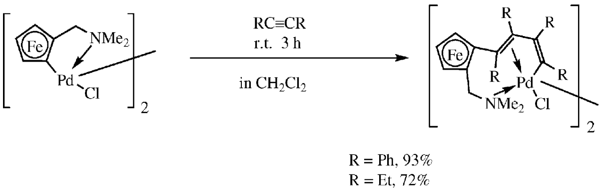


(15)

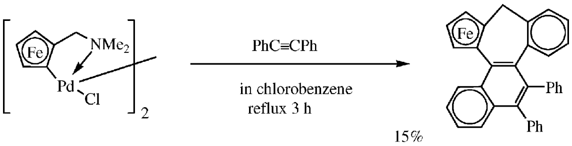


(16)

With dimethylaminomethylferrocene, at a room temperature, the insertion of two alkynes into the Pd–C bond of the cyclopalladate derivatives proceeds in high yield as shown in Eq. (17). When reaction with diphenylacetylene is performed at higher temperatures, depalladation occurs readily to give six- and seven-membered *ortho*-fused rings, that is, a bis-insertion product, through new annulation reactions of phenyl groups, and the formation of one of these also involves the cleavage of a C–N bond as shown in Eq. (18) [84].



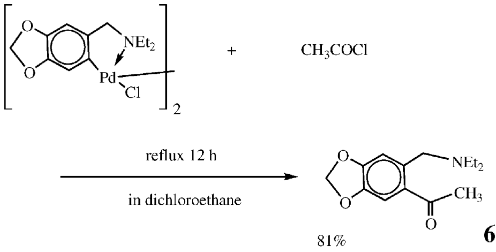
(17)



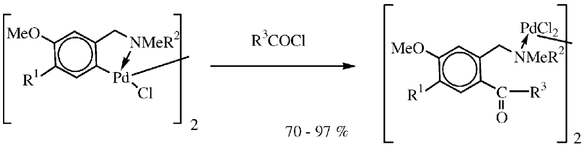
(18)

3.1.3. Reactions with acyl halides

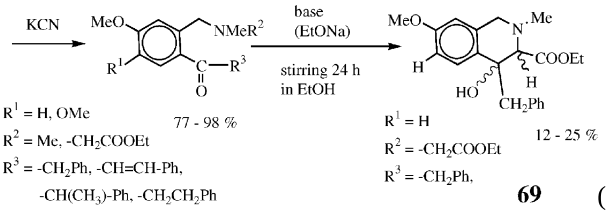
The regio-specific reaction of palladacycles with acyl halides gives a 2-acyl derivative (**67**) in a high yield (Eq. (19)) [85]. Cyclopalladated *N*,*N*-dimethylbenzylamine derivatives bearing methoxy-groups on the ring behave similarly with respect to acetyl and benzoyl chorides also to give the corresponding ketones in high yield as shown in Eq. (20). The heterocyclic compounds **69** are also synthesized by stirring these acyl compounds with a base such as sodium ethoxide in dry ethanol solution. The presence of electron-withdrawing substituent appears to drastically decrease the rate; a complex di-μ-chlorobis[*N*,*N*-dimethyl-5-chlorobenzylamino-2*C*,*N*]dipalladium(II) is recovered unchanged after 3 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 the presumed intermediates **68** [75,86].



67



68 (19)

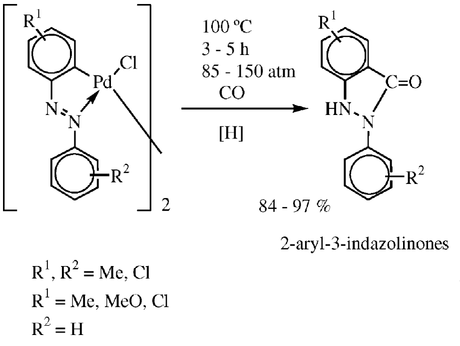


69 (20)

3.2. Carbonylations

Carbonylation together with alkenylation is one of the most important reactions in the application of intramolecular five-membered ring compounds. Heterocyclic ketones are synthesized by the insertion of carbon monoxide into a metal–carbon bond followed by demetalation reactions. Because the metal–carbon or metal–nitrogen σ-bonds are usually very reactive toward carbon monoxide, these bonds undergo carbon monoxide insertion and finally yield heterocyclic compounds by the hydrolysis of the metal–nitrogen bond [65].

In 1967, Takahashi and Tsuji [65] reported that the carbonylation of substituted azobenzene in protic solvents such as alcohols or water proceeded smoothly under mild conditions to afford 2-aryl-3-indazolinones with the separation of metallic palladium in a high yield as shown in Eq. (21). Hence, the reactions are a very good synthetic method for the synthesis of substituted 2-aryl-3-indazolinones **70**.

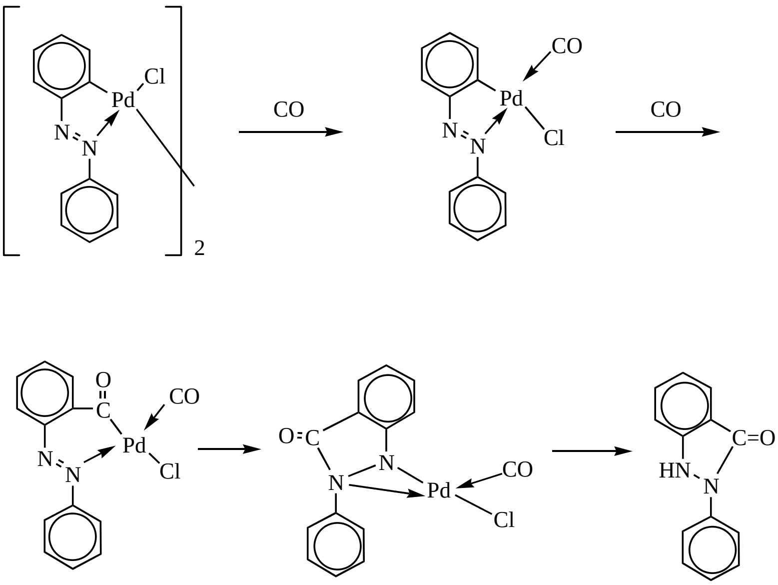


70

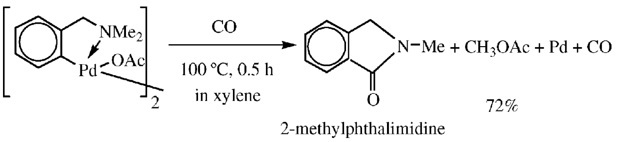
(21)

They tentatively presumed that the mechanisms of these carbonylation reactions are as shown in Scheme 5: The first step is the coordination of CO with splitting of the bridged structure. Then, insertion of CO at the σ-bond gives an acyl–palladium bond. The final step seems to be the insertion of the –N=N– bond into the Pd–acyl bond, followed by hydrogenolysis of the Pd–N bond [65].

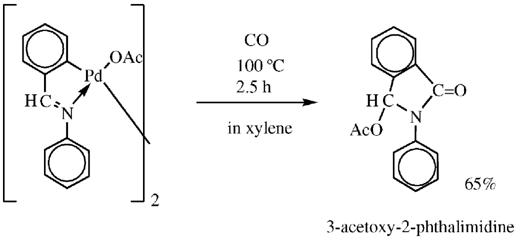
Carbonylations yield various kinds of heterocyclic carbonyl compounds with organopalladium intramolecular five-membered ring compounds of *N*,*N*-dimethylbenzylamine, benzaldehyde-Schiff base compounds and benzylamine-Schiff base compounds, (e.g. forming 2-methylphthalimidine, 3-acetoxy-2-phthalimidine and 2-benzylphthalimidine) as shown in Eqs. (22)–(24) [87]. From Eqs. (23) and (24), Thompson and Heck [87] assumed a similar mecha-



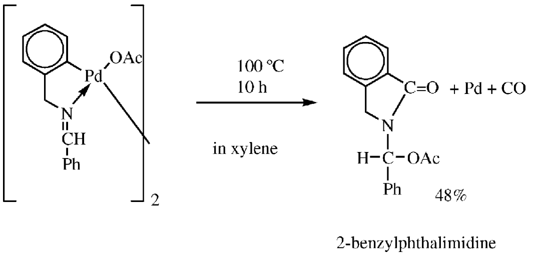
Scheme 5. [65].



(22)



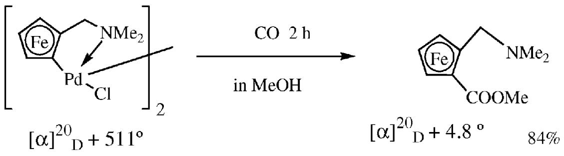
(23)



(24)

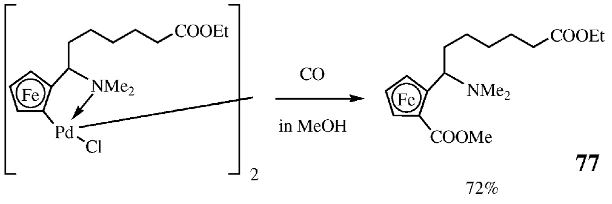
nism for the Takahashi and Tsuji reactions [65]. Initially, carbonyl insertion into the palladium-carbon bond and breaking of the bridge bond formed compound **71**, which may undergo internal addition of the acyl–palladium group to the nitrogen–carbon double bond to form compounds **72**. The simple reductive elimination of compounds **72** yields compounds **74** and **75**. These carbonylations in xylene or benzene form various kinds of heterocyclic compounds as shown in Eqs. (22)–(24) and Schemes 5 and 6.

However, in alcoholic solvents, these carbonylations or carbonylations with ferrocenyl or pyrrol compounds also form various kinds of uncyclized esters as shown in Scheme 6 (the compound **73**) and in Eqs. (25)–(27) (the compounds **76**–**78**) [75,88–90].



76

(25)



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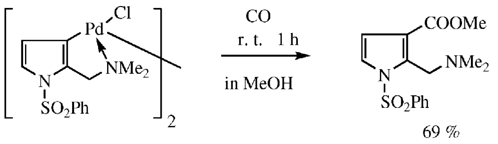
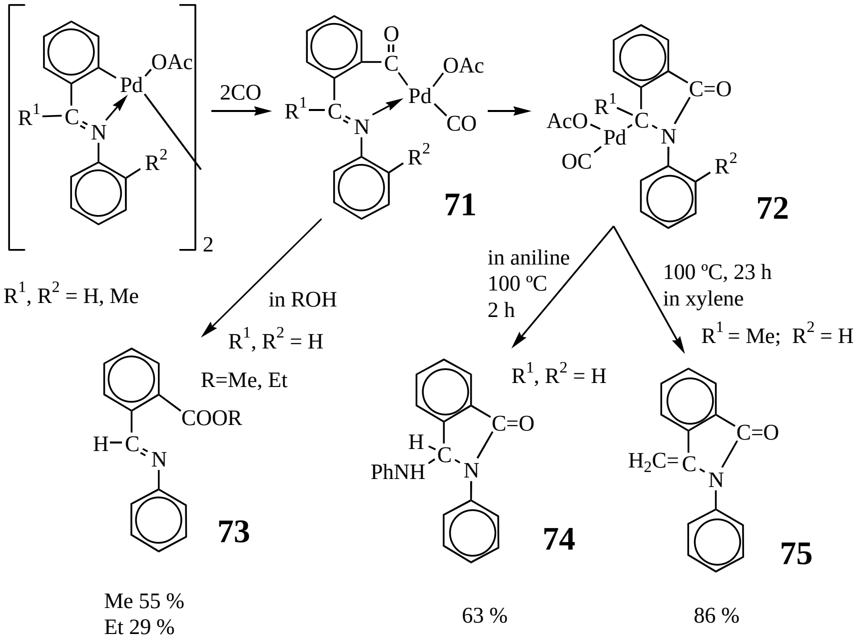
(26)



78 (27)

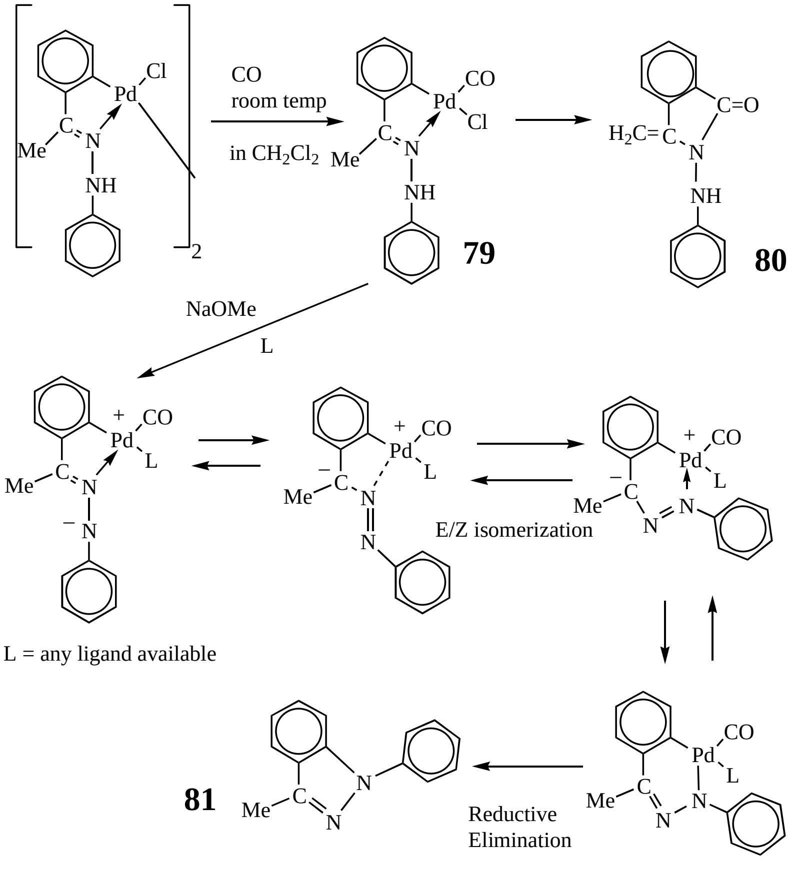
The carbonylation of ortho-palladated acetophenone-phenylhydrazone yields an isoindolinone derivative **80**, which is the same type as the methyleneisoindolinone **75** in Scheme 6 [91]. However, the addition of a stoichiometric amount of NaOMe to the carbonyl inserted product **79** in solution leads instantaneously to reductive elimination yielding the indazole derivative, 3-methyl-1-phenyl-indazole **81** in high yield. This is presumed to proceed by the complete deprotonation of the carbonyl coordinated product **79**, then,



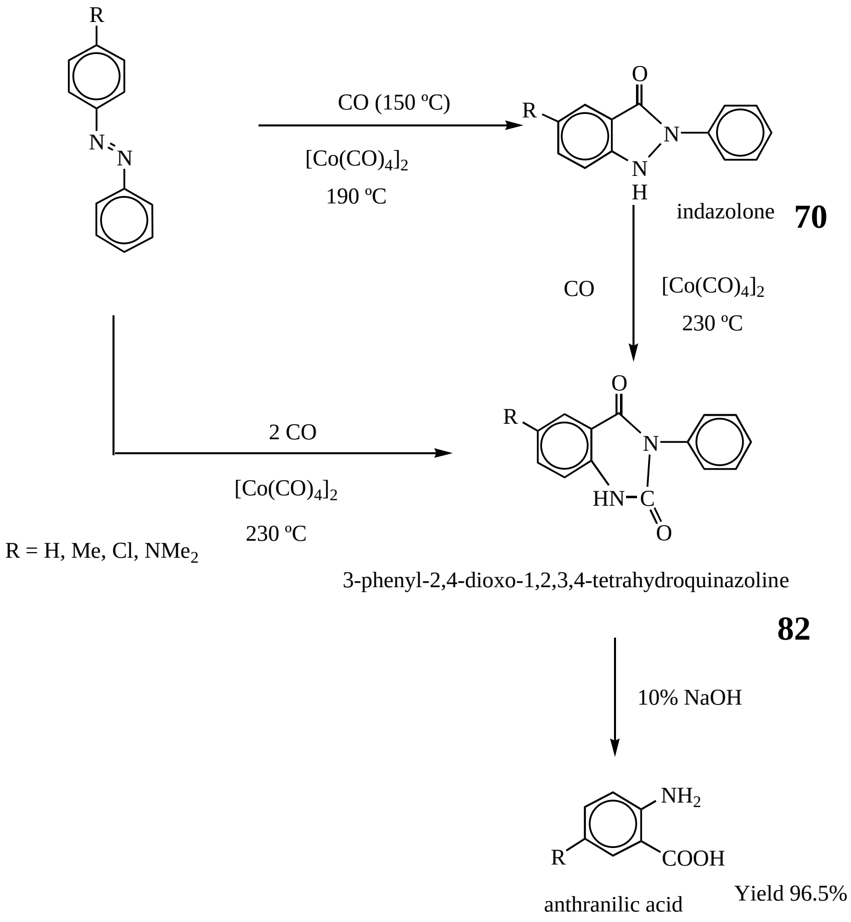
Scheme 6. [87].

an *E*/*Z* isomerization and a reductive elimination as shown in Scheme 7 [91].

In 1956, Murahashi and Horiie [92] reported the carbonylation of azobenzene with an octacarbonyldicobalt catalyst as shown in Scheme 8. The monocarbonylation of azobenzene with the cobalt catalyst at 190 °C forms indazolones **70** as shown in Scheme 8, which is also obtained by the monocarbonylation of the cyclopalladium



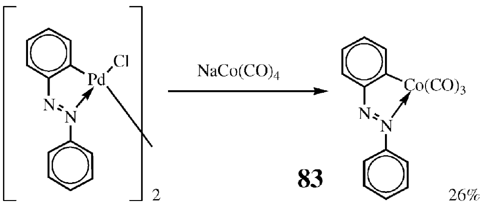
Scheme 7. [91].



Scheme 8. [92–95].

azobenzene complex as shown in Eq. (21) and Scheme 5. The dicarbonylation of azobenzenes at 230 °C forms 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazolines **82** in quantitative yield. The dicarbonylation product is presumed to occur through the further carbonylation of the monocarbonylation product [92–95]. This process may be utilized for the industrial preparation of anthranilic acid because the hydrolysis of the quinazolines **82** gives anthranilic acid in a high yield [93].

On the other hand, a cyclometalated cobalt complex **83** is prepared by the reaction of the cyclopalladated compound with $NaCo(CO)_4$ as shown in Eq. (28), although the cyclometalation of azobenzene with $Co_2(CO)_8$ at a low temperature (80 °C) does not proceed [96]. Hence, the formation of isoindazolones **70** from azobenzene and CO in the presence of $Co_2(CO)_8$ at 190 °C is presumed to proceed via the cyclocobalt complex **83**.



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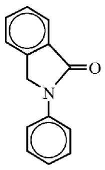
(28)

Therefore, the process of these reactions with the cobalt catalyst in Scheme 8, is easily presumed that the carbonylation proceeds via the cyclometalation reaction of the cobalt compound. Further, 1 year previously, in 1955, Murahashi also reported the same type of heterocyclic compound (2-phenylphthalimine **84**) by the carbonylation of benzylideneaniline **31** (R^1 = H, R^2 = Ph) (Ph–CH=N–Ph) in the presence of $Co_2(CO)_8$ as a catalyst [97,98]. Hence, it is presumed that the cyclometalation was actually performed in 1955, which was 8 years before the publication by Kleiman and Dubeck in 1963, although the product was not isolated as an intermediate. Therefore, the first application of the carbonylation was performed before organotransition-metal intramolecular five-membered ring compounds were first reported [56].



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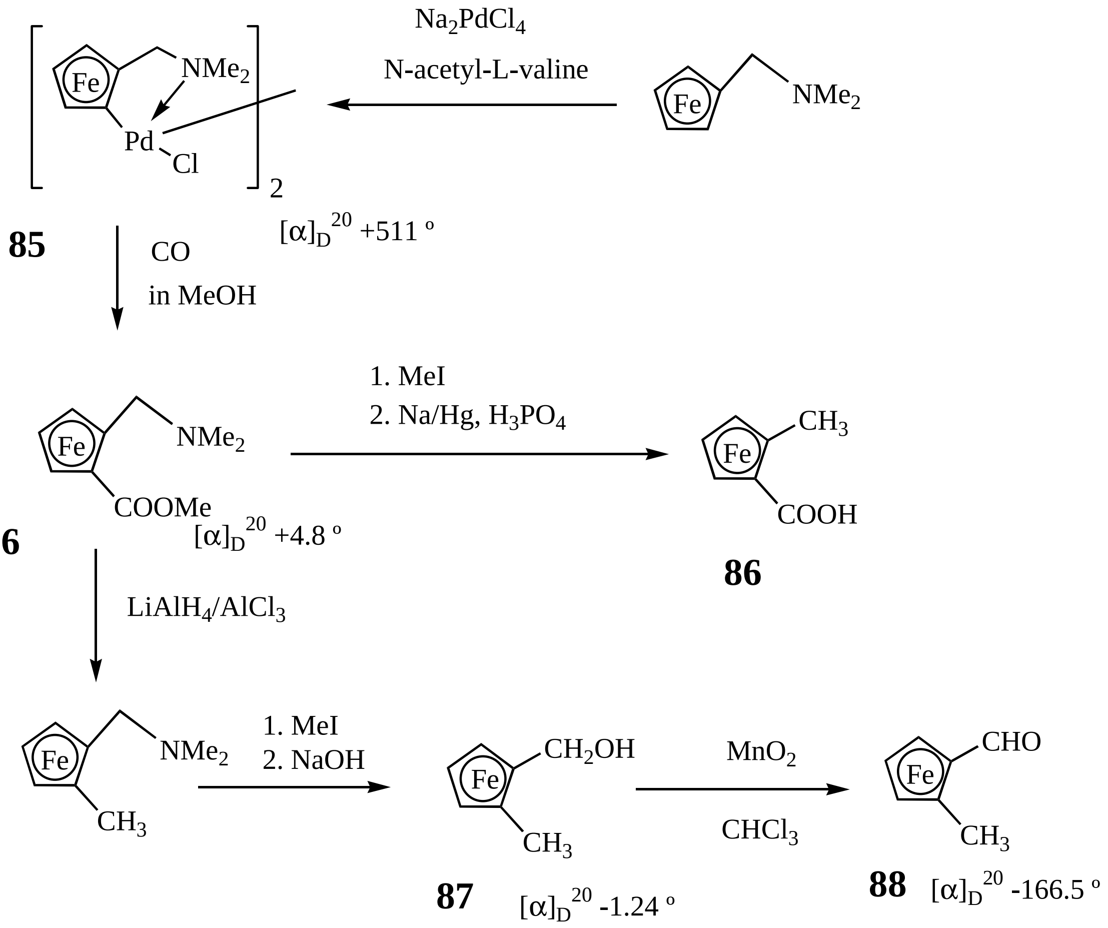
The various kinds of 2-ferrocene derivatives are synthesized by reactions with transition metal compounds similar



Scheme 9. [88].

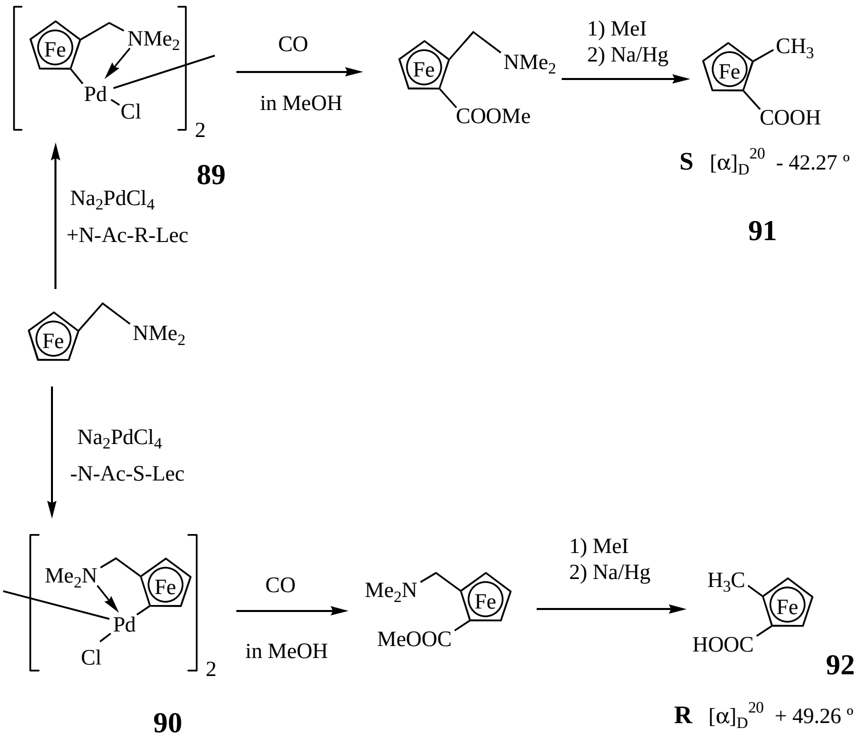
to the orthometalation of phenyl compounds. The palladium compounds **85** of dimethylaminomethylferrocene react with carbon monoxide in methyl alcohol to give the 2-methoxycarbonyl compound **76**, and then the treatment of the compound with methyl iodide, sodium amalgam, and phosphoric acid gives 1-methyl-2-carboxylic acid **86**. The reduction of 2-methoxycarbonyl compound **76** followed by treatment with NaOH, produces an alcohol **87**, and oxidation of the compound **87** yields an aldehyde **88** as shown in Scheme 9. Since the starting material **85** is an optically active compound as shown in Scheme 9, all of its derivatives are also optically active 1,2-ferrocene derivatives [88].

The asymmetric cyclopalladation of dimethylaminomethylferrocene in the presence of *N*-acetyl-(*R*)- or (*S*)-leucine gives an enantiomerically enriched palladacycle (*S*)- or (*R*)-$[Pd\{C_5H_3(CH_2NMe_2)FeC_5H_5\}(\mu\text{-}Cl)]_2$ (**89**,**90**), respectively. The carbonylation of each enantiomer followed by iodomethylation and reduction by sodium amalgam gives (*S*)- or (*R*)-2-methylferrocene carboxylic acid (**91**,**92**) with an optical purity of 80 or 90%, respectively, as shown in Scheme 10 [99].

3.3. Reactions with isocyanates and thermal degradation

The reactions of *N*,*N*-dimetylbenzylamine palladacycles with isocyanates lead to the cleavage of halide bridges to give monocyanate products **93**. On heating the monoisocyanates **93**, intramolecular insertion takes place to give dimeric iminoacyl complexes **94**. The treatment of the monoisocyanates **93** and the insertion products **94** with isocyanide produce diisocyanate products **95**. The reactions of the products **94** with $LiAlH_4$ or Grignard reagent give diamines **96** or ketones **97**, respectively, as shown in Scheme 11 [100].

Some heterocyclic compounds are easily synthesized simply by the thermal degradation of the cyclometalated compounds. For example, the reactions of azobenzene cyclopalldated products with isocyanides proceed with the cleavage of the chloride bridges to yield very stable yellow orange complexes **98**. The thermal degradation of the cleaved products proceeds smoothly at 100–130 °C in toluene to give 3-imino-2-phenylindazolines **99** with the separation of metallic palladium [101]. This indazolines **99** may also be obtained from the reaction of the azoben-



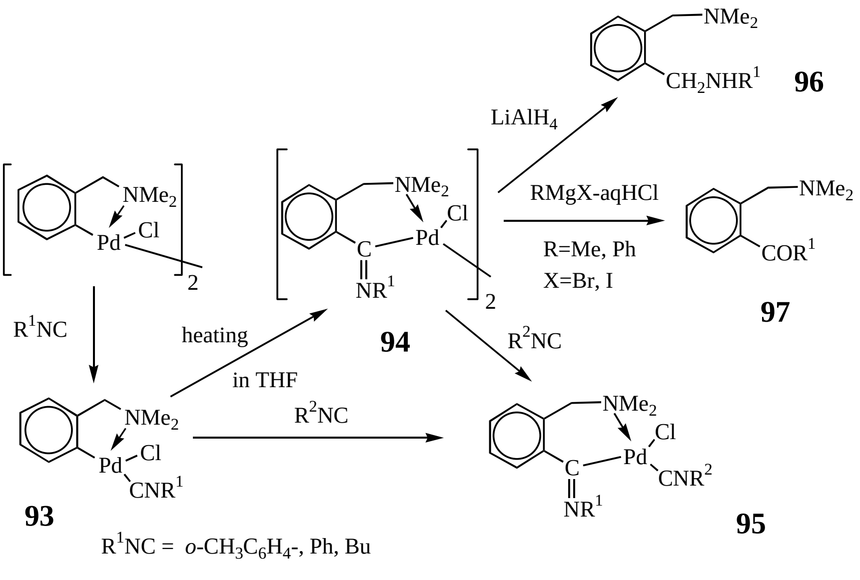
Scheme 10. [99].

zene cyclopalladation products in toluene at 120 °C with isocyanides in a 1:2 molar ratio respectively as shown in Scheme 12 [101].

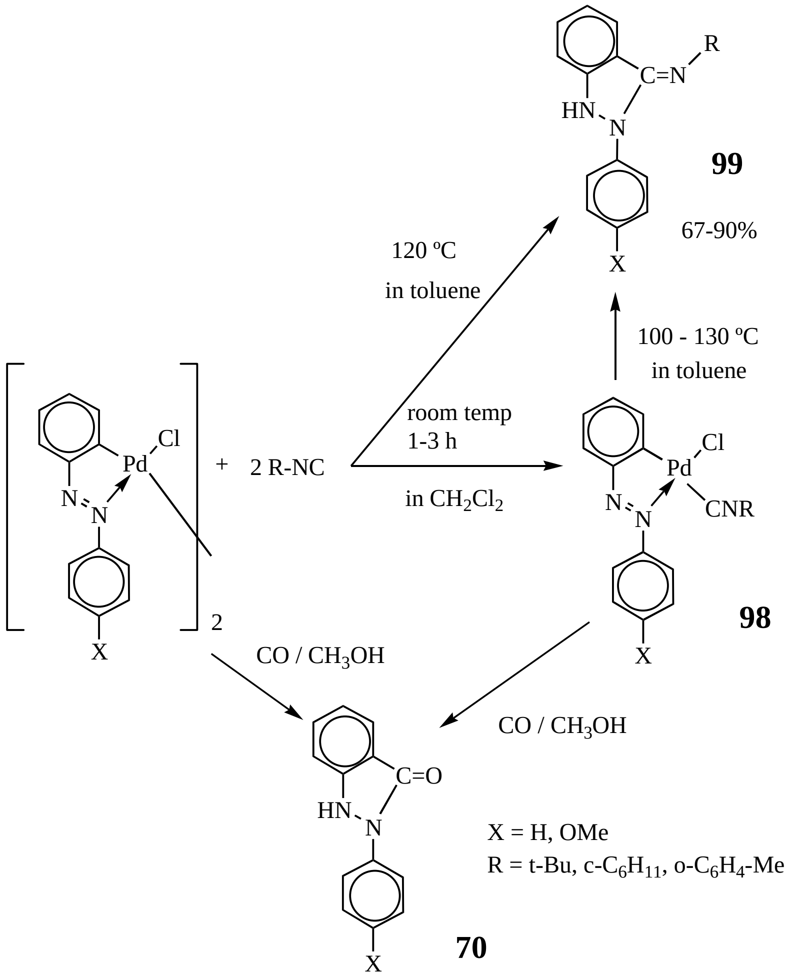
The oxo-2-phenylindazolines **70** that are synthesized by the reaction of the azobenzene cyclopalladated complexes with carbon monoxide, are also obtained from the cleavage products **98** by reaction with monoisocyanides and carbon monoxide in methanol at 40 °C under the pressure of 35 kPa/cm^2 [101].

3.4. Halogenations

It is well documented [102] that the direct halogenation of arenes, bromination in particular, is one of the most se-

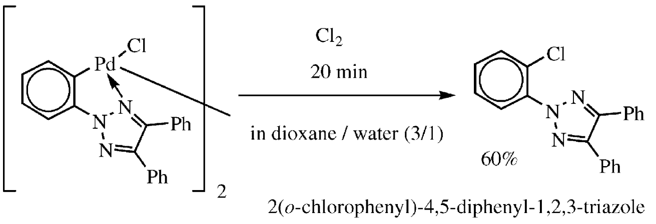


Scheme 11. [100].



Scheme 12. [101].

lective electrophilic reactions yielding almost exclusively *para*-substituted products. However, evidently, the use of cyclometallated compounds might drastically change the selectivity in favor of *ortho*-halogenated compounds as shown in Eq. (29) [75,103]. This halogenation is widely applied, also as a regio-selective reaction method as shown below in Scheme 20 (see Section 3.9).



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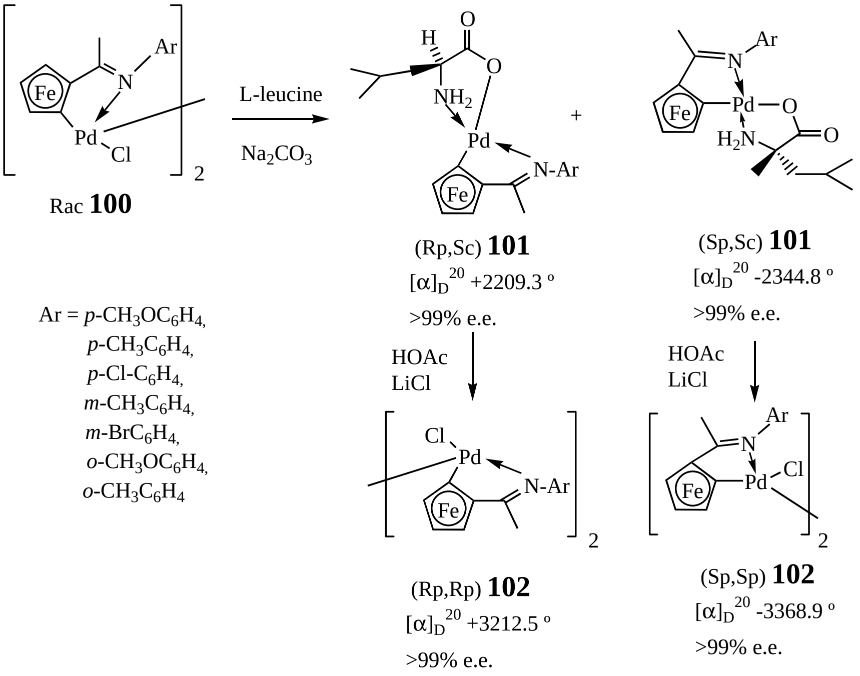
3.5. *Reactions of chiral compounds with amino acids and enantioselective rearrangements*

The optically pure α-amino acids, e.g. L-leucine, are used as a chiral auxiliary for the optical resolution of cyclopalladated ferrocenylimines as shown in Scheme 13 [104,105]. On the other hand, the optically pure cyclomatalated ferrocenylimines were found to be equally useful in the resolution of racemic α-amino acid.

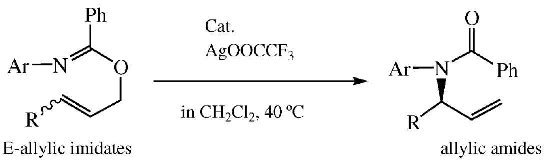
For example, by using a chiral dimer (Rp,Rp) **102** (*R*-configuration) as a resolving agent, the optical resolution of a raceminc α-amino acid was successfully carried out (Scheme 14) [104]. The mixture of diastereomers (Rp,Sc) **103**, (Rp,Rc) **103** could be separated by chromatography. The optically active α-amino acids (Sc **104** and Rc **104**) were obtained by the treatment of compounds (Rp,Sc) **103**, (Rp,Rc) **103**, respectively, with glacial acetic acid and LiCl, and the dimer (Rp,Rp) **102** was recovered without loss of the optical activity [104–106].

Chiral cyclopalladate ferrocenyl compounds rearrange allylic imidates to allylic amides. It is seen that allylic *N*-arylimidates are excellent substrates for providing the allylic amides in good rates, good yields, and moderate enantioselectivities. The variation of the electron donating ability of the *N*-aryl group had little effect on the outcome of the reaction (no. 1–3), whereas the rate of reaction decreased dramatically as the size of the substituent on the alkane increased (no. 3–6). The corresponding *Z*-allylic imidate (no. 7) provided the allylic amide product having an



Scheme 13. [104,105].

opposite absolute configuration with a decrease in reaction rate as shown in Eq. (30) and in Table 5 [107].



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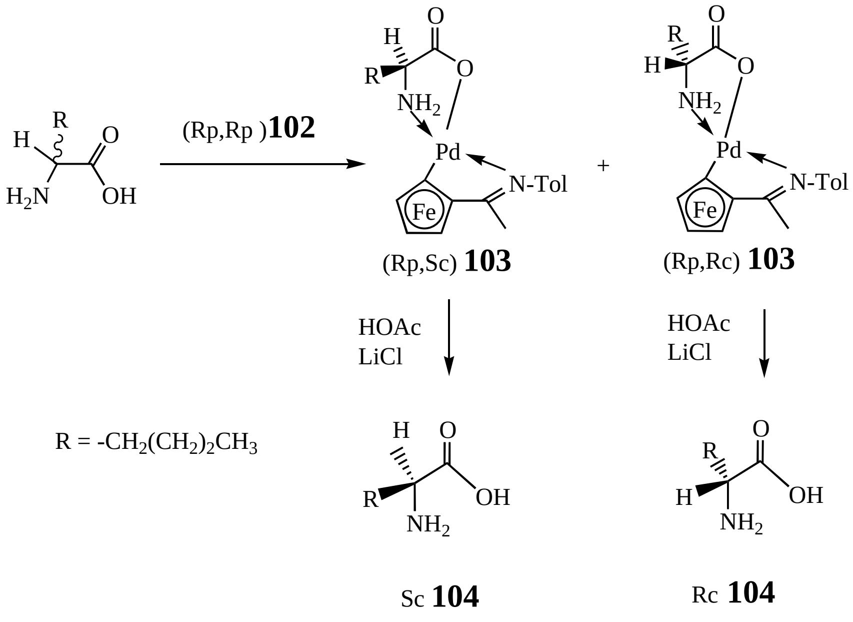
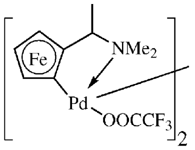
The size of the oxazoline substituent in the catalysts (**106**–**108**) was increased to 3-methoxy-3-pentyl (**108**) and an iodide-bridged dimer was activated in CH_2Cl_2 by deiodination with $Ag(OOCCF_3)$. These in situ-generated species catalyzed the rearrangement of *E*-allylic imidate to allylic amide in moderate to good yields with enantioselectivities of 72–79%e.e. (no. 8–10).



Scheme 14. [104].

Table 5
Rearrangement of allylic imidates catalyzed by the palladacyle catalysts/$AgOOCCF_3$ in CH_2Cl_2

No.	Cat.	R	Ar	Time (h)	Yield (%)	%e.e.
1	105	Pr	4-$CF_3C_6H_4$	24	97	57
2	105	Pr	4-MeC_6H_4	24	69	52
3	105	Pr	Ph	38	84	61
4	105	Me	Ph	16	94	54
5	105	Ph	Ph	27	47	47
6	105	*t*-Bu	Ph	48		
7	105	Pr	4-$CF_3C_6H_4$	6 (days)	76	46
8	106	Pr	4-$CF_3C_6H_4$	2 (days)	57	79(*S*)
9	107	Pr	4-$CF_3C_6H_4$	2.5 (days)	76	76(*S*)
10	108	Pr	4-$CF_3C_6H_4$	3 (days)	95	72(*R*)
11	106	Pr(*Z*)	4-$CF_3C_6H_4$	3 (days)	67	91(*R*)
12	107	Pr(*Z*)	4-$CF_3C_6H_4$	6 (days)	89	90(*R*)
13	108	Pr(*Z*)	4-$CF_3C_6H_4$	6 (days)	81	92(*S*)



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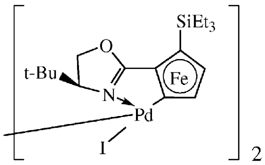

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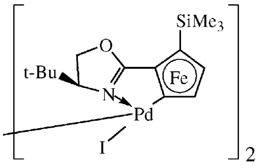

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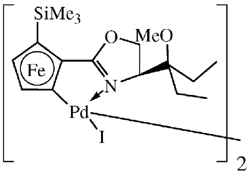

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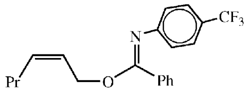


109

By using the catalysts having planar chiral elements such as Pd, O, N, C and Si, enantioselectivity was dramatically improved. For example, cyclopalladated ferrocenyloxazolines (**106**–**108**) catalyzed the rearrangement of several *Z*-allylic imidate **109** to give rearranged allylic amides in >90%e.e. (no. 11–13), as shown in Eq. (30) and in Table 5 [107].

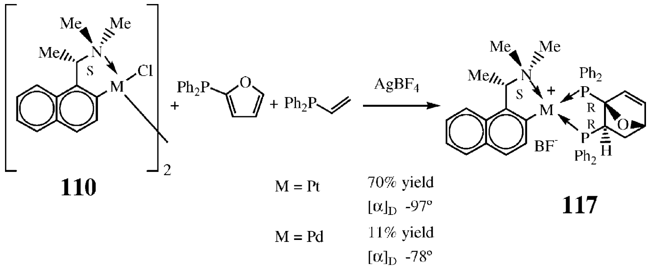
3.6. Asymmetric Diels–Alder reactions

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 cycloaddition reactions between coordinated 3,4-dimethyl-1-phenylphosphole **110** and two dienophiles (*N*,*N*-dimethylacrylamide and styrene) via two pathways of endo (compounds **111**) with X = Cl and exo (compounds **112**) with X = $OClO_3$ that proceed as shown in Scheme 15 [108].

For example, in the reactions with *N*,*N*-dimethylacrylamide, diasteromeric cycyloadducts were separated to pale yellow prisms and yellow blocks by fractional crystallization with dichloromethane and diethyl ether. These molecular structures (compounds **113**,**114**) 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 **115** ($[\alpha]_{365}$ = +5.9) and *S*-endo 116 ($[\alpha]_{365} = -5.7$) forms as shown in Scheme 16 [108].

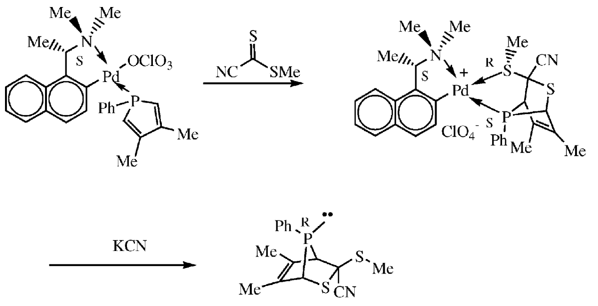
Leug and coworkers [109,110] reported the effect of palladium or platinum metal templates of (1-(dimethylamino) ethyl)naphthalene on the asymmetric Diels–Alder reactions of 2-diphenylphosphinofuran with diphenylvinylphosphine, and, of 1-phenyl-3,4-dimethlylphosphole with methyl cyanodithioformate. They are shown in Eqs. (31)–(32), respectively.

The Diels–Alder reaction of 2-diphenylphosphinofuran with diphenylvinylphosphine in the presence of organoplatinum complex gives the chelating diphosphine *exo*-cycloadduct, 4(*R*), 5(*R*)-bis(diphenylphosphine)-7-oxabicyclo[2.2.1] hepta-2-ene 117 (M = Pt) in 70% isolated yield with many diastereoisomers as shown in Eq. (31). The cycloaddition reaction proceeded at a significantly slower rate and exhibited a markedly lower stereoselectivity when the chiral platinum template was replaced by its organopalladium counterpart **117** (M = Pd) [109].



(31)

As shown in Scheme 15, the reaction of *ortho*-palladated (1-(dimethylamino)ethyl)-naphthalene with perchlorate complex proceeds *exo*-pathway and produce the (+)-*exo*-*syn*-methylthio-substituted phosphanorbornene P–S bidentate chelate **118** as shown in Eq. (32). The generation of the chelating cycloadduct involved an intramolecular cycloaddition mechanism in which both the cyclic diene and the hetero dienophile were coordinated simultaneously to the chiral palladium template during the course of the cycloaddition reaction [110].



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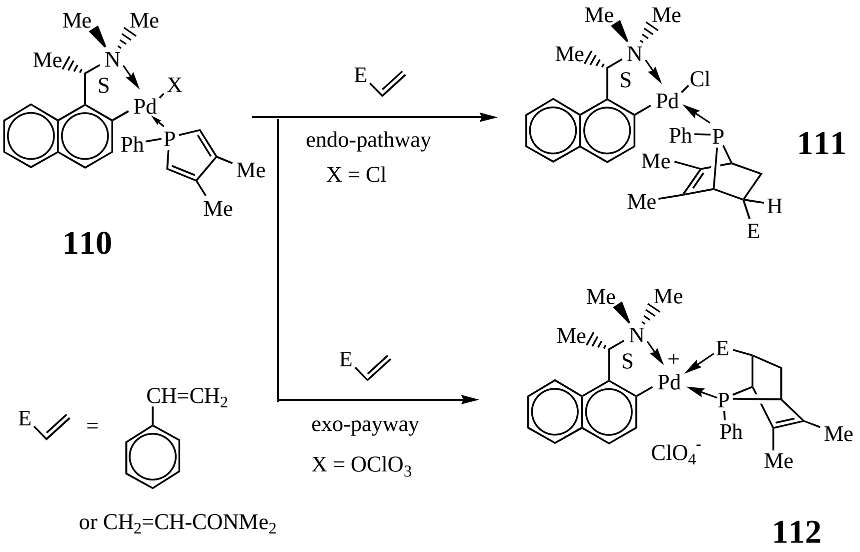
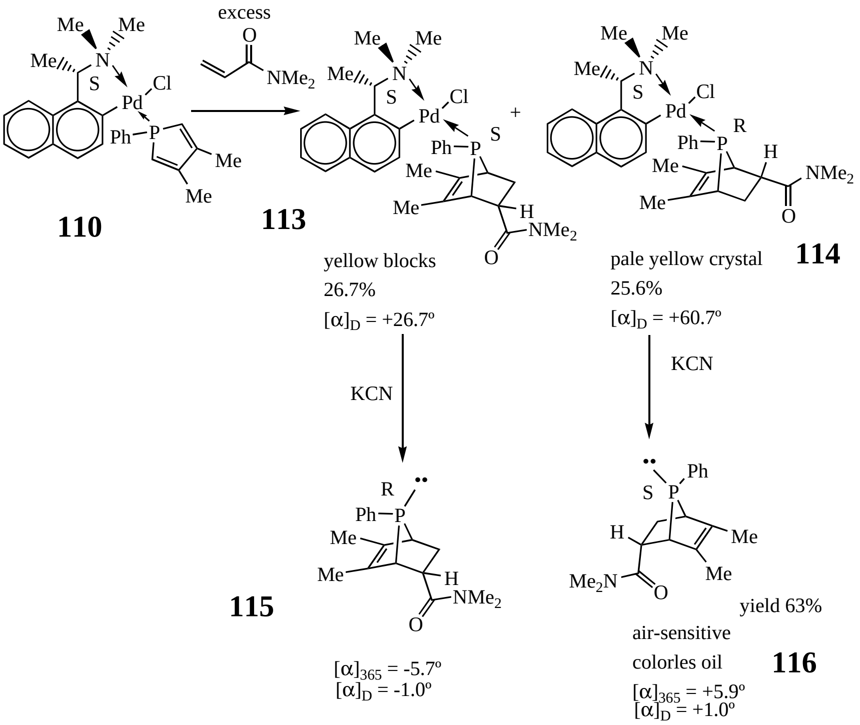


Scheme 15. [108].



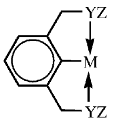
Scheme 16. [108].

3.7. Pincer complexes and dehydrogenations

3.7.1. Pincer complexes

1,3-Bis(dimethylaminomethyl)benzene metal complexes **28** as shown in Table 3, comprise one of the most numerous intramolecular five-membered ring compounds. These bidentate phenyl compounds are called ‘pincer complexes’. Most coordinating atoms in these pincer complexes are nitrogen atoms, however, the other coordinating atoms such as phosphorus, oxygen and sulfur occur, as shown in compounds **119**.

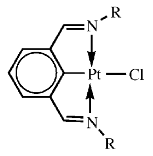
Principal Pincer Complexes



119

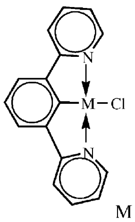
YZ = NR$_2$, PR$_2$, OR, SR, etc.

Some Other Pincer Complexes



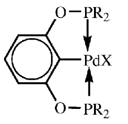
R = t-Bu. n-Bu, Cy, PhCH$_2$-, Ph,

120



M = Ni, Pd, Pt

121



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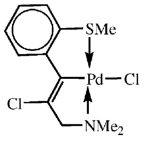

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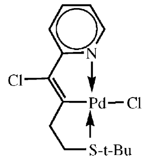

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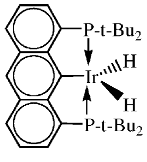

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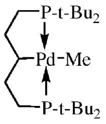

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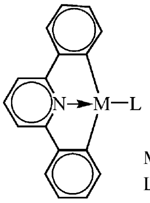
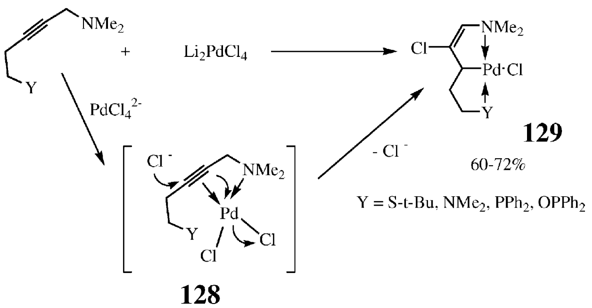


M = Pt, Pd
L = SEt$_2$, pyridine

127

However, similar bidentate compounds such as compounds **120–127**, are also called ‘pincer complexes’ [111–114]. For example, the pincer complexes having asymmetrical coordinating atoms are synthesized by the reaction of a palladium compound with hetero-substituted alkynes ($M_2NH_2C{\equiv}CCH_2H_2Y$) (Y = S-*t*-Bu, NMe$_2$, PPh$_2$ or OPPh$_3$) as shown in Eq. (33). In these reactions, the cyclopalladation reaction is considered to proceed by coordinating only one donor group and then followed by the coordination of a C≡C bond to the metal center after going through an intermediate (**128**). The selective and intermolecular nucleophilic addition of chloride on this activated unsaturated bond affords more thermodynamically stable palladacyclic ring. Finally, the coordination of the second donor groups to the Pd center yields the “pincer” palladacycles **129** [112].



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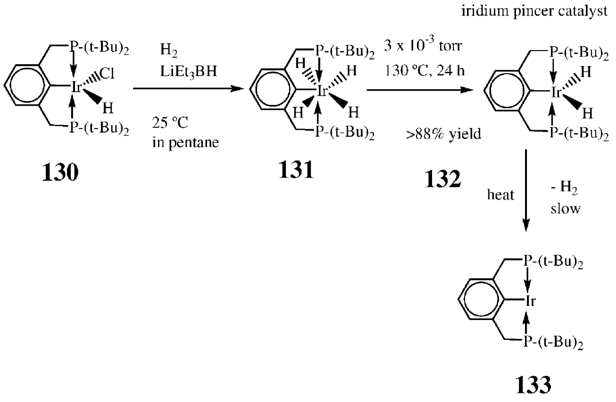
3.7.2. Dehydrogenations

In 2003, van der Boom and Milstein [111] reported on phosphine-based pincer complexes in Chemical Reviews. They pointed out that major recent contributions included efficient dehydrogenation, Heck type catalysts, the activation of strong C–O and C–C bonds, and the trapping of various intermediates and unusual molecules. These compounds possess the unique balance of stability versus reactivity which can be controlled by systematic ligand modifications and/or the variation of the metal center, allowing the enhancement of metal complex reactivity, stability and reaction selectivity.

In 2001, van Koten and Albrecht [115] reported platinum group organometallics based on the pincer complexes in *Angew. Chem. Int. Ed.* They pointed out that these compounds are used for gas sensors, crystalline switches for material processing, alkane dehydrogenation catalysts, sustainable metallodendrimer catalysts for homogeneous reactions, etc.

Fossey and Richards [113] also reported pincer complexes as catalysts for Diels–Alder reactions, Michael reaction, etc. I discuss in this section only dehydrogenation, presented as one of the most important applications of these pincer complexes.

A pincer complex, $IrH_2[C_6H_3(CH_2P\text{-}t\text{-}Bu_2)_2\text{-}2,6\text{-}]$ **132** is an extraordinarily active and robust catalyst for aliphatic dehydrogenation reactions. Its application to alkane dehydrogenation has resulted in the first efficient catalytic systems for homogeneous thermochemical alkane dehydrogenation without the use of a sacrificial hydrogen acceptor (e.g. *t*-butylethylene) and for dehydrogenation of *n*-alkanes to α-olefins. Pincer catalysts also effect other aliphatic dehydrogenations that had not previously been accomplished via homogeneous catalysis including the conversion of cycloalkanes to arenes, ethylbenzene to styrene and tetrahydrofuran to furan. The iridium catalyst **132** is prepared as follows: in the first step, a hydrido chloride complex **130** is converted to a tetrahydride complex **131** by a reaction with $LiEt_3BH$ under an atmosphere of H_2. Then, the iridium catalyst **132** is obtained quantitatively upon heating the tetrahydride **131** at 130 °C in vacuo as shown in Eq. (34).



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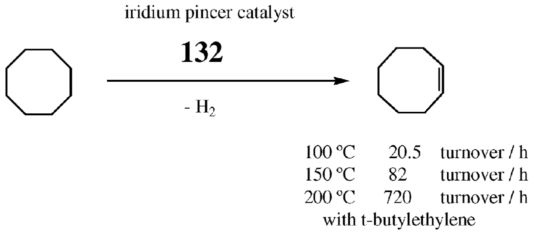


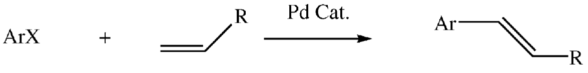
(35)

For example, dehydrogenation of cyclooctane proceeds in the presence of *t*-butylethylene as the hydrogen acceptor as shown in Eq. (35). At 150 °C, the turnover/h is 82, while a rate of 720 turnover/h is observed at 200 °C. The dehydrogenation is required for the formation of the active complex **133** in the reaction without a hydrogen acceptor. However, the formation of the dehydride **133** from a dihydride catalyst **132** is not so fast. Hence, none of these is of practical value due to the requirement for sacrificial acceptors and also due to the following product inhibition problems. All of these catalytic reactions are inhibited by the presence of even traces of nitrogen. This is apparently due to the formation of remarkably stable dinitrogen complexes: $[Ir\{C_6H_3(CH_2PR_2)_2\text{-}2,6\}]_2(\mu\text{-}N_2)$. Mechanistic studies have indicated that the high activity of the pincer catalysts may be in part due to 'agostic promotions' by phosphino aliphatic groups [116].

3.8. Metal-catalyzed cross-coupling reactions

3.8.1. Heck type cross-coupling reactions

In the past 30 years, there have been many reports detailing coupling reactions catalyzed by transition metals. Heck reactions are especially widely known [117–122]. The Heck reactions are the cross-coupling reactions of aryl halides with alkenes in the presence of palladium catalysts as shown in Eq. (36) and Scheme 17 [122]. Mizoroki first reported the same type of cross-coupling reaction as "The Heck reaction" in a Japanese Journal in 1971 [123], while Heck separately reported it in *J. Org. Chem.* in 1972 [124]. Therefore, some articles called these reactions as Mizoroki–Heck reactions [117].

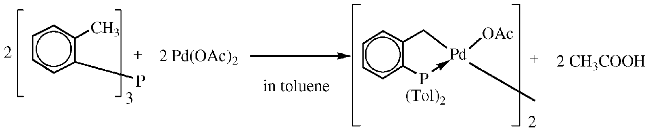


(36)

Similar cross-coupling reactions with transition metal catalysts such as the Kharasch reaction, Negishi reaction, Stille reaction, Suzuki reaction and Sonogashira reaction were also reported in 1970s and 1980s. The Heck reaction is widely applied industrially [119,122,125,126].

Heck reactions have been used for the production of fine chemicals on the scale of 1–500 t per year. In 2001, de Vries [119] reported the following five kinds of chemicals produced by Heck reactions: a herbicide (Prosulfuron^{TM}) **134**, 2-ethylhexyl-*p*-methoxy-cinnamate as a sunscreen agent **135**, an anti-inflammatory analgesic (Naproxen^{TM}) **136**, a benzocyclobutene-containing monomer for coatings of electronic components (Cyclotene^{TM}) **137** and an antiasthma agent (Singulair^{TM}) **138** as shown in Table 6 [119].

Recently, Herrmann et al. [117] reported an excellent palladium catalyst for the Heck reaction and also useful for other metal-catalyzed cross-coupling reactions. This catalyst is the air and moisture stable yellow *trans*-di(μ-acetate)bis[di-*o*-tolylphosphinobenzyl]dipalladium(II) **139**, which is prepared by the reaction of palladium acetate with tri-*o*-tolylphosphine (P(*o*-Tol)$_3$) (Eq. (37)).

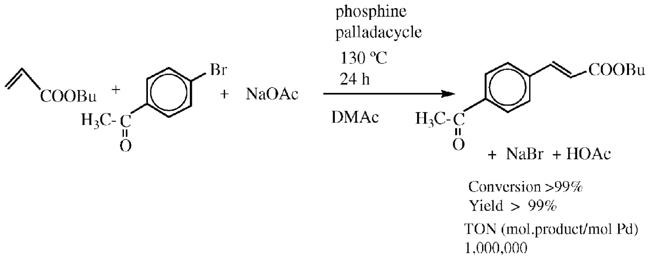


phosphine palladacycle **139**

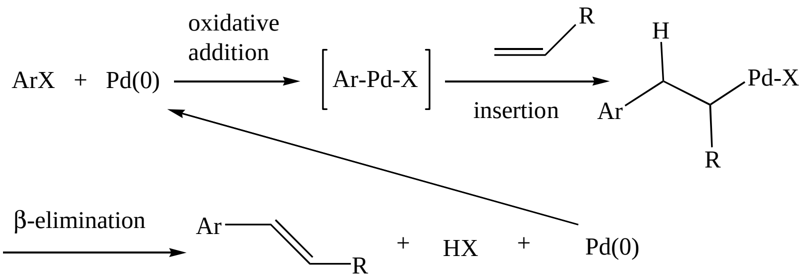
(37)

This has outstanding thermal stability with no decomposition below 250 °C whereas, e.g. *trans*-$Pd(PPh_3)_2(OAc)_2$ decomposes at about 150 °C [117].

For example, the industrially useful cinnamic acids are quantitatively prepared using the tolyphosphine catalyst **139** in the presence of sodium acetate. Activated, electron-poor aryl bromides like 4-bromoacetophenone react with high turnover numbers of up to 10^6 (mol product/mol Pd) as shown in Eq. (38) [117].

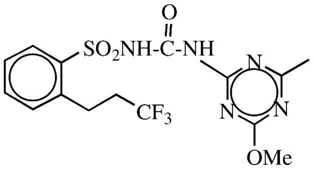
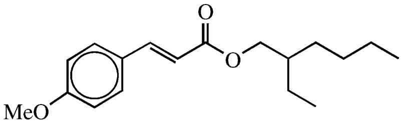
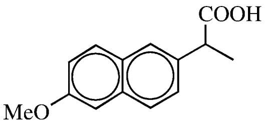
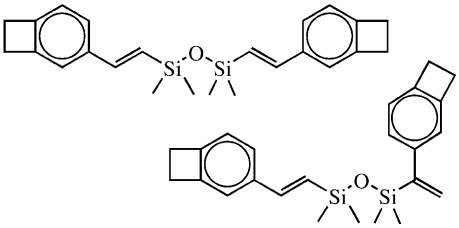
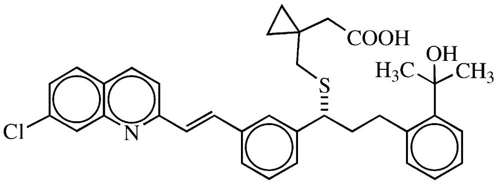


(38)

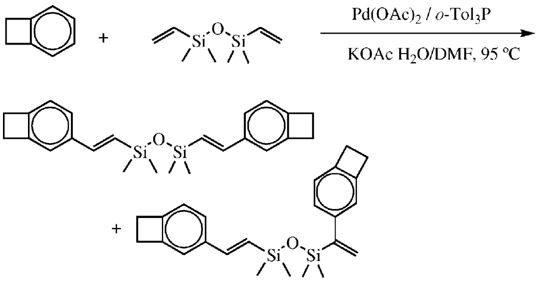


Scheme 17. [122].

Table 6
Fine chemicals produced with Heck reactions [119]

Herbicides (Prosulfuron™)		**134**
Suncreen agent 2-ethylhexyl-*p*-methoxy-cinnamate		**135**
Anti-inflammatory analgesic (Naproxen™)		**136**
Monomer for coatings of electronic components (Cyclotene™)		**137**
Antiasthma agent (Singulair™)		**138**

Generally, the palladacycles such as **139** are much more stable than Pd–phosphine complexes and can be used at high temperatures. The same effect is exhibited in the pincer complexes. In these chemicals, the monomer for a coating of electronic components **137** is actually produced by using the tolylphosphine catalyst **139** as shown in Eq. (39) [119].



137 (39)

3.8.2. *Kharasch, Negishi, Stille, Suzuki and Sonogashira reactions*

The first four reactions; Kharasch, Negishi, Stille and Suzuki reactions, are biaryl coupling reactions. On the other hand, the Sonogashira reactions are the reactions of aryl halides or alkenyl halides with alkynes as shown in Eqs. (40) and (45) [122,127].

Kharach reaction

$$\underset{(X = \text{halogen})}{Ar^1MgX} + \underset{(X = \text{halogen})}{Ar^2X} \longrightarrow Ar^1\text{-}Ar^2 \qquad (40)$$

Negishi reaction

$$\underset{(X = \text{halogen})}{Ar^1ZnX} + \underset{(X = \text{halogen or triflate})}{Ar^2X} \longrightarrow Ar^1\text{-}Ar^2 \qquad (41)$$

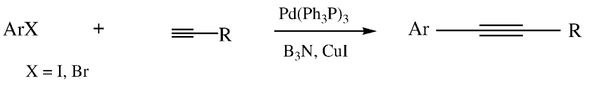
Stille reaction

$$\underset{(R = \text{Me, Bu})}{Ar^1SnR_3} + \underset{(X = \text{halogen or triflate})}{Ar^2X} \longrightarrow Ar^1\text{-}Ar^2 \qquad (42)$$

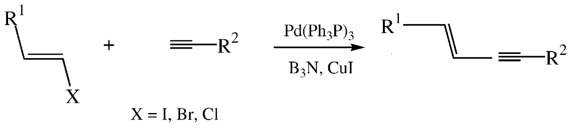
Suzuki reaction

$$Ar^1B(OH)_2 + \underset{(X = \text{halogen or triflate})}{Ar^2X} \longrightarrow Ar^1\text{-}Ar^2 \qquad (43)$$

Sonogashira reaction



(44)



(45)

The Kharasch reactions were reported first in the mid to late 1970s. The reactions are performed, generally, between aryl Grignard reagents and aryl halides in the presence of a catalyst such as ($Ni(Ph_2PCH_2CH_2PPh_2)Cl_2$) to yield the biaryls as shown in Eq. (40). One disadvantage of the Kharasch reaction is that the polar nature of the Grignard reagents precludes the use of several types of functional groups in the coupling partner such as aldehydes, ketones, esters, and nitro group [127].

The Negishi reaction began to assume importance in the mid 1970s. This reaction utilizes arylzinc reagents and aryl halides or triflates as shown in Eq. (41). Unlike the Kharasch reaction, functional groups such as aldehydes, ketones, esters, amines, nitro group, etc. are tolerated as the coupling partner of the arylzinc reagent [127].

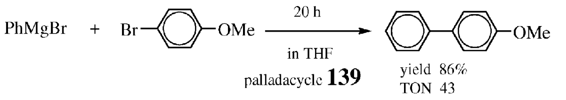
In the late 1970s, the Stille reaction was used initially in biaryl syntheses. This reaction uses arylstannanes and aryl halides or triflates as shown in Eq. (42). The reaction is extremely versatile, proceeds under neutral conditions, and can tolerate a wide range of substituents as coupling partners. Thus, substituents that are not compatible with the Kharasch and Negishi reactions are often tolerated in the Stille reactions [127].

The Suzuki reaction was used first in early 1980s. This reaction, like the Stille reaction, has proven extremely versatile and is extensively used in natural product syntheses. Aryl boronic acids are the usual substrates in this reaction together with aryl halides or triflates although the esters of aryl boronic acids and arylboranes are frequently used as shown in Eq. (43) [127].

The Sonogashira reaction was used initially in mid 1970s. The Sonogashira reaction is a cross-coupling reaction of terminal alkynes with aryl halides or alkenyl halides in the presence of amines with a palladium phosphine catalyst. The reactions proceed smoothly by adding a catalytic amount of CuI as shown in Eqs. (44) and (45) [122].

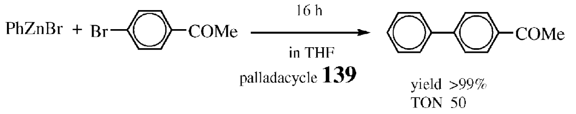
Herrmann et al. [117] also reported Sonogashira reactions using the cyclopalladated tolylphosphine catalyst **139** as shown in Eqs. (46)–(50). These reactions are also applied to amination reactions, which were discovered independently by Buchwald and Hartwig in 1995 [128]. For example, aryl halides react with piperidine or *N*-methylaniline in toluene in the presence of a sterically hindered base NaO-*t*-Bu or KO-*t*-Bu and 0.5 mol% cyclopalladated tolylphosphine catalyst **139** as shown in Eqs. (51) and (52) [117].

Kharach reaction



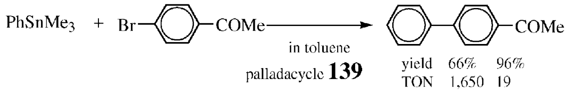
(46)

Negishi reaction



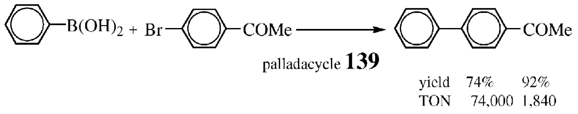
(47)

Stille reaction



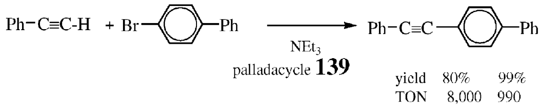
(48)

Suzuki reaction

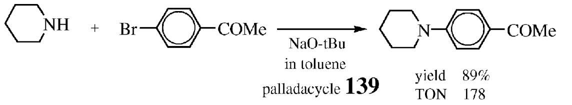


(49)

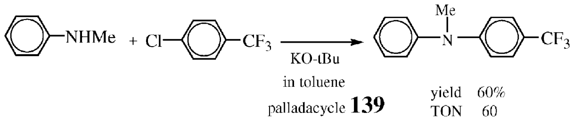
Sonogashira reaction



(50)



(51)

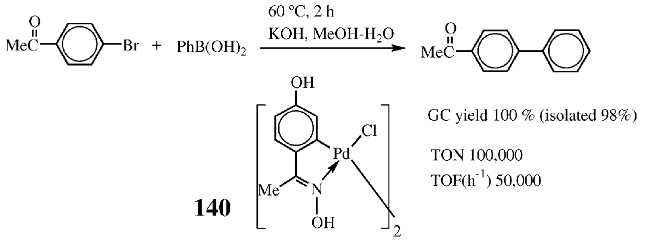


(52)

The phosphine palladium five-membered ring catalyst **139** is suitable for the Heck reaction as a student chemical experimental reaction because it is a stable and easily handled catalyst [129].

The Suzuki reactions are the cross-coupling reactions of organoboron reagents with organic halides or related electrophiles, which represent one of the most straightforward methods for carbon-carbon bond formation. In 1995, Suzuki and Miyaura [130] reported a very wide range of aryl- and 1-alkenylboron reagents that undergo the palladium(0)-catalyzed reaction with alkyl, allylic, alkenyl, aryl, and 1-alkynyl substrates.

Botella and Nájela found the palladacyle **140** derived from phenone-oxymes to be an efficient catalyst for the Suzuki reaction. The reaction of aryl bromides with this catalyst gave biaryls in high yields with high turnover numbers (up to 100,000) as shown in Eq. (53) [131]. Aliphatic boronic acids can also be coupled efficiently in refluxing water with aromatic bromides or chlorides, whereas benzylic and allylic chlorides can be coupled with aryl boronic acids in aqueous acetone at a room temperature [131].

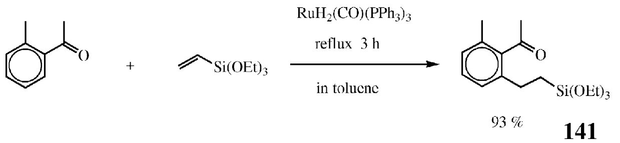


140

(53)

3.8.3. Ruthenium-catalyzed cross-coupling reactions

Murai reported ruthenium catalysts for the cross-coupling reactions of phenylmethylketones at the *ortho*-position in 1993 [132]. The reaction gave a 1:1 adduct in an almost quantitative yield based on both starting materials. The most effective catalysts are $RuH_2(CO)(PPh_3)_3$ and $Ru(CO)_2(PPh_3)_3$. Vinylsilane and allylsilane gave coupling products with *o*-methylacetophenone in excellent yields as shown in Eq. (54) [132–138].

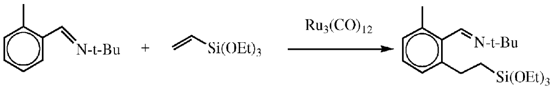


141

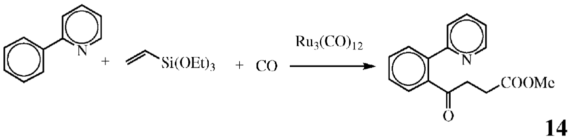
(54)

These reactions are presumed to proceed via a five-membered ring structure by the coordination of the oxygen ligand to a metal atom, followed by bonding the metal to a γ-carbon atom as shown in Scheme 18 (see Eq. (2)) [132].

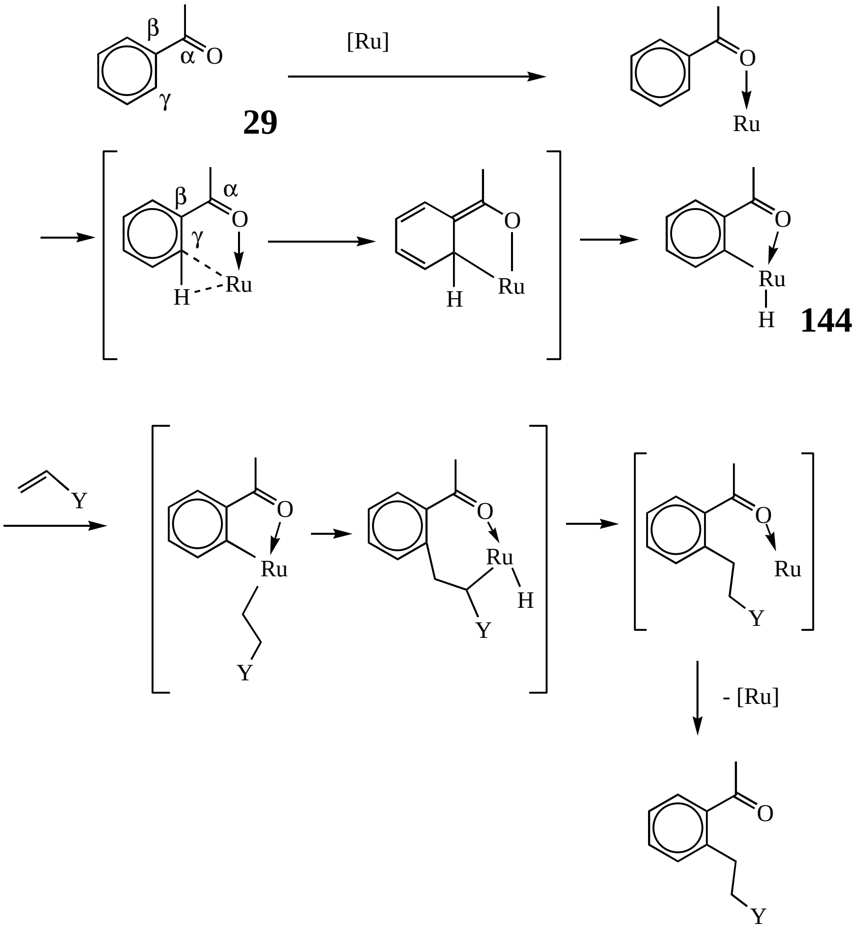
Hence, phenyl compounds, such as the alkylphenylketones which are examples of compounds **29** in Table 3 and Scheme 18, having a coordinating atom such as an oxygen, nitrogen, sulfur or phosphorus, are able to react with vinylsilanes in the presence of ruthenium catalysts. For example, cross-coupling reactions with nitrogen donor ligands are shown in Eqs. (55) and (56) [132].



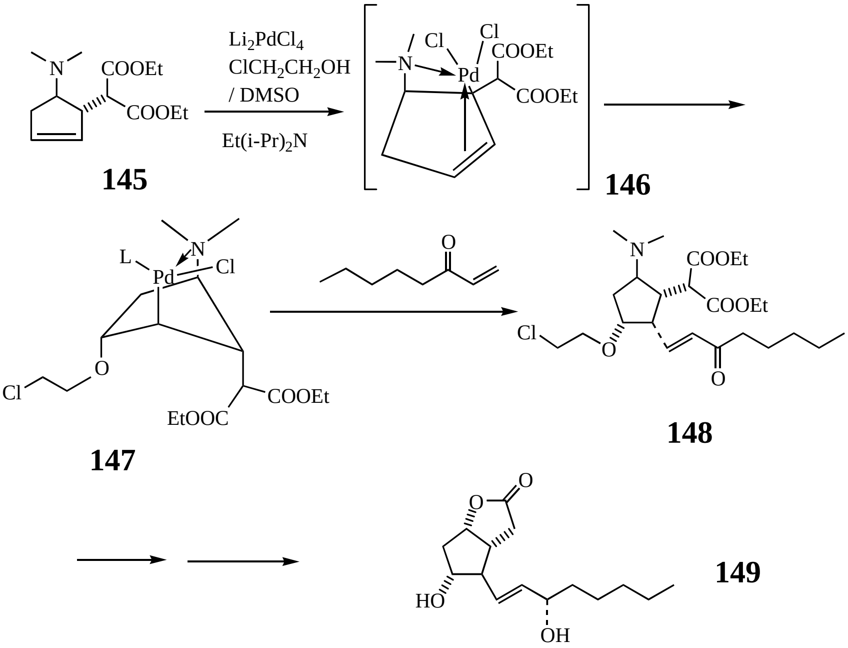
142 (55)



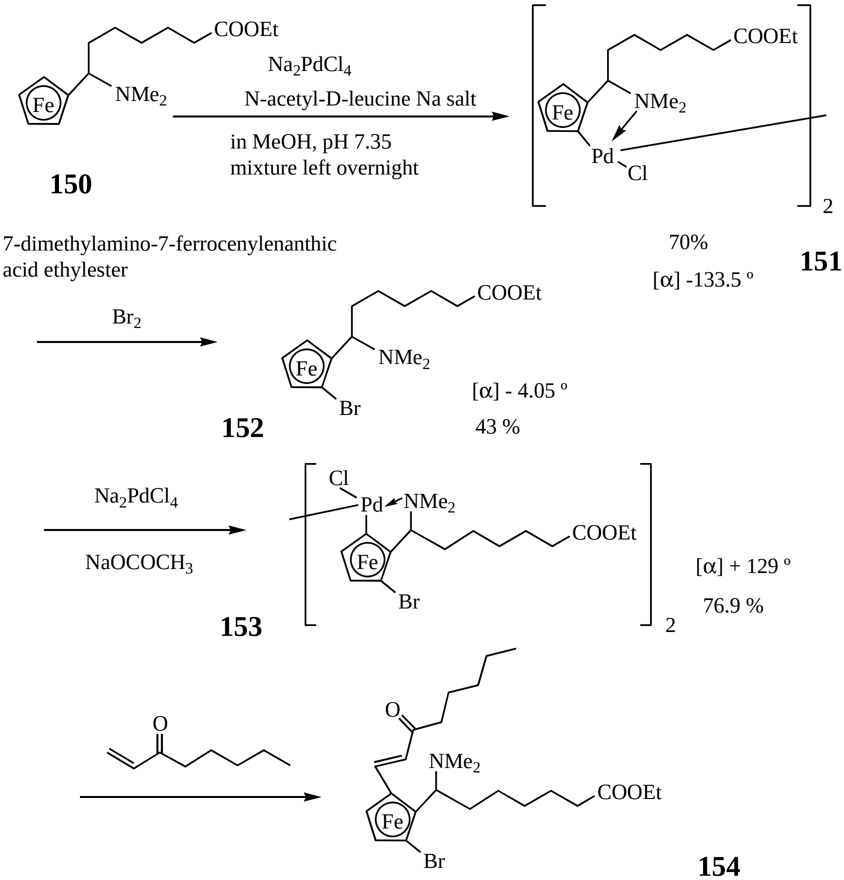
143 (56)



Scheme 18. [132].



Scheme 19. [75,143].



Scheme 20. [144].

3.9. Fine chemicals

The intramolecular five-membered ring compounds are used for the syntheses of many organic compounds. Some fine chemicals produced by the Heck reactions are already shown in Table 6 [119]. The intramolecular five-membered ring compounds are useful for preparation of fine chemicals because they satisfy high regioselectivity. That is to say, the metalations easily proceed with high regio-selectivity since only one five-membered ring can readily form in the cyclometaltion reactions. Then, all reactions such as reduction, acidolysis, transmetalation, alkylation, alkenylation, alkynylation, arylation, carbonylation, halogenation, acylation and isocyanate insertion proceed at the metal position [75,139–144].

For example, the palladation of cyclopenteneamino diester **145** in chloroethanol/dimethylsulfoxide in the presence of diisopropylethylamine affords a bicyclic cyclometalated complex that is immediately treated with *n*-pentyl vinyl ketone to yield a ketovinylation product **148** as a main product. This compound is then converted by routine chemical methods into a Corey lactone diol **149**, the precursor of the prostaglandin $F_2\alpha$ as shown in Scheme 19 [75,143].

A similar alkenyl compound is prepared by ketovinylation as shown in Scheme 20. A chiral cyclopalladated chloro-bridged complex **151** is prepared in the presence of the *N*-acetyl-D-leucine salt. The bromination of the enantiomeric palladacycle **151** gave the desired bromide **152** in fair yield. The repeated cyclopalladation of the enantiomeric monobromide **152** with $NaOCOCH_3$ as a catalyst gave a trisubstituted organopalladium complex **153**, which was then treated with pentyl vinyl ketone to yield the trisubstituted alkenyl ferrocenyl bromide **154**. Finally, the application of the boron hydride reduction of a quaternary ammonium salt, is thought to result in the synthesis of the prostaglandin 11-desoxy-PGF_1 [144].

4. Conclusions

The intramolecular five-membered ring compounds are surprisingly easily and selectively synthesized when compared with other sized ring compounds. Their stability is very high for organometallic compounds. Therefore, a large number of compounds with almost every metal have been reported, particularly since the 1970s. They are utilized for organic syntheses, and their ring formation property is utilized for highly regioselective reactions. Because of their high reactivity, these organometallic compounds are also used for some catalytic processes.

In 1955, Murahashi reported a cross-coupling reaction with cobalt catalysts, and in 1993, Murai also found a cross-coupling reaction with ruthenium catalysts. These two reactions are presumed to proceed via intramolecular five-membered ring compounds. These are but two of many types of reactions in many reaction combinations involving many different metals and many types of five-membered rings as shown in Tables 3 and 4.

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