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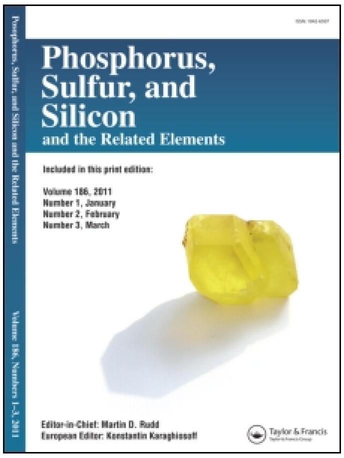

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FIVE-MEMBERED RING COMPOUNDS IN ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS

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FIVE-MEMBERED RING COMPOUNDS IN ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS

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Organometallic intramolecular-coordination five-membered ring compounds show high reactivity and high selectivity. Therefore, these many compounds have been synthesized since around mid 1960s. More than 50 kinds of metals are found as the metal elements, and these compounds are very widely used as intermediates and catalysts for organic syntheses.

Keywords: Compounds; coordination; five-membered ring; intramolecular; organometallic

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Some inorganic ring compounds are called chelate compounds. In these chelate compounds, the five-membered ring compounds are well known as stable compared with those of the four- and six-membered ring compounds.

The ring compounds of organometallic compounds generally are unstable because most of the metal-carbon bonds are unstable. However, their compounds having five-membered ring structures show an unbelievable stability as compared with the relative stability of four- and six-membered ring organometallic compounds.[1–8] Therefore, many researchers have investigated these compounds involving many kinds of metals since around mid 1960s. Now these compounds have been synthesized in conjunction with almost all kinds of metal elements. Applications of organometallic ring compounds as intermediates and catalysts in organic syntheses by utilizing their characteristics have been increasing.

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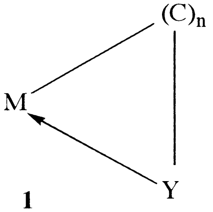
FIVE-MEMBERED RING COMPOUNDS

Organometallic intramolecular-coordination compounds generally are expressed as shown in formula 1. These compounds were first published in 1955 by Bähr and Müller[9] as an organoaluminium metal intramolecular-coordination five- and six-membered ring compound. In 1963, Kleiman and Dubeck[10] reported on the cyclometallation of azobenzene with nickel as a transition metal. Publications on these cyclometallations have increased since then.



1

M = metal

$n \geq 1$

σ-coordination compounds

Y = O, N, S, P, As
Se, F, Cl

π–coordination compound

Y = alkenyl, allyl, alkynyl dienyl
aryl, cyclopentadienyl, etc.

Many articles on organometal intramolecular-coordination five-membered ring compounds have been published, as well as the kinds of metals related to the number of articles. From the many articles, reviews, monographs, Chemical Abstracts Database, and The Cambridge Structural Database, more than 50 kinds of metal elements are found as the metal elements of organometallic intramolecular-coordination five-membered ring compounds. The metal elements are shown in Table I.[1–8] Almost all the metallic elements have been incorporated into organometallic intramolecular-coordination five-membered ring compounds. The metal elements of which five-membered ring structures were not reported in the articles, are only four elements of cesium, barium, hafnium and niobium as ordinary metals.

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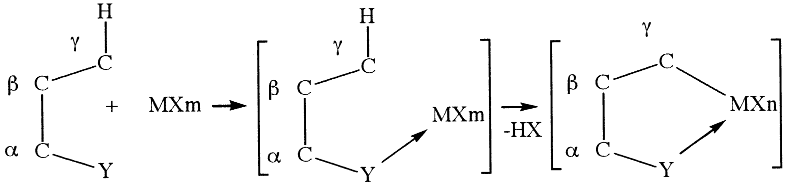
TABLE I Metal Elements of the Organometallic Intramolecular-Coordinaton Five-Membered Ring Compounds

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

Principal donor ligand atoms consist of the five elements nitrogen, phosphorus and arsenic of 15th group, and oxygen and sulfur of 16th group. Other elements are selenium of 16th group and fluorine and chlorine of 17th group. The latter elements have been reported only in few articles.[11–13]

The nine major types of compounds, especially, diemethylaminomethybenzene are prepared regarding most of the metals. The formation of these compounds are considered to be performed by a two step reaction mechanism as shown in Eq. 1. The first step is the coordination of a coordinating atom to a central metal. These coordinating atoms such as nitrogen and oxygen have high electronegativities compared with those of metal atoms. When the metals are coordinated by a coordinating atom, the metal is activated and is able to be situated at a very near position to a γ-carbon atom as shown in Eq. 1. Hence, the metal atom is able to easily bond with the γ-carbon atom and forms a five-membered cyclic ring.



(1)

But, in the case that activation by a coordinating atom is not enough, for example, with an arsenic element which has a low electronegativity, the reaction stops at the first step, that is, the coordination of a coordinating atom to a metal. The cyclization reaction of the second step does not proceed. Further cyclization reaction requires a higher temperature or an accelerating agent such as dehalogenation agent, e.g., sodium amalgam.[1]

Reactions with a strong aromatic C—H bond were generally thought to be difficult compared to a weak alkane C—H bond. But the reactions of aromatic compounds with transition atoms are found to be easily proceed.

In the cyclometalation of phenyl compounds with a transition metal, in the first step, the transition metal is coordinated by a coordinating atom. The metal is located to a position close to the carbon-carbon double bond between a ß-carbon atom and the γ-carbon to the coordinating atom. The metal is easily π-coordinated with the phenyl ring bond, then the π-bond changes to a σ-bond to the γ-carbon atom. It then forms an organometallic intramolecular-coordination five-membered ring compound.

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From 1980s, many reports on an agostic bond have been published. An agostic bond is formed when a transition atom approaches to a C—H bond. The agostic bond forms fluxional structures. Usually, in the agostic bond (M—H—C bond), the M—H bond is longer by 10–20% than that of the ordinary M—H bond, and the C—H bond is longer by 5–10% than ordinary C—H bond. Activation energy of the agostic bond required to change from the ordinary bond, is very little, that is, only 8 kcal/mol or below.[6,14–16]

When a metal is coordinated by a coordinating atom, it is able to be located at a near position to the γ-carbon atom described above. This phenomenon is able to form the agostic bond with the C—H bond at the γ-carbon atom, that is, most cyclometalation proceeds with a low energy via the agostic bond.

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APPLICATIONS OF ORGNAOMETALLIC INTRAMOLECULAR-COORDINATION FIVE-MEMBERED RING COMPOUNDS

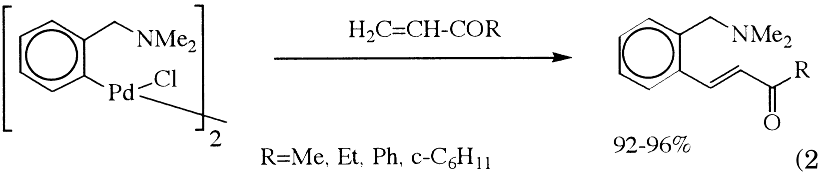
The primary applications of organometallic intramolecular-coordination five-membered ring compounds are the reactions of cyclometalated phenyl compounds. For example, the reactions with alkenes, carbon monoxide, alkynes, acyl halides, isocyanates, halogens, amino acids, etc. are useful.[17]

Especially, alkenylation and carbonylation with alkenes and carbon monoxide to cyclometalated phenyl compounds are the most useful applications. These reactions afford various kinds of vinyl and carbonyl derivatives. These reactions proceed through the most regioseletive passways because of the ortho-arrangements of cyclometaleted compounds.

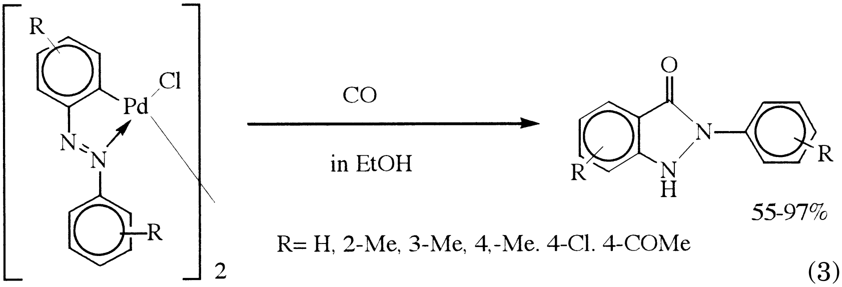
The example of alkenylation is shown as in Eq. 2.[18]

Carbonylations afford many kinds of carbonyl compounds by insertion of carbon monoxide. In the presence of an alcohol at this carbonylation, the carbonyl insertion product affords an esters. These carbonylations are shown in Eq. 3.[19]

In 1956, the carbonylation of azobenzene with octacarbonyldicobalt catalyst was reported to form 2-phenyl-1H-indazolone.[20] This product is the same compound as the carbonylation product of azobenzene cyclopalladeted compound. Cobalt compounds react with azobenzene and form the same types of cyclometalated compounds as the cyclopalladated compounds. From these facts, the carbonylation easily is presumed to proceed via the cyclometalation of azobenzene with the cobalt catalyst and the insertion of 2arbon monoxide as shown in Eq. 3.



(2)



(3)

Therefore, the actual application of the carbonylation was presumed to be older than the finding of the organotransition metal intramolecular-coordination compounds in 1963 by Kleiman and Dubeck.[10]

In the last 30 years, research on coupling reactions catalyzed with transition metals have been published one after another. Heck's reaction is the most widely known. The Heck reaction is the cross coupling reaction of aryl halides with alkenes with palladium catalysts.[21] The Heck reaction is widely and industrially applied, for example, to the synthesis of a cinnamic acid ester.[22]

The similar cross coupling reactions with transition metal catalysts such as the Kharasch reaction, Negishi reaction, Stille reaction, Suzuki reaction, and Sonogashira reaction have been reported in 1970s and 1980s.

Recently, a tri-arylphosphine catalyst is prepared by the reaction of a palladium compound with tri-tolylphosphine as shown in Eq. 4.[23] This has a long catalytic life and high activity. For example, in the Heck reaction, a ratio of 1,000,000 times (mol product/mol Pd) of substrate is used with this catalyst as shown in Eq. 5.[23] The other cross coupling metal-catalyzed reactions with this catalysts show very high yields and long catalytic life. This catalyst is reported to be useful for student chemical experiments of the Heck reaction because it is a stable and easy handling catalyst. This phosphine catalyst is an

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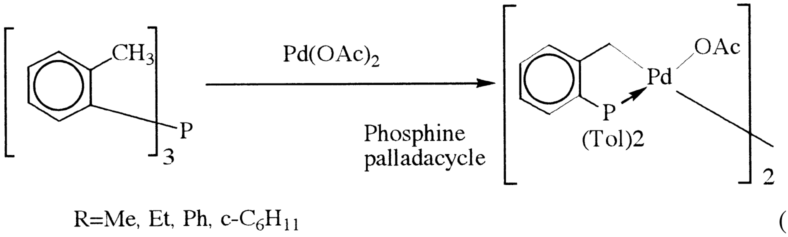
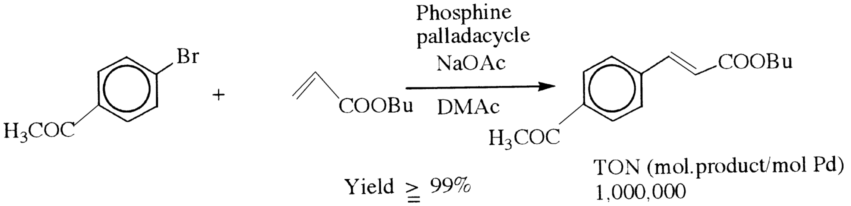
excellent example for exhibiting the characteristic of organometallic intramolecular-coordination five-membered ring compounds.



(4)



Yield ≥ 99%

TON (mol.product/mol Pd) 1,000,000

(5)

Murai et al.[24] in 1993, reported on triphenylphosphinecarbonylruthenium catalysts. The cross coupling reaction of phenylmethylketone with olefins in the presence of this ruthenium catalyst proceeds smoothly at the ortho-position. Vinylsilane and allylsilane gave coupling products with *o*-methylacetophenone in excellent yields. The reaction is presumed to proceed via the intermediate of organometallic intramolecular-coordination five-membered ring compounds. Actually, many cyclomatalled ruthenium compounds having the five-membered ring have been synthesized from these phenyl compounds.

These reactions are applied for the syntheses of various kinds of compounds. Especially, they are used for the preparations of pharmaceuticals. The formation reactions of the five-membered ring of a palladium metal were used for the preparation of prostaglandin precursors.[25]

CONCLUSIONS

Organometallic intramolecular-coordination five-membered ring compounds are already used as excellent catalysts, which show high yields and high turnover numbers, and gave high selective intermediates for organic syntheses such as vinylation and carbonylation. More useful catalysts and intermediates for organic syntheses will continue to be found.

Both of the cross coupling reactions with cobalt catalysts and with ruthenium catalysts are presumed to proceed via these five-membered

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ring compounds. These are only two types of applications of five-membered ring formation reactions; however, there are many types of five-membered ring formation reactions. We easily will be able to find new types of reactions with the other types of the ring formation reactions, with similar coupling reactions in the future.

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