Applied Organometallic Chemistry

Received: 10 September 2008 Revised: 23 November Accepted: 2 December 2008

(www.interscience.com) DOI 10.1002/aoc.1480

Characteristic reactions of group 9 transition metal compounds in organic synthesis

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Group 9 metal compounds in organic synthesis have two characteristic reactions. The first occurs because the group 9 metals have a high affinity to carbon–carbon or carbon–nitrogen π-bonds. The first type of characteristic reactions in these group 9 metal compounds includes Pauson–Khand reactions, the Pauson–Khand-type reactions ([2 + 2 + 1] cyclization), the other cyclizations and coupling reactions. The second occurs because the group 9 metals have a high affinity to carbonyl groups. The second type of characteristic reactions includes carbonylations such as hydroformylations, the carbonylations of methanol, amidocarbonylations and other carbonylations. The first characteristic reactions are applied for the synthesis of fine chemicals such as pharmaceuticals and agrochemicals. However, the second characteristic reactions are utilized not only for fine chemicals but also for important bulk commodity chemicals such as aldehydes, carboxylic acids and alcohols. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: transition metal compounds; Pauson–Khand reaction; Pauson–Khand-type reaction; coupling reaction; carbonylation; hydroformylation; amidocarbonylation; cycloaddition; Monsanto process; Cativa process

Introduction

Some of the properties of the group 9 transition metal, i.e. Co, Rh and Ir, are shown in Table 1.[1,2] The outer electron configurations of Co, Rh and Ir are $[Ar]3d^7 4s^2$, $[Kr]4d^8 5s^1$ and $[Xe]4f^{14} 5d^7 6s^2$, respectively. In these metals, the total number of electrons in their *d*- and *s*-orbital electrons is nine. Therefore, some metal compounds tend to form compounds, being donated by ligands that have nine electrons in accordance with the 18-electron rule. Examples of this are one cyclopentadienyl ring and one diene [e.g. CpCo(cod)], one cyclopentadienyl ring and two phosphines [e.g. $CpRh(PPh_3)_2$], and one hydrogen, one carbonyl and three phosphines [e.g., $HIr(CO)(PPh_3)_3$], as shown in Table 2.[1–3]

The chemical properties in these metal compounds are mutually slightly different because the number of electrons in their *s*-, *d*- and *f*-orbitals is different in addition to the difference in their atom sizes. For example, in studies on the C–H activation of methane by MCp(CO) for the group 9 metals, CoCp(CO) was found to be entirely inert towards alkanes in contrast to the corresponding rhodium and iridium systems.[4]

In the organocobalt compounds, their three characteristic reactions in organic syntheses were reported in an earlier review:[5] the first one occurs because cobalt has a high affinity to carbon–carbon or carbon–nitrogen π-bonds; the second one occurs because cobalt has a high affinity to carbonyl group; and the third one is due to the tendency of cobalt to easily form vitamin B_{12}-type compounds. These three characteristic reactions of organocobalt compounds in organic synthesis are given in Table 3.

The first type of characteristic reactions includes reactions with a $Co_2(CO)_6$ protecting group, Nicholas reactions and Pauson–Khand reactions. These reactions are caused by a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt. However, in organorhodium compounds and organoiridium compounds, only Pauson–Khand-type reactions proceed in a manner similar to the Pauson–Khand reactions in the above three organocobalt reactions.

The third type of characteristic reactions of organocobalt compounds is due to the fact that cobalt easily tends to form square-planar bipyramidal six-coordination structures with four nitrogen atoms or two nitrogen atoms and two oxygen atoms at square-planar positions, and to bond with one or two carbon atoms at axial positions, for example, B_{12}-type compounds. They have recently been used in organic syntheses and are utilized as catalysts for stereoselective synthesis. These reactions have been used as new applications for the organic synthesis.[5] However, articles regarding the B_{12}-type compounds of the rhodium and iridium compounds and their applications are not as common as those on organocobalt compounds.[6–9] This third type of characteristic reactions of organocobalt compounds is considerably different from similar characteristic reactions of organorhodium and organoiridium compounds. For example, those reactions between organocobalt compounds and organorhodium or organoiridium compounds, e.g. hydrogention properties[5] or reaction properties via their carbene complexes,[9a,9b,9c] are also different. Because of the hydrogenation properties of cobalt, cobalt compounds do not act as good catalysts as rhodium compounds, e.g. Wilkinson's complex $[RhCl(PPh_3)_3]$ and iridium compound [Vaska's complex, $IrCl(CO)(PPh_3)_2$].[5] In the latter reactions via carbene complexes, few articles have been published regarding organocobalt compounds as the carbene formations of organorhodium compounds[9a] and organoiridium compounds.[9b,9c]

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Table 1. Some properties of group 9 elements

Property	Co	Rh	Ir
Atomic number	27	45	77
Electronic configuration	[Ar]$3d^7 4s^2$	[Kr]$4d^8 5s^1$	[Xe]$4f^{14} 5d^7 6s^2$
Atomic weight	58.933	102.906	192.217
Electronegativity			
Pauling	1.88	2.28	2.20.
Allred	1.7	1.45	1.55
Ionization potential			
I_1 (kJ mol^{-1})	760	720	880
I_2		1744	
I_3		2997	
Electron affinity (kJ mol^{-1})	64	109.7	151
Metal radius (12-coordinate)/pm	125	134	136
Ionic radius M^{2+}	82	86	
M^{3+}	64	75	82
M^{4+}		67	
Covalent radius	116	125	136

For these reasons, reviews regarding these charactersistic reactions of all group 9 metal compounds in organic synthesis have been infrequently published. For example, reactions of alkynes with group 9 metal were reviewed in 2002.[9d] However, this review was concerned only with the coupling reactions of iridium and rhodium compounds. Recently, a review on group 9 metal complex-catalyzed hydrogen transfer reactions was published.[9e] This was concerned with hydrogen transfer reaction of simply iridium and rhodium compounds.

This article shows the first and the second types of characteristic reactions of the group 9 transition metal compounds in organic synthesis.

Cyclizations and Coupling Reactions

Introduction

Generally, transition metals show high affinities with π-electrons in the carbon–carbon or carbon–nitrogen π-bonds. These π-electrons are able to bond with not only the electrons of *s*- or *p*-orbitals in main-group metals but also electrons of *d*-orbitals (dz^2, $dx^2 - y^2$) in transition metals. Further, the p_x- and d_{xz}-orbitals of the transition metals overlap with the π^* antibonding molecular orbitals of olefins, and participate in the back-bonding.[10]

In the organocobalt compounds, the first type of characteristic reactions occurs because cobalt has a high affinity to the carbon–carbon or carbon–nitrogen π-electron bonds. In particular, the organocobalt compounds are able to form a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt.[5,11–15] For example, dicobalt hexacarbonyl diphenylacetylene can be cited.[16] The reaction of this mutually bridged bond is the most characteristic reaction of the organocobalt compounds. These are (i) the reactions of a $Co_2(CO)_6$ protecting group with a reactive acetylene bond; (ii) the Nicholas reactions; and (iii) the Pauson–Khand reactions as described in the first chapter. However, rhodium and iridium, which are larger atoms than cobalt atom, cannot form completely the same type of compounds, although a few rhodium compounds have mutually bridged bonds between the metal–metal bond and the acetylene triple bond, e.g. $Rh_2(PF_3)_6(PhC{\equiv}CH)$[17] and $Rh_2(PF_3)_4(PPh_3)_2(PhC{\equiv}CPh)$.[18] Therefore, in the rhodium and iridium compounds, the above three reactions do not occur. However, in rhodium and iridium compounds, the Pauson–Khand-type reactions, which are similar to the above third type of Pauson–Khand reactions of the organocobalt compounds, proceed. The Pauson–Khand and Pauson–Khand-type reactions are [2 + 2 + 1] cyclizations.

Hence, the first type of characteristic reactions of organocobalt compounds also proceeds in the other group 9 metal compounds. This first type of characteristic reactions comprises the following three types of reactions with the carbon–carbon or carbon–nitrogen π-bonds bonds:

(1) cyclizations with carbon–carbon π-bonds;
(2) cyclizations with carbon–carbon and carbon–nitrogen π-bonds;
(3) coupling reactions with carbon–carbon and carbon–nitrogen π-bonds.

In the first type of cyclization with the carbon–carbon multiple bonds, there are two types of reactions, i.e. cyclooligomerizations and cycloadditions. The cyclooligomerizations, mainly of organocobalt compounds, proceed with acetylene compounds. These cyclooligomerizations are cyclotrimerizations to yield benzene derivatives.[5]

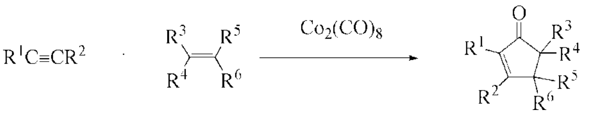
On the other hand, cycloadditions occur in all of the group 9 metal compounds. The cycloadditions are used mainly for the synthesis of cyclopentenones by the Pauson–Khand reactions and Pauson–Khand-type reactions ([2 + 2 + 1] cycloadditions), and for the synthesis of benzene derivatives with three ynes, cyclohexadienes with two ynes and one ene, and cyclohexenes with one yne and two enes by [2 + 2 + 2] cycloadditions.

The second type of cyclization, with carbon–carbon and carbon–nitrogen multiple π-electron bonds, forms heterocyclic compounds. These [2 + 2 + 2] cycloadditions are used for the synthesis of pyridine derivatives.

The third type of coupling reaction with the carbon–carbon or carbon–nitrogen π-bonds bonds, proceeds in the many types of reactions regarding all of the group 9 metal compounds.

Pauson–Khand-type reactions

The Pauson–Khand reactions involve the cyclization of one alkyne, one alkene and a cobalt carbonyl (as a carbon monoxide source, e.g., octacarbonyldicobalt) to yield cyclopentenones by [2 + 2 + 1]cyclization addition as shown in eqn (1):[15]



(1)

Many review articles on the Pauson–Khand reactions have been published.[19–37] Reactions to similar to Pauson–Khand reactions occur with other transition metal compounds besides the

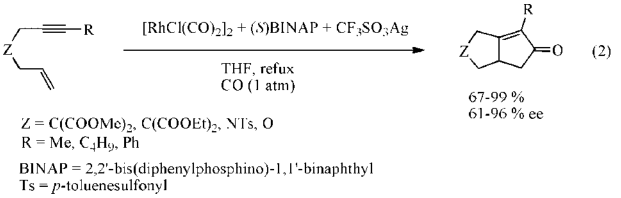
Table 2. Representative metal compounds of group 9 elements[1–3]

Compound	Co	Rh	Ir
Metal carbonyl	$(Co)_2(CO)_8$		
	$(Co)_4(CO)_{12}$	$(Rh)_4(CO)_{12}$	$(Ir)_4(CO)_{12}$
		$(Rh)_6(CO)_{16}$	
Metal halide	$CoCl_2 \cdot 6H_2O$	$RhCl_3 \cdot 3H_2O$	
	$CoBr_2$	K_3RhCl_6	$Na_3IrCl_6 \cdot 6H_2O$
Hydride	$HCo(CO)_4$	$HRh(CO)(PPh_3)_3$	$HIr(CO)(PPh_3)_3$
Metal carbonyl halide	$CoI_2(CO)Cp$	$[RhCl(CO)_2]_2$	$IrCl(CO)(PPh_3)_2$
Metal phosphine	$H_3Co(PPh_3)_3$	$RhCl(PPh_3)_3$	$IrCl(PPh_3)_3$
Metal carbonyl phosphine	$Co_2(CO)_6(P\text{-}n\text{-}Bu_3)_2$	$RhCl(CO)(PPh_3)_2$	$IrCl(CO)(PPh_3)_2$
Biscyclopentadienyl metal	$CoCp_2$	$RhCp_2$	$IrCp_2$
Cyclopenadienyl phosphine	$CoCp(PPh_3)_2$	$RhCp(PPh_3)_2$	
Cyclopentadienyl carbonyl metal	$CoCp(CO)_2$	$RhCp(CO)_2$	$IrCp(CO)_2$
			$[IrCpCl_2]_2$
Cyclooctadienyl metal	CoCp(cod)	$[RhCl(cod)]_2$	$[IrCl(cod)]_2$
Metal nitrogen	$HCo(N_2)(PPh_3)_3$		$IrCl(N_2)(PPh_3)_2$

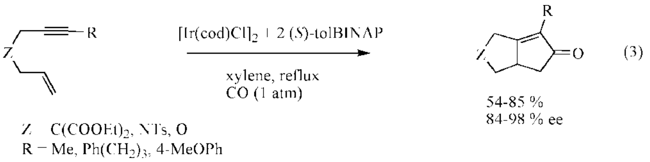
cobaltcarbonyl compounds.[23,26,27,31,38] These reactions are called the Pauson–Khand-type reactions. Rhodium compounds,[38–50] iridium compounds[27,38,51,52] and the compounds of the other metals such as Ti, Zr, Mo, W, Fe, Ru, Ni and Pd[15] are used in these reactions.

Asymmetric Pauson–Khand-type reactions proceed in the presence of transition metal catalysts and chiral compounds, or chiral transition metal catalysts.[27,38,46,49,51]

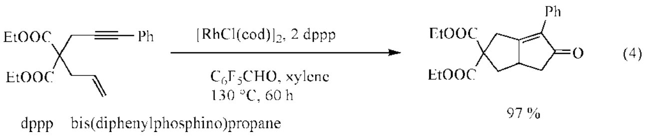
For example, the asymmetric Pauson–Khand-type reactions occur in the presence of a rhodium catalyst and chiral phosphine in high enantioselective yields, as shown in eqn (2). Silver salt, e.g. CF_3SO_3Ag, is required for the ionization of rhodium catalyst in THF.[46]



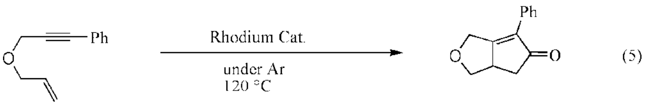
On the other hand, with cyclooctadiene iridium compounds and chiral bis(diphenylphosphine)ligand, the asymmetric Pauson–Khand-type reactions proceed in high enantioselective yields without using the silver salt, as shown in eqn (3).[51]



Aldehydes may be used as a source of carbon monoxide for the Pauson–Khand-type reactions.[27,38,53–61] For example, the Pauson–Khand-type reaction proceeds with electronegative pentafluorobenzaldehyde in high yield. When the reaction time was increased (60 h) untill all of the enyne was consumed, a quantitative yield of the carbonylated product was obtained as shown in eqn (4).[55]



As the other carbon monoxide sources, cinnamaldehyde was found to be able to be utilized for the Pauson–Khand-type reactions. When a noncationic rhodium complex and a chiral phosphine are used as the chiral catalysts, the reactions proceed in high enantioselective yields to give the chiral cyclopentenones, as shown in eqn (5).[53]



Rodium Cat.	CO source(equiv)	yield (%)	%ee
$Rh(dppp)_2Cl$	cinnamaldehyde (20)	98	
$Rh(dppp)_2Cl$	cinnamaldehyde (5)	93	
$Rh(dppp)_2Cl$	benzaldehyde (20)	87	
$Rh(dppp)_2Cl$	hexanal (20)	30	
$[Rh(cod)Cl]2 \cdot 2tolBINAP$	cinnamaldehyde (20)	89	83

The reactions of alkynes having a formyl group at their terminal positions also give the cyclopentenones. This terminal alkynal acts as the alkene and carbonyl sources in the Pauson–Khand-type reactions. It is proposed that the reaction proceeds by reductive elimination of rhodium metal of six-membered metallacycle, as shown in eqn (6).[62a,62b]

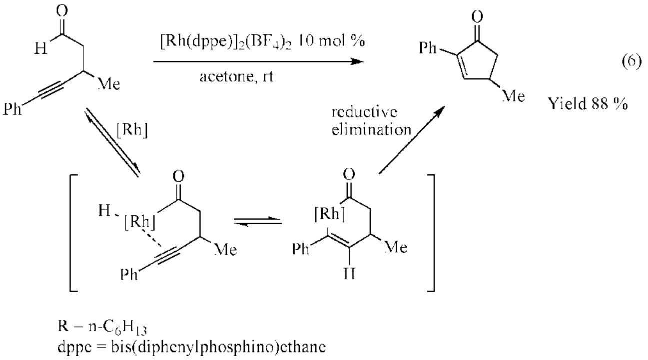
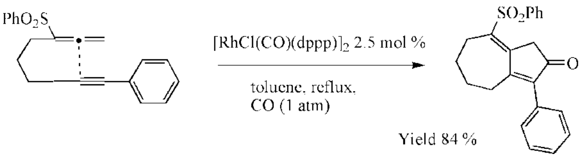


Table 3. Three characteristic reactions of organocobalt compounds in organic synthesis

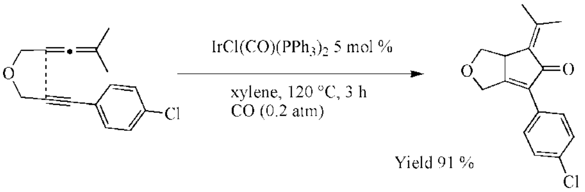
Characteristic property of metal	Reaction type	Reaction
1 High affinity to carbon–carbon or carbon–nitrogen unsataurated π-bonds	Reactions with unsaturated π-bond (i) Reactions with a mutually bridged bond between the two π-bonds of acetylene and the Co–Co bond of $Co_2(CO)_6$	1. Reactions with a $Co_2(CO)_6$ protection group 2. Nicholas reactions 3. Pauson–Khand reactions
	(ii) Reactions with the other π-bonds	1. [2 + 2 + 2] Cyclotrimerizations and other cyclizaitons such as [2 + 2 + 1], [2 + 2], [3 + 2], [4 + 2], etc.
2. High affinity to carbonyl group,especially, to the carbon atom of carbonyl group.	Reactions with carbonyl groups	1. Hydroformylations 2. Hydrocarbonylations 3. Amidocarbonylations 4. Hydrosilylcarbonylations 5. Carbonylations of halides 6. Other carbonylations
3. High affinity to porphyrins, bis(dimethylglyoxim), porphycenesbis(salicylaldehyde)-ethylenediamines, etc.	Reactions with vitamin B_{12} type compounds such as corriroids, porhpyrins and salcomines.	1. Diels–Alder reactions 2. Cyclopropations 3. Carbonyl-ene reactions 4. Henry reactions 5. Boron hydride reductions, etc.

Allenes are used in the presence of rhodium metal compounds as the alkene sources in the Pauson–Khand-type reactions.[63–76] For example, the Pauson–Khand-type reaction with an alkynylsulfonylallene proceeds with high yield via the reaction with the external π-bond under reflux in toluene solution, as shown in eqn (7).[64]



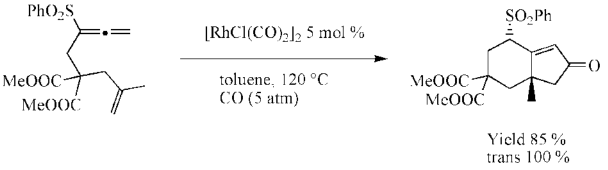
(7)

On the other hand, in the presence of Vaska's complex, $[IrCl(CO)(PPh_3)_2]$, the Pauson–Khand-type reaction with an allene as an olefin source in low partial pressure of carbon monoxide realizes the selective engagement of the internal π-bond of the allene to give a bicyclic cyclopentenone containing an alkylidene substituent as shown in eqn (8).[52]



(8)

Recently, Mukai *et al*. reported on the Pauson–Khand-type reactions with the allene at the terminal position as the alkyne sources. For example, the intramolecular Pauson–Khand-type reactions of sulfonylallenes proceed in the presence of a rhodium carbonyl chloride catalyst with high yield of the *trans*-cyclopentenones as shown in eqn (9).[74]



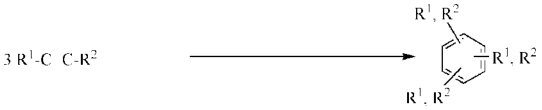
(9)

Other cyclizations

The most representative cyclizations of organocobalt compounds are Pauson–Khand reactions described in the former section, that is, [2 + 2 + 1] cyclizations. The other cyclizations with the organocobalt compounds are the other [2 + 2 + 1] cyclizations and various kinds of cyclizations such as [2 + 2 + 2], [2 + 2], [3 + 2 + 2], [3 + 2], [5 + 2] and [4 + 2].[5]

In the oligomerizations of acetylenes, cyclotetramerizations with only a few kinds of nickel catalysts[77–87] were reported. However, the synthesis of benzene derivatives from acetylene compounds by cyclotrimerizations with many kinds of transition metal catalysts has been reported. In particular, the organocobalts such as cyclopentadienyldicarbonylcobalt are conveniently used for the synthesis of the benzene derivatives. These cyclizations are called [2 + 2 + 2] cyclotrimerization reactions.[5,15]

Many reviews of these [2 + 2 + 2] cyclotrimerizations have been published regarding the group 9 metal acetylene compounds.[78,88–95] In these cyclotrimerizations, there are three types of cyclotrimerizations. The first one is cyclooligomerization-type cyclotrimerizations as shown in eqn (10). The second one is cycloaddition with two ynes and one yne as shown in eqn (11). The third one is intramolecular cycloaddition with three ynes as shown in eqn (12).



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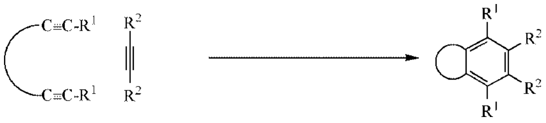

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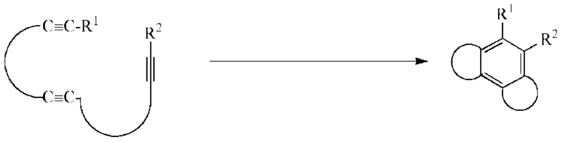
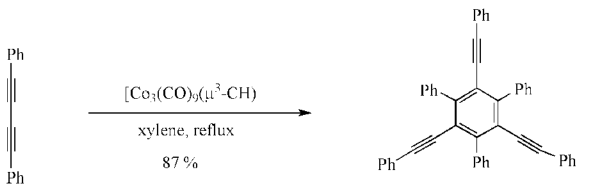


(12)

The first cyclooligomerizations yield many kinds of benzene derivatives and polymeric products. Usually their selectivities are poor. However, the cyclooligomerizations with some bulky or long acetylene derivatives can yield sole products in good yields. For example, in the group 9 metal compounds, these cyclooligomerization with the organocobalt and organorhodium compounds easily proceed to yield the benzene derivatives in high yields, as shown in eqns (13) and (14), respectively.[96,97]



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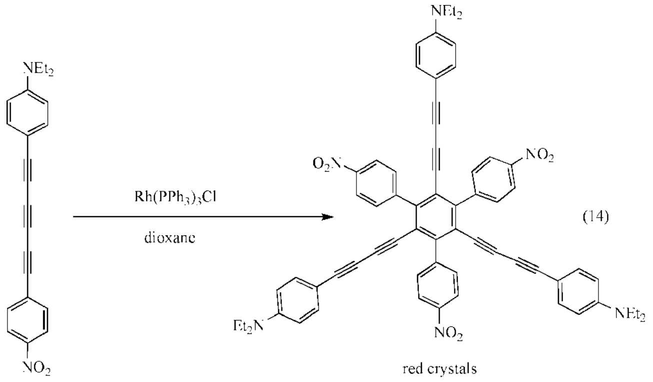
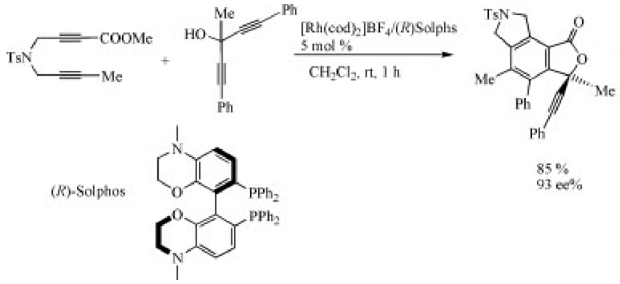


(14)

The second cyclotrimerizations are the most useful organic syntheses for the benzene derivatives. These methods are applied for not only the organocobalt[5] and rhodium metal compounds[98–107] but also organoiridium compounds.[108–111]

For example, one-pot cyclotrimerization with organorhodium catalysts and organoiridium catalyst are shown in eqns (15) and (16), respectively.[100,109]

With the organorhodium catalyst, [2 + 2 + 2] cycloaddition of 1,6-diyne ester with tertiary propargylic alcohol gives an enatioenriched tricyclic 3,3-disubstituted phthalide in high yield. This proceeds by cationic rhodium/Solphos complex-catalyzed asymmmetric one-pot transesterfication as shown in eqn (15).[100] On the other hand, with the iridiium catalyst, [2 + 2 + 2], cycloaddition of 1,6-diyne ether with monoalkyne bisether also gives only the DL isomer of the teraryl compound in high yield, as shown in eqn (16).[109]



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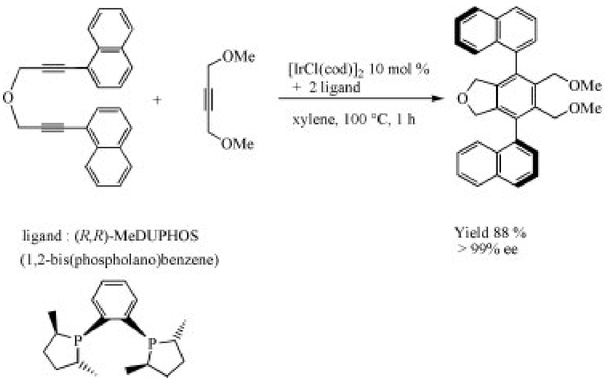
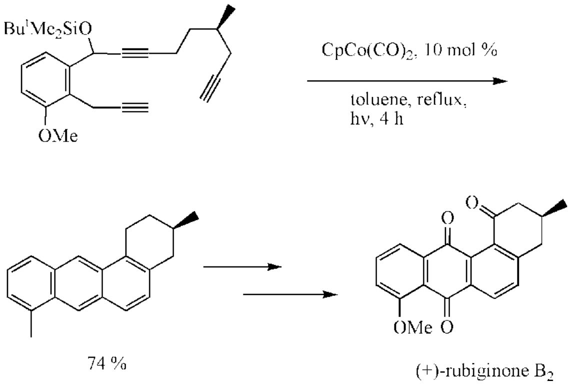


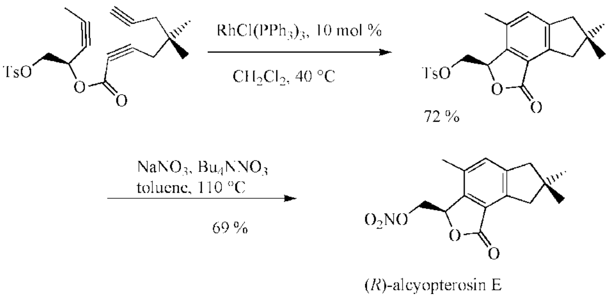
(16)

The third cyclotrimerizations with organocobalt[89–91] and organorhodium compounds.[90,91,112] provide useful organic syntheses of benzene derivatives. For example, the asymmetric total synthesis of an anguracyclinone antibiotic (+)-rubiginone B_2 was achieved by an intramolecular cyclotrimerization in the presence of cyclopentadienyldicarbonylcobalt, as shown in eqn (17).[90,113,114]



(17)

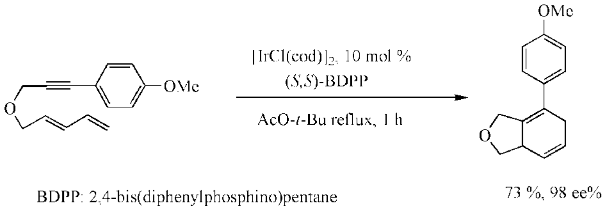
With Wilkinson complex, $RhCl(PPh_3)_3$, an illudalane class sesquiterpene (*R*)-alcyopterocin E, is prepared in good yield by the cyclotrimerization of lactonetriyne in the presence of the rhodium catalyst, as shown in eqn (18).[115] This rhodium-catalyzed intramolecular alkyne cyclotrimerization is a key connection for synthesis of the marine illudalane sesquiterpenoid alcyopterosin E. This reaction gives a single product in 72% yield.



(18)

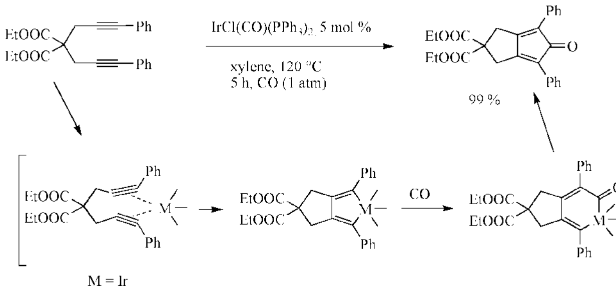
These cyclotrimerizations using [2 + 2 + 2] cycloaddition with three yne components in the presence of the group 9 metal compounds are useful synthetic methods of benzene derivatives.[89] However, pyridine derivatives also are easily synthesized with a nitrile instead of one yne component in [2 + 2 + 2] cyclotrimerization in the presence of the rhodium catalyst, as shown in Scheme 1.[101]

On the other hand, cyclohexadiene or cyclohexene derivatives are also synthesized using [2 + 2 + 2] cycloaddition when one or two triple bonds are replaced by double bonds.[89,116–121] For example, a highly enantiomerically enriched cyclohexadiene is synthesized with a terminal dieneyne using a chiral iridium complex prepared *in situ* from $[IrCl(cod)]_2$ and BDPP [2,4-bis(diphenylphosphine)pentane] as shown in eqn (19).[117] This reaction is also called a [4 + 2] cycloaddition because it involves an intramolecular Diels–Alder-like reaction.



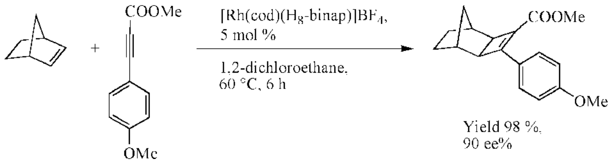
(19)

The Pauson–Khand reactions and Pauson–Khand-type reactions are [2 + 2 + 1] cycloadditions. However, carbonylative alkyne–alkyne couplings are also [2 + 2 + 1] cycloaddition of two ynes and one carbonyl group. For example, a cyclopentadienone derivative is prepared in high yield via a metallacyclohexadienone as the intermediate by the [2 + 2 + 1] cycloaddition of two ynes with carbon monoxide in the presence of an iridium phosphine complex, as shown in eqn (20).[38,122,123]



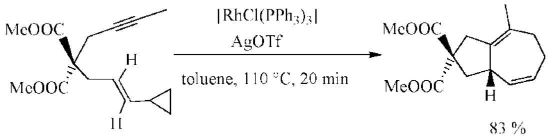
(20)

Many kinds of alkynes, alkenes, carbon monoxide, aldehydes, ketones, diazomethanes, cyclopropanes, etc., are utilized as cyclization components. With alkynyl esters and norbornene, [2 + 2] cycloadditions proceed in the presence of rhodium compounds, as shown in eqn (21).[124]



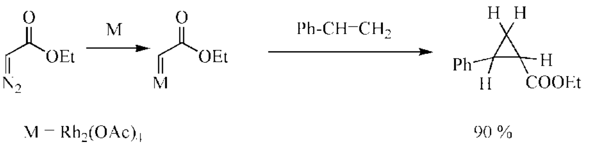
(21)

When alkynyl vinylcyclopropane was treated with Wilkinson's catalyst, the bicyclo[5.3.0]decane was isolated in high yield by [5 + 2] cycloaddition, as shown in eqn (22).[89,125]



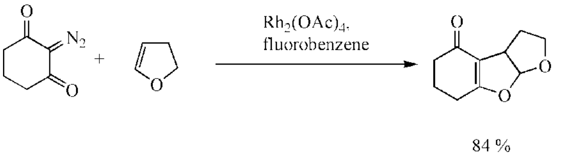
(22)

Cyclopropanation reactions with rhodium carbenes derived from α-diazocarbonyl compounds are [2 + 1] cycloadditions as shown in eqn (23).[89,126a–126d]



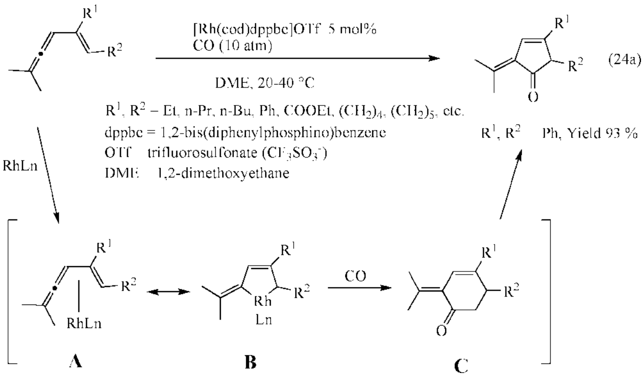
(23)

The reaction of diazodimedone with dihydrofuran in the presence of $Rh_2(OAc)_4$ gives a tricylic product in a high yield via a [3 + 2] cycloaddition as shown in eqn (24).[89,127–129]



(24)

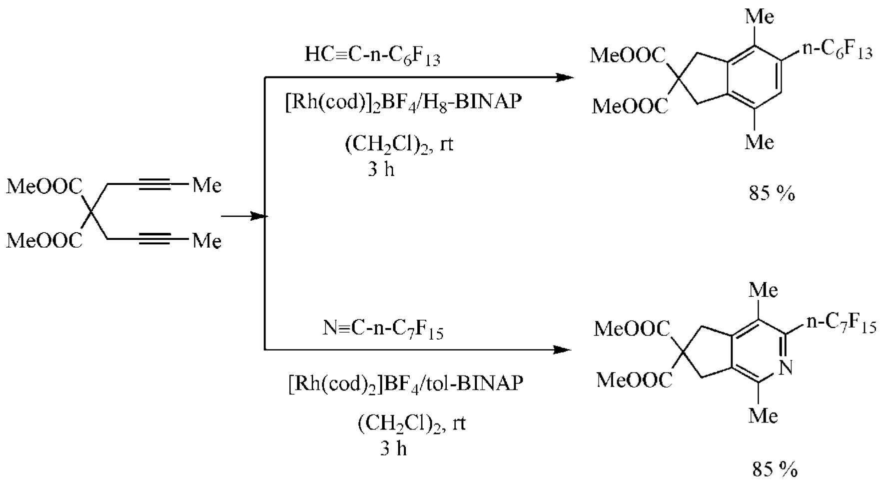
The other cycloadditions such as the carbonylative [4 + 1] cycloaddition of vinylallenes, diene-allene [4 + 2] cycloadditions,[130a,130b] diene-alkyne [4 + 2] cycloadditions,[131] dieneyne-yne [4 + 2 + 2] cycloadditions[131,132] and, further [4 + 3], [6 + 2], [3 + 2 + 2], [5 + 2 + 1], [4 + 2 + 1] and [2 + 2 + 2 + 1] cycloadditions,[133] were also reported, for example, the carbonylative [4 + 1] cycloaddtion of vinylallenes shown in eqn (24a). Vinylallenes undergoing facile carbonylative [4 + 1] cycloaddition in the presence of the rhodium complex give five-membered cyclic ketones in high yields via (η^4-vinylallene)rhodium complex (A), rhodacylopent-3-ene (B) and six-membered cyclic ketone inserted by carbon monoxide (C).[130a,130b]



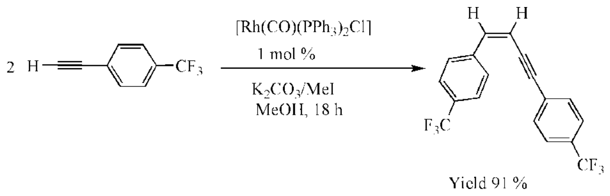
Coupling reactions

The various kinds of cycloadditions proceeds with compounds having carbon–carbon or carbon–nitrogen multiple bonds in the presence of group 9 metal compounds, as described in former sections. In these cyclizations, the key component is an yne moiety having two π-bonds, because of high reactivities to these transition metal compounds. Furthermore, with the alkynes, simple coupling reactions also occur with other compounds having the carbon–carbon or carbon–nitrogen π-bonds such as the other alkynes, alkenes and allenes, and with carbon monoxide, carbon dioxide, aldehydes, ketones, amines, etc.

The coupling reaction of two alkynes, that is, the dimerization of alkynes, proceeds at an ambient temperature in the presence of a rhodium phosphine catalyst to form a (*Z*) enyne product in a high yield and high regioselectivity, as shown in eqn (25).[134,135]

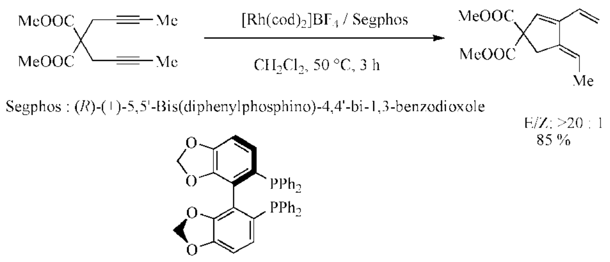


Scheme 1. [2 + 2 + 2] Cyclotrimerizations.



(25)

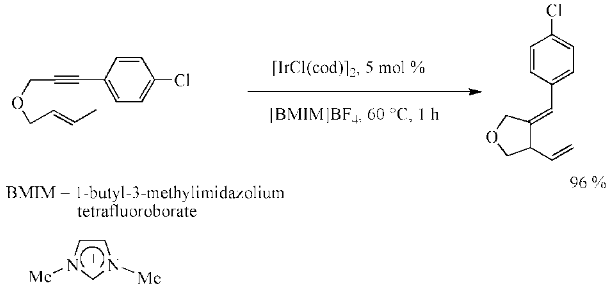
On the other hand, in the intramolecular coupling of 1,6-diynes, cycloisomerizations proceeds to form trienes in the presence of a rhodium catalyst as shown in eqn (26).[136]



(26)

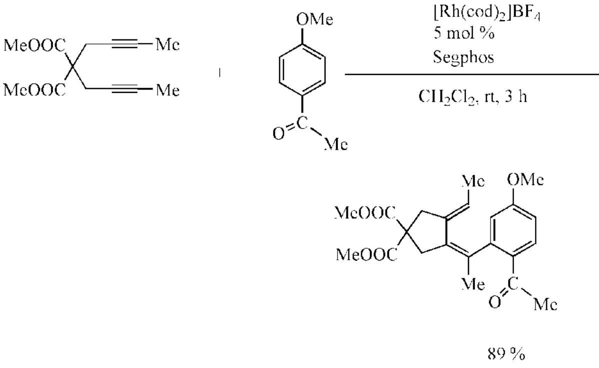
The coupling reactions of a carbon–carbon triple bond with an ene moiety such as an alkenyl and allenyl, and a phenyl ring moiety in the presence of the rhodium and iridium metal compounds, occur.[137–148]

The coupling reactions with simple alkenes, that is, intramolecular enynes-type reactions, proceed in the presence of an iridium compound to give the cyclic 1,4-diene in a high yield as shown in eqn (27).[149]



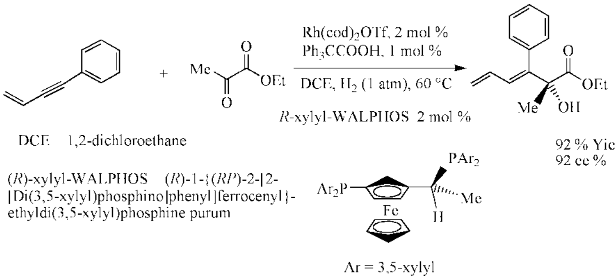
(27)

The coupling reactions of 1,6-diynes with an arylalkylketone proceed in the presence of a rhodium compound in a high yield, as shown in eqn (28).[140]



(28)

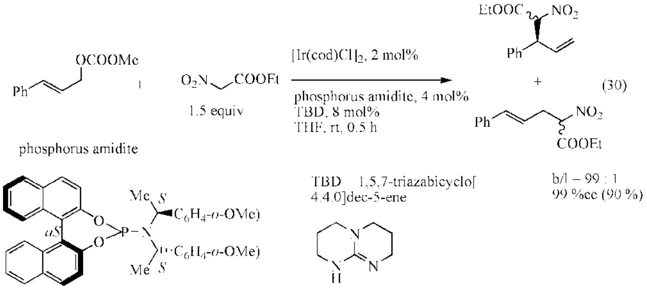
The other coupling reactions of the carbon–carbon triple bond with allene groups,[150] aldehydes,[151–159] ketones,[160] imines,[161] silanes,[162,163] carboxylic acids,[164–166] phenols[167] and acyl halides[168] occur in the presence of rhodium and iridium compounds. For example, the highly enantioselective direct reductive coupling of conjugated alkynes with α-ketoesters proceed via a rhodium catalyzed asymmetric hydrogenation as shown in eqn (29).[160]



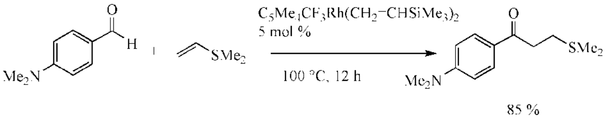
(29)

Alkynes have the two sets of mutually orthogonal π-bonds that are different from the π-bonds of alkenes. These two sets of π-bonds are able to bond with transition metal compounds. Hence, the coupling reactions of alkynes proceed more easily than those of alkenes. However, the coupling reactions of alkenes in the presence of the group 9 metal compounds also occur. Reviews have been published of aryl compounds with olefins[169–171] and terminal olefins,[172] allylations with carbon nucleophiles,[172–174] the addition of ethylene to butadiene,[175] the 1,4-addition of σ,β-unsaturated ketones[176] and an aryl–aryl bond formation.[177]

In these coupling reactions, the representative reactions are allylations.[178–184] The asymmetric allylic substitution has been shown to be a powerful method for the preparation of a wide range of chiral molecules. For example, the allylic alkynylation with commercially available ethyl nitroacetate easily proceeds to form mainly a branched form (99/1) in the presence of iridium catalyst, as shown in eqn (30).[183]



Aldehydes easily couple with olefins similarly to acetylenes, described above. For example, the hydroacylation of the olefins with *p*-dimehtylaminobenzaldehyde proceeds in the presence of the rhodium compounds $[(C_5Me_4CF_3)Rh(vinyltrimethylsilane)_2]$ to give arylketones as shown in eqn (31).[181] The use of a more electron-deficient catalyst results in faster reaction rates, better selectivity for linear ketone products from α-olefins and broader reaction scope.[179]



(31)

Other coupling reactions of olefins with aryl compounds, rhodium-catalyzed Mizoroki–Heck reactions,[185] the arylation of *N*-tosylarylimines,[186] bis-allenyl couplings,[187] olefin-diazo coupling reactions,[188] olefin and ketone coupling reactions,[189] carbonylation allylation reactions,[190] silylformylations,[191,192] the hydrosilylations of alkenes,[141,193,194] etc.,[195–197] have also been reported.

Carbonylations

Introduction

Transition metals easily react with carbon monoxide to yield the metal carbonyl. The bonds between the transition metal and the carbon atom of carbonyl group are shown in Fig. 1.[198] The 5σ lone pair electrons in the carbon atom is donated to the metal center (CO-M σ bond). The LUMO is strongly π^* antibonding and is low enough in energy to act as a good acceptor orbital for interacting with filled *d*-orbitals on the metals (M to CO π backbonding).[198a]

The representative metal compounds of the group 9 elements are shown in Table 2. These compounds are widely utilized as raw materials in organic synthesis. The ligands are carbonyl, dienes, halogens, phosphines, hydrogen and nitrogen. The group 9 transition metals easily bond with these ligands, especially, with carbonyl groups. Transition metal compounds having the metal and carbonyl group are shown in Table 4.[198b] Note that the metals of group 4 and 11 do not form carbonyls.

Table 4 shows that the metals in the central two groups, 8 and 9, in the transition metal groups of the periodical table, are able to form various kinds of metal carbonyl compounds. The group 9 metal compounds form the most complicated metal carbonyl clusters having carbon–metal bonds, bridged carbon–metal bonds and complicated metal–metal bonds.

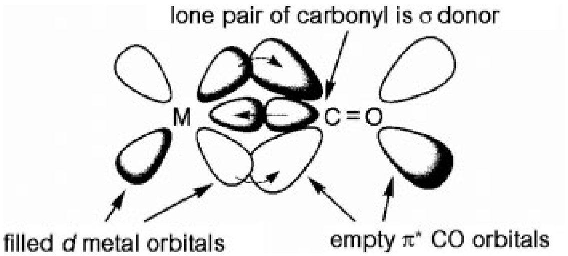


Figure 1. Participation of various orbitals between a transition metal atom and carbon monoxide.[198a].

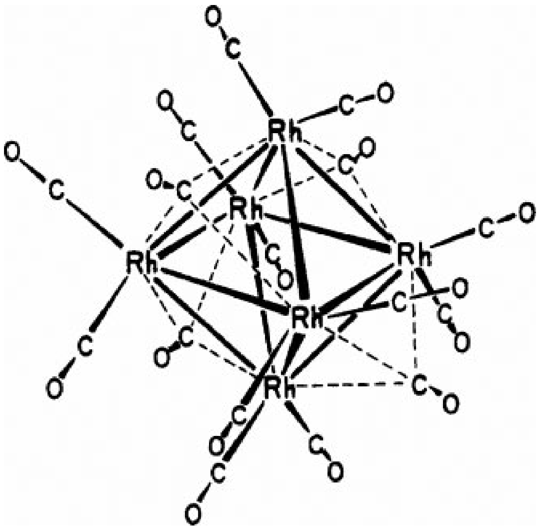


Figure 2. Molecular structure of $Rh_6(CO)_{16}$.[199].

For example, the carbon of the carbonyl group in $Rh_6(CO)_{16}$ forms a metal–carbon σ-bond (the terminal bond) and three metal bridged bonds (triply bridging bond, μ_3) between metal and carbon in the carbonyl group, and a metal–metal bridged bond, as shown in Fig. 2.[199] This shows that the group 9 metals in all transition metals have the highest reactivity to the carbonyl group of all the elements.

The Pauson–Khand reactions and Pauson–Khand-type reactions are the [2 + 2 + 1] cycloadditions of one yne, one ene and one carbonyl group. Hence, they belong not only to the first type of characteristic reactions that show high reactivity to the carbon–carbon or carbon–nitrogen π-bonds, but also to the second type that also shows high reactivity to the carbonyl group.

The second characteristic reactions regarding the organocobalt compounds are hydroformylations, hydrocarbonylations, amidocarbonylations, hydrosilylcarbonylations, carbonylations of halides and other carbonylations.[5]

However, these carbonylation properties regarding the rhodium and iridium compounds are not the same as those of the organocobalt compounds. Hence, their applications for rhodium and iridium compounds are different from those for the cobalt compounds.

Table 4. Common parent metal carbonyls for synthesis of organometallic compounds[198b]

4	5	6	7	8	9	10	11
Ti	$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $Co_4(CO)_{12}$	$Ni(CO)_4$	Cu
Zr	Nb	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	Pd	Ag
Hf	Ta	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_3(CO)_{12}$	$Ir_4(CO)_{12}$	Pt	Au

The second type of characteristic reactions of the group 9 metal compounds, including the organocobalt compounds, hydroformylations, the carbonylation of methanol, amidocarbonylations and other carbonylations, are described below:

Hydroformylation reactions

The hydroformylation reactions[200–216] are used for preparing aliphatic aldehydes whose number of carbon atoms is increased by one, as shown in eqn (32).

$$RCH{=}CH_2 - CO - H_2 \xrightarrow{\text{Co, Rh}} RCH_2CH_2CHO + RCH(CH_3)CHO \quad (32)$$

The hydroformylation reaction requires catalysts at elevated pressures and temperatures. The optimal catalysts for the hydroformylation reaction are complexes such as $HM(CO)_4$ or $HM(CO)_xL_y$ ($x = 3-1$, $y = 1-3$). The approximate and generally accepted ordering of hydroformylation reaction activities of the central atoms is as follows:[202]

	Rh ≫	Co >	Ir, Ru, >	Os >	Pt >	Pd
Relative activities:	>1000	1	10^{-2}	10^{-3}	10^{-4}	10^{-6}

In industrial practice, only rhodium and cobalt are used. Hydroformylation technology, now matured, has grown with the rise of the world economy since 1945. During these exciting developments of propylene hydroformylation, cobalt-catalyzed conversions remained as the foundation for the hydroformylation of higher alkenes for the production of plasticizer and detergent alcohols, because ligand-modified rhodium catalysts are excluded from the conversion of higher-boiling reactants owing to their limited thermal stabilities or the limited solubility of the higher alkenes in the aqueous medium (Table 5).[202,213]

The hydroformylation of alkenes is one of the most important syntheses in the chemical industry. Worldwide oxo capacity in 1993 exceeded 6 million tons per year and increased within five years to more than 9.2 million tons per year, as shown in Table 6.[169]

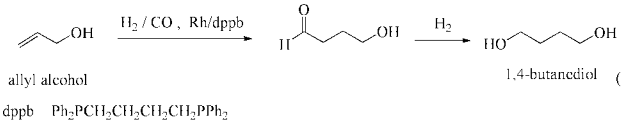
The situation regarding the hydroformylation reaction of alkenes other than propylene is quite different. The cobalt catalysts dominate rhodium catalysts by far with a ratio of 9 : 1. The reasons for this dominance are the low activity of rhodium for branched alkenes having internal double bonds and high boiling points of the products, which causes a considerable thermal stress on the catalysts if distillation is used for rhodium recycling.[202]

With a share of 75%, C_4 products have a major share of the production. Approximately 70% of the total hydroformylation capacity (converting light alkenes such as C_2, C_3 and C_4) is based on the low-pressure oxo processes (LPOs) using phosphine-modified rhodium catalysts (see Table 6). Rhodium LPO technologies claim various advantages over those based on the cobalt catalysts: mild reaction conditions, no need for high-pressure equipment and thus simpler and cheaper processes, higher efficiencies and yields of straight-chain products, and simpler metal recycling.[202]

Table 5. Comparison of Co and Rh hydroformylation processes[202,213]

	Catalyst	
	Cobalt (unmodified) $[HCo(CO)_4]$	Rhodium (ligand-modified) $[HRh(CO)L_3]$
Temperature (°C)	130–180	85–130
Pressure (MPa)	20–30	1–5
Catalyst concentration (%)	0.1–0.5	0.01–0.05
LHSV (h^{-1})	0.5–1.5	0.1–0.3
n/i ratio	80/20	>90/10
Formation of by-products	High	Low
Catalyst recovery and recycle	Complicated	Simple
Restrictions	None	Alkenes $<C_6$

Union Carbide developed the first commercial hydroformylation process using $HRh(CO)(PPh_3)_2$ and excess PPh_3 in the early 1970s. The addition of excess phosphine ligand shifts the phosphine dissociation equilibrium back towards the more selective $HRh(CO)(PPh_3)_2$ catalyst. However, the use of $HRh(CO)(PPh_3)_2$ in the presence of excess PPh_3 leads to relatively rapid catalyst deactivation to unidentified species. The addition of just over 1 equivalent of $Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (dppb) leads to a stable, active hydroformylation catalyst.[181] This is most evident in the hydroformylation of a reactive alkene such as allyl alcohol. ARCO Chemical licensed the Kuraray technology to build the first plant in 1990 for the hydroformylation reaction of allyl alcohol to produce 1,4-butanediol, as shown in eqn (33).[215]



(33)

By using a sulfonated PPh_3 ligand, $P(Ph\text{-}m\text{-}SO_3Na)_3$, a highly water-soluble catalyst is generated: $HRh(CO)[P(Ph\text{-}m\text{-}SO_3Na)_3]_3$. Currently Celanese–Ruhrchemie operates several hydroformyla-

Table 6. Nameplate capacity for production of aldehydes by hydroformylation*[169]

	C_3	C_4	C_5-C_{13}	$>C_{13}$	Sum	2-ethylhexanol	C_9/C_{10} alcohol
Capacity (million tons)	0.285	6.850	1.575	0.470	9.180	3.185	1.210
Share (%)	3	75	17	5	100		

* Estimate for 1998.

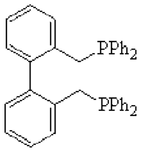
tion plants based on this water-soluble rhodium catalyst technology. Shorter chain alkenes (C_2-C_4) are water soluble enough that their migration into an aqueous catalyst phase occurs to allow the hydrofomylation. Rather high linear to branched regioselectivities of 16–18 : 1 for propylene can be obtained via the water-soluble catalyst. The process is limited to the shorter chain alkenes that have some appreciable water solubility.[208a]

Recently, chelating bisphosphine rhodium catalysts (e.g. Bisbi, Naphos and Xantphos) were found to show remarkably high product regioselectivities and good to high activities. These data are shown in Table 7.[208b]

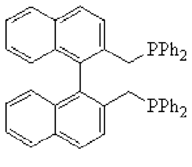
Table 7. Some catalytic comparisons between Rh/PPh_3, Bisbi, Naphos and Xantphos for hydroformylation of 1-hexene[208b]

Catalyst (1 mM)	Init TOF (min^{-1})	Aldehyde L : B	Isomerization (%)
Rh/PPh_3 (1 : 400)	13 (1)	9.1 : 1	<0.5
Rh/Bisbi (1 : 5)	25 (2)	70 : 1	<0.5
Rh/Naphos (1 : 5)	27 (1)	120 : 1	1.5
Rh/Xantphos (1 : 5)	13 (2)	80 : 1	5.0

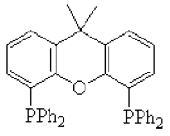
90 °C, 6.2 bar, 1 : 1 H_2-CO, 1000 equiv. 1-hexene.



Bisbi

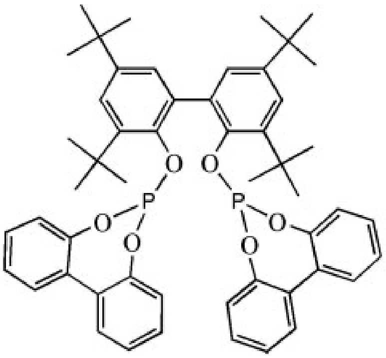


Naphos



Xantphos

Further, a bulkier bisphosphite ligand hydroformylation catalyst (UC-44) shows linear to branched aldehyde product ratios for the hydroformylation of propylene of well over 30 : 1. Because of the presence of the poorly σ-donating phosphite ligands, however, a rhodium center is highly active, giving hydroformylation rates for 1-alkenes that are about 5 times faster than those of Rh/PPh_3 catalysts.[208c]



UC-44

In 2007, Williams *et al*. reported on high-rate and highly selective vinyl acetate hydroformylation in the presence of $Rh(CO)_2(acac)$ with an ionic phosphine ligand in organic solvents, as shown in Scheme 2. The ionic liquid ([1-butyl-3-methylimidazolium][$N(SO_2CF_3)_2$]) had a significant effect on the selectivity of the hydroforymylation of vinyl acetate (89%), with very high TOF (Turnover frequency, 13,600) being realized and branched product at 94% selectivity for aldehyde products. The product, acetoxypropanal, is utilized as an important intermediate in the synthesis of the environmentally friendly solvent ethyl lactate.[216]

Carbonylations of methanol

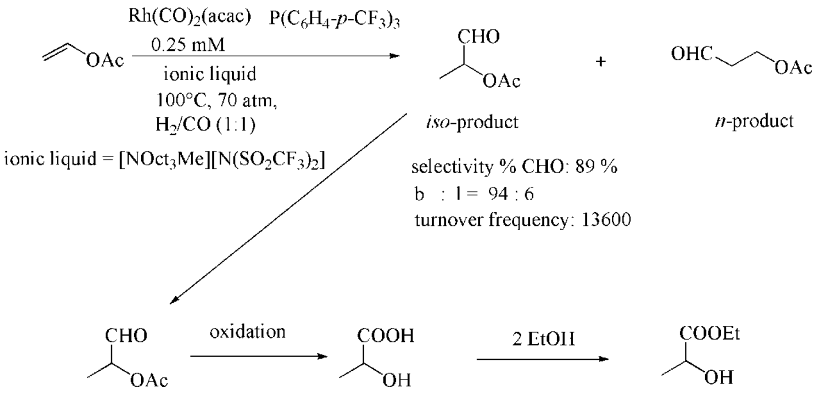
Acetic acid is an important bulk commodity chemical, with the world annual production capacity of *ca* 7 million tons. Acetic acid synthesis via the carbonylation of methanol is one of the most important industrial applications of catalysis using organometallic compounds. All the group 9 metals are active, with processes based on cobalt, rhodium and iridium developed in the 1960s. The carbonylation reaction involves the formal insertion of carbon monoxide into the C–O bond in methanol as shown in eqn 34.[204,206,217–228]

$$CH_3OH + CO \xrightarrow{\text{Co, Rh, Ir}} CH_3COOH \qquad (34)$$

BASF had already found in 1913 that methanol, the primary reaction product from synthesis gas, could be carbonylated to acetic acid. The corrosion problem caused by acetic acid was solved at the end of the 1950s with highly resistant Mo–Ni alloys, and in 1960 the first small plant was brought on-line in the presence of CoI_2 in the liquid phase at 250 °C and 680 bar. The reaction is assumed to proceed as follows: the cobalt iodide initially reacts to form $HCo(CO)_4$ and HI, which is then converted into CH_3I with methanol. $HCo(CO)_4$ and CH_3I react to form the important intermediate $CH_3Co(CO)_4$ which, after CO insertion, hydrolyzes to form acetic acid and regenerate $HCo(CO)_4$ as shown in Scheme 3.[220]

Around the mid 1960s, Monsanto discovered that rhodium combined with iodine was a considerably more active catalyst system for methanol carbonylation than cobalt iodine. The selectivities of the BASF process to acetic acid are 87% (based on MeOH) and 59% (based on CO). However, the selectivities of the Monsanto process using rhodium catalysts are much higher, as shown in Table 8.[222]

During the methanol carbonylation, methyl iodide is generated by the reaction of added methanol with hydrogen iodide (Scheme 4). The major rhodium catalyst species present is $[Rh(CO)_2I_2]^-$, (A). The methyl iodide adds oxidatively to this



Scheme 2. Vinyl acetate hydroformylation.

$$2\,CoI_2 + 3\,H_2O + 11\,CO \longrightarrow 2\,HCo(CO)_4 + 4\,HI + 3CO_2$$

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O$$

$$CH_3I + HCo(CO)_4 \rightleftharpoons CH_3Co(CO)_4 + HI$$

$$CH_3Co(CO)_4 \xrightarrow{CO} CH_3COCo(CO)_4 \xrightarrow{H_2O} CH_3COOH + HCo(CO)_4$$

Scheme 3. Carbonylation of methanol, BASF process.

rhodium species to give $[CH_3Rh(CO)_2I_3]^-$, (B). The key to the process is that this rhodium-methyl complex undergoes a rapid change in which the methyl is shifted to a neighboring carbonyl group, $[CH_3CORh(CO)I_3]^-$, (C). After the subsequent addition of CO, the rhodium complex becomes locked into an acyl form, $[CH_3CORh(CO)_2I_3]^-$, (D). The reductive elimination of the acyl species and attack by water can then occur to liberate the original rhodium dicarbonyl diiodide complex and to form acetic acid and hydrogen iodide.[218]

When the water content is high (>8 wt%), the rate-determining step in the process is the oxidative addition of methyl iodide to the rhodium center.[218]

The iridium catalyst is stable under a wide range of conditions that would cause the rhodium analogs to decompose completely to inactive and largely irrecoverable rhodium salts. Besides this stability, iridium is also much more soluble than rhodium in the reaction medium and thus higher catalyst concentrations can be obtained to make a much higher reaction rate achievable. The anionic iridium cycle is similar to the rhodium cycle and is shown in Scheme 5.[218]

The Cativa process is a route to the manufacture of acetic acid by methanol carbonylation catalyzed with high rates at low water concentrations using an iridium/iodine based catalyst. It was developed by BP Chemicals in 1996.[227]

In the Cativa system, ruthenium carbonyl can enhance the activity of an iridium catalyst. For example, the carbonylation is enhanced by factor of 2.6 using $[Ru(CO)_4I_2]$ as a promoter, the mole raio of which to Ir is 5:1.[217] The effect of water concentration on the carbonylation rates of a rhodium system and an iridium ruthenium system is illustrated in Fig. 3.[221,228] For rhodium, a decline in carbonylation rate is observed as the water content is reduced below about 8 wt%. For a Cativa system, in contrast to the rhodium, the reaction rate increases with decreasing water content. A maximum value is reached at around 5% w/w, as shown in Fig. 3.[218,228]

The Cativa model studies have shown that the oxidative addition of methyl iodide to an iridium center (from A to B in Scheme 5) is

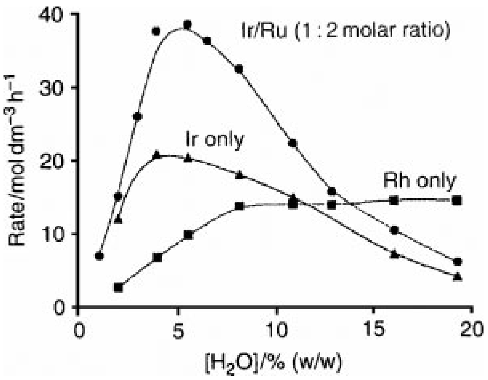


Figure 3. Effect of water concentration on catalytic rate for Rh, Ir and Ir/Ru-catalyzed methanol carbonylation (190 °C, 28 bar).[221,228].

about 150 times faster than the equivalent reaction to rhodium. This Cativa process delivers many benefits over the conventional Monsanto rhodium methanol carbonylation process:

(1) It is an inherently stable catalyst system.
(2) Plants can operate with a higher reactor productivity and higher rates.
(3) The water concentration in the reactor can be reduced as the system has high tolerance to low water conditions.

Amidocarbonylations

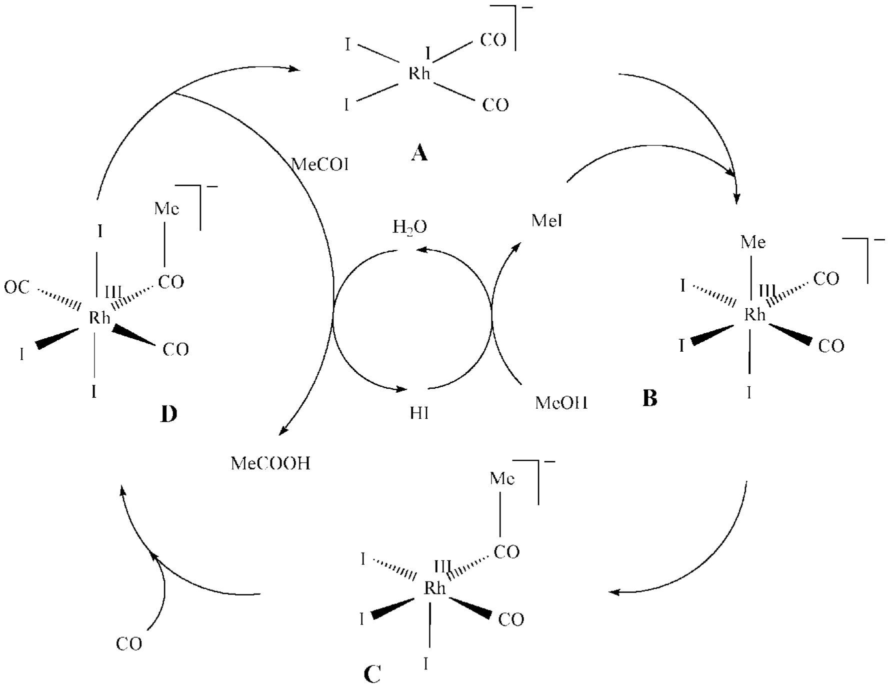
The amidocarbonylations[229–239] are also an important industrial processes for the production of α-amino acids by using the group 9 metal compounds as the catalysts. The hydroformylations and carbonylations of methanol described in the previous two sections are the processes for bulk commodity chemicals; however, the amidocarbonylations are for fine chemicals such as the pharmaceuticals captopril and *N*-acetylcystein, the herbicide Flamprop-isopropyl, anionic sarcosinate tensides, a substrate for enzymatic resolution *N*-acetyl-(*R*,*S*)-AS, and simple dipeptides such as a sweeteners, e.g. aspartame.[195]

The hydroformylations yield aldehydes under CO and H_2 pressure in the presence of $Co_2(CO)_8$ (the active species $HCo(CO)_4$). Under the same conditions, an amide is added to an aldehyde to produce an acylamino acid, as shown in Scheme 6.[229]

The aldehyde reacts with the amide giving an aminoalcohol A, and, as cobalt hydrocarbonyl is a strong acid, the dehydration condensation of the aminoalcohol A with $HCo(CO)_4$ forms a C–Co

Table 8. Comparison of Co, Rh and Ir metal-catalyzed methanol carbonylation[222]

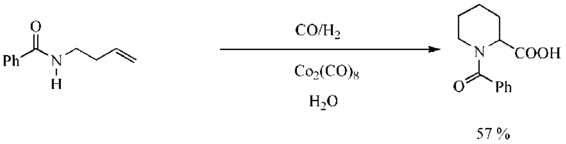
Catalyst	Cobalt	Rhodium	Iridium
Process	BASF process	Monsanto process	BP Chemicals process (Cativa process)
Start	1960	1970	1996
Catalyst	CoI_2	Rh/I_2	Ir/I_2
Catalytic active species	$HCo(CO)_4$	$[Rh(CO)_2I_2]^-$	$[Ir(CO)_2I_2]^-$
Temperature (°C)	210–250	175	
Pressure (MPa)	65	2.8	
Selectivities based on MeOH	87	>99	
Selectivities based on CO	59	>90	
Formation of by-products	High CO_2, H_2, etc. (from the water gas shift reaction)	Low	Low



Scheme 4. Carbonylation of methanol, Monsanto process.

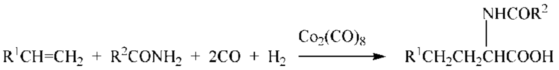
bond B. This is followed by carbonyl insertion and hydrolysis to produce an acyl amino acid C.[229,233]

Aldehydes are the most important starting materials for the amidocarbonylation. With the amides having the formyl group at the terminal position, the intramolecular amidocarbonylation proceeds. For example, *N*-benzoylpipecolinic acid is prepared in good yield as shown in eqn (35).[234]



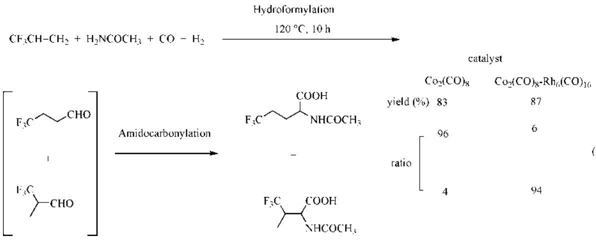
(35)

These reactions directly produce amino acids from olefins and amides under hydroformylation reaction conditions, that is, the Wakamatsu reaction, as shown in eqn (36).[235]



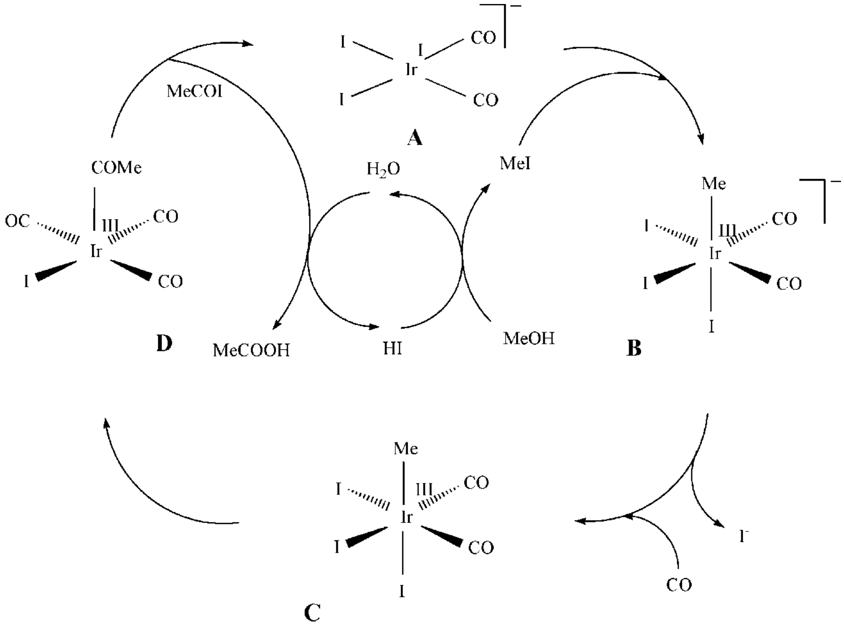
$$R^1CH{=}CH_2 + R^2CONH_2 + 2CO + H_2 \xrightarrow{Co_2(CO)_8} R^1CH_2CH_2\underset{}{\overset{NHCOR^2}{CH}}COOH \qquad (36)$$

Olefins are usually suitable as raw materials and are commercially available in a wide variety in the combination of hydroformylation and amidocarbonylation with *in situ* aldehyde formation in the presence of cobalt catalysts. The addition of a rhodium catalyst, $[Rh_6(CO)_{16}]$, to the cobalt catalyst system achieved a reverse selectivity regarding the production of *N*-acetyltrifluoronorvaline, as shown in eqn (37).[229,236]

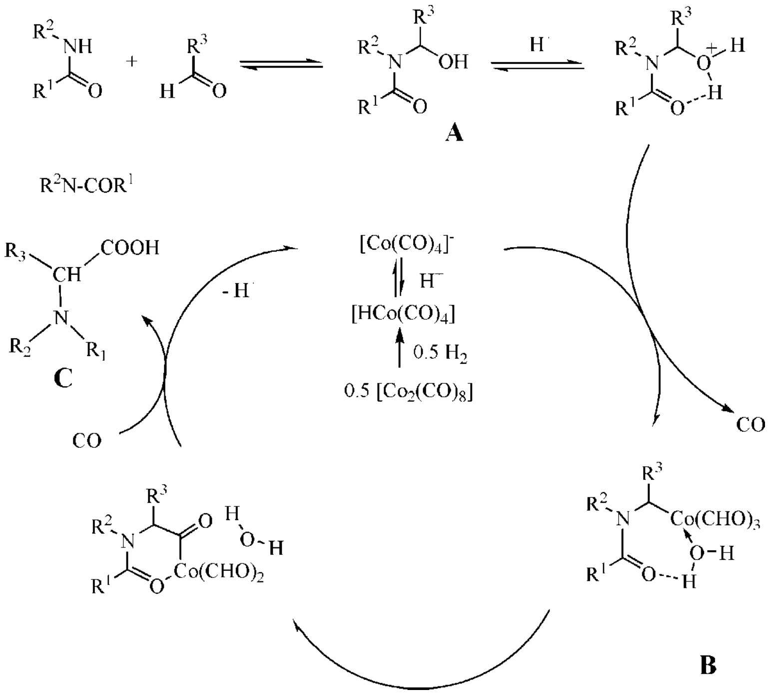


(37)

Beside aldehydes and olefins as the raw materials for amidocarbonylation, acetals, epoxides and allyl alcohols are also

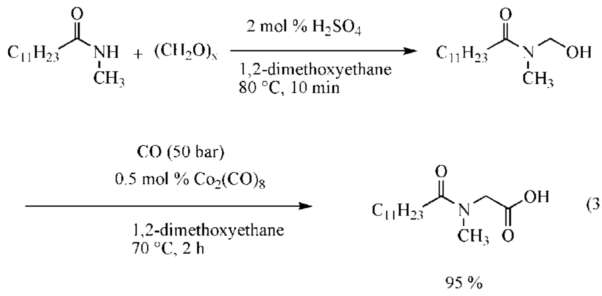


Scheme 5. Carbonylation of methanol, BP Chemical process (Cativa process).



Scheme 6. Amidocarbonylation.

utilized. In 1994, Hoechst AG developed an industrial application of the amidocarbonylation as shown in eqn (38).[229,237,238] After the first stage, methylol was formed by acid catalysis at 80 °C, and amidocarbonylation was carried out under mild conditions by cobalt catalysis at 50–70 °C and 10–50 bar to give glycine derivatives in a high yield. The long-chain *N*-acyl derivatives of sarcosine (*N*-methylglycine) belong to the group of anionic tensides that are used as reverse components of surfactants, soaps and emulsifiers because of their low hardening sensitivities and a good dermatological compatibility.[229,239]

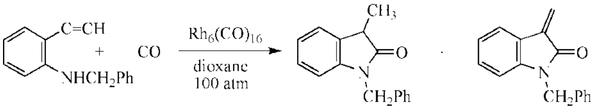


(38)

In addition, Beller and Eckert also reported on the development of palladium-catalyzed amidocarbonylation.[229]

Other Carbonylations

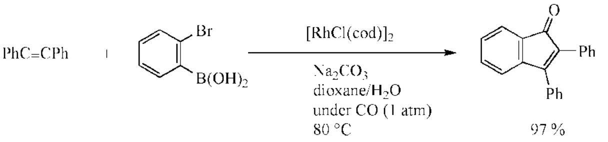
Other carbonylations of the group 9 metal compounds are carbonylative cyclizations, hydrosilylcarbonylations and ring-expanding carbonylations. The carbonylative cyclizations are the cyclization of alkynes or alkenes with carbon monoxide.[240–243] For example, 2-alkynylamines react with carbon monoxide in the presence of a rhodium catalyst under water–gas shift reaction conditions to form amino lactams in high yields, as shown in eqn (39).[241,242] The selectivity of the reaction depends mainly on the amount of H_2O and Et_3N added to the reaction mixture and temperature.



(39)

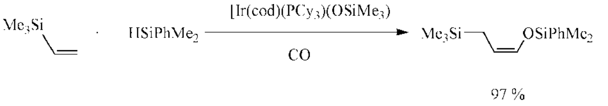
T °C	H_2O(eq)	Et_3N	Yield (%)	
175	4	1	86	0
80	0	0	2	85

The carbonylative cyclization of 2-bromophenylboronic acid with carbon monoxide proceeds in the presence of a rhodium catalyst to yield an indenone in high yield, as shown in eqn (40).[243] The [2 + 2 + 1] cycloaddition of diyne and one carbon monoxide as shown in eqn (20) is also the carbonylative cycloaddition.



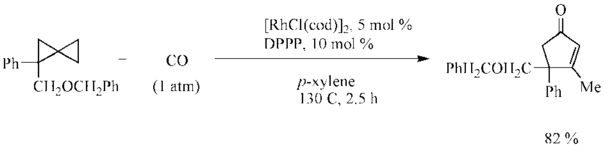
(40)

The hydrosilylcarbonylation of alkenes under carbon monoxide proceeds in the presence of the group 9 metal compounds.[244,245] For example, the hydrosilylcarbonylation of a vinylsilane under a carbon monoxide pressure (10 bar) gives (*Z*)-siloxysilylpropene in high yield as shown in eqn (41).[244]



(41)

The ring-expanding carbonylations of small ring compounds such as three-, four-, and five-membered ring compounds proceed in the presence of the group 9 metal compounds by an insertion of carbon monoxide.[246–253] For example, the ring-expanding carbonylations of three-membered ring spiropentane takes place under an atmosphere of carbon monoxide to afford cyclopentenone in a high yield as shown in eqn (42).[246]



(42)

Furthermore, other carbonylations are the carbonylations of halides such as benzyl chloride,[254] and allenic carbocyclization reactions.[255]

Concluding Remarks

Group 9 metal compounds very easily bond with compounds having carbon–carbon or carbon–nitrogen π-bond such as alkynes, alkenes and cyano compounds, and with carbon monoxide. These high reactivities are the first and second characteristic reaction properties of the group 9 metal compounds, respectively.

The first type of characteristic reactions includes Pauson–Khand reactions, Pauson–Khand-type reactions ([2 + 2 + 1] cyclizations), other cyclizations and coupling reactions. The second type of characteristic reactions includes carbonylation reactions such as hydroformylations, carbonylations of methanol, amidocarbonylations and other carbonyltions.

The first type of characteristic reaction is applied for the synthesis of fine chemicals such as pharmaceuticals and agrochemicals. However, the second type of characteristic reaction is utilized not only for fine chemicals but also for important bulk commodity chemicals such as aldehydes, carboxylic acids and alcohols.

Acknowledgments

I should like to express my sincere appreciation to Dr Sumio Chubachi for reading the full manuscript, who enhanced its accuracy and clarity, and for providing much valuable constructive criticism. I should also like to express my sincere gratitude to Professor Leopold May for making substantial corrections and improvements.

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