APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 318–344
DOI:10.1002/aoc.1213

Review

Three characteristic reactions of organocobalt compounds in organic synthesis

Iwao Omae*

Nihon Pharmaceutical University, 10281, Komuro, Ina-cho, Kita-adachigun, Saitama, 362-0806, Japan

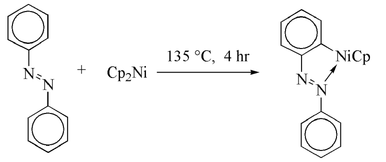
Received 19 December 2006; Accepted 7 January 2007

Organocobalt compounds in organic synthesis have three characteristic reactions. The first occurs because cobalt has a high affinity to carbon–carbon π-bonds or carbon–nitrogen π-bonds. The second occurs because cobalt has a high affinity to carbonyl groups. The third is due to cobalt easily tending to form square-planar bipyramidal six-coordination structures with four nitrogen atoms or two nitrogen atoms and two oxygen atoms at the square-planar position, and to bond with one or two carbon atoms at the axial position. The first characteristic reactions are the representative reactions of organocobalt compounds with a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt. These are reactions with a $Co_2(CO)_6$ protecting group to reactive acetylene bond, the Nicholas reactions, the Pauson–Khand reactions ([2 + 2 + 1] cyclizations), [2 + 2 + 2] cyclizations, etc. These reactions are applied for the syntheses of many kinds of pharmaceutically useful compounds. The second reactions are carbonylations that have been used or developed as industrial processes such as hydroformylation for the manufacture of isononylaldehyde, and carbonylation for the production of phenylacetic acid from benzyl chloride. The third reactions are those reactions with the B_{12}-type catalysts, and they have recently been used in organic syntheses and are utilized as catalysts for stereoselective syntheses. These reactions have been used as new applications for organic syntheses.

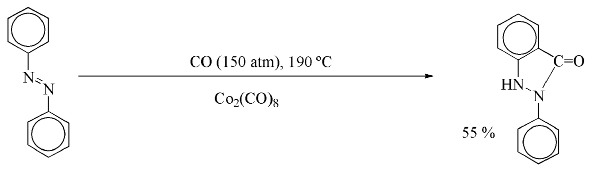
KEYWORDS: organocobalt compound; protecting group; Pauson–Khand reaction; Nicholas reaction; carbonylation; cyclization; vitamin B_{12}

INTRODUCTION

Organometallic intramolecular coordination compounds, especially five-membered ring compounds of organotin compounds, have been studied since 1965, and many reviews[1–13] and some books[14–16] have published on the subject. These compounds are mainly synthesized by cyclometalation reactions with transition metal compounds. The first publication on this subject is generally considered to be the reaction of diazobenzene with nick elocene by Kleiman and Dubeck[17] in 1963 as shown in equation (1).



(1)



(2)

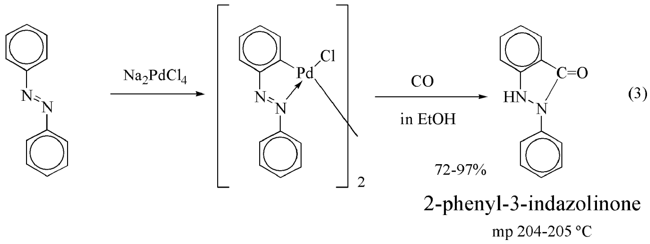
2-phenyl-3-indazolinone

An earlier article on the direct synthesis of 2-phenyl-3-indazolinone by carbonylation of azobenzene with a cobalt

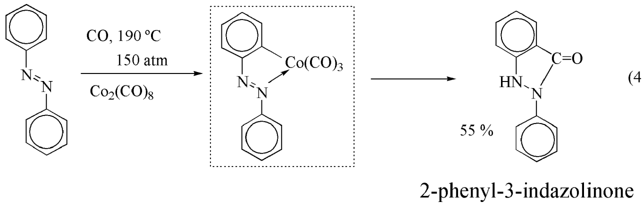
*Correspondence to: Iwao Omae, Nihon Pharmaceutical University, 10281, Komuro, Ina-cho, Kita-adachigun, Saitama, 362-0806, Japan.
E-mail: um5i-oome@asahi-net.or.jp

carbonyl catalyst, as shown in equation (2), was published in 1956.[18] It was also synthesized in 1967 through a two-step reaction, that is, (i) cyclopalladation of azobenzene via the five-membered ring product, and (ii) carbonylation, as shown in equation (3).[19]

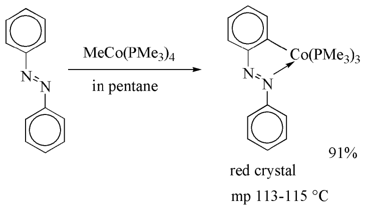
From these two reactions, the former reaction [equation (2)] is presumed also to proceed via cyclometallation, that is, cyclocobaltation with the cobalt carbonyl catalyst, as shown in equation (4). Actually, many cyclomatalations with cobalt compounds have been reported.[20–35] For example, a similar cyclometalated organocobalt compound was prepared by the reaction of azobenzene with methyltetra(trimethylphosphine)cobalt, as shown in equation (5).[20] Further, one year previously, in 1955, the same type of heterocyclic compound was prepared by the same type of carbonylation reaction with an organocobalt compound, as shown in equation (6).[36] This publication by Murahashi[36] may be considered to be the first reaction relating cyclometalation reactions.



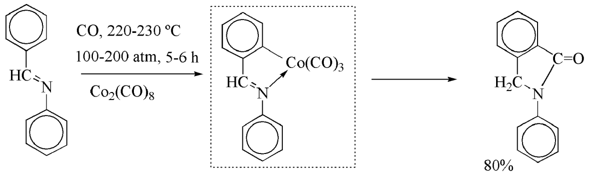
(3)



(4)



(5)



(6)

In the chemical industry, organocobalt is an essential constituent in many important catalysts. Specifically, they are key components in the multimillion-pound technology of hydroformylation; that is, the catalytic transformation of olefins into aldehydes using homogeneous catalysts.[37]

Many reviews on organocobalt compounds in organic synthesis have been published. For examples, Pauson–Khand reactions,[38–52] [2 + 2 + 2] cyclizations and related cyclizations,[39,44,48,53–56] Nicholas and related reactions,[44,57–59] hydroformylations,[60–63] amidocarbonylations (Wakamatsu reactions),[64,65] enantioselective reactions with cobalt–salen complexes,[66,67] and green transformations with B_{12} derivatives.[68]

This article reports on three characteristic reactions of the organocobalt compounds in organic syntheses on the basis of their structures and reactivities.

THREE CHARACTERISTIC REACTIONS OF OGANOCOBALT COMPOUNDS IN ORGANIC SYNTHESIS

Organocobalt compounds in organic synthesis can engage in three characteristic reactions. The first ones occur because cobalt has a high affinity to π-bonds such as carbon–carbon bonds and carbon–nitrogen bonds. These characteristic reactions are understood from the following three facts.

(1) Organocobalt compounds form a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt; for example, dicobalt hexacarbonyl diphenylacetylene, shown in Fig. 1.[69]
(2) The organocobalt compounds easily form many kinds of diene compounds, cyclobutadiene compounds and 5.5-membered ring compounds, as shown in compounds **1–6**. As the CpCo moiety in the compounds **1–4** has 14 electrons, these tend to react with many kinds of moieties

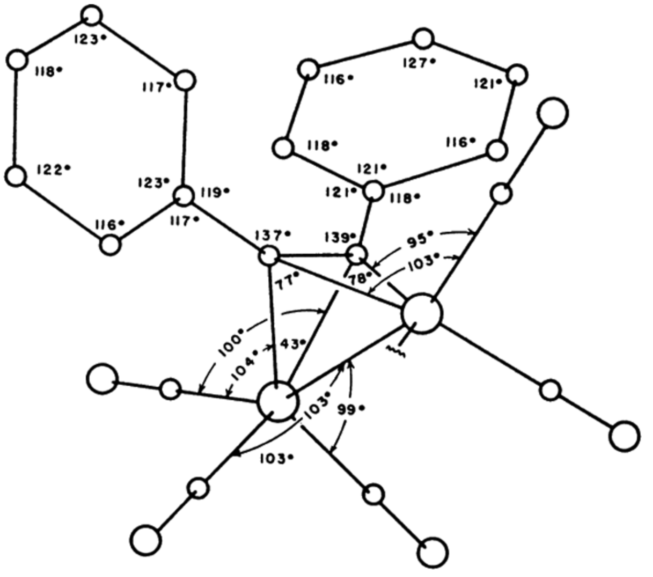
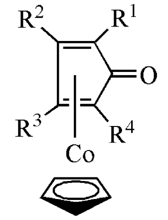


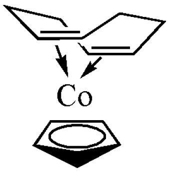
Figure 1. Structure of dicobalt hexacarbonul diphenylacetylene.[69].

having four electrons, such as two pairs of carbon–carbon double bonds[70–77] and cyclobutadiene rings[76,78–103] to form 18-electron compounds. The organocobalt compounds having an alkenyl chain generally can form 5.5-membered ring compounds such as compounds **5** and **6**.[14,104–107]

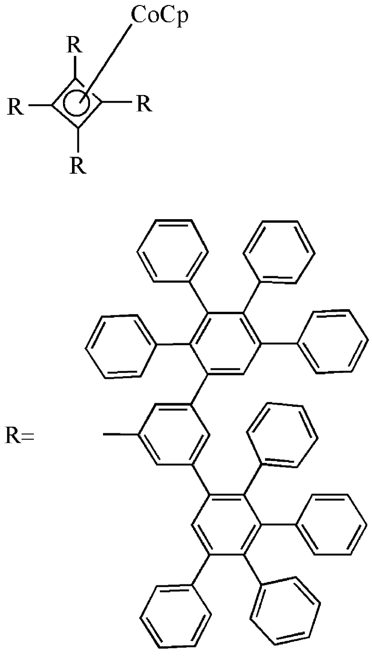


1

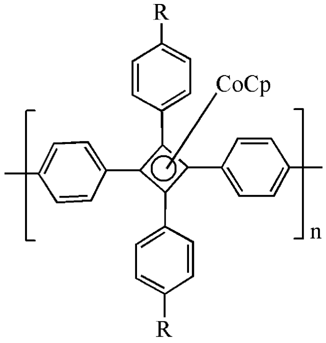
R^1, R^2, R^3, R^4 = H, Me, Ph, Si(Me)$_3$, P(O)(OEt)$_2$, mesityl



2



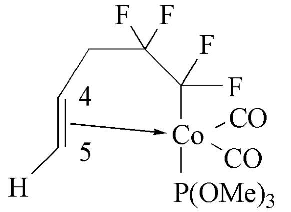
3



*M*n = 16,700 - 17,700

R = $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

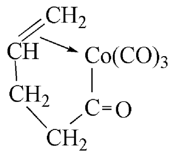
4



Co - C^4 = 2.110 Å

Co - C^5 = 2.116 Å

5



6

(3) The organocobalt compounds can form 19-, 20- and 21-electron sandwich compounds. For example, cobaltocene is a 19-electron compound. The M–C bond length is 2.10 Å in this compound, slightly longer (by 0.06 Å) than in the very stable ferrocene (2.04 Å, eclipsed structure), and much shorter (by 0.08 Å) than in nickelocene (2.18 Å).[108,109] The cobalt is considered to be able to form a relatively strong bond with cyclopentadienyl carbons and also to form the 20-electron compounds of the cyclopentadienyl and phenyl derivatives such as CpCoC$_6$Me$_6$[110] and $[(C_6Me_6)_2Co]^+$,[111] and the 21-electron compound of the bisphenyl sandwich complex $[(C_6Me_6)_2Co]$ (Fig. 2).[111]

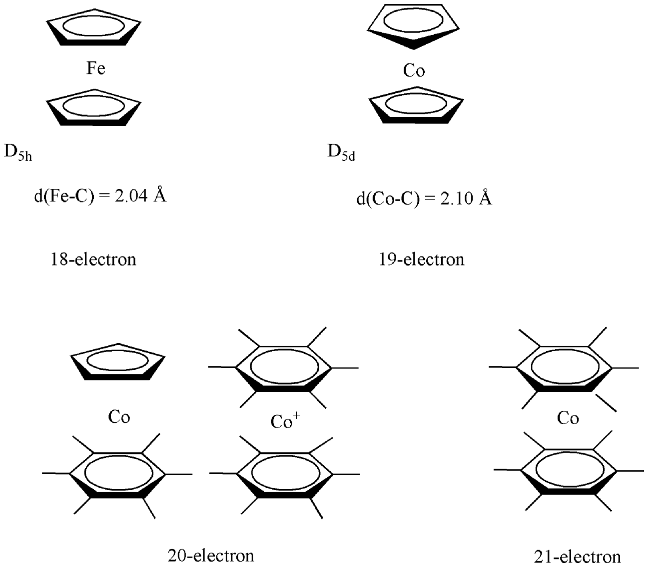


Figure 2. Structure of organocobalt sandwich compounds.[109–111]

The first characteristic reactions of organocobalt compounds relate to its reaction with unsaturated triple bond, that is, acetylene compounds and cyano compounds. There are three types of reactions arising from this property. The first reaction is with a $Co_2(CO)_6$ protecting group with mutually bridged bonds to a triple bond. The second is similar but with the propargyl ion. The third is the cyclizations with triple bonds in acetylenes or cyano compounds, and with other triple bonds or a double bond. The representative reactions of the second reactions are the Nicholas reactions. The third reactions are the Pauson–Khand reactions, $[2+2+2]$ cyclization, $[2+2]$ cyclization, $[3+2+2]$ cyclizations, etc. These first, second and third reactions are discussed below.

The second characteristic reactions occur because of the high affinity of cobalt to carbonyl groups. Many transition metals of Groups 5–10 easily form metal carbonyl compounds. For example, Group 9 elements, cobalt, rhodium and iridium, and Group 8 elements, iron, ruthenium and osmium, form many kinds of metal carbonyl clusters.[112,113] Generally, these metal compounds have high affinity to carbon monoxide, that is, high carbonylation reactivity. Specifically, organocobalt compounds have high reactivity of carbonylation. This reactivity is also easily understood by the following two facts:

(1) The cobaltcarbonyls form many cobaltcarbonyl clusters such as $Co_2(CO)_8$, $Co_4(CO)_{12}$, $Co_6(CO)_{16}$ and $Co_8C(CO)_{18}$.[114,115] $Co_2(CO)_8$ is easily converted to the carbonyl cluster $Co_4(CO)_{12}$ by simply heating only slightly above room temperature,[116] and $Co_6(CO)_{16}$ is derived from $Co_4(CO)_{12}$.[114]
(2) $Co_2(CO)_8$ is able to form many kinds of structures such as C_{2v-} $Co_2(CO)_8$ and D_{2d-} $Co_2(CO)_8$, and many kinds of bonds between Co and CO form, e.g. Co–CO single bond, Co–CO–Co carbon bridged bond, and Co–CO–Co carbonyl π-bond bridged bond.[116–120]

The second characteristic reactions involve organocobalt compounds as catalysts for various kinds of carbonylation reactions as shown below.

The third characteristic reactions involve vitamin B_{12}-type compounds having a bulky square-planar group. These reactions are expected to proceed through a regio- and stereospecific pathway, as shown below.

The third characteristic reactions occur because cobalt tends to easily form a square-planar bipyramidal six-coordination or square-planar five-coordination structure with four nitrogen atoms, square-planar four-coordination with two nitrogen atoms and two oxygen atoms, etc., and to bond with one or two carbon atoms in the axial position.

Vitamin B_{12}, as shown in Fig. 3,[121] is the first compound with a metal–carbon bond to be discovered in natural products. It is stable in the human body, which is an aqueous system, even though it has a metal–carbon bond, as it is an organotransition metal compound. This octahedreal six-coordination structure is involved the third characteristic reaction of organocobalt compounds in organic syntheses, as shown below.

REACTIONS WITH A $CO_2(CO)_6$ PROTECTING GROUP

The organocobalt compounds react vigorously with π-bonds. For example, octacarbonyldicobalt reacts with the acetylene

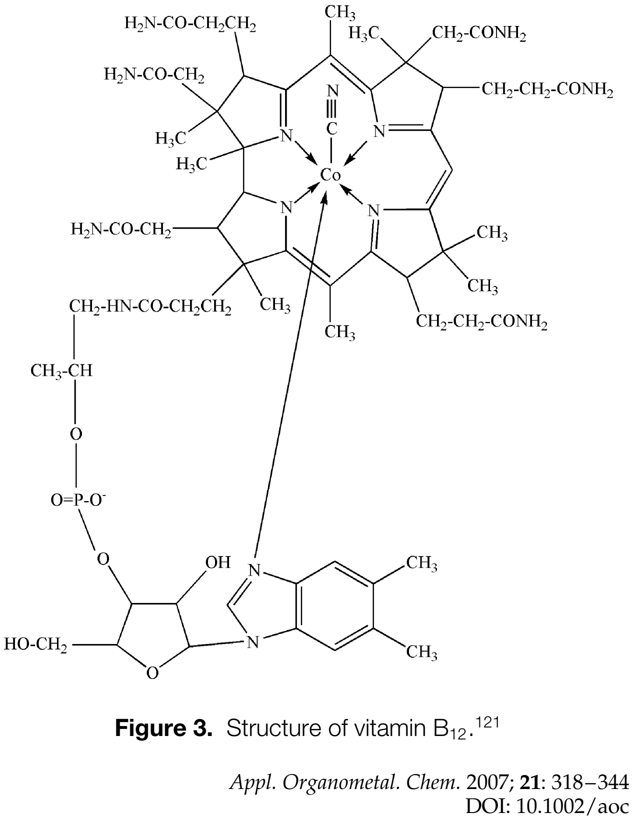
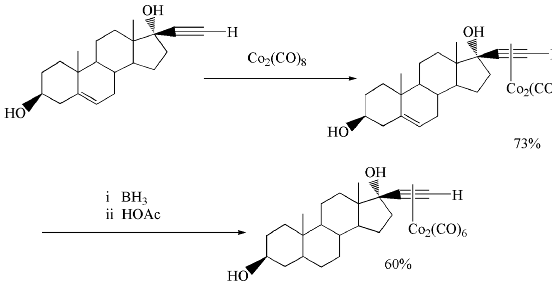


Figure 3. Structure of vitamin B_{12}.[121]

triple bond forming a mutually bridged bond between two π-bonds of acetylene and cobalt–cobalt bond of $Co_2(CO)_6$, as described above. The reactive carbon–carbon triple bond with this bridged bond is converted to an inert bond. This means that the hexacarbonyldicobalt forms as a protecting group for the reactive triple bond of acetylene compounds.

Hence, by protecting the reactive triple bond of the acetylene compounds with the octacarbonyldicobalt, many kinds of reactions such as reductions,[122–124] Friedel–Crafts reactions,[122,125] rearrangements,[126] fluorinations,[127] 1,3-dipolar cycloaddition reactions,[128] Grignard reactions,[129] hydrolyses,[130] oxidations,[131] amidations,[131] pinacol coupling reactions,[132] carbonylative cyclizations,[133] metathesis[134] and radical reactions,[135] have been reported. These many reactions with ocatacarbonyldicobalt for protection of the reactive acetylene triple bond have been applied in organic syntheses.

For example, in steroids with a double bond and triple bond, the double bond is selectively reduced after protecting the triple bond with the cobaltcarbonyl reagent, as shown in equation (7).[122,125]



(7)

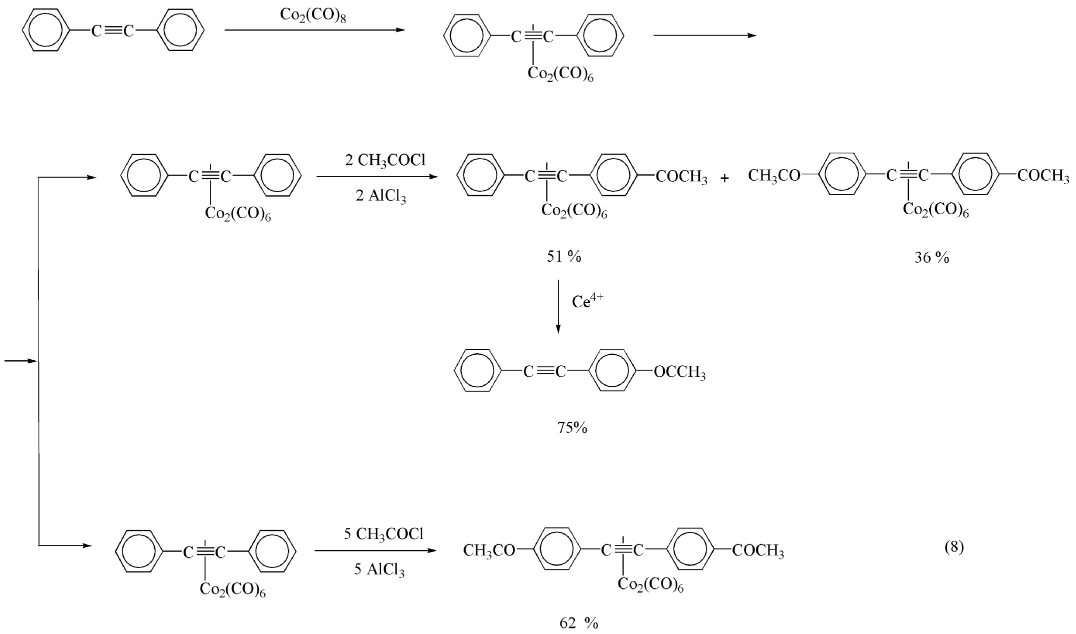
The Friedel–Crafts acylation of diphenylacetylene cannot be accomplished directly. However, by protecting with cobaltcarbonyl, a facile Friedel–Crafts acylation occurs, and the organic ligand in the resulting products is released from their cobalt complexes to give organic compound in a good yield, as shown in equation (8).[122,125]

NICHOLAS REACTIONS

The mutually bridged bonds simply show protective action to the reactive acetylene bond, as shown in the previous section. However, the reactions with this bridged bond frequently proceed regio- and stereo-specifically because this protecting group is a bulky group, as shown in Fig. 1. Furthermore, the mutually bridged bond forms a reaction site at the α-position to the bridged bond. At this position, many kinds of reactions, such as nucleophilic substitutions, and cyclizations also proceed as shown in the next section.

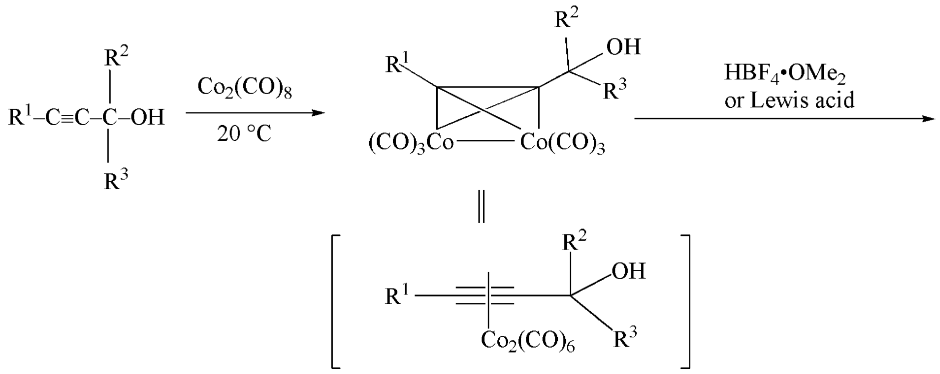
In the formation of the mutually bridged complexes, where the α-carbon of the acetylene compounds bonds with a hydroxy group or alkoxy group in the complexes, or the α-carbon is the carbon of a formyl group or an alkene, the complexes form cations with an acid such as tetrafluoroboric acid and trifluoroacetic acid. The cations easily react with many kinds of nucleophiles to form the corresponding derivatives. The reaction with hydroxy group at the α-carbon is shown in equation (9).[136]

Nicholas and Pettit, in 1971, reported on the reaction of alkyne protected with octacarbonyldicobalt[137] and, in 1972, on the high stability of the cation at the α-position of the alkynes.[138] The reactions of the cation with many kinds of nucleophiles are well known as the Nicholas reactions.[44,57–59,122,139–181] The carbonium ions at the α-position to the alkyne carbon are stabilized with the mutually bridged bond and can react with a variety of

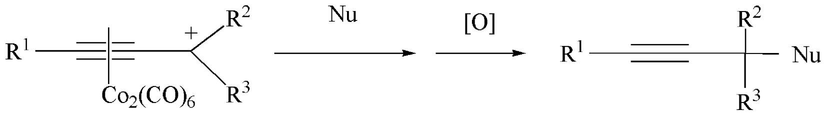


(8)

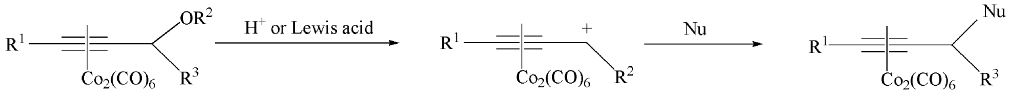
DOI: 10.1002/aoc



mutualy bridged bond between Co-Co and C≡C

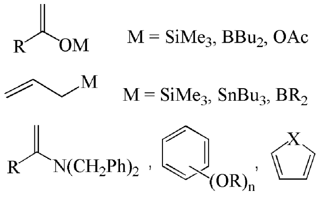


(9)



(10)

Nu = ROH, R_2NH, RSH, H_2NSO_2R, MeCN, R_3P, R_3Al, R_3SiH, R_3SnH, $NaBH_4$, BH_3,

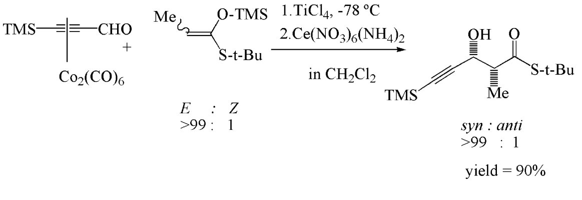


M = $SiMe_3$, BBu_2, OAc

M = $SiMe_3$, $SnBu_3$, BR_2

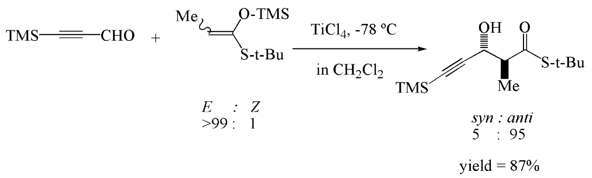
nucleophiles such as alcohols, amines, alcoholates, allysilanes and allyltrialkyltin, as shown in equation (10).[58]

For example, the Nicholas reaction is an aldol-type reaction of the propynal–$Co_2(CO)_6$ complexes with silyl enol nucleophiles and proceeds with highly *syn*-selectivity. The treatment of the propynal–$Co_2(CO)_6$ complexes with (*E*)-*O*, *S*-acetal in methylene chloride, followed by exposure to cerium ammonium nitride gives the *syn* product exclusively in 90% yield. On the other hand, the reaction without the octacarbonyldicobalt gives the *anti*-product exclusively, as shown in equations (11) and (12), respectively.[168,169]



(11)

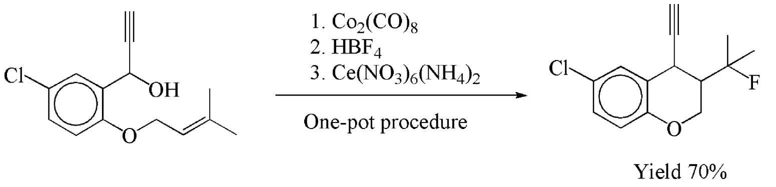
In 2002, syntheses of many kinds of pharmaceuticals with these stereoselective aldol-type reactions were reviewed,[170] e.g. β-lactam antibiotics (±)-PS-5 and (±)-epi-PS-5[170–172], (±)-blastmycinone,[173] and (+)-bengamide E[174–176] and cyclizations, e.g. (+)-syributins 1.[177]



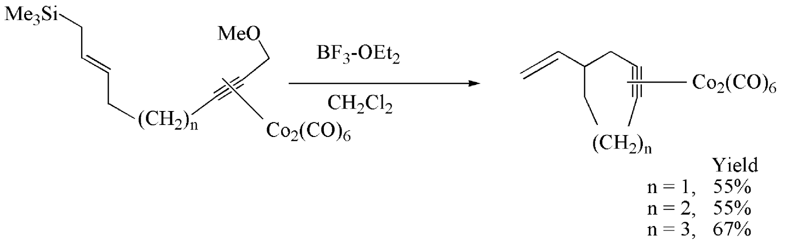
(12)

With long chain groups, an intramolecular Nicholas cyclization easily proceeds at the propargyl position,[58,141,178–181] for example, if octacarbonyldicobalt is added to the hexane solution of a propynyl alcohol, (2-methyl-4-[2-(1-hydroxyprop-2-yn-1-yl)phenoxy]but-2-ene), and the reaction mixture is stirred under an atmospheric pressure of nitrogen at an ambient temperature. A stereospecific cyclization product is obtained in high yield, as shown in equation (13).[141]

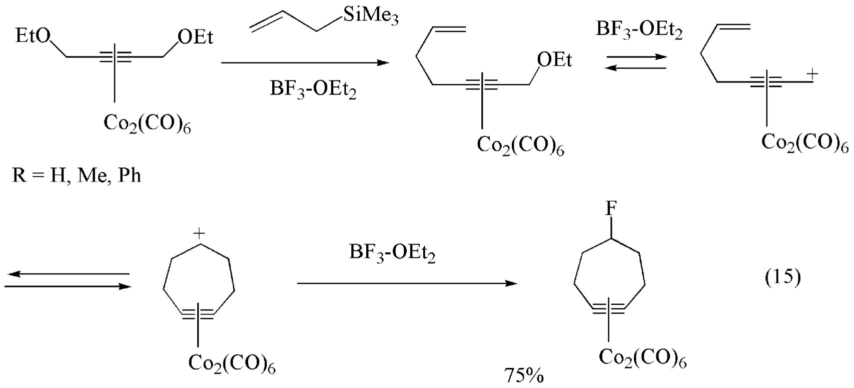
DOI: 10.1002/aoc



(13)



(14)



(15)

In a study in 1986, syntheses of six-, seven- and eight-membered ring systems proceeded by the intramolecular cyclization of cobalt complexed propargylic ether with allylic silyl group, as shown in equation (14).[58]

On the other hand, similar seven-membered ring systems were also synthesized by intermolecular cyclization, that is, [4 + 3] cycloaddition of butyne-1,4-diether hexacarbonyl with allylsilane, as shown in equation (15).[151]

CYCLIZATIONS OF ALKYNES, ALKENES AND NITRILES WITH ORGANOCOBALT COMPOUNDS

Introduction

Cyclization reactions of alkynes proceed by the insertion of other alkynes, alkenes, nitriles, carbon monoxide, etc., to the cobalt–carbon bond of the cobalt carbonyl catalyst. These cyclizations are the [2 + 2 + 1] cyclizations (Pauson–Khand reactions), [2 + 2 + 2] cyclotrimerizations, [2 + 2] cyclizations, [3 + 2 + 2] cyclizations, [3 + 2] cyclizations, [5 + 2] cyclizations, etc. These proceed not only with conventional $Co_2(CO)_8$ but also with the other cobalt carbonyls such as cyclopendadienyl cobalt and cyclooctadienyl cobalt.

In the reactions with the mutually bridged bond between the acetylene two π-bonds with the cobalt–cobalt bond, reactions with a $Co_2(CO)_6$ protecting group and Nicholas reactions were described above.

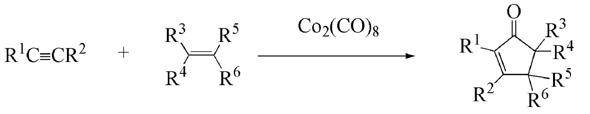
The Pauson–Khand reactions also proceed with the mutually bridged bond between the acetylene two π-bonds with cobalt–cobalt bond, mainly using the $Co_2(CO)_8$ catalyst.

Generally, these cyclizations show one of the first characteristic reactions of the organocobalt compounds. However, Pauson–Khand reactions of the [2 + 2 + 1] cyclizations illustrate the first and second characteristic reactions of the organocobalt compounds because these cyclizations proceed by the insertion of carbon monoxide except for the alkynes and alkenes, as shown in the next section.

[2 + 2 + 1] Cyclizations

Pauson–Khand reactions

Pauson–Khand reactions are the most representative reactions with the organocobalt compounds used in organic synthesis.[38–52,182–237] These reactions involve the cyclization of one acetylene, one olefin and a cobaltcarbonyl (as a carbon monoxide source, e.g. octacarbonyldicobalt) and yield cyclopentenone by the [2 + 2 + 1] cyclization addition, as shown in equation (16).



(16)

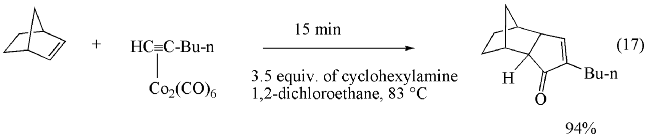
DOI: 10.1002/aoc

Many reviews on this Pauson–Khand reactions have been published.[38–52,216] These reactions also occur with other metal compounds such as Rh, Ru, Ir, Pd, Mo, Ti, Ni, Fe, W, Co–Zn compounds and Co–C, as well as cobalt carbonyl compounds.[46,186,189,200,204,208,221,227,233,235,238–243]

As shown in Scheme 1,[40] at first, two π-bonds in acetylene with two cobalt atoms form the mutually bridged structure **7**, as shown in Fig. 1. Then one olefin is coordinated to one of the cobalt atoms and inserted into the cobalt–carbon bond. Also, one carbonyl is inserted into the new cobalt–carbon bond, and cyclopentenone is obtained by the elimination of $Co_2(CO)_6$.

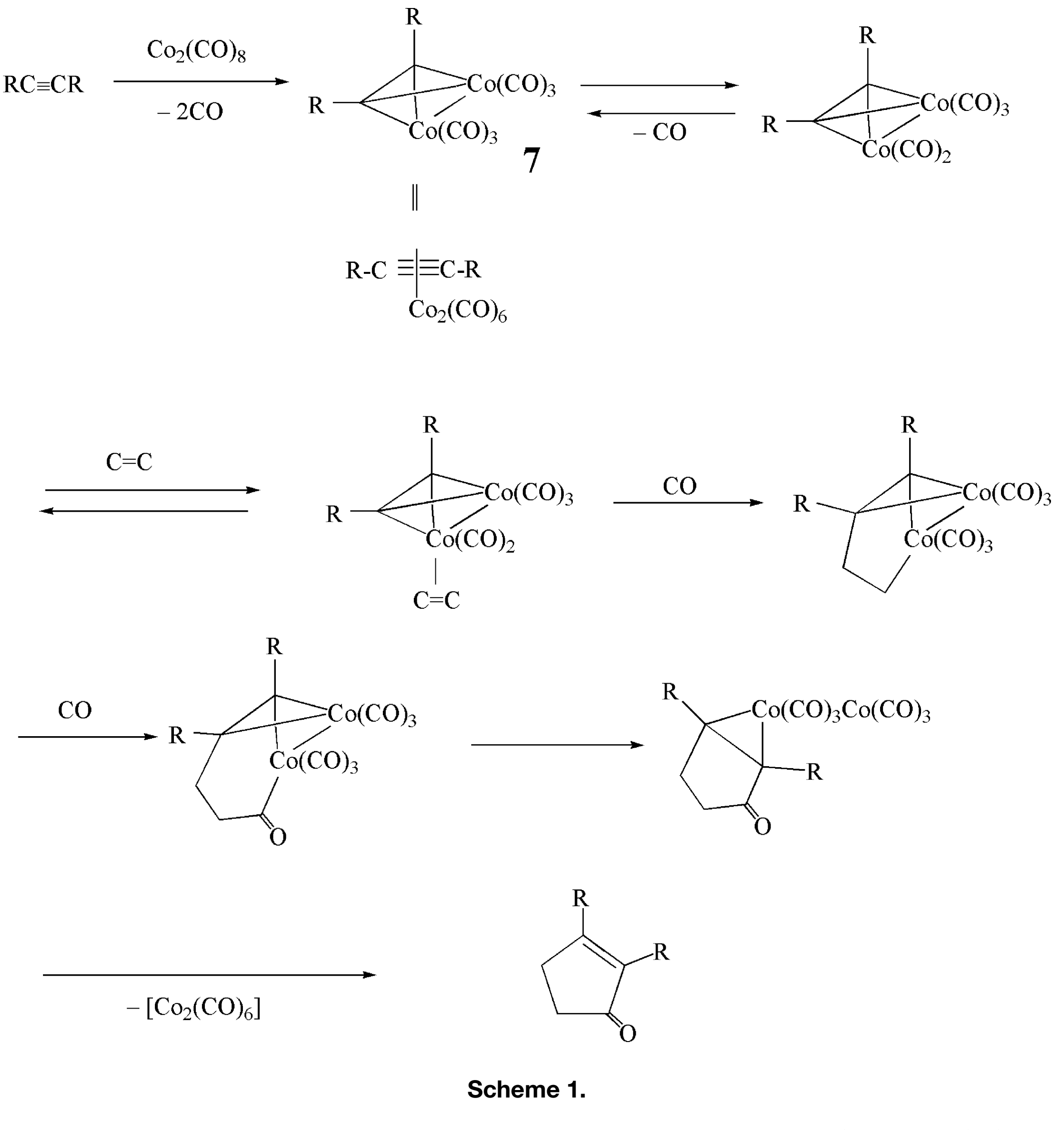
In these reactions, $Co_2(CO)_8$ reacts with acetylene at room temperature for several hours to form a stable acetylene π-complex **7**, then an olefin reacts with the complex under a nitrogen or carbon monoxide atmosphere with heating. Generally, a stoichiometric amount of the metal is required to achieve an acceptable yield because the cobaltcarbonyl compound is used as the carbon monoxide source. The yields of the Pauson–Khand reactions were not very high.[39,40] However, the use of tertiary amine N-oxides, silica, primary amines, alumina and a supersonic wave, leads to a dramatic increase in their yields and reaction rates.[43,185,200,206,207,209,212,232,244,245]

For example, norbornene reacts with hexeyne-1 and $Co_2(CO)_8$ in the presence of cyclohexylamine in 1,2-dichloroethane at 83 °C for 15 min in an argon atmosphere to give the desired cyclopentenone in 94% yield, as shown in equation (17).[207]



(17)

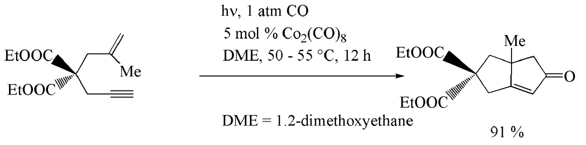
The use of stoichiometric amounts of a transition-metal compound is not acceptable commercially. Therefore, many



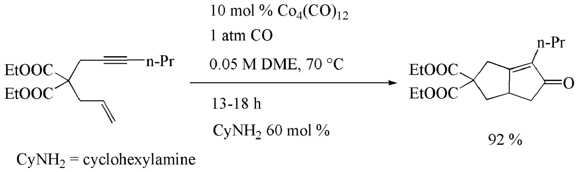
Scheme 1.

research groups have studied the use of various kinds of catalysts, such as $Co_2(CO)_8/P(OPh)_3$, (indenyl)Co(COD) and $Co(acac)_2/NaBH_4$ under CO pressure with additives.[200]

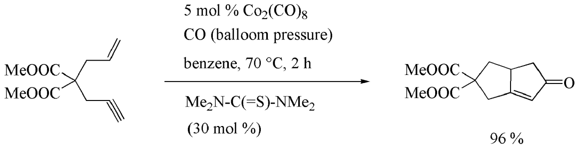
In 1996, the photo-activation (Q-Beam Max million 10^6 candle-power spotlight) of $Co_2(CO)_8$ under a low CO pressure was successful as a practical procedure in giving high yields, as shown in equation (18).[209] In 2001, as a practical example of cobalt carbonyl catalysis in the thermal cyclization, the reaction with $Co_4(CO)_{12}$ in the presence of cyclohexylamine also proceeds in high yield under one atmosphere of CO pressure, as shown in equation (19).[185] Furthermore, in 2005, a similar reaction with a catalytic amount of $Co_2(CO)_8$ in the presence of tetramethylurea $[Me_2N{-}C({=}S){-}NMe_2]$ under a balloon pressure of CO in benzene proceeded with 96% yield, as shown in equation (20).[232]



(18)

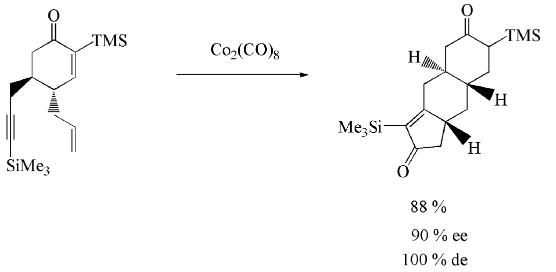


(19)



(20)

The Pauson–Khand reactions tend to proceed stereoselectively because the reactions goes via a bulky mutually bridged structure, as shown in Scheme 1. Furthermore, the reaction with a cobaltcarbonyl catalyst coordinated by a chiral group such as phosphine proceeds with a high enantioselectivity. Recently, many of these diastereospecific and asymmetric reactions,[186–188,191–193,198,202,203,210–212,215–221,223,225,229–231] and syntheses of natural products[216–218,220,225,229–231] have been reported. For example, the Pauson–Khand reaction with an enyne gives a tricyclic product in a high yield and proceeds with complete diasteroselectivity, as shown in equation (21).[215]



(21)

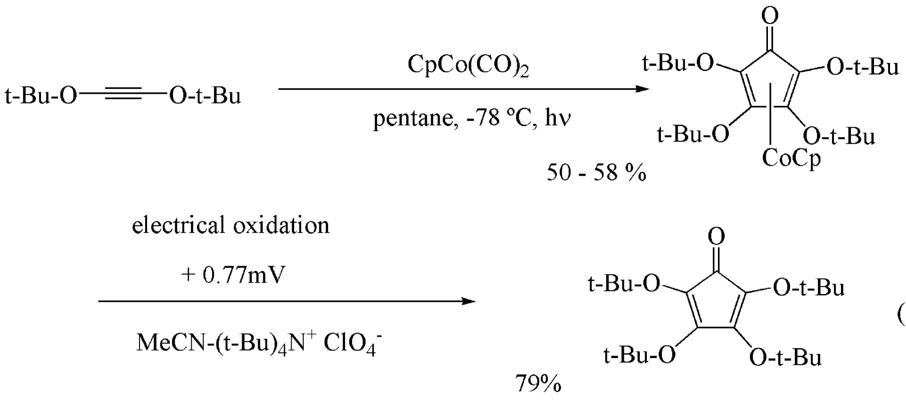
The cycloaddition of two alkynes in the presence of cyclopentadienylcobalt catalyst gives cyclopentadienone instead of the cyclopentenones in the Pauson–Khand reaction, as shown in equation (22).[246–248]

Iwasawa and co-workers[249–254] recorded the reaction of $Co_2(CO)_8$ with cyclopropane compounds in place of the olefins. This is also considered to be one of the modifications of the Pauson–Khand reactions.

[2 + 2 + 2] Cyclotrimerizations

In the oligomerizations of acetylene, only a few catalysts besides nickel catalysts for the tetramerizations to cyclooctatetraene are known.[255,256] However, many kinds of catalysts for the cyclotrimerization to benzene have been found. These catalysts are metals or metal compounds of Ti (Group 4), V, Nb and Tc (Group 5), Cr and W (Group 6), Fe and Ru (Group 8), Co and Rh (Group 9), and Ni and Pd (Group 10).[256–263]

In particular, the organocobalts such as cyclopentadienyldicarbonylcobalt are conveniently used as the best catalysts for the synthesis of benzene derivatives.[264–268] These cyclizations are called [2 + 2 + 2] cyclotrimerization reactions. With the cyclopentadienylcobalt catalysts, not only acetylenes but also olefins, nitriles and the other unsaturated compounds, can be used in these cyclotrimerizations.



(22)

DOI: 10.1002/aoc

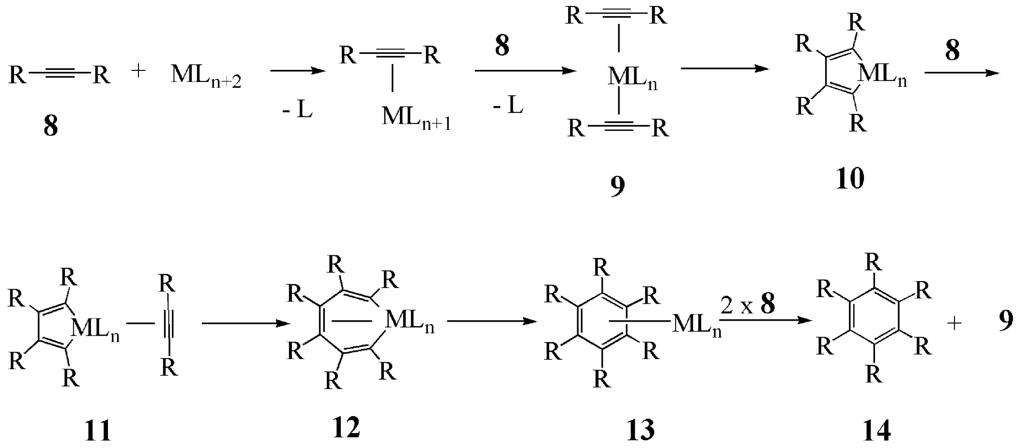
There are mainly three types of the cyclotrimerization reactions, such as acetylene [2 + 2 + 2] cyclotrimerization, acetylene–olefin [2 + 2 + 2] cyclotrimerizations, and hetero [2 + 2 + 2] cyclotrimerizations.[39,44,48,53–56,267,269–325]

The acetylene [2 + 2 + 2] cyclotrimerizations are presumed to proceed as shown in Scheme 2.[262] A metal complex ML_{n+2} is thought to sequentially bind first with an alkyne **8** and then with a second alkyne **8** to give the complex **9**. An ensuing redox reaction would lead to matalacyclopentadienes **10**, which might relieve its coordinative unsaturation by coordinating a third alkyne to give another complex, **11**. In the conversion of **9** to **10**, the alkynes have been reduced with a concomitant carbon–metal bond formation, and the metal has lost two electrons. An insertion of the third alkynes in the complexed alkynes **11** gives metallacycloheptatriene **12** followed by a reductive elimination to an arene **13**. A decomplexation with two alkynes would produce an arene **14** and the complex **9**, completing a catalytic cycle.[262] In these reactions, it may be conceivable that the Diels–Alder reaction partially proceeds between the diene of metalacyclopentadine **10** and alkyne **8**. With the exception of **11**, species **9**–**13** have been isolated. Cobaltcyclopentadienes **10** are easily synthesized, and many compounds are derived from the compounds, as shown in Scheme 3.[264] Therefore, these compounds are utilized as useful intermediates. In the reactions from the species **9** to the cobaltcyclopentadienes **10**, the bulky groups tend to bond with the carbon atom near the cobalt atom.[122]

Cyclic products derived from only two molecules of alkynes include cyclobutadiene complexes **15** and cyclopentadienone complexes **16** via cobaltcyclopentadienes **10**, as shown in equation (23). The cyclopentadienone **16** arises from the incorporation of carbon monoxide with a cobaltcarbonyl catalyst, as shown in Scheme 3. The lower cyclooligomers may predominate over trimers **17** and higher homologues if further alkyne incorporations are found due to steric hindrance at the metal. In these reactions, three types of reactions, i.e. [2 + 2] cyclization (with two alkynes), [2 + 2 + 1] cyclization (with two alkynes and carbon monoxide), and [2 + 2 + 2] cyclotrimerization (with three alkynes) occur.[262]

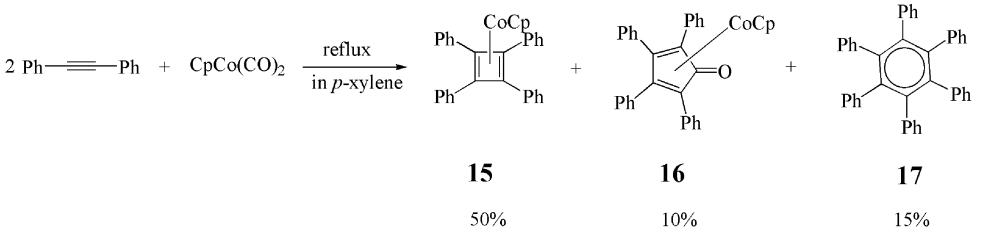
These cyclizations are presumed to proceed not via the mutually bridged structure with the $Co_2(CO)_8$ catalyst (e.g. Scheme 1) but via their acetylene–cobalt π-complexes with the other cobalt catalysts such as $CpCo(CO)_2$ and $CpCo(PPh)_3$, e.g. as shown in Scheme 2.[262]

A partial intramolecular approach of diynes and monoalkyne and a completely intramolecular approach of triynes are also applied as shown in equations (24) and (25), respectively, and these reactions are also called the [2 + 2 + 2] cyclotrimerization or [2 + 2 + 2] cycloaddition.[269,277–279,291–293]

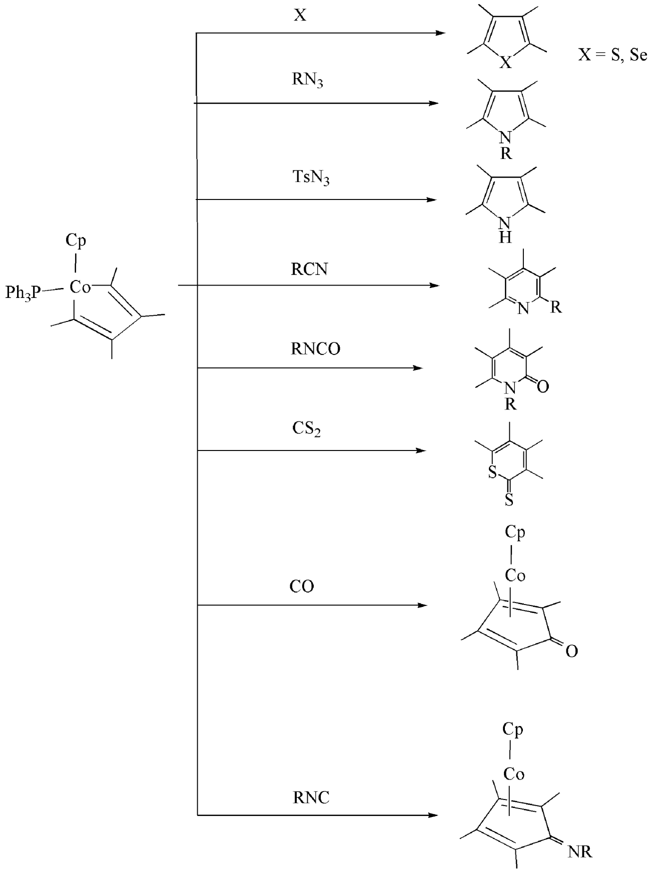


$ML_n = CpCo(PR_3)$

Scheme 2.

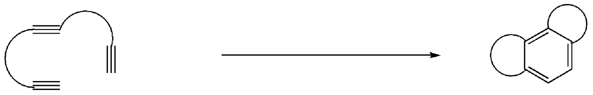


(23)

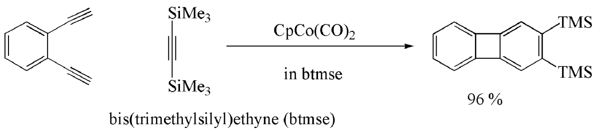


Scheme 3.

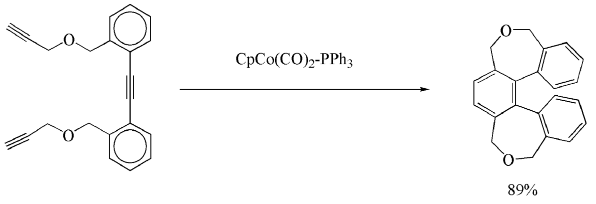

(24)


(25)

Examples of these partial or completely intramolecular cyclotrimerizations with three triple bonds are 1,2-diethynylbenzene combining with bis(trimethylsilyl)ethyne to give bis(trimethylsilyl)[2]phenylene,[294] and the synthesis of helicenes by the cyclotrimerization of triynes with CpCo(CO)$_2$–PPh$_3$ catalyst,[296,297] as shown in equations (26) and (27), respectively.

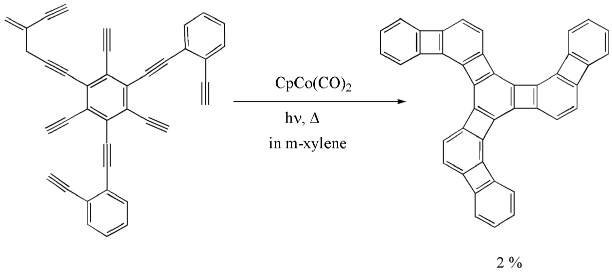


(26)



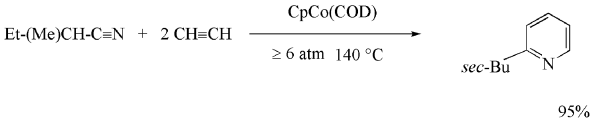
(27)

The total synthesis of C_{3h}-symmetric[7]phenylene has been accomplished by triple cobalt-catalyzed cycloisomerization of nonayne, albeit in low yield as shown in equation (28).[310,321]



(28)

With one cyano compound instead of one monoyne, the cyclotrimerization provides heterocyclic compounds[28,29,183,262,284–289,291,273,298–300,312] such as pyridine derivatives. For example, (+)-(*S*)-2-methylbutanenitrile reacts with acetylene at 140 °C in the presence of CpCo(cyclooctadiene) to yield (+)-(*S*)-2-*sec*-butylpyridine in a high yield, as shown in equation (29).[284]



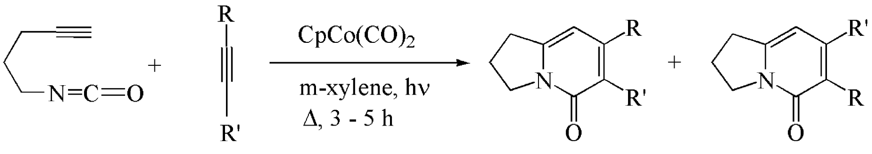
(29)

With isocyanates instead of nitriles, the cyclizations of acetylenes yield 5-indolizinones in a regio-controlling reaction, as shown in equation (30). This reaction is readily applied to a total synthesis of the antitumor alkaloid camptothecin.[301]

The cyclotrimerizations with one alkene instead of one alkyne, give cyclohexadiene derivatives **19**, instead of benzene derivatives.[183,262,280–283,273,302–307] This reaction may be used in the total synthesis of the Torgov intermediate **20**, in the synthesis of estrone. Exposure of enediyne **18** to excess CpCo(CO)$_2$ in boiling isooctane gave the red crystalline cobalt complexes **19**, in a fairly good yield (65%), as shown in equation (31).[306]

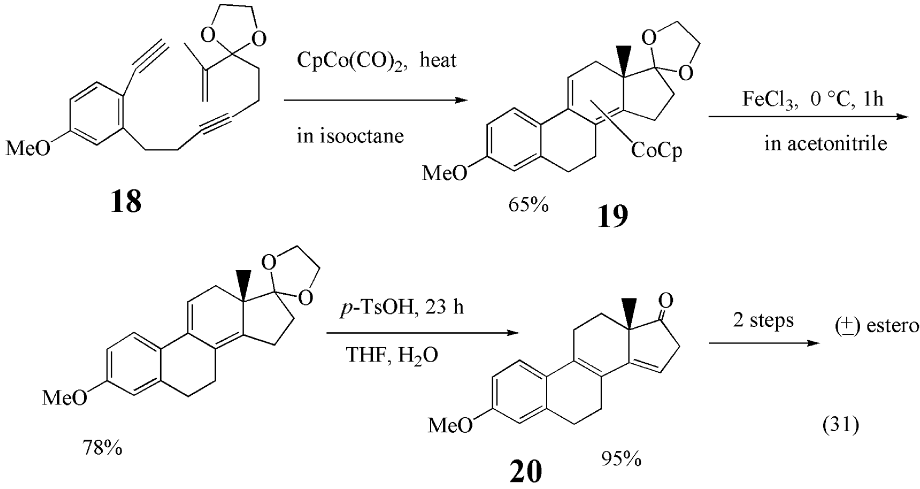
Others

Other cyclizations with the cobalt catalysts have been reported on the [2 + 2], [3 + 2 + 2], [3 + 2], [5 + 2], and [4 + 2] cyclizations, etc. One example of the [2 + 2] cyclization



(30)

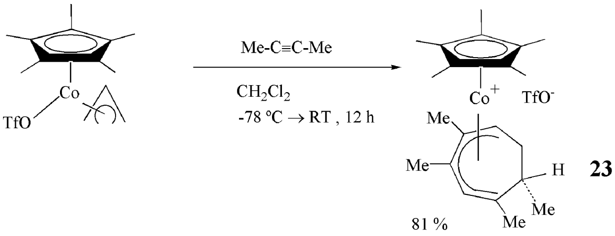
R	R'		
SiMe$_3$	SiMe$_3$	72%	-
n-Pr	SiMe$_3$	68%	5



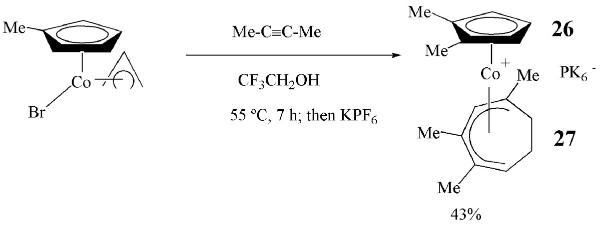
(31)

is shown in equation (23). However, a different type of the [2 + 2] cyclization is the following reaction, shown in Scheme 4.[326,327] In some of the [2 + 2] cyclizations, isomerizations also proceed during the cyclization reaction. Hence, these reactions are called cycloisomerizations. As a cyclopentadienyl cobalt moiety tends to show a high affinity to a diene moiety, as described above. This cycloisomerization forms the two types of cyclopentadienyl cobalt diene complexes, that is, a diene complex **21** and cyclopentadiene complex **22**, as shown in Scheme 4.[326,327]

In the reaction of 2-butyne with η^5-pentamethylcyclopentadienylallyl cobalt or η^5-methylcyclopentadienylallyl cobalt compounds, [3 + 2 + 2], [3 + 2] and [5 + 2] cyclizations were reported.[328–330] The cycloaddition of two 2-butynes to an allyl moiety in the presence of pentamethylcyclopentadienylallyl cobalt complex yields an η^5-cycloheptadienyl ring product **23** by a [3 + 2 + 2] allyl/alkyne, alkyne cycloaddition, as shown in equation (32). The formation of the η^5-cycloheptadienyl ring is considered to follow the insertion of 2-butyne to an allyl-cobalt bond in pentamethylcyclopentadienylallyl cobalt complex that leads to an η^1,η^2-cyclopentenyl ligand **24**, and an agostic η^3-cyclopentenyl intermediate **25** that subsequently undergoes an alkyne insertion and a ring expansion at or below room temperature, as shown in Scheme 5.[328,329] On the other hand, the cycloaddition of 2-butyne to monomethylcylopentadieneylallylcobalt complex forms two cyclization products. One is the [3 + 2] cycloaddition, **26**, of an alkyne to an η^3-allylcobalt moiety. The other is the [5 + 2] cycloaddition, **27**, of an alkyne to methylcyclopentadiene derived from the ring expansion of the original η^5-cyclopentadineyl ring with 2-butyne, as shown in equation (33).[328]

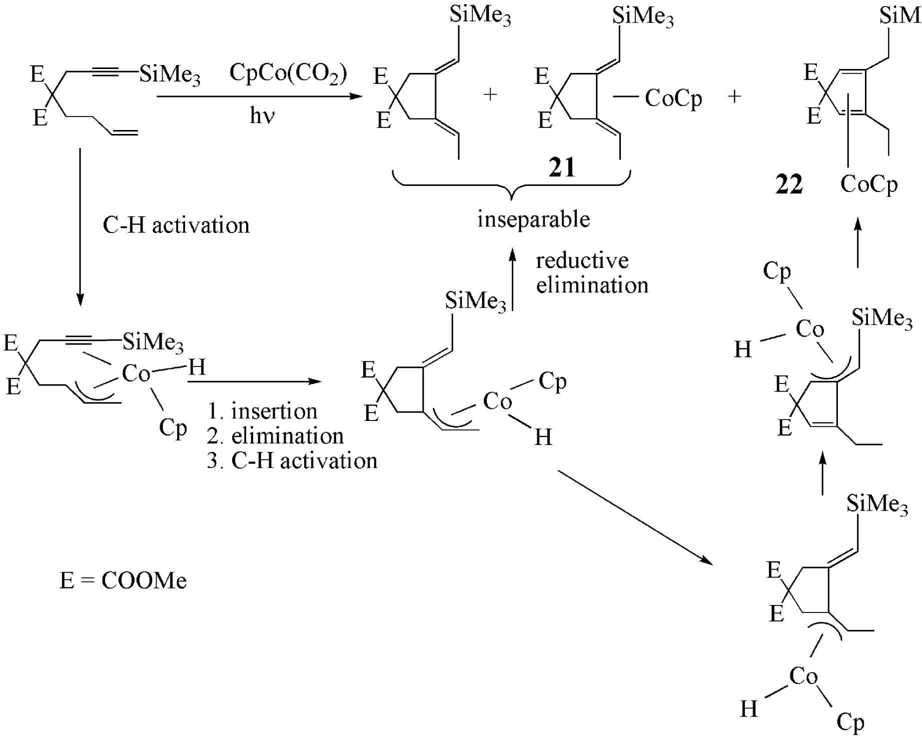


(32)

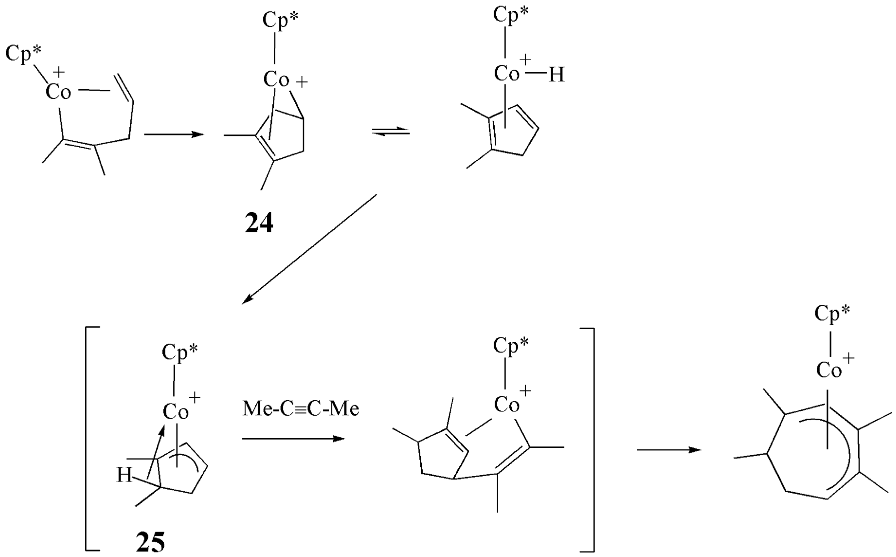


(33)

Recently, many articles regarding Diels–Alder reactions ([4 + 2] cycloadditions),[313–317] [4 + 2 + 2] cycloadditions (diene and two ynes),[313] and [6 + 2] cycloadditon of cycloheptatriene with alkynes[318] also reported using inorganic cobalt catalysts.



Scheme 4.



Scheme 5.

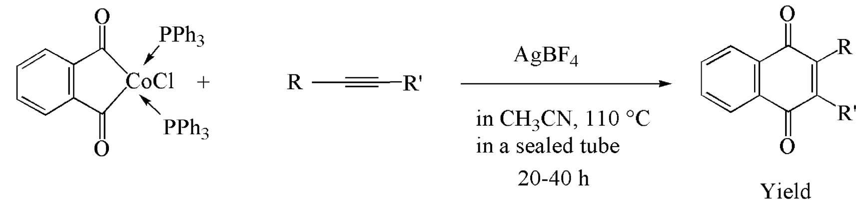
Since 1980, Liebeskind *et al.*[331–340] have reported on many kinds of quinone syntheses by utilizing the property of high affinity of cobalt complexes to alkynes. For example, phthaloyl cobalt complexes react with a wide variety of alkynes to give high yields of 1,4-naphthoquinones as shown in equation (34).[331] They also reported on the applications of regiospecific total syntheses of the natural product (±) nanaomycin using this phthalolyl cobalt complex.[333]

CARBONYLATIONS

Introduction

The second characteristic reaction of organocobalt compounds in organic synthesis is carbonylation. The organocobalt compounds are used as catalysts in these carbonylation reactions.

DOI: 10.1002/aoc



(34)

R, R' = I, Me, Et, CH_2-CH=CH_2,n-Bu, t-Bu, OEt, Ph, $SiMe_3$

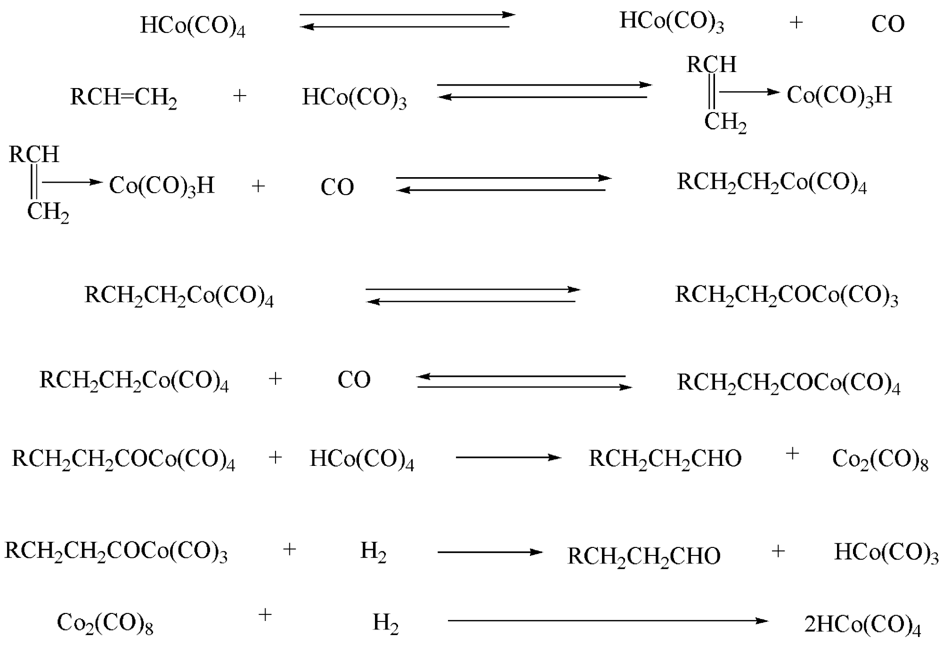
The carbonylations of alkenes with carbon monoxide and hydrogen sing cobaltcarbonyl catalysts are hydroformylations (oxo reactions). The hydrocarbonylations are the carbonylation of alkenes with water or alcohols. Amidocarbonylations (Wakamatsu reactions) are used to manufacture amino acids as an industrial process by the carbonylation of aldehydes with amides. Hydrosilylcarbonylations are the carbonylations with a hydrosilyl group instead of hydrogen in the hydroformylation. The carbonylation of alkyl or aryl halides such as benzyl halides easily proceeds using the cobaltcarbonyl catalysts.[60–65,341–351]

The other carbonylations are also reported on exocylic carbonylations of cycloimino esters,[352] ring-expanding carbonylations of 2-aryl-3-oxazolines,[353] active epoxide carbonylations to β-lactones[354] or polyesters,[355] carboylative silycarbocyclization of 1,6-enynes,[356] hydromethoxycarbonylation of 1,3-butadiene, etc.[357]

Hydroformylations

The hydroformylation is a reaction for preparing aliphatic aldehydes whose carbon number is increased by one, as shown in equation (35).[341] Commercially, butyraldehyde is produced largely from propylene. Butyraldehyde is used as a raw material for butanol, 2-ethylhexanol, etc., with cobalt and rhodium compounds as useful catalysts. The catalytic activity of the cobalt catalysts is less than that of rhodium catalysts. However, the linear product, **28**, of the reaction shown in equation (35) was obtained. The ratio (**28**:**29**) of straight-chain obtained using $HCo(CO)_4$ as the cobalt catalyst is 3:4, but the ratio using $HCo(CO)_3(PBu_3)$ as the catalyst is improved to 6:7.[341] $HCo(CO)_4$ as the hydroformylation catalyst is obtained by the hydrogenation of $Co_2(CO)_8$, and the active species is thought to be $HCo(CO)_3$ formed by the decarbonylation of $HCo(CO)_4$ by one carbonyl. The reaction is presumed to proceed as shown in Scheme 6.[60,343–345]

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[100\,^\circ C,\ 100\ atm]{Co\ or\ Rh} \underset{\mathbf{28}}{RCH_2CH_2CHO} + \underset{\mathbf{29}}{RCH(CH_3)CHO} \quad (35)$$



$$HCo(CO)_4 \rightleftarrows HCo(CO)_3 + CO$$
$$RCH{=}CH_2 + HCo(CO)_3 \rightleftarrows \overset{RCH}{\underset{CH_2}{\|}} \rightarrow Co(CO)_3H$$
$$\overset{RCH}{\underset{CH_2}{\|}} \rightarrow Co(CO)_3H + CO \rightleftarrows RCH_2CH_2Co(CO)_4$$
$$RCH_2CH_2Co(CO)_4 \rightleftarrows RCH_2CH_2COCo(CO)_3$$
$$RCH_2CH_2Co(CO)_4 + CO \rightleftarrows RCH_2CH_2COCo(CO)_4$$
$$RCH_2CH_2COCo(CO)_4 + HCo(CO)_4 \longrightarrow RCH_2CH_2CHO + Co_2(CO)_8$$
$$RCH_2CH_2COCo(CO)_3 + H_2 \longrightarrow RCH_2CH_2CHO + HCo(CO)_3$$
$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4$$

Scheme 6.

DOI: 10.1002/aoc

In 2003, the industrial processes for hydroformylation to make octanol and butanol were reported.[346] The hydroformylation produces octanol (2-ethylhexanol, 3 × 10^6 ton/year), butanol (2.1 × 10^6 ton/year), and isononanol (0.6 × 10^6 ton/year) as worldwide oxoalcohols 2002. In the primary stage of the hydroformylation, cobalt catalysts [e.g. $HCo(CO)_4$] were used. Now, rhodium catalysts [e.g. $HRh(CO)(PPh_3)_4$] have mainly replaced the cobalt catalysts, because the rhodium catalysts have higher reactivity, selectivity and stability than the cobalt catalysts. However, isononylaldehyde is produced using the cobalt catalyst because its recycle is very easy.[346] Other articles on the hydroformylation have also been published.[61–63,345,347–351,358–366]

Hydrocarboxylations

Hydrocarboxylation is the reaction by using water or alcohol in the place of hydrogen in hydroformylation, as shown in equation (35). It produces a carboxylic acid or an ester, as shown in equations (36) and (37).[341]

$$\mathrm{RCH{=}CH_2 \;+\; CO \;+\; H_2O \xrightarrow[Co_2(CO)_8]{140-170\ ^\circ C,\ 100-200\ atm} RCH_2CH_2COOH} \quad (36)$$

$$\mathrm{RCH{=}CH_2 \;+\; CO \;+\; R'OH \xrightarrow[Co_2(CO)_8]{80-100\ ^\circ C,\ ca.\ 35\ atm} RCH_2CH_2COOR'} \quad (37)$$

The hydrocarboxylation of olefins with carbon monoxide and a nucleophilic reaction partner possessing a labile hydrogen atom results in the formation of carboxylic acids or their derivatives in the presence of metal carbonyls (i.e. carbonyls of Ni, Co, Fe, Rh, Ru and Pd), as shown in equation (38).[363] These hydrocarbonylation products are thioesters, amides, anhydrides, and carboxylic acids and their esters. For example, nickel carbonyl [$Ni(CO)_4$] is used as the catalyst for the industrial production of propionic acid from ethylene, CO and H_2O. Other carbonyls such as Co or Fe carbonyl are also catalytically active.[359]

$$\mathrm{RCH{=}CH_2 \;+\; CO \;+\; HX \longrightarrow RCH_2CH_2COX} \quad (38)$$

X = -OH, -OR, -SR, -NHR, -O(O=C)C-R, etc.

Generally, adipic acid is manufactured by a two-stage oxidation process via cyclohexanol/cyclohexanone from cyclohexane. Recently, a new synthesis of adipic acid from butadiene has been used in an industrial process.[341,367,368] Adipic acid is produced by the hydrocarbonylation of butadiene by using the organocobalt catalysts, as shown in equation (39).

$$\mathrm{CH_2{=}CHCH{=}CH_2 \;+\; CO \;+\; MeOH \longrightarrow CH_3CH{=}CHCH_2COOMe}$$

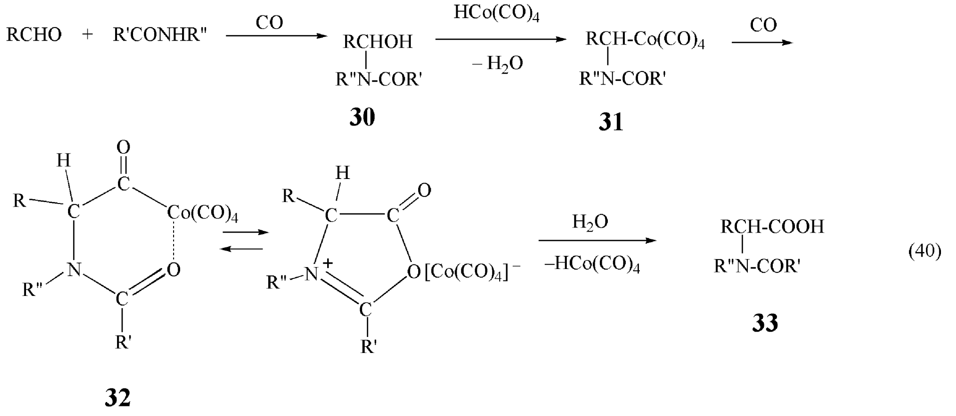
$$\mathrm{CH_3CH{=}CHCH_2COOMe \;+\; CO \;+\; MeOH \longrightarrow MeOCO(CH_2)_4COOMe} \quad (39)$$

Amidocarbonylations

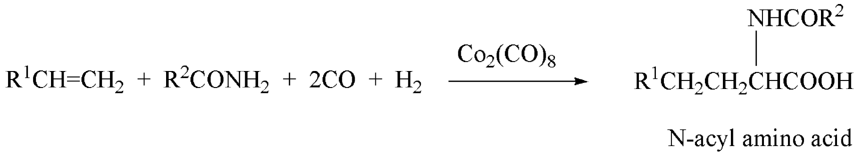
The hydroformylations (oxo reactions) yield aldehydes under carbon monoxide and hydrogen pressure in the presence of the organocobalt catalysts. Under the same conditions, an amide is added to an aldehyde to produce an acylamino acid, as shown in equation (40).[341] The aldehyde reacts with the amide giving an aminoalcohol **30**, and, as cobalthydrocarbonyl ($HCo(CO)_4$) is a strong acid, the dehydration condensation of the aminoalcohol **30** using $HCo(CO)_4$ forms a C–Co bond **31**. This is followed by carbonylation and hydrolysis to produce an acylamino acid **33** via the intermedaite having a six-membered ring **32**.[341,369] For example, acetaldehyde reacts with acetamide under carbon monoxide and hydrogen pressure (200 kg/cm^2) in the presence of octacarbonyldicobalt catalysts at 110–120 °C for 10 min to yield α-alanine (80%).[64]

This reaction is named the Wakamatsu reaction after H. Wakamatsu, who first discovered this reaction in 1971.[370] These reactions directly produce amino acids from olefins and amides under the hydroformylation reaction conditions, as shown in equation (41).

Recently, the reaction mechanism of this cobalt-catalyzed amidocarbonylation was reported as shown in Scheme 7.[65] The applications of the cobalt-catalyzed amidocarbonylation were also reported with *N*-acetyl-D,L-phenylalanine (precursor of L-phenlalanine, the key intermediate in the synthesis of aspartame), sarcosinates (*N*-methylglycine, a group of anionic tensides that are used as components of surfactants, soaps and emulsifiers) and glufosinate (a naturally occurring



DOI: 10.1002/aoc



$$R^1CH{=}CH_2 + R^2CONH_2 + 2CO + H_2 \xrightarrow{Co_2(CO)_8} R^1CH_2CH_2\overset{\overset{NHCOR^2}{|}}{C}HCOOH$$

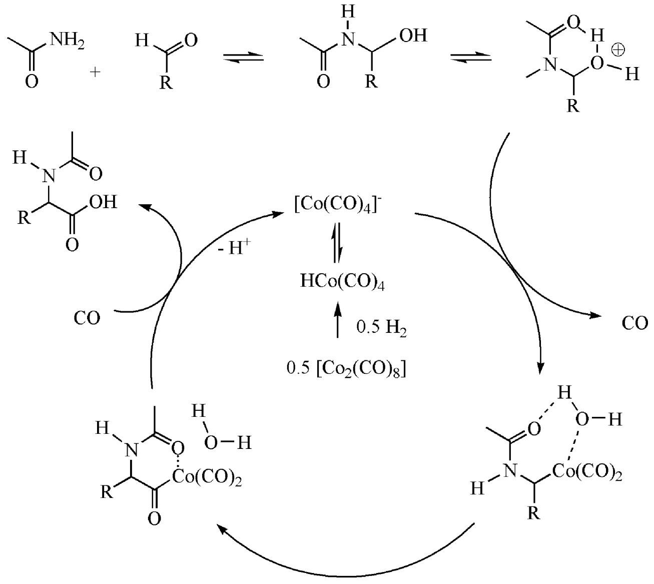
(41)

N-acyl amino acid

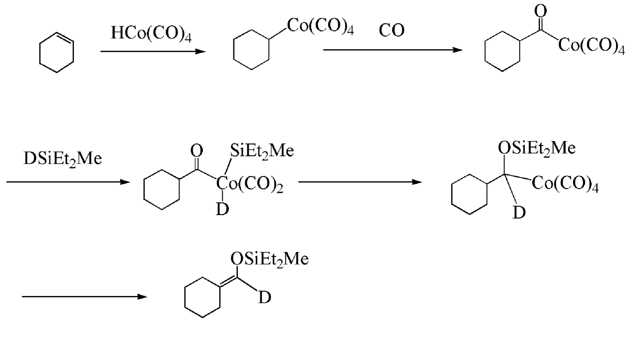
hydroxyphosphorylamino acid with herbicidal and antibiotic properties marketed as a nonselective herbicide under the name BASTA).[65]

Hydrosilylcarbonylations

The hydrosilylcarbonylations are hydroformylations utilizing the hydrosilyl group instead of hydrogen, wherein olefins and carbon monoxide react in the presence of the organocobalt catalyst. These hydrosilylcarbonylations also proceed with cyclic ethers, aldehydes and alkyl acetates besides alkenes.[371–376] For example, the hydrosilylcarbonylation of an alkene and its reaction mechanism are shown in equation (42) and Scheme 8, respectively.[372,373]



Scheme 7.



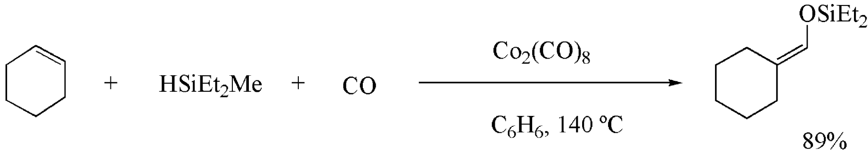
Scheme 8.

Carbonylations of halides

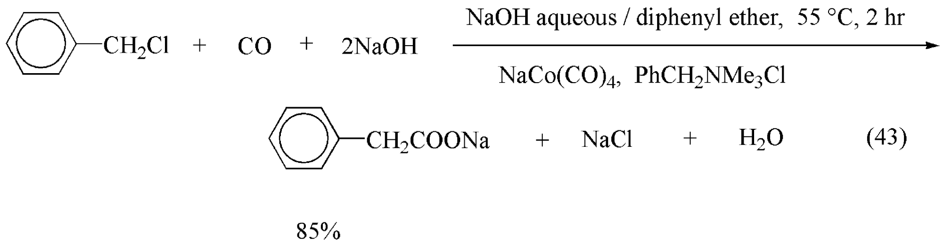
The cobaltcarbonyls are used for the carbonylation of alkyl halides, benzyl halides or aryl halides.[377–383] For example, as shown in equation (43), benzylcarboxylic acid is prepared by the reaction of benzyl halide with carbon monoxide. The reaction mechanism is thought to be the substitution of the halogen of the halide by a cobalt atom followed by the insertion of a carbonyl into the Co–C bond. An example of this is the industrial production of phenylacetic acid from benzyl chloride using a cobalt catalyst.[377]

In the presence of $Ca(OH)_2$, double carbonylations proceed in a high selectivity to give α-keto acids (raw materials for phenylalanine),[377,384,385] as shown in equation (44).[383]

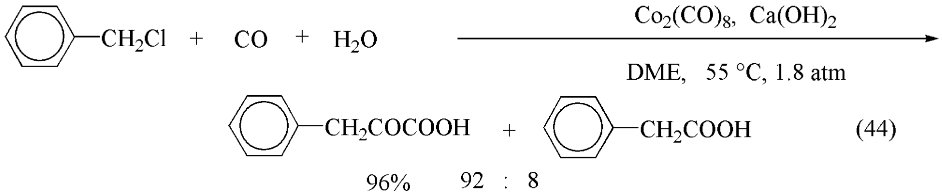
With alcohols, the carbonylation gives esters that are similar to the hydrocarbonylation [equations (36–38)] as shown in equation (45).[380] Under microwave irradiation, the carbonylation of aryl iodides using octacarbonyldicobalt proceeds very rapidly to give diarylketones in 6–10 s, as shown in equation (46)[381] Not only does monocarbonylations with aromatic halides occur in high yields, but also the double carbonylations are liable to proceed.[377,378]



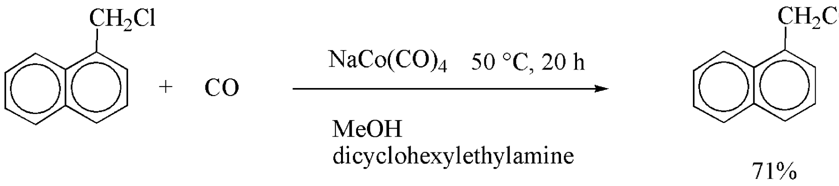
(42)



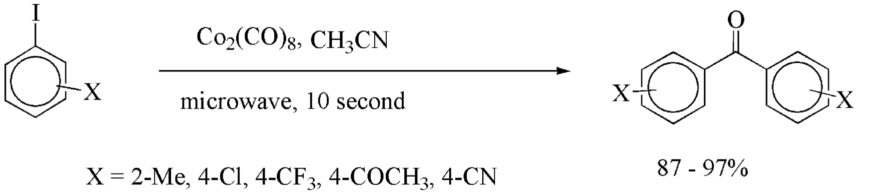
DOI: 10.1002/aoc



(44)



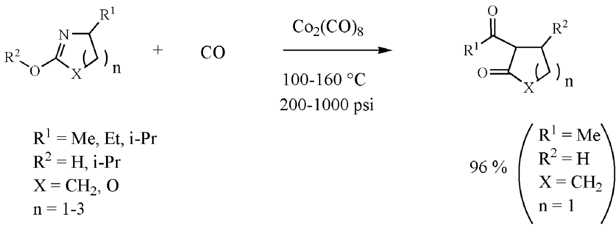
(45)



(46)

Other carbonylations

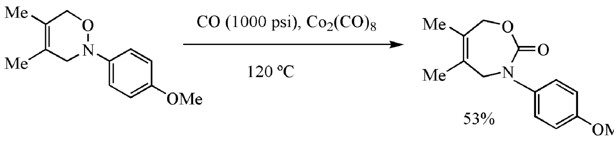
Recently many other carbonylations have been reported.[352–357] Under the catalysis of $Co_2(CO)_8$ in the absence of HI as the copromoter, cycloimino esters are carbonylated to give *N*-acyllactams in high yield under relative mild conditions, as shown in equation (47).[352]



(47)

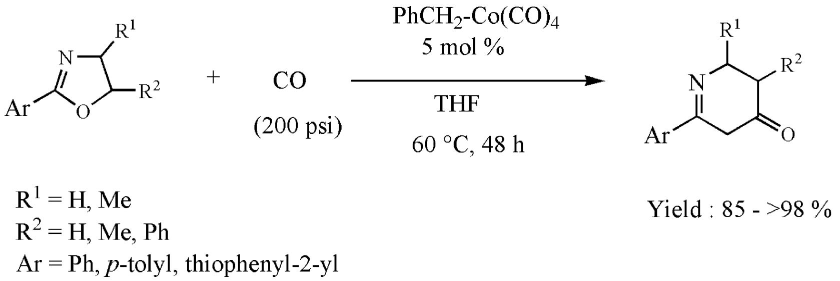
Catalytic ring-expanding carbonylations of 2-aryl-2-oxazolines proceed by carbonylation with $PhCH_2–Co(CO)_4$ under 200 psi of CO pressure, as shown in equation (48).[353] The reaction is considered to proceed via carbonyl insertion to the cobalt–carbon bond and reductive elimination of cobalt catalyst.

The high ring strains of the reactants are considered to be the driving force for the cleavage of a relatively weak bond by octacarbonyldicobalt, resulting in the incorporation of carbon monoxide. For example, the cobaltcarbonyl affects the carbonylation of 3,6-dihydro-2H-1,2-oxazines, giving in moderate yields 4,7-dihydro-1,3-oxazepin-2(3H)-one by a ring expansion reaction caused by insertion of carbon monoxide into the N–O bond as shown in equation (49).[386]



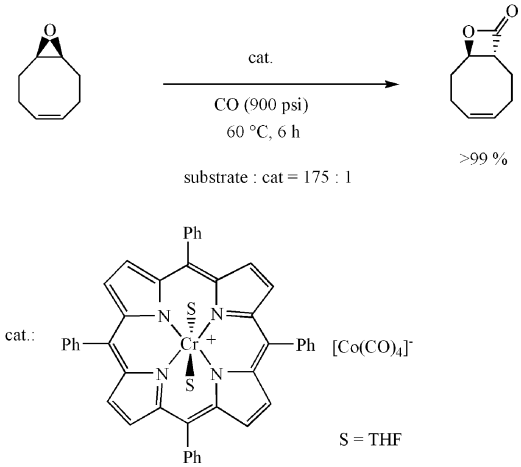
(49)

Carbonylation of epoxide in the presence of chromium(III) porphyrin cation and $Co(CO)_4$ anion easily gives lactones in quantitative yields with not only linear epoxides but also bicyclic epoxides. For example, the eight-membered ring bicyclic lactone is synthesized with a small amount of catalyt, as shown in equation (50). It is proposed that the reaction proceeds via the epoxide ring opening and reacting with



(48)

the Co(CO)$_4$ anion, followed by carbonyl insertion into the cobalt–carbon bond.[354]



(50)

Other carbonylations have been reported for the synthesis of lactones or polyesters from carbonylation of epoxides with [Lewis acid]$^+$[Co(CO)$_4$]$^-$ as a catalyst,[355] carbonylative silylcarbocyclization of 1,6-enynes with immobilized cobalt/rhodium heterobimetallic catalyst,[355] synthesis of metyl-3-pentenoate by hydromethoxycarbonylation of 1,3-butadiene with pyridine-modified cobalt catalyst,[357] etc.

REACTIONS WITH VITAMIN B$_{12}$-TYPE COMPOUNDS

Vitamin B$_{12}$ forms an octahedral structure having a cobalt–carbon bond at its axial position and a stable square-planar bipyramidal six-coordination with nitrogen atoms of a corrin ring, as shown in Fig. 3. The active site of the vitamin B$_{12}$ is the axial cobalt–carbon bond. The compounds of vitamin B$_{12}$ group are cyanocobalamin (B$_{12}$), adenosylcobalamin (a vitamin B$_{12}$ coenzyme), methylcobalamin (a vitamin B$_{12}$ coenzyme), hydroxycobalamin (B$_{12a}$), etc. This vitamin B$_{12}$ and its derivatives show different reactivities in living organisms.

These compounds of vitamin B$_{12}$ group are also usable as catalysts for organic syntheses. These are not only vitamin B$_{12}$ corrinoid cobalt compounds but also the other square-planar bipyramidal six-coordination, square-planar five-coordination, square-planar four-coordination cobalt compounds, as well as three-coordination cobalt compounds. There are two types of four-coordination cobalt compounds on the square plane. One is four-coordination with all nitrogen atoms on the plane. The other is four-coordination with two nitrogen and two oxygen atoms or two sulfur atoms on the plane.

These four-coordination compounds on the square plane include corrinoids (vitamin B$_{12}$ group),[68,387–400] porphyrins,[387,401–419] phthalocyanines,[387] bisdimethylglyoxims,[387,420] porphycenes,[387] etc.[387,421–429] The other types of four coordination compounds are bis(salicylaldehyde)-ethylenediamine (salen),[387,430–442] bis(acetylacetone)ethylenediamine (BAE) type compounds,[66,67,387,443–486] etc. The three-coordination cobalt compounds are 2,6-bis(imino)pyridyl cobalt compounds.[487–495] Examples of these representative vitamin B$_{12}$ type compounds are shown in Fig. 4.[66,387,405,406,420,487]

The salcomine **37** is a cobalt complex [Co(salen)] of salen, a Schiff base of salicylaldehyde with ethylenediamine. This cobalt complex has a square-planar four-coordination structure with two nitrogen and two oxygen atoms. The cobalt atom of this salen-type compound is able to bond with the carbon atom at the axial position, similar to the compounds of the vitamin B$_{12}$ group. Therefore, the salen-type cobalt compound is conveniently used as the model compound of the vitamin B$_{12}$-type compounds.[387,430–442]

The dienyl complexes of optically active square-planar four-coordination compounds such as the salen-type compounds, undergoes Diels–Alder reactions with high enantioselectivity with dimethylfumarate. The Diels–Alder cycloadduct cobalt complexes are cleanly cleaved at the cobalt–carbon bond. Using an optically active cobalt complex, an optically active cycloadduct is recovered. For

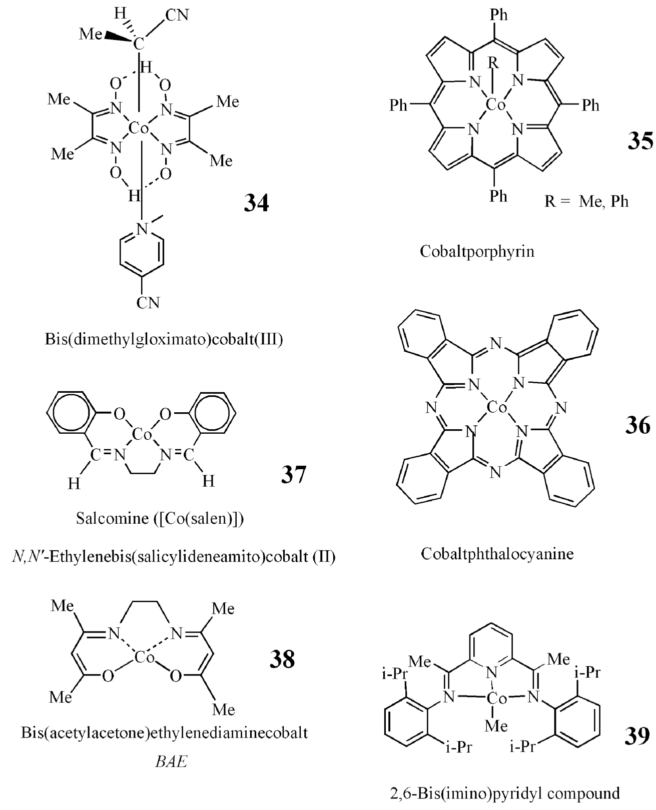


Figure 4. Examples of representative vitamin B$_{12}$-type compounds.[66,387,405,406,420,487].

example, the optical active salen cobalt complex **40** reacts with sodium amalgam to give the corresponding anion. The anion reacts with 4-tosyl-1,2-butadiene to give the corresponding optically active (*R*, *R*)-(+)*N*,*N*-bis(3,5-di-*tert*-butylsalicylideneaminato)-1,2-cyclohexanediamine)][(1,3-butadiene-2-yl)cobalt(III) **41** in high yield. The optically active dienyl complex **41** then reacts with dimethyl fumarate in a Lewis acid-catalyzed Diels–Alder reaction. The cycloadduct *trans*-1,2-dicarbomethoxy-3-cyclohexene **42** is obtained in high optical activity yield by demetalation with sodium boron hydride, as shown in equation (51).[434]

Yamada and coworkers have reported on many reactions with the bis(acetylacetone)ethylenediamine (BAE)-type four-coordination cobalt complexes, e.g. enantioselective borohydride reductions,[443–459] cyclopropanations,[460–463] enantioselective hetero Diels–Alder reactions,[464–467] enantioselective carbonyl-ene reactions,[468,469] enantioselective 1,3-dipolar cycloadditions,[470–474] enantioselective Henry reactions,[475,476] and enantioselective CO_2 fixations, etc.[478–483]

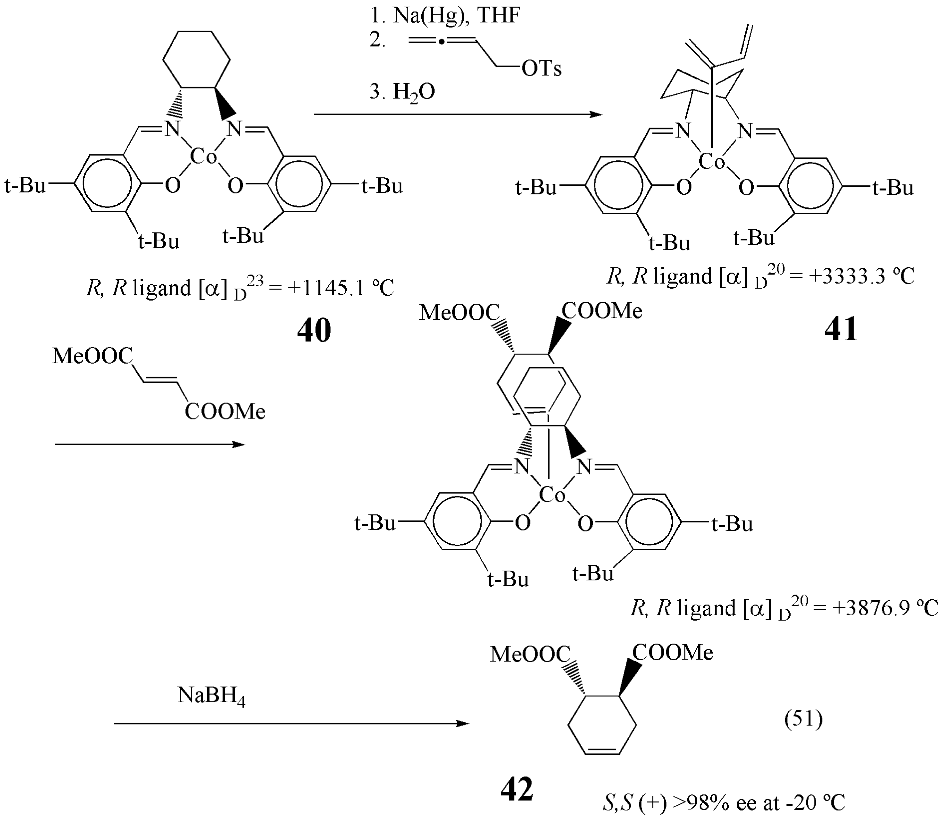
One of their representative bis(acetylacetone)ethylenediamine (BAE)-type cobalt catalysts, that is, an optically active β-ketoiminato cobalt complex (II), (*N*, *N*′-bis{2-(2,4,6-trimethylbenzoyl)-3-oxobutylidene}-(1*S*, 2*S*)-1,2-diphenylethylenediamine), is synthesized as shown in Scheme 9.[449]

The enantioselective boron hydride reduction in the presence of the optical active β-ketoiminato cobalt complexes is used in the efficient preparation of an optically active alcohol in quantitative yield with a high enantiomeric excess, as shown in equation (52).[66,450] Using X-ray crystallography, the reaction mechanism was found to be the enantiofacial discrimination in the boron hydride reduction influenced by the structure of bulky aryl groups bonded with square-planar four coordination ring structure.[66,449]

These optically active cobalt catalysts can be applied for an enantioselective CO_2 fixation. *N*,*N*-diphenylaminomethyloxirane (racemate) reacts with gaseous carbon dioxide in the presence of optically active β-ketoiminate cobalt(II) complex to give an optically active carbonate along with the optically active epoxide, as shown in equation (53).[477]

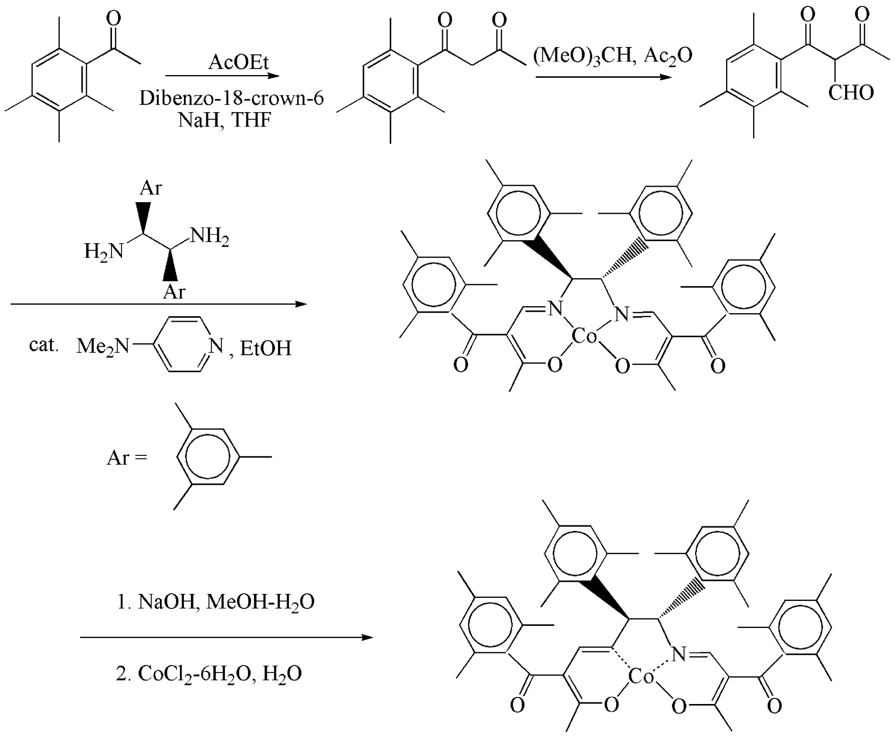
Carbonyl-diene reactions also proceed in the presence of vitamin B_{12}, chromium dichloride and water. For example, 1,3-cyclohexadiene reacts with nonyl aldehyde in the presence of vitamin B_{12}, water and $CrCl_2$ to give stereoselectively a syn adduct, as shown in equation (54).[394]

In 2000, the photoreduction of CO_2 to CO and formic acid in the presence of vitamin B_{12} group catalysts was reported.[395] The photoreduction is carried out in acetonitrile/methanol solution containing *p*-terphenyl as a photosensitizer and triethylamine as a reductive quencher. The photolysis leads to the production of CO and formic acid as well as hydrogen. The rate of production of all three products is considerably higher with the vitamin B_{12} group of cyanocobalamin (vitamin B_{12}), hydroxycobalamin (vitamin B_{12a}) and their similar cobinamide than with cobalt tetra-*m*-tolyporphyrin (similar to cobaltporphyrin **35**). The presumed mechanism of CO_2 reduction is shown in Scheme 10.[395] The initial

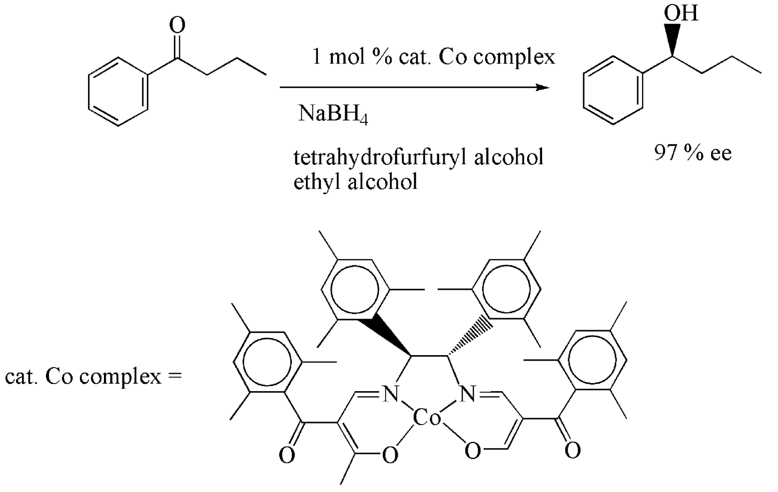


(51)

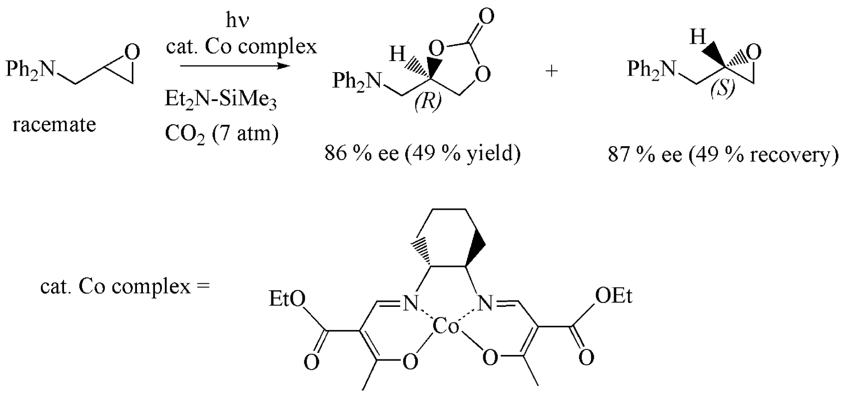
DOI: 10.1002/aoc



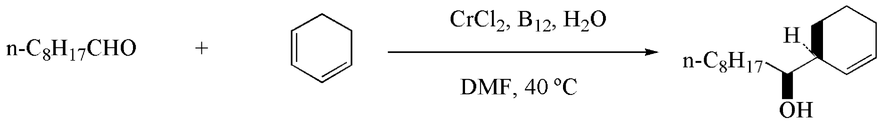
Scheme 9.



(52)

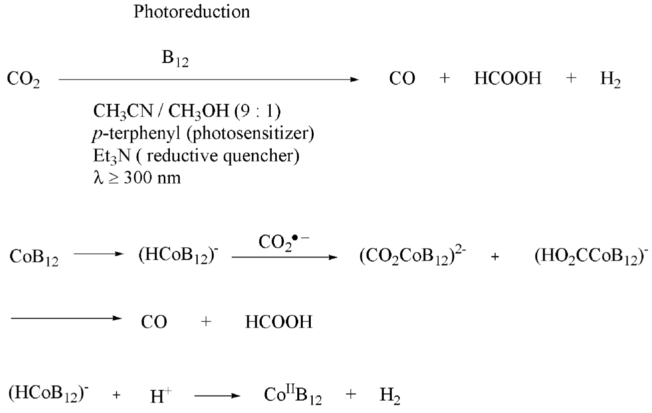


(53)



(54)

Yield 93 %
anti / syn = <1 / >99



Scheme 10.

photoreduction product is mainly a hydride $[(HCoB_{12})^-]$ formed by the protonation of Co(0) corrin. The product of the reaction with carbon dioxide is an adduct $(CO_2CoB_{12})^{2-}$ or its protonated form $(HOOCCoB_{12})^-$ that proceeds to produce CO or HCOOH. Hydrogen is formed by the reaction of the hydride with a proton.[395]

With the presence of vitamin B_{12}-type compounds, other reactions such as reduction of alkyl halides,[396] reductive dechlorinations[397,399] and intramolecular rearrangements,[389] have also been reported.

CONCLUSIONS

There are three characteristic reactions of organocobalt compounds in organic syntheses. The first involves the reactions of a mutually bridged bond between the two π-bonds of acetylene and the cobalt–cobalt bond of hexacarbonyldicobalt. This first type has reactions with a $Co_2(CO)_6$ protecting group, Nicholas reactions, Pauson–Khand reactions, $[2 + 2 + 2]$ cyclizations, etc. The second one is carbonylations, and the third is reactions with vitamin B_{12}-type compounds.

Although the second and third reactions proceed in the presence of the organoiron compounds, organoosmium compounds or organorhodium compounds, the first reactions are the most characteristic reactions of the organocobalt compounds. In particular, these reactions are used in the syntheses of many kinds of pharmaceutically useful compounds.

The second reactions have been used or developed as industrial production processes such as the production of isononylaldehyde, adipic acid, phenylacetic acid and amino acids.

Recently, many articles on the third type of reactions have been published, and we expect an increase in industrial application of synthesis of fine chemicals through the development of such reactions in the near future.

Acknowledgements

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.

REFERENCES

1. Omae I. *Chem. Rev.* 1979; **79**: 287.
2. Omae I. *Coord. Chem. Rev.* 1979; **28**: 97.
3. Omae I. *Coord. Chem. Rev.* 1980; **32**: 235.
4. Omae I. *Coord. Chem. Rev.* 1982; **42**: 31.
5. Omae I. *Coord. Chem. Rev.* 1982; **42**: 245.
6. Omae I. *Coord. Chem. Rev.* 1983; **51**: 1.
7. Omae I. *Coord. Chem. Rev.* 1984; **53**: 261.
8. Omae I. *Coord. Chem. Rev.* 1988; **83**: 137.
9. Omae I. *Coord. Chem. Rev.* 2004; **248**: 995.
10. Omae I. *Kagaku no Ryoiki.* 1979; **33**: 767.
11. Omae I. *Yuki Gosei Kagaku Kyokaishi.* 1982; **40**: 147.
12. Omae I. *Kagaku Kogyo.* 1982; **33**: 989.
13. Omae I. *Angew. Chem. Int. Edn* 1982; **21**: 889.
14. Omae I. *Organometallic Intramolecular-coordination Compounds., J. Organomet. Chem. Library* 18. Elsevier: Amsterdam, 1986.
15. Omae I. *Organotin Chemistry. J. Organometallic Chemistry Library* 21. Elsevier: Amsterdam, 1989.
16. Omae I. *Applications of Organometallic Compounds.* Wiley: New York. 1998.
17. Kleiman JP, Dubeck M. *J. Am. Chem. Soc.* 1963; **85**: 1544.
18. Murahashi S, Horiie S. *J. Am. Chem. Soc.* 1956; **78**: 4816.
19. Takahashi H, Tsuji J. *J. Organomet. Chem.* 1967; **10**: 511.
20. Klein H-F, Helwig M, Koch U, Flörke U, Haupt H-J. *Z. Naturforsch.* 1993; **48b**: 778.
21. Avilés T, Dinis A, Calhorda, MJ, Pinto P, Félix V, Drew MGB. *J. Organomet. Chem.* 2001; **625**: 186.
22. Klein H-F, Beck R, Flörke U, Haupt H-J. *Eur. J. Inorg. Chem.* 2002; 3305.
23. Klein H-F, Beck R, Flörke U, Haupt H-J. *Eur. J. Inorg. Chem.* 2002; 853.
24. Klein H.-F, Beck R, Flörke U, Haupt H-J. *Eur. J. Inorg. Chem.* 2002; 1380.
25. Kein H-F, Camadanli S, Beck R, Leukel D, Flörke U. *Angew. Chem. Int. Edn* 2005; **44**: 975.
26. Robitzer M, Bouamaïed I, Sirlin C, Chase PA, van Koten G, Pfeffer M. *Organometallics* 2005; **24**: 1756.
27. Avilés T, Dinis A, Calhorda MJ, Pinto P, Félix V, Drew MGB. *J. Organomet. Chem.* 2001; **625**: 186.

DOI: 10.1002/aoc

28. Janecki T, Pauson PL, Pietrzykowski A. *J. Organomet. Chem.* 1987; **325**: 247.
29. Heck RF, Breslow DS. *J. Am. Chem. Soc.* 1962; **84**: 2499.
30. Bruce MI, Goodall BL, Stone FGA. *J. Chem. Soc. Dalton Trans.* 1975; 1651.
31. Robitzer M, Sirlin C, Kyritsakas N, Pfeffer M. *Eur. J. Inorg. Chem.* 2002; 2312.
32. Meneghetti MR, Grellier M, Pfeffer M, Dupont J, Fisher J. *Organometallics* 1999; **18**: 5560.
33. Shin S, Matsuda A, Nakayama J, Bando K. *Chem. Lett.* 1997; 115.
34. Heck RF. *J. Am. Chem. Soc.* 1968; **90**: 313.
35. Robitzer M, Bouamaïed I, Sirlin C, Chase PA, van Koten G, Pfeffer M. *Organometallics* 2005; **24**: 1756.
36. Murahashi SJ. *J. Am. Chem. Soc.* 1955; **77**: 6403.
37. Schwab E. *Chem. Eng. News.* 2003; **Sept. 8**: 80.
38. Pauson PL. *Tetrahedron* 1985; **41**: 5855.
39. Schore NE. *Chem. Rev.* 1988; **88**: 1081.
40. Schore NE. *Organic Reaction* 1991; **40**: 1.
41. Schore NE. *Comprehensive Organometallic Chemistry II*, Wilkinson G, Stone FGA, Abel EW (eds), Vol. 5. Pergamon Press: Oxford, 1991; 1037.
42. Brummond KM, Kent JL. *Tetrahedron* 2000; **56**: 3263.
43. Sugihara T, Yamaguchi M, Nishizawa M. *Chem. Eur. J.* 2001; **7**: 1589.
44. Welker ME. *Current Organic Chemistry* 2001; **5**: 785.
45. Gibson SE, Stevenazzi A. *Angew. Chem. Int. Edn* 2003; **42**: 1800.
46. Shibata T. *Yuki Gosei Kagaku Kyokaishi* 2003; **61**: 834.
47. Boñaga LVR, Krafft ME. *Tetrahedron* 2004; **60**: 9795.
48. Nakamura I, Yamamoto Y. *Chem. Rev.* 2004; **104**: 2127.
49. Blanco-Urgoiti J, Añorbe L, Pérez-Serrano L, Domínguez G, Pérez-Castells J. *Chem. Soc. Rev.* 2004; **33**: 32.
50. Park KH, Chung YK. *Synlett* 2005; 545.
51. Gibson SE, Mainolfi N. *Angew. Chem. Int. Edn* 2005; **44**: 3022.
52. Laschat S Becheanu A, Bell T, Baro A. *Synlett* 2005; 2547.
53. Bönnemann H, Brijoux W. *Adv. Heterocycl. Chem.* 1990; **48**: 177.
54. Bönnenmann H, Brijoux W. *Synthetic Methods of Orgnaometallic and Inorganic Chemistry*, Hermann WA (ed), Vol. 10. Thieme: Stuttgard, Germany, 2002; 149.
55. Gandon V, Aubert C, Malacria M. *Current Org. Chem.* 2005; **9**: 1699.
56. Kotha S, Brahmachary E, Lahiri K. *Eur. J. Org. Chem.* 2005; 4741.
57. Caffyn AJM, Nicholas KM. *Comprehensive Organometallic Chemistry II*, Abel EW, Stone FGA, Wilkinson G. (eds), Vol. 12. Pergamon Press: Oxford, 1995; 685.
58. Green JR. *Current Org. Chem.* 2001; **5**: 809.
59. Teobald BJ. *Tetrahedron* 2002; **58**: 4133.
60. Chalk AJ, Harrod JF. *Ad. Organomet. Chem.* 1968; **6**: 119.
61. Pruett RL. *Ad. Organomet. Chem.* 1979; **17**: 1.
62. Ojima I, Eguchi M, Tzamarioudaki M. *Comprehensive Organometallic Chemistry II*, Abel EW, Stone FGA, Wilkinson G. (eds), Vol. 12. Pergamon Press: Oxford, 1995; 9.
63. Bohnen H-W, Cornils B. *Adv. Catal.* 2002; **47**: 1.
64. Wakamatsu H. *Sekiyu Gakkaishi* 1974; **17**: 105.
65. Beller M, Eckert M. *Angew. Chem. Int. Edn* 2000; **39**: 1011.
66. Yamada T, Nagata T, Ohtsuka Y, Ikeno T, Mukaiyama T. *Yuki Gosei Kagaku Kyokaishi* 2003; **61**: 843.
67. Kezuka S, Miya T, Iwakura I, Ikeno T, Yamada T. *Yuki Gosei Kagaku Kyokaishi* 2005; **63**: 604.
68. Hisaeda Y, Shimakoshi H. *Yuki Gosei Kagaku Kyokaishi* 2005; **63**: 780.
69. Sly WG. *J. Am. Chem. Soc.* 1959; **81**: 18.
70. Baxter RJ, Knox GR, McLaughlin M, Pauson PL, Spicer MD. *J. Organomet. Chem.* 1999; **579**: 83.
71. Gutnov A, Heller B, Drexler H-J, Spanneneberg A, Oehme G. *Organometallics* 2003; **22**: 1550.
72. Costa M, Dalcanale E, Dias FS, Graiff C, Tiripicchio A, Bigliardi L. *J. Organomet. Chem.* 2001; **619**: 179.
73. Perthuisot C, Edelbach BL, Zubris DL, Jones WD. *Organometallics* 1997; **16**: 2016.
74. Wadepohl H, Paffen F.-J, Pritzkow HJ. *J. Organomet. Chem.* 1999; **579**: 391.
75. Baldridge KK, O'Connor JM, Chen M-C, Siegel JS. *J. Phys. Chem. A* 1999; **103**: 10126.
76. Enders M, Kohl G, Pritzkow H. *Organometallics* 2004; **23**: 3832.
77. Schaefer C, Werz DB, Staeb TM, Gleiter R, Rominger F. *Organometallics* 2005; **24**: 2106.
78. Gleiter R, Pflästerer G. *Organometallics* 1993; **12**: 1886.
79. Waybright SM, McAlpine K, Laskoski M, Smith MD, Bunz UHF. *J. Am. Chem. Soc.* 2002; **124**: 8661.
80. Roidly G, Enkelmann V, Bunz UHF. *Organometallics* 1999; **18**: 4.
81. Benisch C Werz DB, Gleiter R, Romingser F, Oeser T. *Eur. J. Inorg. Chem.* 2003; 1099.
82. Bunz UHF. *J. Organomet. Chem.* 2003; **683**: 269.
83. Bunz UHF, Roidl G, Altmann M, Enkelmann V, Shimizu KD. *J. Am. Chem. Soc.* 1999; **121**: 10719.
84. Harrison RM, Brotin T, Noll BC, Michl J. *Organometallics* 1997; **16**: 3401.
85. Roers R, Rominger F, Nuber B, Gleiter R, *Organometallics* 2000; **19**: 1578.
86. Elwahy AHM, Hafner K. *Tetrahedron Lett.* 2000; **41**: 2859.
87. Ito S, Inabe H, Okujima T, Morita N, Watanabe M, Harada N, Imafuku K. *Tetrahedron Lett.* 2001; **42**: 1085.
88. Sawada Y, Tomita I, Rozhanskii, IL, Endo T. *J. Inorg. Organomet. Polym.* 2000; **10**: 221.
89. Jones G, Butler DCD, Richards CJ. *Tetrahedron Lett.* 2000; **41**: 9351.
90. Virtue GA, Coyne NE, Halmilton DG. *J. Org. Chem.* 2002; **67**: 6856.
91. Waybright SM, Singleton CP, Wachter K, Murphy CJ, Bunz UHF. *J. Am. Chem. Soc.* 2001; **123**: 1828.
92. Gleiter R, Kratz D. *Acc. Chem. Res.* 1993; **26**: 311.
93. Rozhanskii IL, Tomita I, Endo T. *Macromolecules* 1996; **29**: 1934.
94. Rausch MD, Genetti RA. *J. Org. Chem.* 1970; **35**: 3888.
95. Maitlis PM. *Ad. Organomet. Chem.* 1996; **4**: 95.
96. Cava MP, Mitchell MJ, Simmons HE, Anastassiou AG. *Cyclobutadiene and Related Compounds.* Academic Press: New York, 1996; 88.
97. Meyers AG, Sogi M, Lewis MA, Arvedson SP. *J. Org. Chem.* 2004; **69**: 2516.
98. Ito S, Inabe H, Okujima T, Morita N, Watanabe M, Hrada N, Imafuku K. *J. Org. Chem.* 2001; **66**: 7090.
99. Werz DB, Schulte JH, Gleiter R, Rominger F. *J. Organomet. Chem.* 2004; **689**: 3132.
100. Laskoski M, Steffen W, Morton JGM, Smith MD, Bunz UHF. *J. Organomet. Chem.* 2003; **673**: 25.
101. Laskoski M, Roidl G, Ricks HL, Morton JGM, Smith MD, Bunz UHF. *J. Organomet. Chem.* 2003; **673**: 13.
102. Schaefer C, Gleiter R, Rominger F. *Organometallics* 2004; **23**: 2225.
103. Prasad RS, Anderson CE, Richards CJ, Overman LE. *Organometallics* 2005; **24**: 77.
104. Heck RF, Breslow DS. *J. Am. Chem. Soc.* 1961; **83**: 1097.
105. Bottrill M, Goddard R, Green M, Woodward P. *J. Chem. Soc. Dalton Trans.* 1979; 1671.
106. Greco A, Green M, Stone FGA. *J. Chem. Soc. A* 1971; 3476.
107. Heck RF. *Ad. Organomet. Chem.* 1966; **4**: 243.
108. Elschenbroich Ch, Saltzer A. *Organometallics.* VCH: Weinheim, 1989; 322.
109. Bünder W, Weiss EJ. *J. Organomet. Chem.* 1975; **92**: 65.
110. Elschenbroich Ch, Saltzer A *Organometallics.* VCH: Weinheim, 1989; 277.
111. Elschenbroich Ch, Saltzer A *Organometallics.* VCH: Weinheim, 1989; 348.
112. *McGraw-Hill Encyclopedia of Scienece & Technology*, 9th edn, Vol. 10. McGraw-Hill: New York, 2002; 733.

113. Lukehart CM. *Fundamental Transition Metal Organometallic Chemistry*. Brooks/Cole: California, 1985; 20.
114. Kemmitt RDW, Russell DR. *Comprehensive Organometallic Chemistry*, Wilkinson G, Stone FGA, Abel EW (eds), Vol. 5. Pergamon Press: Oxford, 1982; 1.
115. *Ullmann's Encyclopedia of Industrial Chemistry*, 6th edn, Vo. 8. VCH: Weinheim, 2003; 759.
116. Sumner GG, Klug HP, Alexander LE. *Acta Crystallogr.* 1964; **17**: 732.
117. Schaefer III HF, King RB. *Pure Appl. Chem.* 2001; **73**: 1059.
118. Noack N. *Spectrochimica. Acta* 1963; **19**: 1925.
119. Bor G. *Spectrochim.* 1963; **19**: 2065.
120. Kenny JP, King RB, Schaefer III HF. *Inorg. Chem.* 2001; **40**: 900.
121. Hodgkin DC, Kamper J, Mackay M, Pickworth J, Trueblood KN, White JG. *Nature* 1956; **178**: 64.
122. *Jikken Kagaku Kouza 25*, 4th edn, *Yuki Gousei* VII. Maruzen: Tokyo, 1991; 331.
123. Nicholas KM, Pettit R. *Tetrahedron Lett.* 1971; **37**: 3475.
124. Nicholas KM. *J. Am. Chem. Soc.* 1985; **107**: 4999.
125. Seyferth D, Wehman AT. *J. Am. Chem. Soc.* 1970; **92**: 5520.
126. Carbery DR, Reignier S, Myatt JM, Miller ND, Harrity JPA. *Angew. Chem. Int. Edn* 2002; **41**: 2584.
127. Grée D, Madiot V, Grée R, *Tetrahedron Lett.* 1999; **40**: 6399.
128. Dare S, Ducroix B, Bernard S, Nicholas KM. *Tetrahedron Lett.* 1996; **37**: 4341.
129. Nagasawa T, Yaya K, Kitamura M, Suzuki K. *J. Am. Chem. Soc.* 1996; **118**: 8949.
130. Magnus P, Pitterna T. *J. Chem. Soc. Chem. Commun.* 1991; 541.
131. Magnus P, Miknis GF, Press NJ, Grandjiean D, Taylor GM, Harling J. *J. Am. Chem. Soc.* 1997; **119**: 6739.
132. Lake K, Dorrell M, Blackman N, Khan MA, Nicholas KM. *Organometallics* 2003; **22**: 4260.
133. Iwasawa N, Satoh H. *J. Am. Chem. Soc.* 1999; **121**: 7951.
134. Young DGJ, Burlison JA, Peters U. *J. Org. Chem.* 2003; **68**: 3494.
135. Melikyan GG, Sepanian S, Riahi B, Villena F, Jerome J, Ahrens B, McClain R, Matchett J, Scanlon S, Abrenica E, Paulsen K, Hardcastle KI. *J. Organomet. Chem.* 2003; **683**: 324.
136. Nicholas KM. *Acc. Chem. Res.* 1987; **20**: 207.
137. Nicholas KM, Pettit R. *Tetrahedron Lett.* 1971; 3475.
138. Nicholas KM, Pettit R. *J. Organomet. Chem.* 1972; **44**: C21.
139. Lockwood RF, Nicholas KM. *Tetrahedron Lett.* 1977; 4163.
140. Nicholas KM, Siegel J. *J. Am. Chem. Soc.* 1985; **107**: 4999.
141. Mann A, Muller C, Tyrrell E. *J. Chem. Soc. Perkin Trans.1* 1998; 1427.
142. Conor RE, Nicholas KM. *J. Organomet. Chem.* 1977; **125**: C45.
143. Berge J, Claridge S, Mann A, Muller C, Tyrrell E. *Tetrahedron Lett.* 1977; **38**: 685.
144. Díaz DD. Martín VS. *Tetrahedron Lett.* 2000; **41**: 9993.
145. Gibe R, Green JR. *Royal. Soc. Chem.* 2002; 1550.
146. Mayr H, Kuhn O, Schlierf C, Ofial AR. *Tetrahedron* 2000; **56**: 4219.
147. Carpenter NE, Nicholas KM. *Polyhedron* 1999; **18**: 2027.
148. Vizniowski CS, Green JR, Breen TL, Dalacu AV. *J. Org. Chem.* 1995; **60**: 7496.
149. Guo R, Green JR. *Chem. Commun.* 1999; 2503.
150. Guo R, Green JR. *Synlett* 2000; 746.
151. Lu Y, Green JR. *Synlett* 2001; 243.
152. Gibe R, Green JR. *Chem. Chem.* 2002; 1550.
153. Gibe R, Green JR, Davidson G. *Org. Lett.* 2003; **5**: 1003.
154. Mohamed AB, Green JR. *Chem. Chem.* 2003; 2936.
155. Guo R, Gibe R, Green JR. *Can. J. Chem.* 2004; **82**: 366.
156. Schreiber SL, Sammakia T, Crowe WE. *J. Am. Chem. Soc.* 1986; **108**: 3128.
157. Mukai C, Miyakoshi N, Hanaoka M. *J. Org. Chem.* 2001; **66**: 5875.
158. Laskoski M, Steffen W, Morton JGM, Smith MD, Bunz UHF. *J. Am. Chem. Soc.* 2002; **124**: 13814.
159. Cassel JA, Leue S, Gachkova NI, Kann NC. *J. Org. Chem.* 2002; **67**: 9460.
160. Díaz D, Martín VS. *Org. Lett.* 2000; **2**: 335.
161. Takase M, Morikawa T, Abe H, Inouye M. *Org. Lett,* 2003; **5**: 625.
162. Sui M, Panek JS. *Org. Lett.* 2001; **3**: 2439.
163. Amouri H, Béqué J-P, Chennoufi A, Bonnet-Delpon D, Gruselle M, Malézieux B. *Org. Lett.* 2000; **2**: 807.
164. Quintal MM, Closser KD, Shea KM. *Org. Lett.* 2004; **6**: 4949.
165. Shea KM, Closser KD, Quintal MM. *J. Org. Chem.* 2005; **70**: 9088.
166. Isobe M, Kira K. *Yuki Gosei Kagaku Kyokaishi* 2000; **58**: 23.
167. Álvaro W, de la Torre MC, Sierra MA. *Org. Lett.* 2003; **5**: 2381.
168. Mukai C, Nagami K, Hanaoka M. *Tetrahedron Lett.* 1989; **30**: 5623.
169. Mukai C, Hanaoka M. *Synlett* 1996; 11.
170. Mukai C. *Yakugaku Zasshi* 2002; **122**: 889.
171. Mukai C, Kataoka O, Hanoka M. *Tetrahedron Lett.* 1991; **32**: 7553.
172. Mukai C, Kataoka O, Hanaoka M. *J. Chem. Soc. Perkin Trans. 1* 1993; 563.
173. Mukai C, Kataoka O, Hanaoka M. *J. Org. Chem.* 1993; **58**: 2946.
174. Mukai C, Moharram SM, Kataoka O, Hanaoka M. *J. Chem. Soc. Perkin Trans. I* 1995; 2849.
175. Mukai C, Kataoka O, Hanaoka M. *J. Org. Chem.* 1995; **60**: 5910.
176. Mukai C, Kataoka O, Hanaoka M. *Tetrahedron Lett.* 1994; **35**: 6899.
177. Mukai C, Moharram SM, Azukizawa S, Hanaoka M. *J. Org. Chem.* 1997; **62**: 8095.
178. Salazar KL, Khan MA, Nicholas KM. *J. Am. Chem. Soc.* 1997; **119**: 9053.
179. Salazar KL, Nicholas KM. *Tetrahedron* 2000; **56**: 2211.
180. Iwasawa N, Matsuo T. *Chem. Lett.* 1997; 341.
181. Mukai C, Sugimoto Y, Ikeda Y, Hanaoka M. *Tetrahedron Lett.* 1994; **35**: 2183.
182. Sternberg ED, Vollhardt KPC. *J. Org. Chem.* 1984; **49**: 1574.
183. Brien DJ, Naiman A, Vollhardt KPC. *J. Chem. Soc. Chem. Commun.* 1982; 133.
184. Krafft ME, Scott IL, Romero RH, Feibelmann S, Van Pelt CE. *J. Am. Chem. Soc.* 1993; **115**: 7199.
185. Krafft ME, Boñaga LVR, Hirosawa C. *J. Org. Chem.* 2001; **66**: 3004.
186. Verdaguer X, Vázquez J, Fuster G, Bernardes-Génisson V, Greene AE, Moyano A, Pericàs MA, Riera A. *J. Org. Chem.* 1998; **63**: 7037.
187. Marco-Contelles J. *J. Org. Chem.* 1996; **61**: 7666.
188. Park H-J, Lee BY, Kang YK, Chung YK. *Organometallics* 1995; **14**: 3104.
189. Rajesh T, Periasamy M. *Tetrahedron Lett.* 1999; **40**: 817.
190. Carbery DR, Miller ND, Harrity JPA. *Chem. Commun.* 2002; 1546.
191. Kennedy AR, Kerr WL, Lindsay DM, Scott JS, Watson SP. *J. Chem. Soc. Perkin Trans. 1* 2000; 4366.
192. Pagenkopf BL, Belanger DB, O'Mahony DJR, Livinghouse T. *Synthesis* 2000; 1009.
193. Robert F, Milet A, Gimbert Y, Konya D, Greene AE. *J. Am. Chem. Soc.* 2001; **123**: 5396.
194. Vázquez J, Fonquerna S, Moyano A, Pericàs MA, Riera A. *Teterahedron Asymmetry* 2001; **12**: 1837.
195. Khand IU, Knox GR, Pauson PL, Watts WE, Foreman MI. *J. Chem. Soc. Perkin Trans. 1* 1973; 977.
196. Krafft ME, Fu Z, Boñaga VR. *Tetrahedron Lett.* 2001; **42**: 1427.
197. Dolaine R, Gleason JL. *Org. Lett.* 2000; **2**: 1753.
198. Mukai C, Uchiyama M, Sakamoto S, Hanaoka M. *Tetrahedron Lett.* 1995; **36**: 5761.
199. de Bruin TJM, Milet A, Greene AE, Gimbert Y. *J. Org. Chem.* 2004; **69**: 1075.
200. Geis O, Schmalz H-G. *Angew. Chem. Int. Edn* 1998; **37**: 911.
201. Smit WA, Gybin AS, Shashkov AS, Strychkov YT, Kyz'mina LG, Mikaelian GS, Caple R, Swanson ED. *Tetrahedron Lett.* 1986; **27**: 1241.
202. Mukai C, Sonobe H, Kim JS, Hanaoka M. *J. Org. Chem.* 2000; **65**: 6654.
203. Strula SJ, Buchwald SL. *J. Org. Chem.* 2002; **67**: 3398.

204. Son SU, Park KH, Chung YK. *Org. Lett.* 2002; **4**: 3983.
205. Castro J, Moyano A, Pericàs MA, Riera A, Alvarez-Larena A, Piniella JF. *J. Am. Chem. Soc.* 2000; **122**: 7944.
206. Gordon AR, Johnstone, C, Kerr WJ. *Synlett* 1995; 1083.
207. Sugihara T, Yamada M, Ban H, Yamaguchi M, Kaneko C. *Angew. Chem. Int. Edn* 1997; **36**: 2801.
208. Rajesj T, Periasamy M. *Tetrahedron Lett.* 1998; **39**: 117.
209. Pagenkopf BL, Livinghouse T. *J. Am. Chem. Soc.* 1996; **118**: 2285.
210. Bladon P, Pauson PL, Brunner H, Eder R. *J. Organomet. Chem.* 1988; **355**: 449.
211. Brunner H, Niedernhuber A. *Tetrahedron Asymmetry* 1990; **1**: 711.
212. Hay AM, Kerr WJ, Kirk GG, Middlemiss D. *Organometallics*, 1995; **14**: 4986.
213. Jamison TF, Shambayati S, Crowe WE, Schreiber SL. *J. Am. Chem. Soc.* 1994; **116**: 5505.
214. Jamison TF, Shambayati S, Crowe WE, Schreiber SL. *J. Am. Chem. Soc.* 1997; **119**: 4353.
215. Quattropani A, Anderson G, Bernardinelli G, Kündig EP. *J. Am. Chem. Soc.* 1997; **119**: 4773.
216. Ishizaki M, Hoshino O. *Yuki Gosei Kagaku Kyokaishi,* 2003; **61**: 1166.
217. Krafft ME, Boñaga LVR, Felts AS, Hirosawa C, Kerrigan S. *J. Org. Chem.* 2003; **68**: 6039.
218. Moriarty RM, Rani N, Enache LA, Rao MS, Batr H, Guo L, Penmasta RA, Staszewski JP, Tuladhar SM, Prakash O, Crich D, Hirtopeanu A, Gilardi R. *J. Org. Chem.* 2004; **69**: 1890.
219. Winkler JD, Lee ECY, Nevels LI. *Org. Lett.* 2005; **7**: 1489.
220. Günter M, Gais H-J. *J. Org. Chem.* 2003; **68**: 8037.
221. Rios R, Paredes S, Pericàs MA, Moyano A. *J. Organomet. Chem.* 2005; **690**: 358.
222. Lagunas A, Payeras AM, Jimino C, Pericàs MA. *Org. Lett.* 2005; **7**: 3033.
223. Rivero MR, de la Rosa JC, Carretero JC. *J. Am. Chem. Soc.* 2003; **125**: 14992.
224. Rivero MR, Carretero JC. *J. Org. Chem.* 2003; **68**: 2975.
225. Verdaguer X, Pericàs MA, Riera A, Maestro MA, Mahía J. *Organometallics* 2003; **22**: 1868.
226. Verdaguer X, Lledó A, López-Mosquera C, Maestro MA, Pericàs MA, Riera A. *J. Org. Chem.* 2004; **69**: 8053.
227. Gibson SE, Kaufmann KAC, Lock JA, Steed JW, White AJP. *Chem. Eur. J.* 2005; **11**: 2566.
228. Gibson SE, Johnstone C, Loch JA, Steed JW, Stevenazzi A, *Organometallics* 2003; **22**: 5374.
229. Nomura I, Mukai C. *J. Org. Chem.* 2004; **69**: 1803.
230. Ishikawa T, Ishii H, Shimizu K, Nakao H, Urano J, Kudo T, Saito S. *J. Org. Chem.* 2004; **69**: 8133.
231. Pérez-Serrano L, Domínguez G, Pérez-Castells J. *J. Org. Chem.* 2004; **69**: 5413.
232. Tang Y, Deng L, Zhang Y, Dong G, Chen J, Yang Z. *Org. Lett.* 2005; **7**: 593.
233. Tang Y, Zhang Y, Dai M, Luo T, Deng L, Chen J, Yang Y. *Org. Lett.* 2005; **7**: 885.
234. del Valle CP, Milet A, Gimbert Y, Greene AE. *Angew. Chem. Int. Edn* 2005; **44**: 5717.
235. Park KH, Jung IG, Chung YK. *Org. Lett.* 2004; **6**: 1183.
236. Hayashi M, Hashimoto Y, Yamamoto Y, Usuki J, Saigo K. *Angew. Chem. Int. Edn* 2000; **39**: 631.
237. Kraft ME, Boñaga LVR, Wright JA, Hirosawa C. *J. Org. Chem.* 2002; **67**: 1233.
238. Yeh M-CP, Tsao W-C, Ho J-S, Tai C-C, Chiou D-Y, Tu L-H. *Organometallics* 2004; **23**: 792.
239. Cao H, Van Omum SG, Deschamps J, Flippen-Anderson J, Laib F, Cook JM. *J. Am. Chem. Soc.* 2005; **127**: 933.
240. Cao H, Flippen-Anderson J, Cook JM. *J. Am. Chem. Soc.* 2003; **125**: 3230.
241. Itami K, Mitsudo K, Fujita K, Chashi Y, Yoshida J. *J. Am. Chem. Soc.* 2004; **126**: 11058.
242. Tang Y, Deng L, Zhang Y, Dong G, Chen J and Yang Z. *Org. Lett.*, 2005; **7**: 1657.
243. Adrio J, Rivero MR, Carretero JC. *Org. Lett.* 2005; **7**: 431.
244. Shambayati S, Crowe WE, Schreiber SL. *Tetrahedron Lett.* 1990; **31**: 5289.
245. Tsuji J. *Sen-i-kinzoku ga Hiraku Yukigosei*, Kagaku Dojin: Tokyo, 1997; 174.
246. Bou A, Pericàs MA, Serratosa F. *Tetrahedron Lett.* 1982; **23**: 361.
247. Bou A, Pericàs MA, Serratosa F, Claret J, Feliu JM, Muller CJ. *J. Chem. Soc. Chem. Commun.* **982**: 1305.
248. Serratosa F. *Acc. Chem. Res.* 1983; **16**: 170.
249. Iwasawa N, Matsuo T. *Chem. Lett.* 1993; 997.
250. Iwasawa N, Iwamoto M. *Chem. Lett.* 1993; 1257.
251. Iwasawa N. *Chem. Lett.* 1992; 473.
252. Iwasawa N. *Synlett,* 1993; 13.
253. Iwasawa N, Matsuo T. *Chem. Lett.* 1997; 341.
254. Iwasawa N. *Yuki Gosei Kagaku Kyokaishi* 1998; **56**: 1058.
255. Reppe W, Schlichting O, Klager K, Toepel T. *Liebigs Ann. Chim.* 1948; **560**: 1.
256. Bird CW. *Transition Metal Intermediates in Organic Synthesis.* Logos Press/Academic Press: London 1997; 1.
257. Lautens M, Klute W, Tam W. *Chem. Rev.* 1996; **96**: 49.
258. Peter K, Vollhardt C. *Angew. Chem. Int. Edn* 1984; **23**: 539.
259. Maitlis PM. *Acc. Chem. Res.* 1976; **9**: 93.
260. Keim W, Behr A, Röper M. *Comprehensive Organometallic Chemistry*, Wilkinson G, Stone FGA, Abel EW (eds), Vol. 1.8. Pergamon Press: Oxford, 1982; 371.
261. Iwashita Y, Tamura F. *Bull. Chem. Soc. Jpn.* 1970; **43**: 1517.
262. Grotjahn DB. *Comprehensive Organometallic Chemistry II*, Abel EW, Stone FGA, Wilkinson G. (eds), Vo. 1.8. Pergamon Press: Oxford, 1995; 741.
263. Pearson AJ. *Metallo-organic Chemistry.* Wiley: New York, 1985; 84.
264. Vollhardt KPC. (translator: Yamazaki H). *Kagaku Zokan* 1985; **105**: 165.
265. Yamazaki H, Wakatsuki Y. *J. Organomet. Chem.* 1977; **139**: 157.
266. McAlister DR, Bercaw JE, Bergman RG. *J. Am. Chem. Soc.* 1977; **99**: 1666.
267. Borwieck H, Walter O, Dinjus E, Rebizant J. *J. Organomet. Chem.* 1998; **570**: 121.
268. Mamane V, Gref A, Lefloch G, Riant O. *J. Organomet. Chem.* 2001; **637–639**: 84.
269. Diercks R, Eaton BE, Gürtzgens S, Jalisatgi S, Matzger AJ, Radde RH, Vollhard KPC. *J. Am. Chem. Soc.* 1998; **120**: 8247.
270. Skoda-Földes R *Chem. Rev.* 2003; **103**: 4095.
271. Fechtenkötter A, Tchebotareva N, Watson M, Müller V *Tetrahedron,* 2001; **57**: 3769.
272. Maderna A, Pritzkow H, Siebert W. *Angew. Chem. Int. Edn* 1996; **35**: 1501.
273. Vollhardt KPC. *Angew. Chem. Int. Edn* 1984; **23**: 539.
274. Grotjahn DB, Vollhardt KPC. *Synthesis* 1993; 579.
275. Frühauf H-W. *Chem. Rev.* **97**: 1997; 523.
276. Funk RL, Vollhardt KPC. *J. Am. Chem. Soc.* 1980; **102**: 5253.
277. Chouraqui G, Petit M, Aubert C, Malacria M. *Org. Lett.* 2004; **6**: 1519.
278. Cruciani P, Aubert C, Malcria M. *J. Org. Chem.* 1995; **60**: 2664.
279. Lecker SH, Nguye NH, Vollhardt KPC. *J. Am. Chem. Soc.* 1986; **108**: 856.
280. Zhou Z, Battaglia LP, Chiusoli GP, Costa M, Nardelli M, Pelizzi C, Predieri G. *J. Chem. Soc. Chem. Commun.* 1990; 1632.
281. Boese R, Harvey DF, Malaska MJ, Vollhardt KPC. *J. Am. Chem. Soc.* 1994; **116**: 11153.
282. Eichberg MJ, Dorta RL, Lamottke K, Vollhardt KPC. *Org. Lett.* 2000; **2**: 2479.
283. Halterman RL, Vollhardt KPC. *Organometallics* 1988; **7**: 883.
284. Tatone D, Dich TC, Nacco R, Botteghi C. *J. Org. Chem.* 1975; **40**: 2987.

285. Fatland AW Eaton BE. *Org. Lett.* 2000; **2**: 3131.
286. Bönnemann H *Angew. Chem. Int. Edn* 1978; **17**: 505.
287. Bönnemann H, Brinkmann R, Schenkluhn H. *Synthesis* 1974; 575.
288. Bönnemann H *Angew. Chem. Int. Ed.* 1985; **24**: 248.
289. Boñaga LVR, Zhang H-C, Gauthier DA, Reddy I, Maryanoff BE. *Org. Lett.* 2003; **5**: 4537.
290. Mao F, Schut DM, Tyler DR. *Organometallics* 1996; **15**: 4770.
291. Saito S, Yamamoto Y. *Chem. Rev.* 2000; **100**: 2901.
292. Kalogerakis A, Groth U. *Org. Lett.* 2003; **5**: 843.
293. Dosa OI, Whitener Vollhardt GD. *Org. Lett.* 2002; **4**: 2075.
294. Vollhardt KPC. *Pure & Appl. Chem.* 1993; **65**: 153.
295. Berri BC, Hovakeemian GH, Lai Y-H, Mestdagh H, Vollhardt KPC. *J. Am. Chem. Soc.* 1985; **107**: 5670.
296. Stará IG, Starý I, Kollárović A, Teplý F, Šaman D, Tichý M. *J. Org. Chem.* 1998; **63**: 4046.
297. Stará IG, Starý I, Kollárovič A, Teplý F, Vyskoćil Š, Šaman D. *Tetrahedron Lett.* 1999; **40**: 1993.
298. Varela JA, Saá C. *Chem. Rev.* 2003; **103**: 3787.
299. Osei-Owusu A, Martin GC, Gotro JT. *Polym. Engng Sci.* 1992; **32**: 535.
300. Naiman A, Vollhardt KPC. *Angew. Chem. Int. Edn* 1977; **16**: 708.
301. Earl RA, Vollhardt KPC. *J. Am. Chem. Soc.* 1983; **105**: 6991.
302. Slowinski F, Aubert C, Malacria M. *Tetrahedron Lett.* 1999; **40**: 707.
303. Slowinski F, Aubert C, Malacria M. *Tetrahedron Lett.* 1999; **40**: 5849.
304. Pérez D, Siesel BA, Malaska MJ, David E, Vollhardt KPC. *Synlett* 2000; 306.
305. Pelissier H, Rodriguez J, Vollhardt KPC. *Chem. Eur. J.* 1999; **5**: 3549.
306. Sternberg ED, Vollhardt KPC. *J. Org. Chem.* 1982; **47**: 3447.
307. Slowinski F, Aubert C, Malacria M. *J. Org. Chem.* 2003; **68**: 378.
308. Kalogerakis A, Groth U. *Org. Lett.* 2003; **5**: 843.
309. Gandon V, Leca D, Aechtner T, Vollhardt KPC, Malacria M, Aubert C. *Org. Lett.* 2004; **6**: 3405.
310. Bruns D, Miura H, Vollhardt KPC. *Org. Lett.* 2003; **5**: 549.
311. Petit M, Aubert C, Malacria M. *Org. Lett.* 2004; **6**: 3937.
312. Gutnov A, Heller B, Fischer C, Drexler H-J, Spannenberg A, Sundermann B, Sundermann C. *Angew. Chem. Int. Edn* 2004; **43**: 3795.
313. Hilt G, Hess W, Vogler T, Hengst C. *J. Organomet. Chem.* 2005; **690**: 5170.
314. Pickin KA, Kindy JM, Day CS, Welker ME. *J. Organomet. Chem.* 2003; **681**: 120.
315. Hilt G, Lüers S, Harms K. *J. Org. Chem.* 2004; **69**: 624.
316. Hilt G, Smolko KI. *Angew. Chem. Int. Ed.* 2003; **42**: 2795.
317. Wei K, Li W, Koike K, Nikaido T. *Org. Lett.* 2005; **7**: 2833.
318. Achard M, Tenaglia A, Buono G. *Org. Lett.* 2005; **7**: 2353.
319. Ajamian A, Gleason JL. *Org. Lett.* 2003; **5**: 2409.
320. Chang K-J, Rayabarapu DK, Cheng C-H. *Org. Lett.* 2003; **5**: 3963.
321. Miljanić OŠ, Holmes D, Vollhardt KPC. *Org. Lett.* 2005; **7**: 4001.
322. Chang K-J, Rayabarapu DK, Cheng C-H. *J. Org. Chem.* 2004; **69**: 4781.
323. Hilt G, Lüers S, Smolko KI. *Org. Lett.* 2005; **7**: 251.
324. Hillard III RL, Parnell CA, Vollhardt KPC. *Tetrahedron*, 1983; **39**: 905.
325. Boñaga LVR, Zhang H-C, Moretto AF, Ye H, Gauthier DA, Li J, Leo GC, Maryanoff BE. *J. Am. Chem. Soc.* 2005; **127**: 3473.
326. Llerena D, Aubert C, Malacria M. *Tetrahedron Lett.* 1996; **37**: 7353.
327. Buisine O, Aubert C, Malacria M. *Chem. Eur. J.* 2001; **7**: 3517.
328. Etkin N, Dzwiniel TL, Schwiebert KE, Stryker JM. *J. Am. Chem. Soc.* 1998; **120**: 9702.
329. Dzwiniel TL, Etkin N, Stryker JM. *J. Am. Chem. Soc.* 1999; **121**: 10640.
330. Dzwiniel TL, Stryker JM. *J. Am. Chem. Soc.* 2004; **126**: 9184.
331. Liebeskind LS, South MS. *J. Am. Chem. Soc.* 1980; **102**: 7398.
332. Baysdon SL, Liebeskind LS. *Organometallics*, 1982; **1**: 771.
333. South MS, Liebeskind LS. *J. Am. Chem. Soc.* 1984; **106**: 4181.
334. Liebeskind LS, Leeds JP, Baysdon SL, Iyer S. *J. Am. Chem. Soc.* 1984; **106**: 645.
335. Jewell CF Jr, Liebeskind LS, Williamson M. *J. Am. Chem. Soc.* 1985; **107**: 6715.
336. Liebeskind LS, Jewell. Jr. CF. *J Organomet. Chem.* 1985; **285**: 305.
337. Liebeskind LS, Baysdon SL, Goedken V, Chidambaram R. *Organometallics* 1986; **5**: 1086.
338. Iyer S, Liebeskind LS. *J. Am. Chem. Soc.* 1987; **109**: 2759.
339. Liebeskind LS, Chidambaram R. *J. Am. Chem. Soc.* 1987; **109**: 5025.
340. Liebeskind LS, Chidambaram R, Nimkar S, Liotta D. *Tetrahedron Lett.* 1990; **31**: 3723.
341. *Yuki Kinzoku no Kagaku, Shinkagaku Library*. Japan Chemical Society (ed.). Dai Nippon Tosho: Tokyo, 1989; 170.
342. Matsuda A. *Yuki Gosei Kagaku Kyokaishi* 1978; **36**: 173.
343. Ziegler T, Cavallo L, Bérces A. *Organometallics* 1993; **12**: 3586.
344. Miller AES, Beauchamp JL. *J. Am. Chem. Soc.* 1991; **113**: 8765.
345. Bird CW. *Transition Metal Intermediates in Organic Synthesis.* Logos Press/Academic Press: London, 1967; 117.
346. Yokomori M, Ohara S. *Shokubai* 2003; **45**: 580.
347. Watanabe Y, Mitsudo T, Tanaka M, Yamamoto K, Takegami Y. *Yukagaku* 1974; **23**: 304.
348. Weber E, Englert U, Ganter B, Keim W, Möthrath M *Chem. Commun.* 2000; 1419.
349. Crause C, Bennie L, Damoense L, Dwyer CL, Grove C, Grimmer N, Van Rensburg WJ, Kirk MM, Mokheseng KM, Otto S, Steynberg PT. *Dalton Trans*. 2003; 2036.
350. Wender I, Friedel RA, Orchin M. *Science* 1951; **113**: 206.
351. Kuno K. *Yuki. Gosei Kagaku Kyokaishi* 1977; **35**: 683.
352. Xu H, Jia L. *Org. Lett.* 2003; **5**: 3955.
353. Xu H, Jia L. *Org. Lett.* 2003; **5**: 1575.
354. Schmidt JAR, Mahadevan V, Getzler YDYL and Coates GW. *Org. Lett.* 2004; **6**: 373.
355. Allmendinger M, Zintl M, Eberhardt R, Luinstra GA, Molnar F, Rieger B. *J. Organomet. Chem.* 2004; **689**: 971.
356. Park KH, Jung IG, Kim SY, Chung YK. *Org. Lett.* 2003; **5**: 4967.
357. Tuba R, Mika LT, Bodor A, Pusztai Z, Tóth I, Horváth IT. *Organometallics,* 2003; **22**: 1582.
358. Crabtree RH. *The Organometallic Chemistry of the Transition Metals,* 3rd edn. Wiley: New York, 2001; 240.
359. Collman Hegedus JP, Norton JR, Finke RG. *Principles and Applications of Organotransition Metal Chemistry*. University Science Books: California, 1987; 621.
360. Davies SG. *Organotransition Metal Chemistry: Applications to Organic Synthesis*. Pergamon Press: Oxford, 1982; 348.
361. Pearson AJ. *Metallo-organic Chemistry*. Wiley: New York, 1985; 56.
362. Green MM, Wittcoff HA. *Organic Chemistry Principles and Industrial Practice.* Wiley-VCH: Weinheim, 2003; 238.
363. Weissermel K, Arpe H-J. *Industrial Organic Chemistry*, 4th edn, translated by Lindley CR, Hawkins S. Wiley-VCH: Weinheim, 2003; 127.
364. Huo C-F, Li Y-W, Beller M, Jiao H. *Organometallics* 2003; **22**: 4665.
365. van Rensburg H, Tooze RP, Foster DF, Slawin AMZ. *Inorg. Chem.* 2004; **43**: 2468.
366. Weissermel K, Arpe H-J. *Industrial Organic Chemistry,* 4th edn, translated by Lindley CR, Hawkins S. Wiley-VCH: Weinheim, 2003; 141.
367. Matsuda A. *Kagaku Kogyo* 1974; **25**: 1180.
368. Matsuda A. *Bull. Chem. Soc. Jpn* 1973; **46**: 524.
369. Tsuji J. *Yuki Gosei okaeta Sen-i Kinzoku*. Kagaku Dojin: Tokyo, 1991.
370. Wakamatsu H, Uda J, Yamakami N. *J. Chem. Soc. Chem. Commun.* 1971; 1540.
371. Murai S, Sonoda N. *Kagaku Zokan* 1982; **96**: 95.

372. Tsuji J. *Sen-i-kinzoku ga Hiraku Yukigosei*. Kagaku Dojin: Tokyo, 1997; 163.
373. Murai S, Sonoda N. *Angew. Chem. Int. Edn* 1979; **18**: 837.
374. Murai S, Sonoda N. *Yuki Gosei Kagaku Kyokaishi* 1981; **39**: 301.
375. Seki Y, Hidaka A, Murai S, Sonoda N. *Angew. Chem. Int. Edn* 1977; **16**: 174.
376. Chatani N, Murai S. *Synlett* 1996; 414.
377. Cassar L, Foa M. *J. Organomet. Chem.* 1977; **134**: C15.
378. Kashimura T, Kudo K, Mori S, Sugita N. *Chem. Lett.* 1986; 483.
379. Miura M, Akase F, Nomura M. *J. Org. Chem.* 1987; **52**: 2623.
380. Heck RF, Breslow DS. *J. Am. Chem. Soc.* 1963; **85**: 2779.
381. Enquist P-A, Nilsson P, Larhed M. *Org. Lett.* 2003; **5**: 4875.
382. des Abbayes H, Buloup A. *J. Chem. Soc. Chem. Commun.* 1978; 1090.
383. Foà M, Francalanci F. *J. Mol. Catal.* 1978; **41**: 89.
384. Yamazaki H, Hagihara N. *J. Organomet. Chem.* 1970; **21**: 431.
385. Wakatsuki Y, Nomura O, Kitaura K, Morokuma K, Yamazaki H. *J. Am. Chem. Soc.* 1983; **105**: 1907.
386. Okuro K, Khumtaveeporn K, Alper A. *Tetrahedron Lett.* 1996; **37**: 2713.
387. Pratt JM, Craig PJ. *Ad. Organomet. Chem.* 1973; **11**: 331.
388. Freindorf M, Kozlowski PM. *J. Am. Chem. Soc.* 2004; **126**: 1928.
389. Bernhauer K, Müller O, Wagner F. *Angew. Chem. Int. Edn* 1964; **3**: 200.
390. Warncke K, Utada AS. *J. Am. Chem. Soc.* 2001; **123**: 8564.
391. Polson SM, Hansen L, Marzilli LG. *J. Am. Chem. Soc.* 1996; **118**: 4804.
392. Polson SM, Cini R, Pifferi C, Marzilli LG. *Inorg. Chem.* 1997; **36**: 314.
393. Giorgetti M, Berrettoni M, Conti P, Cicco AD, Marassi R, Ascone I. *Organometallics* 1996; **15**: 3491.
394. Takai K, Toratsu C. *J. Org. Chem.* 1998; **63**: 6450.
395. Grodkowski J, Neta P. *J. Phys. Chem. A* 2000; **104**: 1848.
396. Takai K, Nitta K, Fujimura O, Utimoto K. *J. Org. Chem.* 1989; **54**: 4732.
397. McCauley KM, Wilson SR, van der Donk WA. *Inorg. Chem.* 2002; **41**: 393.
398. Ramdhanie B Telser J, Caneschi A, Zakharov LN, Rheigold AL, Goldberg DP. *J. Am. Chem. Soc.* 2004; **126**: 2515.
399. Argüello JE, Costentin C, Griveau S, Savéant J-M. *J. Am. Chem. Soc.* 2005; **127**: 5049.
400. van Doorslaer S, Jeschke G, Epel B, Goldfarb D, Eichel R-A, Kräutler B, Schweiger A. *J. Am. Chem. Soc.* 2003; **125**: 5915.
401. Sutton LR, Scheloske M, Pirner KS, Hirsch A, Guldi DM, Gisselbrecht J-P. *J. Am. Chem. Soc.* 2004; **126**: 10370.
402. Imaoka T, Horiguchi H, Yamamoto K. *J. Am. Chem. Soc.* 2003; **125**: 340.
403. Gao G-Y, Harden JD, Zhang XP. *Org. Lett.* 2005; **7**: 3191.
404. Xu X-P, Au-Yeung SCF. *J. Am. Chem. Soc.* 2000; **122**: 6468.
405. Yoshimoto S, Higa N, Itaya K. *J. Am. Chem. Soc.* 2004; **126**: 8540.
406. Fukuzumi S, Nakanishi I, Tanaka K, Tabard A, Guilard R, Van Caemelbecke E, Kadish KM. *Inorg. Chem.* 1999; **38**: 5000.
407. Hayashi T, Okazaki K, Urakawa N, Shimakoshi H, Sessler JL, Vogel E, Hisaeda Y. *Organometallics* 20012; **20**: 3074.
408. Huang L, Chen Y, Gao G-Y, Zhang XP. *J. Org. Chem.* 2003; **68**: 8179.
409. Debuigne A, Caille J-R, Jérôme R *Angew. Chem. Int. Edn* 2005; **44**: 1101.
410. Lee M-Y, Chen Y, Zhang XP. *Organometallics* 2003; **22**: 4905.
411. Fukuzumi S, Noura SJ. *Porphyrins Phthalocyanines* 1997; **1**: 251.
412. Fukuzumi S, Miyamoto K, Suenobu T, Van Caemelbecke E, Kadish KM. *J. Am. Chem. Soc.* 1998; **120**: 2880.
413. Stolzenberg AM, Cao Y. *J. Am. Chem. Soc.* 2001; **123**: 9078.
414. Uyemura M, Aida T. *J. Am. Chem. Soc.* 2002; **124**: 11392.
415. Uyemura M, Aida T. *Chem. Eur. J.* 2003; **9**: 3492.
416. Krattinger B, Callot H. *Bull. Soc. Chim. Fr.* 1996; **133**: 721.
417. Wayland BB, Basickes L, Mukerjee S, Wei M, Fryd M. *Macromolecules* 1997; **30**: 8109.
418. Cao Y, Petersen JL, Stolzenberg AM. *Inorg. Chim. Acta* 1997; **263**: 139.
419. Kadish KM, Frémond L, Ou Z, Shao J, Shi C, Anson FC, Burdet F, Gros CP, Barbe J-M, Guilard R. *J. Am. Chem. Soc.* 2005; **127**: 5625.
420. Arai Y, Ohgo Y. *Bull. Chem. Soc. Jpn.* 1988; **71**: 1871.
421. Kovacs JA. *Chem. Rev.* 2004; **104**: 825.
422. Kato K, Mukaiyama T. *Chem. Lett.* 1989; 2233.
423. Isayama S, Mukaiyama T. *Chem. Lett.* 1989; 573.
424. Isayama S, Mukaiyama T. *Chem. Lett.* 1989; 1071.
425. Isayama S, Mukaiyama T. *Chem. Lett.* 1989; 569.
426. Isayama S. *Bull. Chem. Soc. Jpn.* 1990; **63**: 1305.
427. McCauley KM, Wilson SR, van der Donk WA. *Inorg. Chem.* 2002; **41**: 5844.
428. Waser J, González-Gómez JC, Nambu H, Huber P, Carreira EM. *Org. Lett.* 2005; **7**: 4249.
429. Waser J, Carreira EM. *J. Am. Chem. Soc.* 2004; **126**: 5676.
430. Dreos R, Nardin G. Randaccio L, Siega P, Tauzher G, Vrdoljak V. *Inorg. Chem.* 2003; **42**: 6805.
431. Kingma IE, Wiersma M, van der Baan JL, Balt S, Bickelhaupt F, de Bolster MWG, Klumpp GW, Spek AL. *J. Chem. Soc. Chem. Commun.* 1993; 832.
432. Blaauw R, Kingma IE, Laan JH, van der Baan JL, Balt S, de Bolster MWG, Klumpp GW, Smeets WJJ, Spek AL. *J. Chem. Soc. Perkin Trans. 1* 2000; 1199.
433. Li G, Zhang FF, Chen H, Yin HF, Chen HL, Zhang SY. *J. Chem. Soc. Dalton Trans.* 2002; 105.
434. Chapman JJ, Day CS, Welker ME. *Organometallics* 2000; **19**: 1615.
435. Dreos R, Nardin G, Randaccio L, Siega P, Tauzher G, Vrdoljak V. *Inorg. Chem.* 2003; **42**: 6805.
436. Nakano T, Tamada D, Miyazaki J, Kakiuchi K, Okamoto Y. *Macromolecules* 2000; **33**: 1489.
437. Greatrex BW, Taylor DK. *J. Org. Chem.* 2005; **70**: 470.
438. Lu X-B, Wang Y. *Angew. Chem. Int. Ed.* 2004; **43**: 3574.
439. Nandy JP, Prabhakaran EN, Kumar SK, Kunwar AC, Iqbal J. *J. Org. Chem.* 2003; **68**: 1679.
440. Qin Z, Thomas CM, Lee S, Coates GW. *Angew. Chem. Int. Edn* 2003; **42**: 5484.
441. Cohen CT, Chu T, Coates GW. *J. Am. Chem. Soc.* 2005; **127**: 10869.
442. Caselli A, Gallo E, Ragaini F, Oppezzo A, Cenini S. *J. Organomet. Chem.* 2005; **690**: 2142.
443. Sugi KD, Nagata T, Yamada T, Mukaiyama T. *Chem. Lett.* 1997; 493.
444. Miyazaki D, Nomura K, Ichihara H. Ohtsuka Y, Ikeno T, Yamada T. *New J. Chem.* 2003; **27**: 1164.
445. Miyazaki D, Nomura K, Yamashita T, Iwakura I, Ikeno T, Yamda T. *Org. Lett.* 2003; **5**: 3555.
446. Miyazaki D, Nomura K, Yamashita T, Iwakura I, Ikeno T, Yamada T. *Org. Lett. Web Release Date*: Sept. 2003; **3**: 3671.
447. Yamada T, Nagata, T, Sugi KD, Yorozu K, Ikeno T, Ohtsuka Y, Miyazaki D, Mukaiyam T. *Chem. Eur. J.* 2003; **9**: 4485.
448. Ohtsuka Y, Koyasu K, Miyazaki D, Ikeno T, Yamada T. *Org. Lett.* 2001; **3**: 3421.
449. Yamada T, Nagata T, Ikeno T, Ohtsuka Y, Sagara A, Mukaiyama T. *Inorg. Chim. Acta* 1999; **296**: 86.
450. Dugi KD, Nagata T, Yamada T, Mukiiyama T. *Chem. Lett.* 1996; 737.
451. Nagata T, Dugi KD, Yamada T, Mukaiyama T. *Synlett* 1996; 1076.
452. Sugi KD, Nagata T, Yamada T, Mukaiyama T. *Chem. Lett.* 1996; 1081.
453. Ohtsuka Y, Ikeno T, Yamada T. *Tetrahedron Asy.* 2003; **14**: 967.
454. Ohtsuka Y, Ikeno T, Yamada T. *Tetrahedron Asy.* 2000; **11**: 3671.
455. Sato H, Watanabe H, Ohtsuka Y, Ikeno T, Fukuzawa S, Yamada T. *Org. Lett.* 2002; **4**: 3313.

456. Ohtsuka Y, Koyasu K, Ikeno T and Yamada T. *Org. Lett.* 2001; **3**: 2543.
457. Ohtsuka Y, Miyazaki D, Ikeno T, Yamada T. *Chem. Lett.* 2002; 24.
458. Nagata T, Yorozu K, Yamada T, Mukaiyama T. *Angew. Chem. Int. Edn* 1995; **34**: 2145.
459. Yamada T, Ohtsuka Y, Ikeno T. *Chem. Lett.* 1998; 1129.
460. Ikeno T, Nishizuka A, Sato M, Yamada T. *Synlett* 2001; 406.
461. Ikeno T, Iwakura I, Yamada T. *Bull. Chem. Soc. Jpn.* 2001; **74**: 2151.
462. Ikeno T, Sato M, Sekino H, Nishizuka A, Yamada T. *Bull. Chem. Soc. Jpn.* 2001; **74**: 2139.
463. Ikeno T, Iwakura I, Yamada T. *J. Am. Chem. Soc.* 2002; **124**: 15152.
464. Yamada T, Kezuka S, Mita T, Ikeno T. *Heterocycles* 2000; **52**: 1041.
465. Kezuka S, Mita T, Ohtsuki N, Ikeno T, Yamada T. *Chem. Lett.* 2000; 824.
466. Kezuka S, Mita T, Ohtsuki N, Ikeno T, Yamada T. *Bull. Chem. Soc. Jpn.* 2001; **74**: 1333.
467. Yamada T Ashizawa T, Iwakura I, Ikeno T. *Shokubai* 2005; **47**: 436.
468. Kezuka S, Kogami Y, Ikeno T, Yamada T. *Bull. Chem. Soc. Jpn.* 2003; **76**: 49.
469. Kezuka S, Ikeno T, Yamada T. *Org. Lett.* 2001; **3**: 1937.
470. Mita T, Ohtsuki N, Ikeno T, Yamada T. *Org. Lett.* 2002; **4**: 2457.
471. Ikeno T, Iwakura I, Yabushita S, Yamada T. *Org. Lett.* 2002; **4**: 517.
472. Mita T, Ohtsuki N, Ikeno T, Yamada T. *Org. Lett.* 2002; **4**: 2457.
473. Ohtsuki N, Kezuka S, Kogami Y, Mita T, Ashizawa T, Ikeno T, Yamada T. *Synthesis* 2003; 1462.
474. Kezuka S, Ohtsuki N, Mita T, Kogami Y, Ashizawa T, Ikeno T, Yamada T. *Bull. Chem. Soc. Jpn* 2003; **76**: 2197.
475. Kogami Y, Nakajima T, Ashizawa T, Kezuka S, Ikeno T, Yamada T. *Chem. Lett.* 2004; 614.
476. Kogami Y, Nakajima T, Ikeno T, Yamada T. *Synthesis* 2004; 1947.
477. Tanaka H, Kitaichi Y, Sato M. Ikeno T, Yamada T. *Chem. Lett.* 2004; **33**: 676.
478. Iwakura I, Ikeno T, Yamada T. *Org. Lett.* 2004; **6**: 949.
479. Ohba S, Nagata T, Yamada Y. *Acta Cryst.* 2001; **E57**: m124.
480. Ohba S, Nagata T, Yamada T. *Acta Cryst.* 2001; **E57**: 1.
481. Iwakura I, Tanaka H, Ikeno T, Yamada T. *Chem. Lett.* 2004; **33**: 140.
482. Akitsu T, Iwakura I, Tanaka H, Ikeno T, Einaga Y, Yamada T. *Acta Crst.* 2004; **E60**: m149.
483. Sato M, Gunji Y, Ikeno T, Yamada T. *Synthesis* 2004; 1434.
484. Kato K, Yamada T, Takai T, Inoki S, Isayama S. *Bull. Chem. Soc. Jpn.* 1990; **63**: 179.
485. Ikeno T, Kimura K, Ohtsuka Y, Yamada T. *Synlett* 1996; 96.
486. Ohtsuka Y, Kubota T, Ikeno T, Nagata T, Yamada T. *Snylett* 2000; 535.
487. Humphries MJ, Tellmann KP, Gibson VC, White AJP, Williams DJ. *Organometallics* 2005; **24**: 2039.
488. Small BL. *Organometallics*, 2003; **22**: 3178.
489. Chen Y, Chen R, Qian C, Dong X, Sun J. *Organometallics* 2003; **22**: 4312.
490. Chen Y, Qian C, Sun J. *Organometallics* 2003; **22**: 1231.
491. Takeuchi D, Anada K, Osakada K. *Angew. Chem. Int. Edn* 2004; **43**: 1233.
492. Sato Y, Nakayama Y, Yasuda H. *J. Organomet. Chem.* 2004; **689**: 744.
493. Tellmann KP, Humphries MJ, Rzepa HS, Gobson VC. *Organometallics* 2004; **23**: 5503.
494. Tellmann KP, Gibson VC, White AJP, Williams DJ. *Organometallics* 2005; **24**: 280.
495. Liu J-Y, Zheng Y, Li Y-G, Pan L, Li Y-S, Hu N-H. *J. Organomet. Chem.* 2005; **690**: 1233.