Review

Applied
Organometallic
Chemistry

Received: 25 October 2007 Accepted: 25 November 2007

(www.interscience.com) DOI 10.1002/aoc.1367

Three characteristic reactions of alkynes with metal compounds in organic synthesis

Iwao Omae*

Alkynes have two sets of mutually orthogonal π-bonds that are different from the π-bonds of alkenes. These π-bonds are able to bond with transition metal compounds. Alkynes easily bond with the various kinds of compounds having a π-bond such as carbon monoxide, alkenes, other alkynes and nitriles in the presence of the transition metal compounds. The most representative reaction of alkynes is called the Pauson–Khand reaction. The Pauson–Khand reactions include the cyclization of alkynes with alkenes and carbon monoxide in the presence of cobalt carbonyls. Similar Pauson–Khand reactions also proceed in the presence of other transition metal compounds. These reactions are the first type of characteristic reaction of alkynes. Other various kinds of cyclizations with alkynes also proceed in the presence of the transition metal compounds. These reactions are the second type of characteristic reaction of alkynes. These include cyclooligomerizations and cycloadditions. The cyclooligomerizations include mainly cyclotrimerizations and cyclotetramerizations, and the cycloadditions are [2 + 2], [2 + 2 + 1], [2 + 2 + 2], [3 + 2], [4 + 2], etc., type cycloadditions. Alkynes are fairly reactive because of the high *s* character of their σ-bonds. Therefore, simple coupling reactions with alkynes also proceed besides the cyclizations. The coupling reactions are the third type of characteristic reactions of alkynes in the presence of, mainly, the transition metal compounds. These reactions include carbonylations, dioxycarbonylations, Sonogashira reactions, coupling reactions with aldehydes, ketones, alkynes, alkenes and allyl compounds.

Keywords: alkynes; transition metal compounds; cyclization; Pauson–Khand reaction; Pauson–Khand-type reaction; coupling reaction; cyclooligomerization; cycloaddition; cyclotrimerization

Introduction

Both alkynes and alkenes are compounds having at least one π-electron bond. Therefore, in these compounds, reactions such as the addition of hydrogen, the addition of halogens, the addition of hydrogen halides, metathesis, oxidation and polymerization, proceed in the presence of metal compounds.

However, alkynes have another set of π-electron bonds. These two sets of π-electron bonds in alkynes are mutually orthogonal. Hence, the reactions of alkynes in the presence of the metal compounds are different from the reactions of alkenes.

As described in the next section, the two sets of mutually orthogonal π-electron bonds tend to easily bond with *d*-electrons in transition metals. Consequently, the characteristic reactions of alkynes occur in the presence of the transition metals. In these transition metal compounds, especially, a Co–Co bond in $(CO)_4Co–Co(CO)_4$, very easily form a mutually bridged bond with the two sets of π-electron bonds in alkynes. These reactions of alkynes with alkenes in the presence of $Co_2(CO)_8$ are the most characteristic reactions of alkynes with the transition metals in organic synthesis.

This first type of characteristic reaction of alkynes with organocobalt compounds is the Pauson–Khand reactions. Reactions that are similar to the Pauson–Khand reactions, Pauson–Khand-type reactions, occur in the presence of the other transition metal compounds besides the cobalt carbonyl compounds, and also proceed as the first type of characteristic reactions. The Pauson–Khand reactions and Pauson–Khand-type reactions are the reactions of alkynes, alkenes and carbon monoxide. In these three components, alkynes and carbon monoxide have two sets of π-electron bonds and alkenes have one set of π-electron bond. These reactions are also called as the [2 + 2 + 1] cyclizations.

The second type of characteristic reactions of alkynes with the transition metal compounds is other cyclizations in which alkynes react with compounds having π-electron bonds such as other alkynes, alkenes, allenes, aldehydes, ketones, imines, carbon monoxide, carbon dioxide and nitriles. These reactions are cyclooligomerizations and cycloadditions.

The third type of characteristic reaction of alkynes in the presence of the metal compounds is coupling reactions in which the negative charge of the carbon atom in alkynes is involved in addition to the high reactivity to the π-electron bond. The reactions are carbonylations, dioxycarbonylations, coupling reactions with aldehydes, ketones, imines, alkenes, allyl compounds, alkynes, other oxygen-containing compounds or nitrogen-containing compounds, Sonogashira reactions and other coupling reactions.

The characteristic reactions of alkynes with organocobalt compounds in organic synthesis have been reported in a previous review article.[1] This present review reports mainly on three characteristic reactions of alkynes with the metal compounds in organic synthesis, excluding the organocobalt compounds.

---

* *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*

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

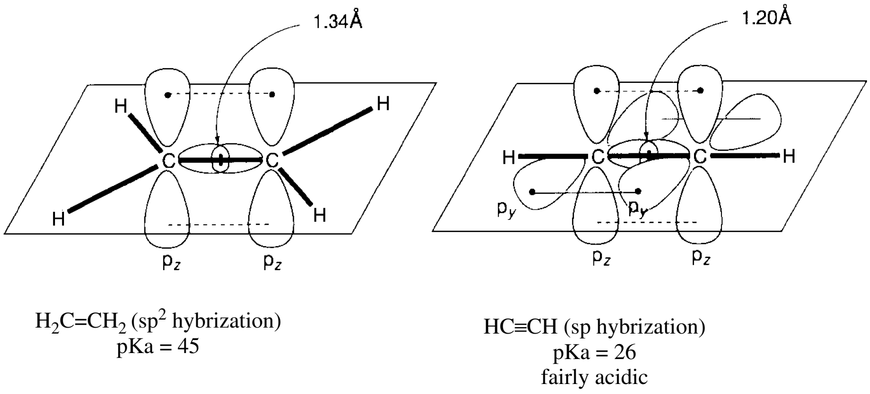


Figure 1. Structures of ethylene and acetylene.[2]

Structures of Unsaturated Carbon–Carbon Compounds, Their Metal Compounds, and Unsaturated Carbon–Oxygen Compounds

Ethylene and acetylene are the simplest compounds of alkenes and alkynes. Ethylene has one double bond consisting of one sp^2-sp^2 σ-bond and one p_z π-bond. On the other hand, acetylene has one triple bond consisting of one $sp-sp$ σ-bond, one p_z π-bond and one p_y π-bond as shown in Fig. 1.[2]

The *s* character in alkyne *sp* orbital is higher (50%) than that of alkene sp^2 orbital (33%). Electrons in an orbital having the more *s* character are closer to the nucleus and more strongly held, and so there is a greater electrostatic stabilization of the electron pair. Therefore, the conjugate base of the alkyne is the most stable and the most readily formed. A terminal alkyne with a strong base such as sodium and *n*-butyllithium gives the anion of the terminal alkyne, i.e. acetylide anion, which is synthetically useful as a strong nucleophile, and it can participate in C–C bond-forming reactions.[3]

C=C π- electrons in alkenes bond with metals as shown in Fig. 2.[4] The filled C=C π-electrons are donated to empty *s*, p_z, d_{z^2} or dx^2-y^2 orbitals in metal bonds. On the other hand, the π-electrons in the filled p_x or d_{xz} orbitals in metal bonds are donated to the empty antibonding C–C π^*-electron orbitals.

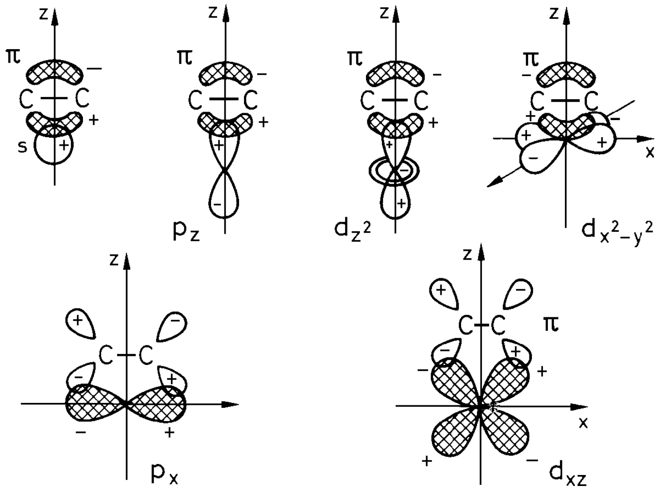


Figure 2. Participation of various orbitals in the formation of π-alkyne complexes.[4]

The molecular orbital interactions between alkynes and metal compounds are shown in Fig. 3.[5–8] The A (σ-type donation) in Fig. 3 corresponds to the bond between the C–C filled π-electrons and *s*, p_z, d_{z^2} and $d_{x^2-y^2}$ orbitals in the metals in Fig. 2 and the B (π-type back donations) in Fig. 3 corresponds to the bond between C–C empty antibonding π^*-orbitals and filled p_x or d_{xz} orbitals in the metals in Fig. 2.

On the other hand, in alkynes, another set of C–C π-bond sits at the orthogonal position. In the C (π-type donation), the filled alkyne π-orbital donates to the empty *d*-orbitals in the transition metals, and in the D (δ-type back donation), filled *d*-orbitals in the transition metals donate to the empty alkyne antibonding π^*-orbital as shown in Fig. 3.

Alkynes have the two sets of mutually orthogonal π-bonds, and the plane of another bond which is a perpendicular π-donor bond **C**, has a good overlap and must be considered. However, the perpendicular empty C=C antibonding orbitals (π^*-acceptor orbitals) can only overlap with a metal *d* orbital **D** in an *xy* plane, resulting in a δ bond of which the overlap is poor. The overlaps in the orbitals decrease in the order: **A** > **B** > **C** > **D**.[5–8]

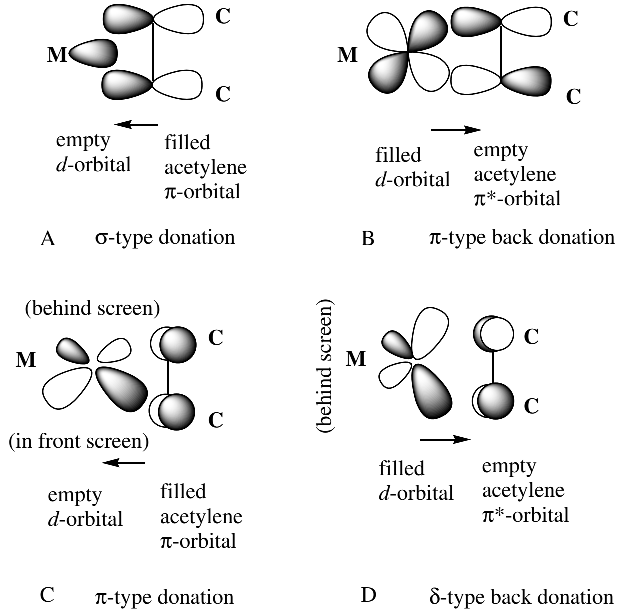


Figure 3. Molecular orbital interactions for coordinated acetylene.[5–8]

Alkyne ligand can coordinate like two orthogonal alkene units and it can formally occupy one, two, three or four coordination sites. Therefore, the alkynes are able to form monodentate **E** to quadridentate **I**, as shown in Fig. 4.[9] The **E** (monodentate) is the bond between one π-electron in the C=C bond and one metal atom. The **F** (bidentate) is the bond between two π-electrons in the C=C bond and one metal atom. The **I** (quadridentate) is the bond between four π-electrons in alkynes and two transition metal atoms. The alkyne ligand can be chelated in dimerized, trimerized or tetramerized form. These alkyne cyclization reactions can also involve the incorporation of carbonyl group and/or the metal atom.[9]

The structures of alkyne metal complexes are shown in Table 1.[10–29] The C–C bond lengths of the representative alkene and alkyne compounds, i.e. those of ethylene and acetylene, are 1.34 and 1.20 Å, and their CCR bond angles are 120 and 180°, respectively. In the monodentate **E**, the CCR bond angle may be close to 180° and the C–C bond length may be close to 1.20 Å. On the other hand, in the bidentate **F**, the CCR bond angle may be close to 120° and the C–C bond length may be close to 1.34 Å.

However, in the alkyne metal complexes in Table 1, the C–C bond lengths and CCR bond angles are 1.235–1.384 Å and 127–165.3°, respectively. For example, $[(Cl_2)(MeC_6H_4NH_2)Pt(t\text{-}Bu\text{-}C \equiv C\text{-}t\text{-}Bu)]$ is considered to be the

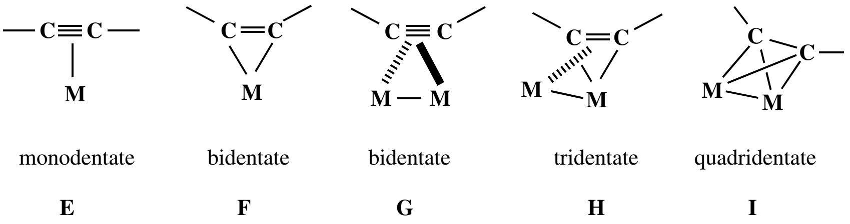


Figure 4. Structures of alkyne complexes.[9]

Table 1. Distances and angles between atoms in alkyne metal complexes

	C≡C (Å)	M-C (Å)	∠C-C-R (°)	Ref.
		2.138(13)	161.6(1.4)	
$((Cl_2)(MeC_6H_4NH_2)Pt(t\text{-}Bu\text{-}C{\equiv}C\text{-}t\text{-}Bu)$	1.235(18)	2.180(13)	165.3(1.4)	[10]
		2.023	127	
$((Ph_3P)_2)Pt(C_6H_4)$(cyclohexyne)	1.289	2.055	128	[11]
$(Ph_3P)_2Pt(PhC{\equiv}CPh)$	1.32	2.01, 2.06	139, 140	[12]
$Me(HB\text{-}(N_2C_3H_3)_3)Pt(F_3CC{\equiv}CCF_3)$	1.292(12)	2.018(16)	145.6(4)	[13]
		2.024(5)	140.62(63)	
$((Ph_3P)_2)Pt(F_3CC{\equiv}CCF_3)$	1.255(9)	2.031(5)	139.55(59)	[14]
		2.11(4)	150(4)	
$(MeAs)_2(Cl)(Me)Pt(F_3CC{\equiv}CCF_3)$	1.32(4)	2.03(4)	135(4)	[15]
		2.074(6)	146.4(9)	
$((Ph_3P)_2)Pd(MeOOCC{\equiv}CCOOMe)$	1.279(11)	2.051(6)	144.9(7)	[16]
	1.291(20)	1.989(14)	150(1)	
$[(Ph_3P)Pd(Ph_2PC{\equiv}CCF_3)]_2$	1.281(20)	2.039(14)	156(1)	[17]
$(Me_3C\text{-}N{\equiv}C)_2Ni(PhC{\equiv}CPh)$	1.284(16)	1.899(19)	148.6(1.4)	[18]
$Ni(HOEt_2CC{\equiv}CCEt_2OH)$	1.259(3)	1.875(1)	155.34(6)	[19]
		2.07(1)	139.2(13)	
$((Ph_3P)_2)(\text{-}C(CN{=}CHCN)Ir(NCC{\equiv}CCN)$	1.29(2)	2.10(1)	139.8(13)	[20]
		2.07(4)	142(4)	
$(Ph)(Cp)(O)W(PhC{\equiv}CPh)$	1.29(3)	2.15(4)	145(4)	[21]
$(CO)W(PhC{\equiv}CPh)_3$	1.30	2.06	139.6	[22]
$(S_2CNEt_2)_2(CO)W(C_2H_2)$	1.29(1)	2.015(9), 2.038(8)		[23]
		2.05(1)	136(1)	
$(Me_3P)(CO)(Cl)_2W(PhC{\equiv}C\text{-}OH)$	1.32(1)	1.97(1)	135(1)	[24]
		2.014(9)	142.8(9)	
$(Me_3P)_2(CO)(Cl)_2W(PhC{\equiv}CNH\text{-}t\text{-}Bu)$	1.34(1)	1.995(9)	146.8(9)	[25]
		2.16, 2.23	136, 140	
$Cp(CO)Nb(PhC{\equiv}CPh)$	1.33, 1.37	2.17, 2.21	138, 139	[26]
			1.38	
$(Cp)(Ph_2C_4Ph_2(CO)Nb(PhC{\equiv}CPh)$	1.26	2.21, 2.29	144	[27]
		2.069(2)	146.48(21)	
$Cl_3(THF)_2Nb(PhC{\equiv}CSi(t\text{-}BuMe_2)$	1.306(3)	2.067(2)	137.19(24)	[28]
$(\eta^5\text{-}C_5Me_5)Me_2TaC_6H_4$ (benzyne)	1.384(4)	2.06(3), 2.53(3)	–	[29]

monodentate **E** because >CCR is shown as the biggest angle, e.g. 165.3 and 161.6°, which are close to 180° and the C–C bond length is the shortest, 1.235 Å, in these compounds. On the other hand, $(Ph_3P)Pt(PhC{=}CPh)$ is better described as metallacyclopropene, that is, the bidentate **F**, because the C=C bond length and the angles >CCPh are 1.32 Å and 139 and 140°, respectively.[12]

Two sets of π-bonds at the orthogonal position tend to form a bridged bond, that is, the quadridentate **I**, as shown in Fig. 4.[2] In particular, $(CO)_4Co{-}Co(CO)_4$ easily forms the bridged bond by the reaction of alkynes as described in a previous review.[1] For example, in $(CO)_3Co{-}Co(CO)_3\cdot PhC{\equiv}CPh$ bridged compound,[29] the C–C bond length is 1.46 Å and the >RCC is 138°. This bridged compound is considered to be the quadridentate **I** in Fig. 4. These quandridentates are not only Co–Co bridged compounds but also Co–M (M is another metal) and M–M bridged compounds, as shown in Table 2.[30–40] These bridged bonds mean that the C–C triple bond perpendicularly bonds with the metal–metal bond.

Surprisingly, there have been many reports on the Pauson–Khand reactions' reports since early in the 1970s.[1] These show that it is easily considered that the alkyne metal complexes show high reactivities to both carbon monoxide and alkenes in the presence of organocobalt compounds (see Figs 1 and 5). Similarly, in the many reports on the reaction, it is also considered that the alkynes show high reactivity to the compounds having at least one π-electron bond such as other alkynes, alkenes, allyl compounds, aryl compounds, carbon monoxide, carbon dioxide (see Fig. 5), nitriles, imines, aldehydes and ketones in the presence of the transition metal compounds.

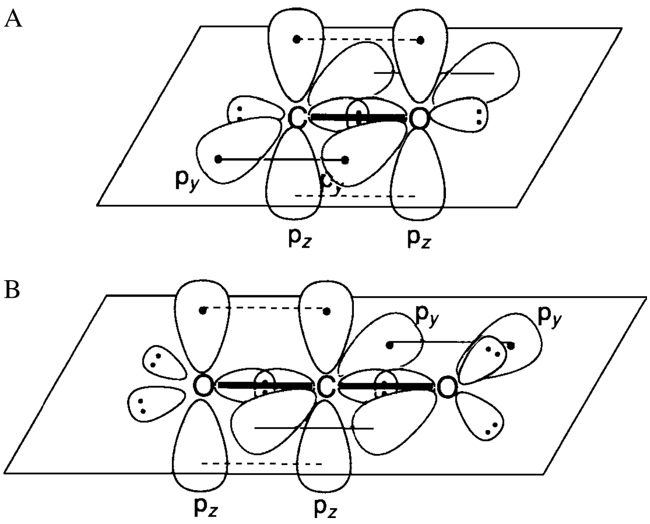


Figure 5. Structures of CO (A) and CO_2 (B).[2]

Pauson–Khand Reactions and Pauson–Khand-Type Reactions

Introduction

Alkynes can form the mutually bridged bonds of the quandridentate I as shown in Fig. 4 and in Table 2 by the reactions of two sets of mutually orthogonal π-bonds with metal–metal compounds, especially $(CO)_4Co{-}Co(CO)_4$. The reactions via their

Table 2. Distances between atom bridged alkyne metal complexes

	C≡C (Å)	M-M (Å) M-M′ (Å)	M-C	Ref.
$(CO)_3Co{-}Co(CO)_3(PhC{\equiv}CPh)$	1.46	2.47	1.93, 1.89 2.01, 2.02	[30]
$(CO)_3Co{-}Co(CO)_3(C_6F_6)$ (cyclohex-1-yne-3-ene)	1.29	2.52	1.88, 1.83 1.92, 1.95	[31]
$(CO)_3Co{-}Co(CO)_3(HOOCC{\equiv}CCOOH)$	1.350(5)	2.471(1)	1.946(4), 1.923(4) 1.924(4), 1.931(3)	[32]
$(CO)_3Co{-}Co(CO)_3(HOH_2CC{\equiv}CCH_2OH)$	1.338(4)	2.461(1)	1.963(3), 1.962(3) 1.978(3), 1.963(3)	[32]
$(CO)_3Co{-}Co(CO)_3(PhC{\equiv}CSiPh_3)$	1.343(6)	2.465(1)	2.002(5), 1.957(5) 1.985(3), 1.996(4)	[33]
$(CO)_3Co{-}Co(CO)_3$(t-Bu-C≡C-t-Bu)	1.349(2)	2.462(1)	1.984(2), 1.985(2) 1.988(1), 1.983(1)	[34]
$(CO)_3$Co-Ni(Cp)(PhC≡CPh)	1.337(5))	2.3656(8)	1.917(4), 1.904(4) Ni 1.963(3), 1.989(4) Co	[35]
$[Cp(CO)_2Mo\text{-}Co(CO)_2(Cp)(2\text{-propynylbornyl})]BF_4$		2.677(2)	2.19 Mo 1.93 Co	[36]
$(MeOOC\text{-}C_5H_4)(CO)_2Mo\text{-}Co(CO)_3(PhC{\equiv}CPh)$	1.347(5)	2.6873(6)	2.188(4), 2.147(4) Mo 1.976(4), 1.972(4) Co	[37]
$(CO)_3Co\text{-}Mo(CO)_2Cp(F_3CC{\equiv}CCF_3)$		2.692(1)	2.116(5), 2.138(5) Mo 1.960(5), 1.934(5) Co	[38]
$(Cp)(CO)_2W\text{-}Co(CO)_2(PhCC{\equiv}CMe)$	1.381(5)	2.693(1)	2.000(4), 2.027(4) Co 2.151(3), 2.120(3) W	[39]
$(CO)_3Co\text{-}W((CO)_2(CO)_3(\mu\text{-}EtC{=}CEt)_2(EtC{\equiv}CEt)$	1.36(2)	2.732(1)	2.15(1), 2.16(1) W 2.04(1), 2.01(1) Co	[40]
$[(Cp)(CO)_2Mo\text{-}Mo(CO)_2Cp((2\text{-propynylbornyl})]BF_4$		2.960	2.20 Mo	[36]

mutually bridged bonds between the Co–Co carbonyl compounds and alkynes proceed as per the following three types of reactions of the organocobalt compounds as described in the previous review.[1]

The first type reactions are those with a $Co_2(CO)_6$ protecting group because the mutually bridged bond $[C{\equiv}C{-}Co_2(CO)_6]$ stabilizes the reactive carbon–carbon triple bond in alkynes.

The second type of reactions are Nicholas reactions in which cations in the formation of the mutually bridged compounds, where the α-carbon at the C≡C bond in alkynes bonds with hydroxyl group, alkoxy group, etc., easily react with many kinds of nucleophiles to form the corresponding derivatives.

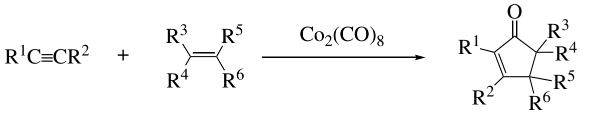
The third type of reactions are the Pauson–Khand reactions. These reactions proceed with Co–Co carbonyl compounds, alkynes and alkenes via mutually bridged bonds by [2 + 2 + 1]cyclizations.

The latter Pauson–Khand reaction is the most characteristic reaction of organocobalt compounds in organic synthesis. They easily form cyclopentenones by the reactions of many kinds of alkynes in the presence of Co–Co carbonyl compounds.[1] Many kinds of alkynes can form bridged compounds not only with the Co–Co compounds but also with Co–M compounds and M–M compounds, as shown in Table 2. The similar Pauson–Khand reactions also proceed with the other metal compounds besides the organocobalt compounds. These reactions are called the Pauson–Khand-type reactions.

The Pauson–Khand reactions and Pauson–Khand-type reactions are the reactions of the two sets of π-electrons in both alkynes and carbon monoxide with the one set of π-electrons of alkenes, as shown in Figs 1 and 5.

Pauson–Khand reactions

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



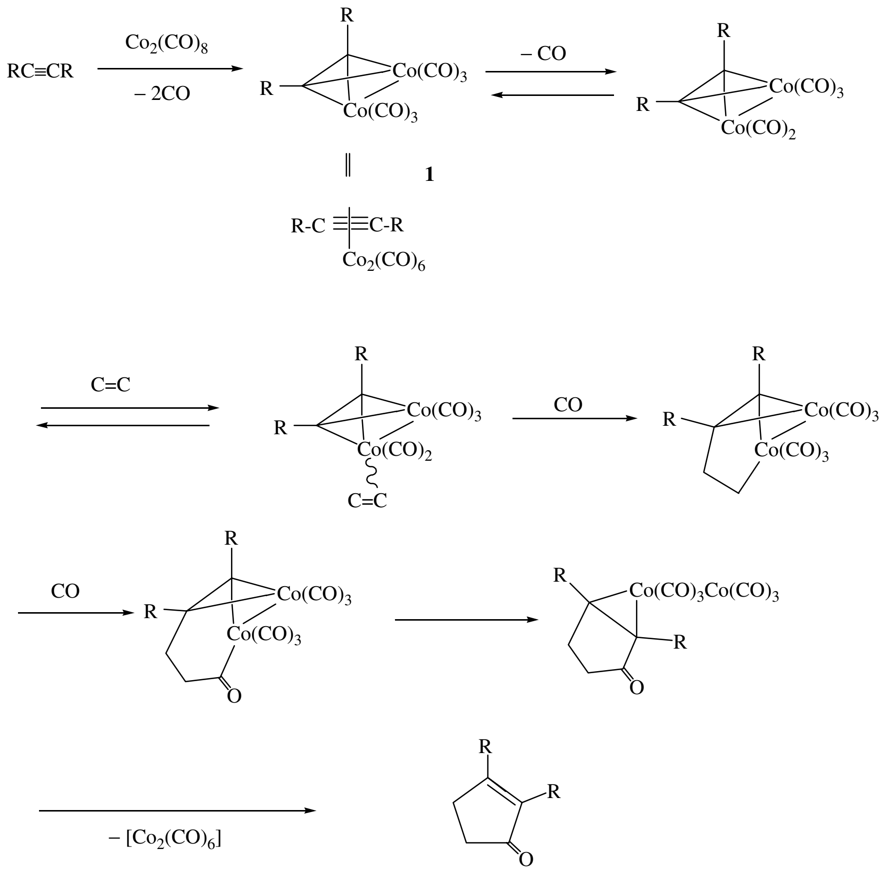
(1)

Many review articles on the Pauson–Khand reactions have been published.[41–56] As shown in Scheme 1,[43] at first, two π-bonds in alkyne with two cobalt atoms form the mutually bridged structure **1**. Then, one alkene is coordinated with one of the cobalt atoms and inserted into a cobalt–carbon bond. Also, one carbonyl is inserted into the new cobalt–carbon bond, and cyclopentenone is obtained by the elimination of $Co_2(CO)_6$. Please refer to the previous review article[1] for detail on the characteristic reactions of organocobalt compounds in organic synthesis.

Pauson–Khand-type reactions

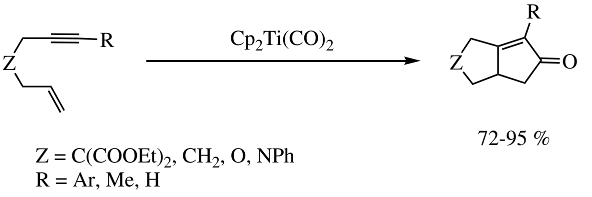
Pauson–Khand-type reactions

Similar Pauson–Khand reactions occur with the other transition metal compounds besides the organocobalt compounds,

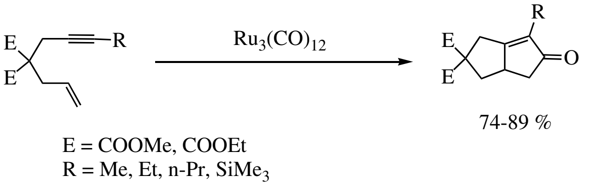


Scheme 1. The proposed mechanism of the Pauson-Khand reaciton.

as described in the former section. These reactions are called the Pauson–Khand-type reactions. The metals and alloys, Ti,[57–68] Zr[68–71] (4 Group), Mo,[72–77], W[74,76,78,79] (6 Group), Fe,[80,81] Ru[82–88] (8 Group), Rh,[89–95] Ir[96] (9 Group), Ni,[97,98] Pd[89,99] (10 Group), Raney cobalt,[100] Ru–Co,[101] Mo–Co,[102] $Co_2Rh_2(CO)_{12}$,[103] homogeneneous Pd, Co/C,[104] Co nanoparticle or Co/C,[105–108] are used in these reactions. Some of the Pauson–Khand-type reactions are shown in eqns (2)[61] and (3).[82]



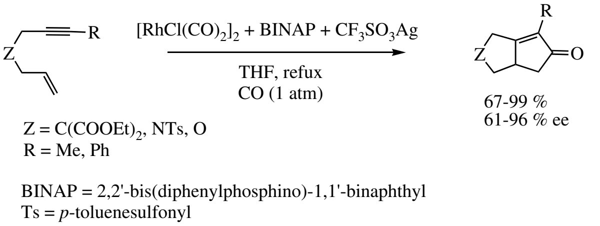
(2)



(3)

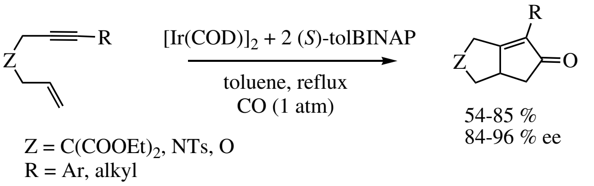
Asymmetric Pauson–Khand-type reactions

Asymmetric Pauson–Khand-type reactions proceed in the presence of transition metal catalysts, chiral compounds or chiral transition metal catalysts.[49,62,65,67,96,104,109–115] For example, the asymmetric Pauson–Khand-type reactions proceed in the presence of a rhodium carbonyl and chiral phosphine in high enantioselective yields, as shown in eqn (4). Silver salt, e.g. CF_3SO_3Ag, is required for the ionization of rhodium carbonyl in THF.[109]



(4)

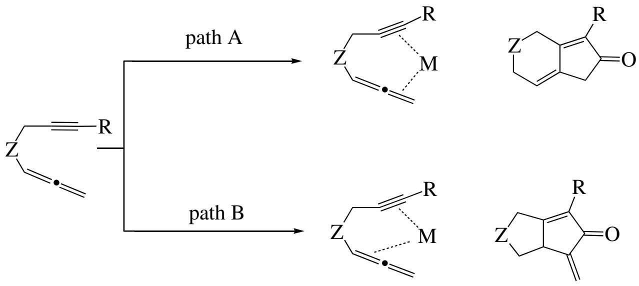
On the other hand, with cyclooctadiene iridium compounds and chiral bisdiphenylphosphine complex catalysts the asymmetric Pauson–Khand-type reactions proceed in high enatioselective yields without silver salt, as shown in eqn (5).[96]



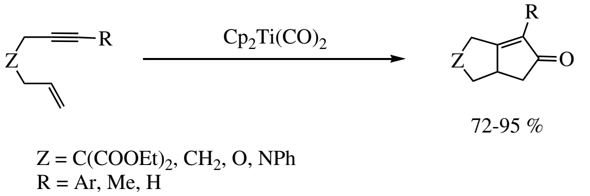
(5)

Pauson–Khand-type reactions with allenes as the alkene sources

Allenes are used as alkene sources in the Pauson–Khand-type reactions.[49,72,116–131] These reactions proceed along two paths, path A and path B depending upon the catalysts and substrates as shown in Scheme 2.[49] For example, the path A using iron carbonyl catalysts is shown in eqn (6).[129]

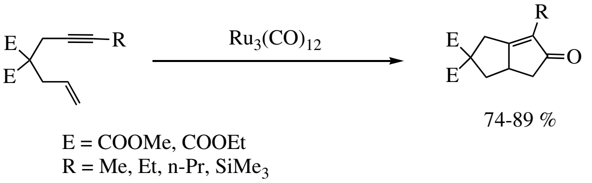


Scheme 2.



(6)

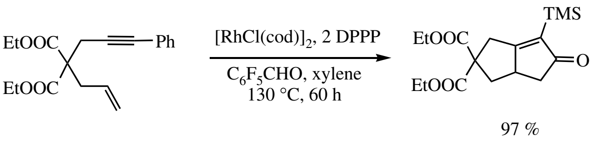
On the other hand, α-methylene cyclopentenone is prepared through the path B with molybdenum carbonyl compounds in good yields as shown in eqn (7).[72]



(7)

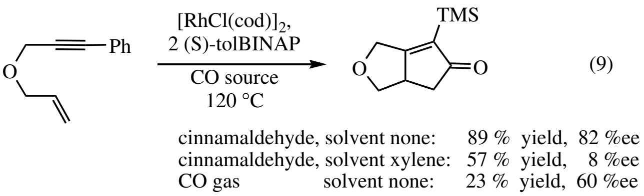
Pauson–Khand-type reactions with aldehydes as the carbon monoxide sources

Aldehydes may be used as a source of carbon monoxide for the Pauson–Khand-type reactions.[49,132–139] For example, the Pauson–Khand-type reactions proceed with elelctronegative pentafluorobenzaldehyde in high yields by carbonylations, as shown in eqn (8).[134]



(8)

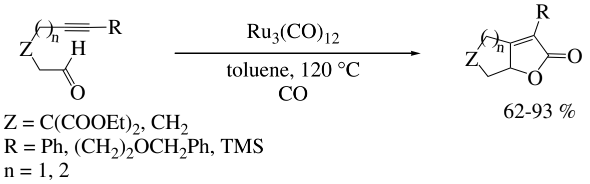
On the other hand, cinnamaldehyde has been found to be the best carbon monoxide source for the Pauson–Khand-type reaction. When a noncationic rhodium complex with a chiral phosphine was used as a chiral catalyst, the reactions proceeded highly enantioselectivity to give chiral cyclopentenones as shown in eqn (9).[132]



(9)

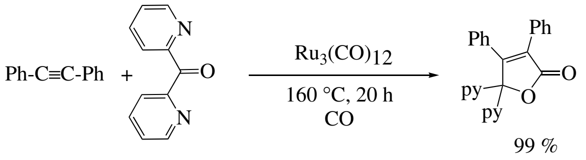
Hetro Pauson–Khand-type reactions

In the Pauson–Khand-type reactions with aldehydes (C=O π-bond), ketones (C=O π-bonds) or imines (C=N π-bond) instead of the alkenes as a C=C π-bond source, hetero Pauson–Khand-type reactions occur in the presence of the metal catalysts.[49,140–145] For example, the compounds having the carbon–carbon triple bond and formyl group reacted with carbon monoxide in the presence of ruthenium catalysts to give two cyclic α,β-unsaturated γ-lactones in high yields as shown in eqn (10).[143]



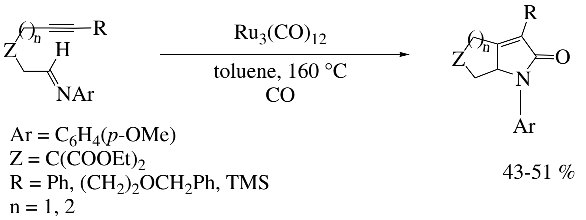
(10)

On the other hand, the reactions with di-2-pyridyly ketone give lactones in high yields as shown in eqn (11).[142]



(11)

With imines as the alkene sources, the hetero Pauson–Khand reactions also proceed in good yields in the presence of the ruthenium catalyst by cyclocarbonylation as shown in eqn (12).[144]



(12)

Other Cyclizations

Introduction

The first type of characteristic reaction in alkynes, i.e. the Pauson–Khand reactions and Pauson–Khand-type reactions is the cyclization of the two sets of π-electrons in alkynes and carbon monoxide with the one set of π-electron of alkynes, that is, [2 + 2 + 1] cyclizations. These cyclizations especially easily proceed with not only cobalt carbonyl but also with the other various kinds of transition metal compounds. Three components of the reaction show high affinity to the transition metal because two components, in particular, have the two sets of π-electron bonds.

The other cyclizations of alkynes in the presence of the transition metal compounds, are the second type characteristic reactions. These cyclizations proceed with the two sets of π-electrons of alkynes and the other compounds having at least one π-electron bond such as other alkynes, alkenes, allenes, carbon monoxide, carbon dioxide, aldehydes, ketones, imines and nitriles in the presence of transition metal comopunds. These reactions include two kinds of cyclizations, that is, cyclooligomerizations and cycloadditions.

The cyclooligomerizations of alkynes produce mainly benzene derivatives and cyclooctatetraene derivatives, as shown in Table 3.[146–155] On the other hand, the cycloadditions form many kinds of ring compounds such as four-, five-, six- and seven-membered compoumds by the [2 + 2], [3 + 2], [4 + 2], [5 + 2], [2 + 2 + 1], [2 + 2 + 2], [3 + 2 + 2], [4 + 2 + 1] and [2 + 2 + 1 + 1] cycloadditions.

The [2 + 2 + 1] cyclizations in the second type of characteristic reactions are different from those of the Pauson–Khand reactions or Pauson–Khand-type reactions, for example, the components are two alkynes and one carbonyl group [see eqn (24)].

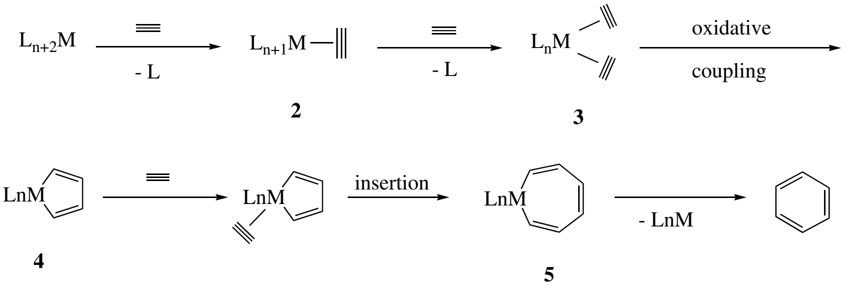
Cyclooligomerizations

The representative cyclooligomerizations of alkynes are cyclotrimerizations to form the benzene derivatives. The intermolecular cyclotrimerization of alkynes are considered to proceed as shown in Scheme 3.[42] In the first step, a metal atom in the metal compound is coordinated by one alkyne and forms an alkyne metal complex **2**. The sequential coordination of another alkyne molecule to a single metal center **3** is followed

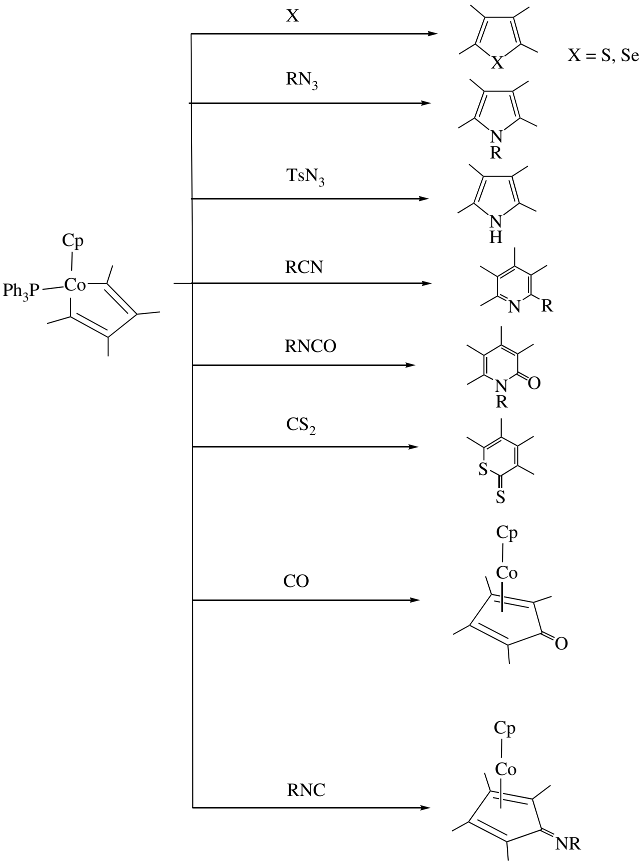
Table 3. Oligomerization of alkynes

Alkyne	Catalyst	Main product	Ref.
HC≡CH	$Ni(CN)_2$	cyclooctatetraene	[146]
HC≡CH	$Ni(CH_2{=}CHCN)_2$	cyclooctatetraene	[147]
HC≡CCOOEt	$Ni(PCl_3)_4$	1,2,4,6- or 1,3,5,7-tetraethoxycarbonylcyclooctatetraene	[148]
HC≡CH	$Ni(CO)_2(Ph_3P)_2$	benzene	[149]
HC≡CH	$NbCl_5$, WCl_6	benzene	[150]
HC≡CR[a]	$[NiL_2]$[b]	1,3,5- or 1,2,4-trisubstituteed benzene	[151]
HC≡CBu	$[NiCl(\eta^3\text{-}C_3H_5)]_2$	1,3,5-tri-*n*-butylbenzene	[152]
HC≡CH	$[NiCl(\eta^3\text{-}C_3H_5)]_2$	1,3,4-tri-*n*-butylbenzene	[152]
PhC≡CPh	$Co_4(CO)_{12}$; $Rh_4(CO)_{12}$	hexaphenylbenzene	[153]
MeC≡CPh	$PdCl_2(PhCN)_2$	1,3,5-trimethyl-2,4,6-triphenylbenzene	[154]
MeC≡C-C≡CMe	$Ni(CO)_2(Ph_3P)_2$	1,2,4-trimethyl-3,5,6-tripropylbenzene	[155]

[a] R = $CMe\text{-}CH_2$, CH_2OH, $CHMeOH$, CMe_2OH, $COOMe$, CH_2NMe_2, $CH_2CH_2NEt_2$, CH_2OEt.
[b] L = trithymyl phosphite.



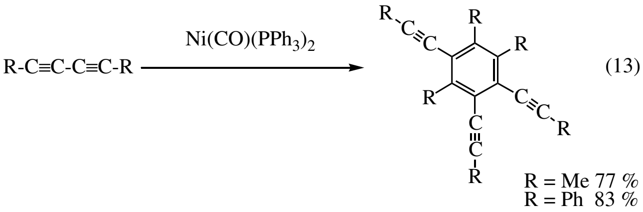
Scheme 3. Intermolecular cyclotrimerizations of alkynes.[42].



Scheme 4.

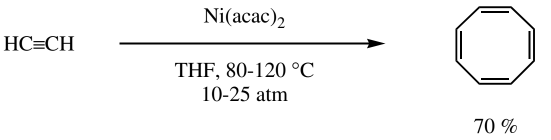
by metallacyclopentadiene formation **4** that simultaneously forms a carbon–carbon bond, formally oxidizes the metal and opens a coordination site. They may also complex with a third alkyne molecule, which may be inserted to give a transient metallacycloheptatriene **5** from which the benzene product is finally released.[156] The intermediates **2–5** are isolated.[157] For example, the intermediates **2** are already shown in Table 2. Metallacyclopentadiene **4**, e.g. cobaltcyclopentadienes, are easily synthesized, and many compounds are derived from the compounds **4** as shown in Scheme 4.[158] Therefore, these compounds are utilized as useful intermediates.

Many kinds of catalysts for the synthesis of benzene derivatives by these cyclotrimerizations have been found.[5,42,146,148,149] These catalysts are the metals or metal compounds such as U[159] (Group3), Ti[160] (Group 4), Nb[28,50,162] and Ta[163] (Group 5), Cr[164] and W[165] (Group 6), Fe[166] and Ru[161] (Group 8), Co,[153,158,167–171] Rh[153] and Ir[156,172,173] (Group 9), and Ni[148,155,164,174–176] and Pd[154,158,177] (Group 10). For example, the cyclotrimerizations of conjugated acetylenes produce solely unsymmetrical isomers in high yields in the presence of $Ni(CO)(PPh_3)_2$, as shown in eqn (13).[155] In particular, the organocobalts such as cyclopentadienyldicarbonylcobalt are conveniently used for the synthesis of the benzene derivatives.[178–182]



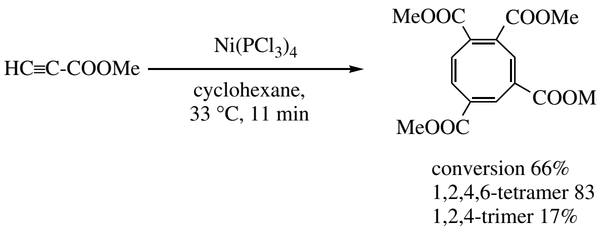
(13)

On the other hand, the cyclotetramerizations proceed mainly with nickel catalysts such as $Ni(acac)_2$, $Ni(CN)_2$, $[Ni(CH_2{=}CHCN)_2]$ and $[Ni(PCl_3)_4]$.[146–148,183–187] The cyclotetramerizations of acetylene is one of the famous Reppe's reactions in the transition metal chemistry of alkynes.[146] The reaction of acetylene with $Ni(acac)_2$ is shown in eqn (14).[146]



(14)

Monosubstituted alkynes are also readily cyclotetramerized and both simple and functionalized tetramers may be synthesized.[151] With methyl propiolate, 66% of the monomer is converted in the presence of $Ni(PCl_3)_4$ catalyst at 33 °C, the yield of 1,2,4,6-tetramer is 83% and the remaining product (17%) is 1,2,4-tricarbomethoxybenzene, as shown in eqn (15).[147,148,188]

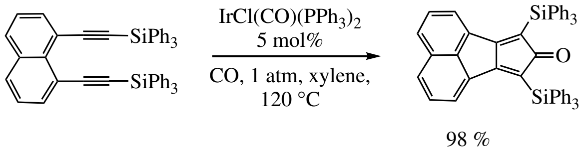


(15)

Cycloadditions

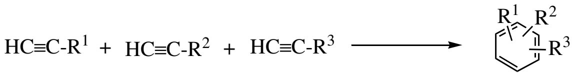
In the second type characteristic reactions of alkynes, the [2+2+1] cycloadditions are carbonylative alkyne–alkyne couplings.[189,190]

For example, cyclopentadienone is prepared in a high yield by the [2 + 2 + 1] cycloadditions of a diyne in the presence of an iridium phosphine complex, as shown in eqn (16).[189]



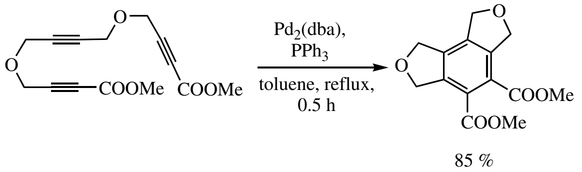
(16)

The cyclooligomerizations of three alkynes form the benzene derivatives. However, the cycloaddition of three kinds of alkynes that are the [2 + 2 + 2] cycloadditions, also forms some benzene derivatives in the presence of the transition metal catalysts, as shown in eqn (17).[191]

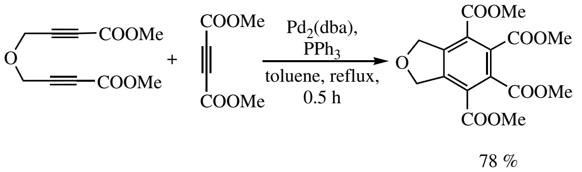


(17)

However, the intramolecular cyclization of alkynes having three triple bonds in the same molecule or cyclization of alkynes having two triple bonds with one alkyne tends to form one kind of compound, as shown in eqns (18) and (19),[197] respectively. These cyclizations are conveniently applied for organic syntheses.[157,171,191–210]

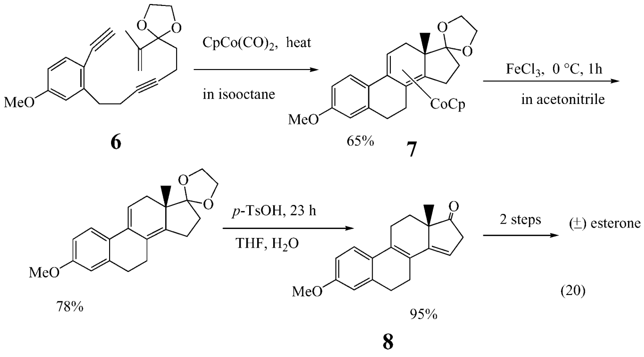


(18)

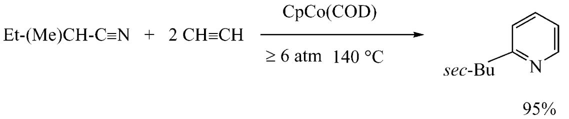


(19)

The intramolemolecular cyclizations of one alkene instead of one alkyne give cyclohexadiene derivatives, e.g. compound **7**, instead of the benzene derivatives.[157,179,211–219] This reaction may be used in the total synthesis of the Torgov intermediate **8**, in the synthesis of estrone. The exposure of enediyne **6** to excess CpCo(CO)$_2$ in boiling isooctane gave a red crystalline cobalt complex **8**, in a fairly good yield (65%) as shown in eqn (20).[217]

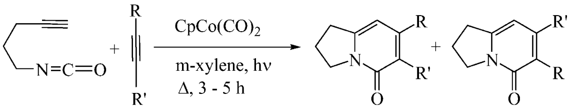


With one cyano compound instead of one monoyne, the [2+2+2] cycloaddition gives heterocyclic compounds[157,179,220–237] such as pyridine derivatives. For example, (+)-(*S*)-2-methylbutanenitrile reacts with acetylene at 140 °C in the presence of CpCo(cyclooctadiene) giving (+)-(*S*)-2-*sec*-butylpyridine in a high yield, as shown in eqn (21).[223]



(21)

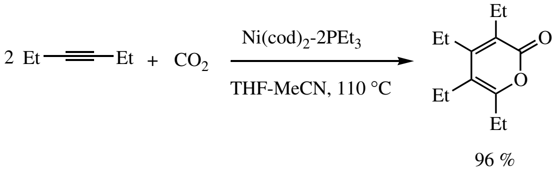
With isocyanates instead of nitriles, the cyclization of acetylenes gives 5-indolizinones in a regio-controlling reaction, as shown in eqn (22).[238] This reaction is readily applied to the total synthesis of an antitumor alkaloid camptothecin.[238–240]



(22)

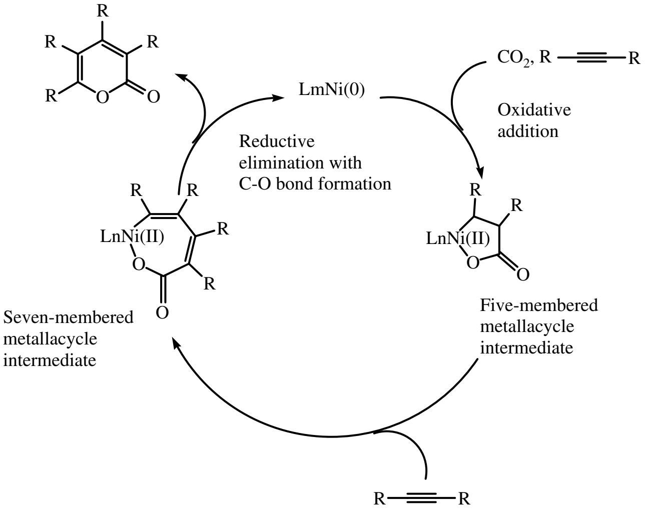
R	R'		
SiMe$_3$	SiMe$_3$	72%	-
n-Pr	SiMe$_3$	68%	5

The reaction of alkynes with carbon dioxide in the presence of nickel catalysts give doubly substituted pyrones by the [2 + 2 + 2] cycloadditions of two alkynes and one carbonyl group in carbon dioxide as shown in eqn (23).[241,242]



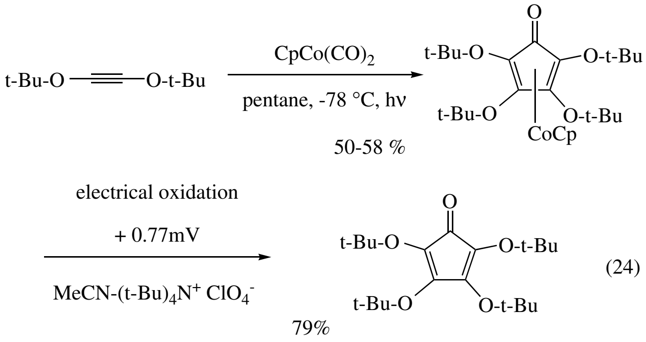
(23)

The mechanism involves an oxanickel cyclopentene complex that undergoes ring enlargement by the insertion of an alkyne to give a seven-membered ring. The decomposition of the seven-membered ring liberates the pyrone and the nickel catalyst is regenerated as shown in Scheme 5.[243]



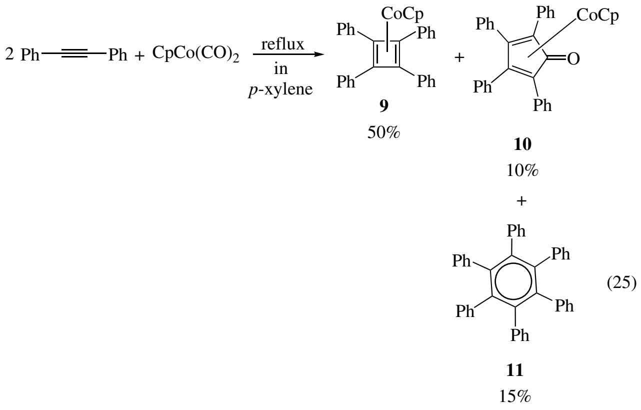
Scheme 5.

The cycloaddition ([2 + 2 + 1] cyclization) of two alkynes in the presence of a cyclopentadienylcobalt catalyst gives cyclopentadienone instead of the cyclopentenones in the Pauson–Khand reaction, as shown in eqn (24).[244–246]



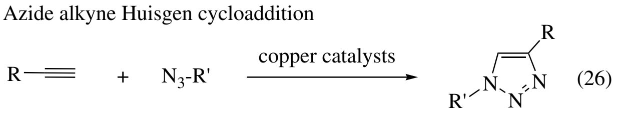
(24)

Cyclic products derived from only two molecules of alkynes include cyclobutadiene complexes **9** ([2 + 2] cycloaddition) and cyclopentadienone complexes **10** ([2 + 2 + 1] cycloaddition) via cobaltcyclopentadienes (see Scheme 4), as shown in eqn (25).[192] As for the [2 + 2] cycloaddition, the other cyclodimerization of alkynes,[194] alkyne–alkene cycloaddition[195] and alkyne fluoroallene cycloaddition[196] were also reported.



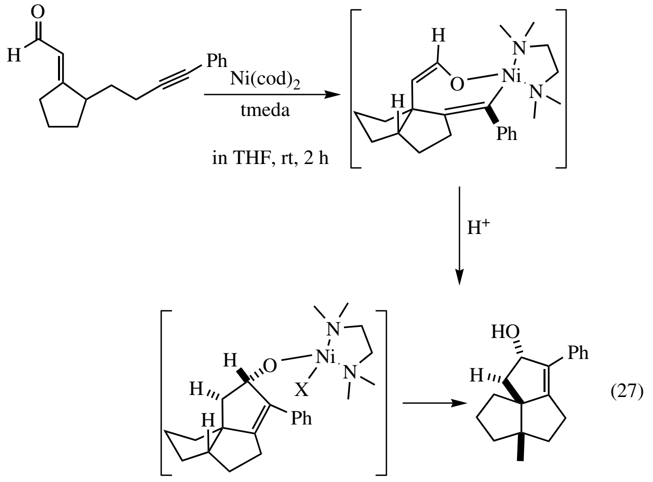
(25)

Azide alkyne Huisgen cycloaddition[247–252] is the [3 + 2] cycloaddtion of alkyne and azide in the presence of copper catalysts to give 1,2,3-triazole. The reaction is shown basically in eqn (26).[248]



(26)

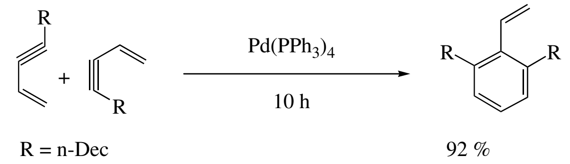
Enol–alkyne reductive cycloadditions[253,254] are also the [3 + 2] cycloadditions. For example, the intramolecular cyclization of the enol–alkyne proceeds in the presence of a nickel catalyst to give a tricyclic single diastereomer in 71% yield, as shown in eqn (27).[254]



(27)

Yied 71 %, from MeOH quench

Monosubstituted conjugated enynes smoothly undergo [4 + 2] homodimerization by the cyclization of the enyne and monoyne cyclization in the presence of palladium catalyst to give styrene derivatives as shown in eqn (28).[255] These [4 + 2] cycloadditions also proceed by the diene and monoyne cycloaddition,[256–258] and by the enyne and diyne cycloaddition.[259,260]



(28)

In the reaction of 2-butyne with η^5-pentamethylcyclopentadienylallyl cobalt or η^5-methylcyclopentadienylallyl cobalt compound, the [3 + 2 + 2], [3 + 2] and [5 + 2] cycloadditions were reported[261–263] (see previous review[1]).

The other cycloadditions such as the [3 + 3 + 2] cycloadditions (cyclopropylidene, alkyne, alkyne),[264,265] [4+2+1] cycloadditions (diene, alkyne, diazomethane derivative)[266], [4 + 2 + 2] cycloadditions (diynes, cyclobutenone)[267] and [5 + 2] cycloaddiitons (vinylcyclopropane, alkyne)[268] were also reported.

Very recently, many kinds of cycloadditions have been reported, such as the [2 + 2 + 2] cycloadditions of two alkynes and one alkenes,[269–273] [2 + 2 + 2] cycloadditions of triynes,[274–276] [2 + 2 + 2] cycloadditions of *ortho*-alkynylaryl aldehyde[277], [2+2+2] cycloadditions of aryl enyne[278], [2+2+2] cycloadditions of diynes and isothiocyanates[279] and [2 + 2 + 2] cycloadditions of diynes or tetraynes.[280,281]

Coupling Reactions

Introduction

Alkynes are fairly acidic because the negative charge in alkynes is stabilized as a result of the high *s* character of the *sp* orbital, as described above. The terminal alkyne with a strong base such as sodium and *n*-butyllithium gives the anion of the terminal alkyne. The acetylide anion is synthetically useful as a strong nucleophile, and it can participate in C–C bond forming reactions.[3]

Furthermore, the two sets of π-bonds at the orthogonal position show high reactivities to the other π-electron bonds, such as carbon monoxide, carbon dioxide, aldehydes, ketones, alkenes, allenes and nitrile in the presence of transition metal compounds as described above.

Hence, in alkynes in the presence of not only the transition metal compounds but also main group metal compounds, their coupling reactions also proceed in addition to the cyclizations. These coupling reactions are the third type characteristic reactions of alkynes with the metal compounds in organic synthesis and proceed in the presence of mainly the transition metal compounds.

Carbonylations

As alkynes are reactive with carbonyl group in the presence of the transition metal compounds, the cyclizations with carbon monoxide easily proceed as shown in the Pauson–Khand reactions [eqn (1)] and the Pauson–Khand-type reactions, as the [2 + 2 + 2] cyclizations, and as the other [2 + 2 + 1] cyclizations [eqns (16), (24) and (25)].

However, the coupling reactions also proceed in the presence of the transition metal compounds. The representative Reppe carbonylations are the production process of acrylic acid, acrylic acid esters and acrylic acid amides. These reactions involve alkynes, carbon monoxide, and HX (X = OH, water, X = OR, alcohol, X = NR_2, amines) in the presence of the tranisition metal compounds such as $HCo(CO)_4$, $Ni(CO)_4$, $NiBr_2$ and $Fe(CO)_5$ as shown in eqns (29)–(31).[282]

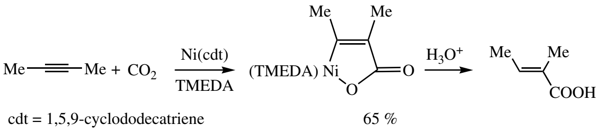
$$HC \equiv CH + CO + HOH \longrightarrow CH_2 = CHCOOH \qquad (29)$$

$$HC \equiv CH + CO + ROH \longrightarrow CH_2 = CHCOOR \qquad (30)$$

$$HC \equiv CH + CO + R_2NH \longrightarrow CH_2 = CHCONR_2 \qquad (31)$$

Dioxycarbonylations

Carbon dioxide is generally an inert compound. However, carbon dioxide has the two sets of carbon oxygen π-electron bonds, as shown in Fig. 5. As it was previously described, it reacts with alkynes in the presence of nickel catalysts to give the [2 + 2 + 2] cyclization products, as shown in eqn (23). With other nickel catalysts, 2-butyne reacts with carbon dioxide in the presence of Ni(cdt) (cdt = 1,5,9-cyclododecatriene) and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (TMEDA) to give a five-membered nickelacyclolactone. Its protonolysis leads to 2-methylcrotonic acid, as shown in eqn (32).[283] Hence, the synthetic reaction of the 2-methylcrotonic acid is the coupling reaction via the [2 + 2 + 1] cycloaddition of C–C bond, C=O bond and a metal atom.



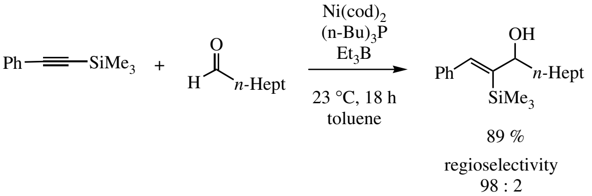
(32)

cdt = 1,5,9-cyclododecatriene

TMEDA = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine

Coupling reactions with aldehydes

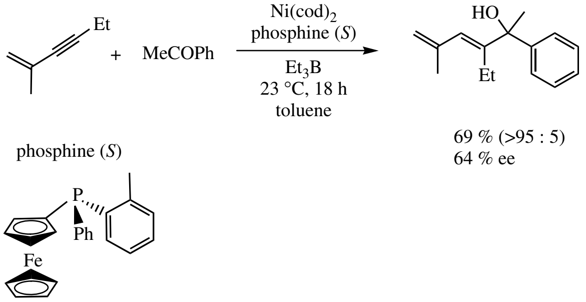
In the section, *Pauson-Khand type reactions with aldehydes as the carbon monoxide sources*, the aldehydes are described that are used as the carbon monoxide sources in the Pauson–Khand reaction and Pauson–Khand-type reactions. Thus, the coupling of alkynes with aldehydes also proceed in the presence of the transition metal compounds such as nickel and rhodium.[284–298] For example, the reductive coupling of alkyne with aldehyde in the presence of a nickel catalyst proceeds in a high yield and high regioselectivity as shown in eqn (33).[284]



(33)

Coupling reactions with ketones

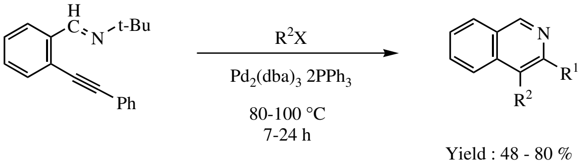
Ketones have one set of carbon oxygen moiety having a π-electron bond. Therefore, the coupling reactions of alkynes with the ketones also easily proceed in the presence of the transition metal compounds such as nickel, rhodium and iridium.[299–303] For example, the highly regioselective and asymmetric reductive coupling of 1,3-enyne with ketone has been achieved in the presence of a nickel compound and a phosphorus chiral, monodentate ferrocenyl phosphine ligand, as shown in eqn (34).[301]



(34)

Coupling reactions with imines

An unsaturated carbon–nitrogen π-electron bond (imino group: C=N) is expected to have a similar reactivity to the unsaturated carbon–oxygen π-electron bond with alkynes in the presence of the transition metal compounds. Hence, the coupling reactions between imino compounds and alkynes proceed with the transition metal compounds.[304–312] For example, a wide variety of 4-substituted isoquinolines are synthesized by the coupling of *o*-(1-alkynyl)benzaldimines and organic halides in the presence of a palladium catalyst as shown in eqn (35).[304]



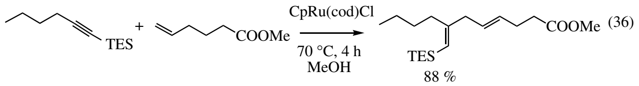
(35)

R^1 = Ph, n-Bu, 1-cyclohexenyl, *p*-$MeOC_6H_4$
R2 = PhI, I-C_6H_4-NO_2-*p*, Br-C_6H_4-NO_2-*p*.
I-C_6H_4-NO_2-*m*, I-C_6H_4-COOEt-,
I-C_6H_4-COOEt-*m*, I-C_6H_4-CF_3-*p*,
I-C_6H_4-CF_3-*m*, I-C_6H_4-CH_3-*p*,
3-iodepyridine

Coupling reactions with alkenes

The [2 + 2 + 1] cyclizations (Pauson–Khand reactions and Pauson–Khand-type reactions) of alkynes, alkenes and carbon monoxide, and the [2 + 2 + 2] cycloadditions of two alkynes and one alkene, [2 + 2] alkyne–alkene cycloadditions and [4 + 2] enyne and monoyne cyclizations (e.g., E 28), easily proceed in the presence of the metal compounds as described above. These cyclization reactions show that the π-electron bond of alkenes has a high reactivity with the two sets of π-bonds in alkynes in the presence of the transition metal compounds.

Alkynes also easily couple with alkenes in the presence of the metal compounds such as ruthenium, palladium, cobalt, rhodium and platinum compounds.[313–322] For example, the cross-coupling reaction of a silylalkyne and terminal alkene carboxylic acid methyl ester proceeds under the control of regioselectivity by a silyl substituent to give a geometrically defined vinylsilane in a high yield, as shown in eqn (36).[313]



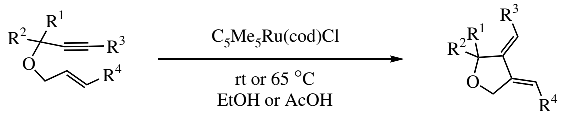
(36)

88 %

TES = triethylsilane

(Isolated yield corrected for the amount of unreacted starting material)

On the other hand, in the compounds having one triple bond and one double bond, intramolecular enyne coupling cyclization reactions easily proceed in the presence of the transition metal compounds. These coupling cyclization reactions are simple enyne cyclizations, the various kinds of cycloisomerization, reductive cyclizations, tandem cyclizations, electrocyclizations, etc.[323–351a] For example, the one-step synthesis of 3,4-dialkylidenetetrahydrofurans from allyl propargyl ethers by enyne cycloisomerization in the presence of a ruthenium catalyst is shown in eqn (37).[323]

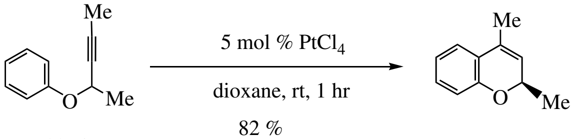


(37)

R^1-R^4 = H, Me, n-Bu, -$(CH_2)_5$-, Ph

58-94 %

The coupling reactions of alkynes with arenes or heteroarenes in the presence of the metal compounds also proceed similarly to those of alkenes. These coupling reactions are intramolecular arene–alkyne coupling,[352,353] the Friedel–Crafts alkenylations of arenes,[354] the heteroarylations of alkynes,[355,356] and the isomerizations of an α-arylprogargl alcohol,[357,358] etc.[359] For example, platinium-catalyzed coupling reaction of arene–alkyne proceed via intramolecular electrophilic hydroarylation as shown in eqn (38).[353]



(38)

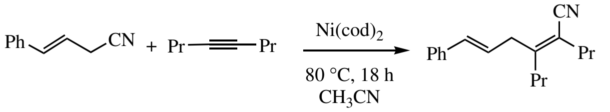
89 %ee

82 %

89 %ee

Coupling reactions with allyl compounds

The allylations of alkynes also proceed in the presence of the transition metal complexes such as ruthenium, nickel, platinum, gold and copper metal.[360–362] For example, allycyanation of alkyne proceeds regio- and stereoselectively as shown in eqn (39).[360]



(39)

86 %

5*E*,
5*Z*
>99:1

Coupling reacions with alkynes

Alkynes are fairly reactive because the negative charge in alkynes is stabilized as described above. Therefore, the alkyne–alkyne coupling reactions easily proceed because the electron charge is stabilized in the alkyne's carbon.

The alkyne–alkyne coupling reactions such as Glaser coupling, Hay coupling, Cadiot–Chodiewicz coupling and Eglington coupling reactions proceed in the presence of copper catalysts, as shown in eqns (40)–(44), respectively.[363–368] For example, the Cadiot–Chodiewicz coupling of 4-ethynylpridine with 1-bromo-2-(triethylsilyl) acetylene in the presence of CuCl proceeds with high yields as shown in eqn (44).[369]

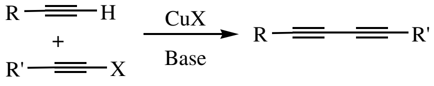
Glaser coupling

$$2\ Ph-\!\equiv\!-H\ +\ 1/2\ O_2 \xrightarrow[NH_4OH,\ EtOH]{CuCl} Ph-\!\equiv\!-\!\equiv\!-Ph\ +\ H_2O \qquad (40)$$

Hay coupling

$$2\ R-\!\equiv\!-H\ +\ 1/2\ O_2 \xrightarrow[TMEDA,\ acetone]{CuCl} R-\!\equiv\!-\!\equiv\!-R\ +\ H_2O \qquad (41)$$

Cadiot-Chodkiewicz coupling

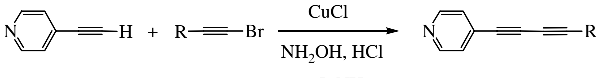


$$R-\!\equiv\!-H\ +\ R'-\!\equiv\!-X \xrightarrow[Base]{CuX} R-\!\equiv\!-\!\equiv\!-R' \qquad (42)$$

Eglington coupling

$$2\ R-\!\equiv\!-H\ +\ 1/2\ O_2 \xrightarrow[pyridine]{Cu(OAc)_2} R-\!\equiv\!-\!\equiv\!-R\ +\ H_2O \qquad (43)$$

Cadiot-Chodkiewicz coupling

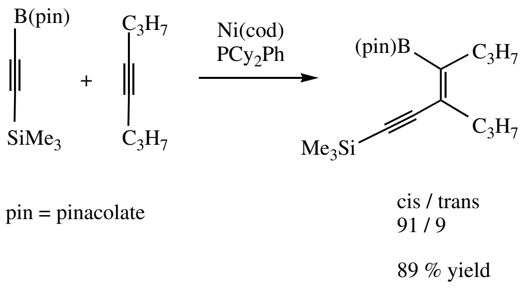


(44)

R = $SiEt_3$

82 %
isolated yield

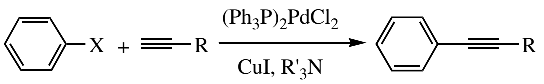
With a nickel catalyst, the addition of alkynylboranes with alkynes proceeds stereoselectively, as shown in eqn (45).[370]



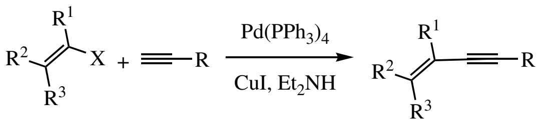
(45)

Sonogashira reactions

Sonogashira reactions are widely used for organic synthesis as the coupling reactions between terminal alkynes with aryl or vinyl halides in the presence of a palladium catalyst, a copper(I) cocatalyst, and an amine base as shown in eqns (46) and (47).[364,371–384]

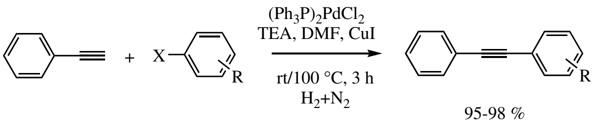


(46)



(47)

The side product from the homocoupling reaction of two terminal acetylenes in the Sonogashira reaction can be reduced to about 2% by using an atmosphere of hydrogen gas diluted with nitrogen or argon as shown in eqn (48).[374]



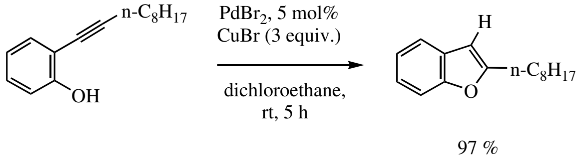
(48)

$R = 2,4$-dimethyl, 4-OMe, 4-CN
4-NO_2, 4-CHO, 4-$COCH_3$
$X = Br, I$

Coupling reactions with other oxygen-containing compounds or with nitrongen-containing compounds

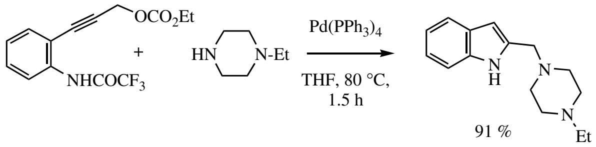
Alkynes easily couple with many kinds of heteroatom-containing compounds.[385–402] These coupling reactions generate heterocyclic compounds generally by electrophilic acetylenic additions. The heteroatom-containing compounds are oxygen-, nitrogen- and sulfur-containing compounds.[385]

The oxygen-containing compounds are alcohols,[386–388] carboxylic acid,[389–391] esters,[392] ethers[393], etc.[385] For example, the coupling reaction of 2-alkynylphenol easily proceeds in the presence of a palladium catalyst and a copper cocatalyst to give 2-octylbenzo[b]furan in a high yield by an intramolecular coupling reaction as shown in eqn (49).[387]



(49)

The nitrogen-containing compounds are primary amines,[394–396] secondary amies,[399–400] tertiary amines,[401] etc.[385] For example, ethyl 3-(*o*-trifluoroacetamidophenyl)-1-propargyl carbonate reacts with piperazine in the presence of a palladium phosphine catalyst to yield an indole piperazin derivative in a high yields as shown in eqn (50).[397]

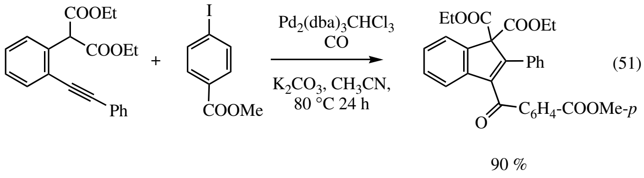


(50)

Other coupling reactions

As the carbon atom in alkynes are reactive, the carbon atom easily couples with the other alkyl carbons, aryl carbons and various kinds of metal atoms. These coupling reactions are, e.g. carbonylative cyclizations by C–C coupling reactions,[403–406] hydroarylations by C–C coupling reactions,[407,408] the reductive cyclization of diynes with hydrogen,[409] the reductive cyclization of acetylenic aldehydes with hydrogen,[410] and the hydrosilation of acetylenes by a C–Si coupling,[411] etc.[384]

For example, the C–C coupling reaction between alkynyl carbon and the methyl carbon of diethylmalonate proceeds in the presence of palladium catalyst under a balloon pressure of carbon monoxide to produce the 3-aroylindene in a high yield, as shown in eqn (51).[405]



(51)

Concluding Remarks

Alkynes have the two sets of π-electron bonds at the orthogonal position which are different from the bond of alkenes. These π-electron bonds are able to bond with the transition metal compounds. These bonds easily bond with the various kinds of compounds having π-electron bonds such as alkynes, alkenes, carbon monoxide, aldehydes, ketones and nitriles to form cyclization products or coupling reaction products in the presence of the trasition metal compounds.

The first type of characteristic reaction of alkynes with the transition metal compounds is the Pauson–Khand reactions and Pauson–Khand-type reactions by the cyclization of alkynes with alkenes and carbon monoxide. The second type of characteristic reaction is the other cyclizations such as the cyclooligomerizations and cycloadditions. The third type of characteristic reaction is the coupling reactions. The first and second type of characteristic cyclization reaction proceeds in the presence of the transition metal compounds. The third type of characteristic coupling reactions proceeds also mainly with the transition metal catalysts. All these characteristic reactions of alkynes are widely applied for organic synthesis with varioius kinds of the metal compounds.

Acknowledgments

The author would like to express sincere appreciation to Dr Sumio Chubachi for reading the full manuscript, enhancing its accuracy and clarity, and for providing much valuable constructive criticism, and also expresses sincere gratitude to Professor Leopold May for making substantial corrections and improvements.

References

[1] Omae I. *Appl. Organomet. Chem.* 2007; **21**: 318.
[2] Miyoshi K. *Hajimete Manabu Daigaku no Mukikagaku*, Kagaku Dojin: Kyoto, 1998.
[3] Wikipedia, the free encyclopedia, http://en.wikipedia.org/wiki/Alkyne.
[4] Haiduc I, Zuckerman JJ. *Basic Organometallic Chemistry*, Walter de Gruyter: Berlin, 1985.
[5] Otsuka S, Nakamura A. *Adv. Organomet. Chem.* 1976; **14**: 245.
[6] *The Organometallic Hyper TextBook: Alkyne Complexes*, www.ilpi.com/organomet/alkyne.html, 2006/12/22.
[7] Collman JP, Hegedus LS, Norton JR, Finke RG. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1987; p. 156.
[8] Maitlis PM. *The Organic Chemistry of Palladium*, Academic Press: New York, 1971.
[9] Elschenbroich C, Salzer A. *Organometallics*, VCH: New York, 1987; p. 272.
[10] Davies GR, Hewertson W, Mais RHB, Owston PG, Patel CG. *J. Chem. Soc. A*, 1970; 1873.
[11] Robertson GB, Whimp PO. *J. Organomet. Chem.* 1971; **32**: C69.
[12] Glanville JO, Stewart JM, Grim SO. *J. Organomet. Chem.* 1967; **7**: P9.
[13] Davies BW, Payne NC. *Inorg. Chem.* 1974; **13**: 1843.
[14] Davies BW, Payne NC. *Inorg. Chem.* 1974; **13**: 1848.
[15] Davies BW, Puddephatt RJ, Payne NC. *Can J. Chem.* 1972; **50**: 2276.
[16] McGinnety JA. *J. Chem. Soc. Dalton Trans.* 1974; 1038.
[17] Jacobson S, Carty AJ, Mathew M, Palenik GJ. *J. Am. Chem. Soc.* 1974; **96**: 4330.
[18] Dickson RS, Ibers JA. *J. Organomet. Chem.* 1972; **36**: 191.
[19] Walther D, Klettke T, Schmidt A, Görls H, Imhof W. *Organometallics* 1996; **15**: 2314.
[20] Kirchner RM, Ibers JA. *J. Am. Chem. Soc.* 1973; **95**: 1095.
[21] Bokiy NG, Gatilov YuV, Struchkov YuT, Ustynyuk NA. *J. Organomet. Chem.* 1973; **54**: 213.
[22] Laine RM, Moriarty RE, Bau R. *J. Am. Chem. Soc.* 1972; **94**: 1402.
[23] Ricard L, Weiss R, Newton WE, Chen GJ-J, McDonald JW. *J. Am. Chem. Soc.* 1978; **100**: 1318.
[24] Mayr A, Bastos CM, Chang RT, Haberman JX, Robinson KS, Belle-Qudry DA. *Angew. Chem. Int. Edn* 1992; **31**: 747.
[25] Mayr A, Bastos CM. *J. Am. Chem. Soc.* 1990; **112**: 7797.
[26] Nesmeyanov AN, Gusev AI, Pasynskii AA, Amisimov KN, Kolovova NE, Struchkov YuT. *J. Chem. Soc. Chem. Commun.* 1969; 277.
[27] Nesmeyanov AN, Gusev AI, Pasynskii AA, Amisimov KN, Kolovova NE, Struchkov YuT. *J. Chem. Soc. Chem. Commun.* 1969; 739.
[28] Hartung JB, Jr., Pedersen SF. *Organometallics* 1990; **9**: 1414.
[29] McLain SJ, Schrock RR, Sharp PR. *J. Am. Chem. Soc.* 1979; **101**: 263.
[30] Sly WG. *J. Am. Chem. Soc.* 1959; **81**: 18.
[31] Bailey NA, Churchill MR, Hunt R, Mason R, Wilkinson G. *Proceedings Chem. Soc. (Lond.)*, 1964; 401.
[32] Baert F, Guelzim A, Coppens P. *Acta Crystallogr.* 1984; **B40**: 590.
[33] Happ B, Bartik T, Zucchi C, Rossi MC, Váradi G, Szalontai G, Horváth IT, Chiesi-Villa A, Guastini C. *Organometallics*, 1995; **14**: 809.
[34] Baert F, Guelzim A, Poblet JM, Wiest R, Demuynck J, Bénard M. *Inorg. Chem.* 1986; **25**: 1830.
[35] Freeland BH, Hux JE, Payne NC, Tyers KG. *Inorg. Chem.* 1980; **19**: 693.
[36] Gruselle M, El Hafa H, Nikolski M, Jaouen G, Vaissermann J, Li L, McGlinchey MJ. *Organometallics* 1993; **12**: 4917.
[37] Song LC, Shen JYu, Hu OM, Han BS, Wang RJ, Wang HG. *Inorg. Chim Acta* 1994; **219**: 93.
[38] Jensen SD, Robinson BH, Simpson J. *Organometallics* 1986; **5**: 1690.
[39] Wido TM, Young GH, Wojcicki A, Calligaris M, Nardin G. *Organometallics* 1988; **7**: 452.
[40] Scott D, Smith DO, Went MJ, Farrugia L. *J. Chem. Soc. Dalton Trans.* 1989; 1375.
[41] Pauson PL. *Tetrahedron* 1985; **41**: 5855.
[42] Schore NE. *Chem. Rev.* 1988; **88**: 1081.
[43] Schore NE. *Organic Reaction* 1991; **40**: 1.
[44] Schore NE. *Comprehensive Organometallic Chemistry, II, Vol. 5* (Eds.: Wilkinson G, Stone FGA and Abel EW), Pergamon Press: Oxford, 1991; p. 1037.
[45] Brummond KM, Kent JL. *Tetrahedron* 2000; **56**: 3263.
[46] Sugihara T, Yamaguchi Nishizawa M. *Chem. Eur. J.* 2001; **7**: 1589.
[47] Welker ME. *Curr. Org. Chem.* 2001; **5**: 785.
[48] Gibson SE, Stevenazzi A. *Angew. Chem. Int. Edn* 2003; **42**: 1800.
[49] Shibata T. *Yuki Gosei Kagaku Kyokaishi* 2003; **61**: 834.
[50] Boñaga LVR, Krafft ME. *Tetrahedron* 2004; **60**: 9795.
[51] Nakamura I, Yamamoto Y. *Chem. Rev.* 2004; **104**: 2127.
[52] Blanco-Urgoiti J, Añorbe L, Pérez-Serrano L, Domínguez G, and Pérez-Castells J. *J. Chem. Soc. Rev.* 2004; **33**: 32.
[53] Park KH, Chung YK. *Synlett* 2005; 545.
[54] Gibson SE, Mainolfi N. *Angew. Chem. Int. Edn* 2005; **44**: 3022.
[55] Laschat S, Becheanu A, Bell T, Baro A. *Synlett* 2005; 2547.
[56] Geis O, Schmalz HG. *Angew. Chem. Int. Edn* 1998; **37**: 911.
[57] Berk SC, Grossman RB, Buchwald SL. *J. Am. Chem. Soc.* 1993; **115**: 4912.
[58] Berk SC, Grossman RB, Buchwald SL. *J. Am. Chem. Soc.* 1994; **116**: 8593.
[59] Hicks FA, Kablaoui NM, Buchwald SL. *J. Am. Chem. Soc.* 1996; **118**: 9450.
[60] Hicks FA, Buchwald SL. *J. Am. Chem. Soc.* 1996; **118**: 11688.
[61] Hicks FA, Kablaoui NM, Buchwald SL. *J. Am. Chem. Soc.* 1999; **121**: 5881.
[62] Hicks FA, Buchwald SL. *J. Am. Chem. Soc.* 1999; **121**: 7026.
[63] Sturla SJ, Buchwald SL. *Organometallics* 2002; **21**: 739.
[64] Subburaj K, Okamoto S, Sato F. *J. Org. Chem.* 2002; **67**: 1024.
[65] Sturla SJ, Buchwald SL. *J. Org. Chem.* 1999; **64**: 5547.
[66] Zhao Z, Ding Y, Zhao G. *J. Org. Chem.* 1998; **63**: 9825.
[67] Urabe H, Hideura D, Sato F. *Org. Lett.* 2000; **2**: 381.
[68] Grossman RB, Buchwald SL. *J. Org. Chem.* 1992; **57**: 5803.
[69] Negishi E, Holmes SJ, Tour JM, Miller JA. *J. Am. Chem. Soc.* 1985; **107**: 2568.
[70] Negishi E, Holmes SJ, Tour JM, Miller JA, Cederbaum FE, Swanson DR, Takahashi T. *J. Am. Chem. Soc.* 1989; **111**: 336.
[71] Uesaka N, Saitoh F, Mori M, Shibasaki M, Okamura K, Date T. *J. Org. Chem.* 1994; **59**: 5633.
[72] Brummond KM, Wan H, Kent JL. *J. Org. Chem.* 1998; **63**: 6535.
[73] Cao H, Flippen-Anderson J, Cook JM. *J. Am. Chem. Soc.* 2003; **125**: 3230.
[74] Mukai C, Uchiyama M, Hanaoka M. *J. Chem. Soc. Chem. Commun.* 1992; 1014.
[75] Adrio J, Rivero MR, Carretero JC. *Org. Lett.* 2005; **7**: 431.
[76] Hoye TR, Suriano JA. *Organometallics* 1992; **11**: 2044.
[77] Jeong N, Lee SJ, Lee BY, Chung YK. *Tetrahedron Lett.* 1993; **34**: 4027.
[78] Hoye TR, Suriano JA. *J. Am. Chem. Soc.* 1993; **115**: 1154.
[79] Jordi L, Segundo A, Camps F, Ricart S, Moretó JM. *Organometallics* 1993; **12**: 3795.
[80] Peason AJ, Dubbert RA. *J. Chem. Soc. Chem. Commun.* 1991; 202.
[81] Pearson AJ, Dubbert RA. *Organometallics* 1994; **13**: 1656.
[82] Kondo T, Suzuki N, Okada T, Mitsudo T. *J. Am. Chem. Soc.* 1997; **119**: 6187.
[83] Itami K, Mitsudo K, Fujita K, Ohashi Y, Yoshida J. *J. Am. Chem. Soc.* 2004; **126**: 11058.
[84] Morimoto T, Chatani N, Fukumoto Y, Murai S. *J. Org. Chem.* 1997; **62**: 3762.
[85] Itami K, Mitsudo K, Yoshida J. *Angew. Chem. Int. Edn* 2002; **41**: 3481.
[86] Mitsudo T, Kondo T. *Synlett* 2001; 309.
[87] Itami K, Mitsudo K, Fujita K, Chashi Y, Yoshida J. *J. Am. Chem. Soc.* 2004; **126**: 11058.

[88] Kondo T, Nakamura A, Okada T, Suzuki N, Wada K, Mitsudo T. *J. Am. Chem. Soc.* 2000; **122**: 6319.
[89] Jeong N, Seo SD, Shin JY. *J. Am. Chem. Soc.* 2000; **122**: 10220.
[90] Evans PA, Robinson JE. *J. Am. Chem. Soc.* 2001; **123**: 4609.
[91] Jeong N, Sung BK, Kim JS, Park SB, Seo SD, Shin JY, In KY, Choi YK. *Pure Appl. Chem.* 2002; **74**: 85.
[92] Kobayashi T, Koga Y, Narasaka K. *J. Organomet. Chem.* 2001; **624**: 73.
[93] Wender PA, Deschamps NM, Deschamps TM, Williams TJ. *Angew. Chem. Int. Edn* 2004; **43**: 3076.
[94] Koga Y, Kobayashi T, Narasaka K. *Chem. Lett.* 1998; 249.
[95] Yeh MCP, Tsao WC, Ho JS, Tai CC, Chiou DY, Tu LH. *Organometallics* 2004; **23**: 792.
[96] Shibata T, Takagi K. *J. Am. Chem. Soc.* 2000; **122**: 9852.
[97] Pagès L, Llebaria A, Camps F, Molins E, Miravitlles C, Moretó JM. *J. Am. Chem. Soc.* 1992; **114**: 10449.
[98] Zhang M, Buchwald SL. *J. Org. Chem.* 1996; **61**: 4498.
[99] Tang Y, Deng L, Zhang Y, Dong G, Chen J, Yang Z. *Org. Lett.* 2005; **7**: 1657.
[100] Muller JL, Rickers A, Leitner W. *Adv. Synth. Catal.* 2007; **349**: 287.
[101] Park KH, Son SU, Chung YK. *Chem. Commun.* 2003; 1898.
[102] Rios R, Paredes M, Pericàs A, Moyano A. *J. Organomet. Chem.* 2005; **60**: 358.
[103] Park KH, Jung IG, Chung YK. *Org. Lett.* 2004; **6**: 1183.
[104] Son SU, Park KH, Seo H, Chung YK, Lee SG. *Chem. Commun.* 2001; 2440.
[105] Kim SW, Son SU, Lee SS, Hyeon T, Chung YK. *Chem. Commun.* 2001; 2212.
[106] Son SU, Lee SI, Chung YK, Kim SW, Hyeon T. *Org. Lett.* 2002; **4**: 277.
[107] Son SU, Lee SI, Chung YK. *Angew. Chem. Int. Edn* 2000; **39**: 4158.
[108] Son SU, Park KH, Chung YK. *Org. Lett.* 2002; **4**: 3983.
[109] Jeong N, Sung BK, Choi YK. *J. Am. Chem. Soc.* 2000; **122**: 6771.
[110] Sturla SJ, Buchwald SL. *J. Org. Chem.* 2002; **67**: 3398.
[111] Hiroi K, Watanabe T, Kawagishi R, Abe I. *Tetrahedron Lett.* 2000; **41**: 891.
[112] Hiroi K, Watanabe T, Kawagishi R, Abe I. *Tetrahedron Asymm.* 2000; **11**: 797.
[113] Gibson SE, Kaufmann KAC, Lock JA, Steed JW, White AJP. *Chem. Eur. J.* 2005; **11**: 2566.
[114] Solà J, Riera A, Verdaguer X, Maestro MA. *J. Am. Chem. Soc.* 2005; **127**: 13629.
[115] Verdaguer X, Pericàs MA, Riera A, Maestro MA, Mahía J. *Organometallics* 2003; **22**: 1868.
[116] Brummond KM, Gao D. *Org. Lett.* 2003; **5**: 3491.
[117] Mukai C, Nomura I, Yamanishi K, Hanaoka M. *Org. Lett.* 2002; **4**: 1755.
[118] Brummond KM, Mitasev B. *Org. Lett.* 2004; **6**: 2245.
[119] Brummond KM, Lu J, Petersen J. *J. Am. Chem. Soc.* 2000; **122**: 4915.
[120] Evans PA, Robinson JE. *J. Am. Chem. Soc.* 2001; **123**: 4609.
[121] Cao H, Flippen-Anderson J, Cook JM. *J. Am. Chem. Soc.* 2003; **125**: 3230.
[122] Cao H, van Omum SG, Deschamps J, Flippen-Andeson J, Laib F, Cook JM. *J. Am. Chem. Soc.* 2005; **127**: 933.
[123] Mukai C, Nomura I, Kitagaki S. *J. Org. Chem.* 2003; **68**: 1376.
[124] Brummond KM, Kerekes AD, Wan H. *J. Org. Chem.* 2002; **67**: 5156.
[125] Brummond KM, Wan H. *Tetrahedron Lett.* 1998; **39**: 931.
[126] Kent JL, Wan H, Brummond KM. *Tetrahedron Lett.* 1995; **36**: 2407.
[127] Aumann R, Weidenhaupt HJ. *Chem. Ber.* 1987; **120**: 23.
[128] Shibata T, Kadowaki S, Hirase M, Takagi K. *Synlett* 2003; 573.
[129] Shibata T, Koga Y, Narasaka K. *Bull. Chem. Soc. Jpn* 1995; **68**: 911.
[130] Narasaka K, Shibata T. *Chem. Lett.* 1994; 315.
[131] Brummond KM, Chen H, Fisher KD, Kerekes AD, Richards B, Sill PC, Geib SJ. *Org. Lett.* 2002; **4**: 1931.
[132] Shibata T, Toshida N, Takagi K. *Org. Lett.* 2002; **4**: 1619.
[133] Shibata T, Toshida N, Takagi K. *J. Org. Chem.* 2002; **67**: 7446.
[134] Morimoto T, Fuji K, Tsutsumi K, Kakiuch K. *J. Am. Chem. Soc.* 2002; **124**: 3806.
[135] Fuji K, Morimoto T, Tsutsumi K, Kakiuchi K. *Angew. Chem. Int. Edn* 2003; **42**: 2409.
[136] Morimoto T, Fuji K, Tsutsumi K, Kakiuchi K. *J. Am. Chem. Soc.* 2002; **124**: 3806.
[137] Shibata T, Toshida N, Takagi K. *Org. Lett.* 2002; **4**: 1619.
[138] Shibata T, Toshida N, Tagagi K. *J. Org. Chem.* 2002; **67**: 7446.
[139] Park KH, Jung IG, Chung YK. *Org. Lett.* 2004; **6**: 1183.
[140] Kablaoui NM, Hicks FA, Buchwald SL. *J. Am. Chem. Soc.* 1996; **118**: 5818.
[141] Kablaoui NM, Hicks FA, Buchwald SL. *J. Am. Chem. Soc.* 1997; **119**: 4424.
[142] Tobisu M, Chatani N, Asaumi T, Amako K, Ie Y, Fukumoto Y, Murai S. *J. Am. Chem. Soc.* 2000; **122**: 12663.
[143] Chatani N, Morimoto T, Fukumoto Y, Murai S. *J. Am. Chem. Soc.* 1998; **120**: 5335.
[144] Chatani N, Morimoto T, Kamitani A, Fukumoto Y, Murai S. *J. Organomet. Chem.* 1999; **579**: 177.
[145] Hicks FA, Berk SC, Buchwald SL. *J. Org. Chem.* 1996; **61**: 2713.
[146] Reppe W, Schlichting O, Klager K, Toepel T. *Liebigs Ann. Chem.* 1948; **560**: 1.
[147] Schrauzer GN. *Chem. Ber.* 1961; **94**: 1403.
[148] Leto JR, Leto MF. *J. Am. Chem. Soc.* 1961; **83**: 2944.
[149] Reppe W, Schweckendiek WJ. *Liebigs Ann. Chem.* 1948; **560**: 104.
[150] Dändliker G. *Helv. Chim. Acta* 1969; **52**: 1482.
[151] Reppe W, von Kutepow N, Magin A. *Angew. Chem. Int. Edn Engl.* 1969; **8**: 727.
[152] Rejchsfel'd VO, Lein BI, Makoveckij KL. *Dokl. Akad. Nauk SSSR* 1971; 190.
[153] Iwashita Y, Tamura F. *Bull. Chem. Soc. Jpn* 1970; **43**: 1517.
[154] Dietl H, Reinheimer H, Moffat J, Maitlis PM. *J. Am. Chem. Soc.* 1970; **92**: 2276.
[155] Chalk AJ, Jerussi RA. *Tetrahedron Lett.* 1972; 61.
[156] Collman JP, Wang JW, Little WF, Sullivan MF. *Inorg. Chem.* 1968; **7**: 1298.
[157] Grotjahn DB. *Comprehensive Organometallic Chemistry, II, Vol. 8* (Eds.: Abel EW, Stone FGA and Wilkinson G), Pergamon Press: Oxford, 1995; p. 741.
[158] Vollhardt KPC (translator, Yamazaki H), *Kagaku Zokan* 1985; **105**: 165.
[159] Wen TC, Chang CC, Chuang YD, Chiu JP, Chang CT. *J. Am. Chem. Soc.* 1981; **103**: 4576.
[160] Hill JE, Balaich G, Fanwick PE, Rothwell IP. *Organometallics* 1993; **12**: 2911.
[161] Hashizumi K, Mizobe Y, Hidai H. *Organometallics* 1995; **14**: 5367.
[162] Willams AC, Sheffels P, Sheehan D, Livinghouse T. *Organometallics* 1989; **8**: 1566.
[163] Peters C, Fischbeck U, Tabellion F, Regitz M, Preuss F. *Naturforschung* 2003; **58b**: 44.
[164] Tsutsui M, Zeiss H. *J. Am. Chem. Soc.* 1959; **81**: 6090.
[165] Moulijn JA, Reitsma HJ, Boelhouwer C. *J. Catal* 1972; **25**: 434.
[166] Ferré K, Toupet L, Guerchais V. *Organometallics* 2002; **21**: 2578.
[167] Yamazaki H, Wakatsuki Y. *J. Organomet. Chem.* 1977; **139**: 157.
[168] McAlister DR, Bercaw JE, Bergman RG. *J. Am. Chem. Soc.* 1977; **99**: 1666.
[169] Borwieck H, Walter O, Dinjus WE, Rebizant EJ. *J. Organomet. Chem.* 1998; **570**: 121.
[170] Mamane V, Gref A, Lefloch G, Riant O. *J. Organomet. Chem.* 2001; **637–639**: 84.
[171] Diercks R, Eaton RE, Gürtzgens S, Jalisatgi S, Matzger AJ, Radde RH, Vollhard KPC. *J. Am. Chem. Soc.* 1998; **120**: 8247.
[172] Bianchini C, Caulton KG, Chardon C, Eisenstein O, Folting K, Johnson TJ, Meli A, Peruzzini M, Rauscher DJ, Streib WE, Vizza F. *J. Am. Chem. Soc.* 1991; **113**: 5127.
[173] Bianchini C, Caulton KG, Chardon C, Doublet ML, Eisenstein O, Jackson SA, Johnson TJ, Meli A, Peruzzini M, Streib WE, Vacca A, Vizza F. *Organometallics* 1994; **13**: 2010.
[174] Maitlis PM. *J. Organomet. Chem.* 1980; **200**: 161.
[175] Eisch JJ, Galle JE, Aradi AA, Boleslawski MP. *J. Organomet. Chem.* 1986; **312**: 399.
[176] Eisch JJ, Aradi AA, Lucarelli MA, Qian Y. *Tetrahedron* 1998; **54**: 1169.
[177] Jhingan AK, Maier WF. *J. Org. Chem.* 1987; **52**: 1161.
[178] Maderna A, Pritzkow H, Siebert W. *Angew. Chem. Int. Edn* 1996; **35**: 1501.
[179] Vollhardt KPC. *Angew. Chem. Int. Edn* 1984; **23**: 539.
[180] Grotjahn DB, Vollhardt KPC. *Synthesis* 1993; 579.
[181] Frühauf HW. *Chem. Rev.* 1997; **97**: 523.
[182] Funk RL, Vollhardt KPC. *J. Am. Chem. Soc.* 1980; **102**: 5253.
[183] Colborn RE, Vollhardt KPC. *J. Am. Chem. Soc.* 1981; **103**: 6259.
[184] Wilke G. *Pure & Appl. Chem.* 1978; **50**: 677.
[185] Hagihara N. *Shokubai*, 1980; **22**: 323.
[186] Dierck HT, Lauer AM, Stamp L, Diercks R. *J. Mol. Cat.* 1986; **35**: 317.
[187] Lawrie CJ, Gable KP, Carpenter BK. *Organometallics* 1989; **8**: 2274.

[188] Leadbeater NE. *J. Org. Chem.* 2001; **66**: 7539.

[189] Shibata T, Yamashita K, Ishida H, Takagi K. *Org. Lett.* 2001; **3**: 1217.

[190] Shibata T, Yamashita K, Katayama E, Takagi K. *Tetrahedron* 2002; **58**: 8661.

[191] Saito S, Yamamoto Y. *Chem. Rev.* 2000; **100**: 2901.

[192] Rausch MD, Genetti RA. *J. Org. Chem.* 1970; **35**: 3888.

[193] Skoda-Földes R, Kollár L. *Chem. Rev.* 2003; **103**: 4095.

[194] Song Z, Li Y, Liu M, Cong L, Liu Y. *Organometallics* 2006; **25**: 5035.

[195] Shibata T, Takami K, Kawachi A. *Org. Lett.* 2006; **8**: 1343.

[196] Shen Q, Hammond GB. *J. Am. Chem. Soc.* 2002; **124**: 6534.

[197] Yamamoto Y, Nagata A, Itoh K. *Tetrahedron Lett.* 1999; **40**: 5035.

[198] Sato Y. *Yakukagaku Kenkyu no Shinpo* 2003; **19**: 43.

[199] a) Yamamoto Y. *Yuki Gosei Kagaku Kyokaishi* 2005; **63**: 112; b) Yamamoto Y. *Current Org. Chem.* 2005; **9**: 503.

[200] Diercks R, Eaton BE, Gürtzgens S, Jalisatgi S, Matzger AJ, Radde RH, Vollhard KPC. *J. Am. Chem. Soc.* 1998; **120**: 8247.

[201] Evenzahav A, Turro NJ. *J. Am. Chem. Soc.* 1998; **120**: 1835.

[202] Kezuka S, Tanaka S, Ohe T, Nakaya Y, Takeuchi R. *J. Org. Soc.* 2006; **71**: 543.

[203] Sato Y, Tamura T, Kinbara A, Mori M. *Adv. Synth. Catal.* 2007; **349**: 647.

[204] Lian J, Odedra A, Wu C, Liu R. *J. Am. Chem. Soc.* 2005; **127**: 4186.

[205] Lian J, Lin C, Chang H, Chen P, Liu R. *J. Am. Chem. Soc.* 2006; **128**: 9661.

[206] Onodera G, Matsumoto H, Milton MD, Nishibayashi Y, Uemura S. *Org. Lett.* 2005; **7**: 4029.

[207] Kim D, Pestersen JL, Wang KK. *Org. Lett.* 2006; **8**: 2313.

[208] Taduri BP, Ran Y, Huang C, Liu R. *Org. Lett.* 2006; **8**: 883.

[209] Magnus P, Carter PA. *J. Am. Chem. Soc.* 1988; **110**: 1626.

[210] Diercks R, Vollhardt KPC. *J. Am. Chem. Soc.* 1986; **108**: 3150.

[211] Sternberg ED, and Vollhardt KPC. *J. Org. Chem.* 1984; **49**: 1574.

[212] Peter K, Vollhardt C. *Angew. Chem. Int. Edn* 1984; **23**: 539.

[213] Zhou Z, Battaglia LP, Chiusoli GP, Costa M, Nardelli M, Pelizzi C, Predieri GJ. *Chem. Soc. Chem. Commun.* 1990; 1632.

[214] Halterman RL, and Vollhardt KPC. *Organometallics* 1988; **7**: 883.

[215] Slowinski F, Aubert C, Malacria M. *Tetrahedron Lett.* 1999; **40**: 707.

[216] Slowinski F, Aubert C, Malacria M. *Tetrahedron Lett.* 1999; **40**: 5849.

[217] Sternberg ED, Vollhardt KPC. *J. Org. Chem.* 1982; **47**: 3447.

[218] Slowinski F, Aubert C, and Malacria M. *J. Org. Chem.* 2003; **68**: 378.

[219] Kezuka S, Okado T, Niou E, Takeuchi R. *Org. Lett.* 2005; **7**: 1711.

[220] Tanaka H, Yamada H, Matsuda A, Takahashi T. *Synlett* 1997; 381.

[221] Kanno K, Takahashi T. *Kagaku Kogyo* 2004; **55**: 1.

[222] Brien DJ, Naiman A, Vollhardt KPC. *J. Chem. Soc. Chem. Commun.* 1982; 133.

[223] Tatone D, Dich TC, Nacco R, Botteghi C. *J. Org. Chem.* 1975; **40**: 2987.

[224] Fatland AW, Eaton BE. *Org. Lett.* 2000; **2**: 3131.

[225] Bönnemann H. *Angew. Chem. Int. Edn* 1978; **17**: 505.

[226] Bönnemann H, Brinkmann R, Schenkluhn H. *Synthesis* 1974; 575.

[227] Bönnemann H. *Angew. Chem. Int. Edn* 1985; **24**: 248.

[228] Boñaga LVR, Zhang H-C, Gauthier DA, Reddy I, Maryanoff BE. *Org. Lett.* 2003; **5**: 4537.

[229] Saito S, Yamamoto Y. *Chem. Rev.* 2000; **100**: 2901.

[230] Varela JA, Saá C. *Chem. Rev.* 2003; **103**: 3787.

[231] Osei-Owusu A, Martin GC, Gotro JT. *Polym. Engng Sci.* 1992; **32**: 535.

[232] Naiman A, Vollhardt KPC. *Angew. Chem. Int. Edn* 1977; **16**: 708.

[233] Gutnov A, Heller B, Fischer C, Drexler H-J, Spannenberg A, Sundermann B, Sundermann C. *Angew. Chem. Int. Edn* 2004; **43**: 3795.

[234.] a) Hrdina B, Kadlčíková A, Valterová I, Hodačová J, Kotora M. *Tetrahedron Asymm.* 2006; **17**: 3185; b) Hrdina R, Stará IG, Dufková L, Mitchel S, Císaová I, Korora M. *Tetrahedron* 2006; **62**: 968.

[235] McCormick MM, Duong HA, Zuo G, Louie J. *J. Am. Chem. Soc.* 2005; **127**: 5030.

[236] Kase K, Goswami A, Ohtaki K, Tanabe E, Saino N, Okamoto S. *Org. Lett.* 2007; **9**: 931.

[237] Dazinger M, Torres-Rodrigues M, Kirchner K, Calhorda MJ, Costa PJ. *J. Organomet. Chem.* 2006; **691**: 4434.

[238] Earl RA, Vollhardt KPC. *J. Am. Chem. Soc.* 1983; **105**: 6991.

[239] Yu RT, Rovis T. *J. Am. Chem. Soc.* 2006; **128**: 12370.

[240] Yu RT, Rovis T. *J. Am. Chem. Soc.* 2006; **128**: 2782.

[241] Wakter H, Schönberg WH, Dinjus E, Sieler J. *J. Organomet. Chem.* 1987; **334**: 337.

[242] Walther H. *Coord. Chem. Rev.*, 1987; **79**: 135.

[243] Tsuda T. *Kagaku Kogyo*, 1992; **43**: 654.

[244] Bou A, Pericàs MA, and Serratosa F. *Tetrahedron Lett.* 1982; **23**: 361.

[245] Bou A, Pericàs MA, Serratosa F, Claret J, Feliu JM, Muller CJ. *J. Chem. Soc. Chem. Commun.* 1982,; 1305.

[246] Serratosa F. *Acc. Chem. Res.* 1983; **16**: 170.

[247] http,//en.wikipedia.org/wiki/Azide_alkyne_Huisgen_cycloaddition.

[248] Girard C, Önen E, Aufort M, Beauvière S Samson E, Herscovici J. *Org. Lett.* 2006; **8**: 1689.

[249] Detz RJ, Heras SA, de Gelder R, van Leeuwen PWNM, Hiemstra H, Reek JNH, van Maarseveen JH. *Org. Lett.* 2006; **8**: 3227.

[250] Thibault RJ, Takizawa K, Lowenhellm P, Helms B, Mynar JL, Fréchet JMJ, Hawker CJ. *J. Am. Chem. Soc.* 2006; **128**: 12084.

[251] Pirali T, Tron GC, Zhu J. *Org. Lett.* 2006; **8**: 4145.

[252] Partyka DV, III Updegraff JB, Zeller M, Hunter AD, Gray TG. *Organometallics* 2007; **26**: 183.

[253] Herath A, Montgomery J. *J. Am. Chem. Soc.* 2006; **128**: 14030.

[254] Mahandru GM, Skauge ARL, Chowdhury SK, Amarasinghe KKD, Heeg MJ, Montgomery J. *J. Am. Chem. Soc.* 2003; **125**: 13481.

[255] Gevorgyan V, Yamamoto Y. *J. Organomet. Chem.* 1999; **576**: 232.

[256] Aikawa K, Akutagawa S, Mikami K. *J. Am. Chem. Soc.* 2006; **128**: 12648.

[257] Lian J, Lin C, Chang H, Chen P, Liu R. *J. Am. Chem. Soc.* 2006; **128**: 9661.

[258] Hilt G, Hess W, Harms K. *Org. Lett.* 2006; **8**: 3287.

[259] Rubina M, Conley M, Gevorgyan V. *J. Am. Chem. Soc.* 2006; **128**: 5818.

[260] Gevorgyan V, Yamamoto Y. *J. Organomet. Chem.* 1999; **576**: 232.

[261] Etkin N, Dzwiniel TL, Schwiebert KE, Stryker JM. *J. Am. Chem. Soc.* 1998; **120**: 9702.

[262] Dzwiniel TL, Etkin N, Stryker JM. *J. Am. Chem. Soc.* 1999; **121**: 10640.

[263] Dzwiniel TL, Stryker JM. *J. Am. Chem. Soc.* 2004; **126**: 9184.

[264] Saito S, Masuda M, Komagawa S. *J. Am. Chem. Soc.* 2004; **126**: 10540.

[265] Komagawa S, Saito S. *Angew. Chem. Int. Edn* 2006; **45**: 2446.

[266] Ni Y, Montgomery J. *J. Am. Chem. Soc.* 2006; **128**: 2609.

[267] Murakami M, Ashida S, Matsuda T. *J. Am. Chem. Soc.* 2006; **128**: 2166.

[268] Trost BM, Frederiksen MU, Rudd MT. *Angew. Chem. Int. Ed.* 2005; **44**: 6630.

[269] Gandon V, Agenet N, Vollhardt KPC, Malacria M, Aubert C. *J. Am. Chem. Soc.* 2006; **128**: 8509.

[270] Varela JA, Rubin SG, González-Rodriguez C, Castedo L, Saá C. *J. Am. Chem. Soc.* 2006; **128**: 9262.

[271] Tsuchikama K, Kuwata Y, Shibata T. *J. Am. Chem. Soc.* 2006; **128**: 13686.

[272] Chen C, Xi C, Ai Z, Hong X. *Org. Lett.* 2006; **8**: 4055.

[273] Xi C, Chen C, Lin J, Hong X. *Org. Lett.* 2005; **7**: 347.

[274] Tanaka K, Takeishi K, Noguchi K. *J. Am. Chem. Soc.* 2006; **128**: 4586.

[274a] Novák P, Pohl R, Kotora M, Hocek M. *Org. Lett.* 2006; **8**: 2051.

[275] Saino N, Kogure D, Kase K, Okamoto S. *J. Organomet. Chem.* 2006; **691**: 3129.

[276] Deng L, Chan H, Xie Z. *J. Am. Chem. Soc.* 2006; **128**: 7728.

[277] Yao X, Li C. *Org. Lett.* 2006; **8**: 1953.

[278] Xu J, Wang Y, Burton DJ. *Org. Lett.* 2006; **8**: 2555.

[279] Tanaka K, Wada A, Noguchi K. *Org. Lett.* 2006; **8**: 907.

[280] Nishida G, Suzuki N, Noguchi K, Tanaka K. *Org. Lett.* 2006; **8**: 3489.

[281] Yamamoto Y, Hattori K, Nishiyama H. *J. Am. Chem. Soc.* 2006; **128**: 8336.

[282] Elschenbroich C, Salzer A. *Organometallics*, VCH: New York, 1989; p. 249.

[283] Burkhart GH, Hoberg H. *Angew. Chem. Int. Edn* 1982; **21**: 76.

[284] Huang W, Chan J, Jamison TF. *Org. Lett.* 2000; **2**: 4221.

[285] Takai K, Sakamoto S, Isshiki T. *Org. Lett.* 2003; **5**: 653.

[286] Miller KM, Huang WS, Jamison TF. *J. Am. Chem. Soc.* 2003; **125**: 3442.

[287] Jang HY, Huddleston RR, Krische MJ. *J. Am. Chem. Soc.* 2004; **126**: 4664.

[288] Mahandru GM, Liu G, Montgomery J. *J. Am. Chem. Soc.* 2004; **126**: 3698.

[289] Luanphaisarnnont T, Ndubaku CO, Jamison TF. *Org. Lett.* 2005; **7**: 2937.

[290] Moslin RM, Jamison TF. *Org. Lett.* 2006; **8**: 455.

[291] Komanduri V, Krische MJ. *J. Am. Chem. Soc.* 2006; **128**: 16448.

[292] Wolf C, Liu S. *J. Am. Chem. Soc.* 2006; **128**: 10996.

[293] Guillarme S, Plé K, Banchet A, Liard A, Haudrechy A. *Chem. Rev.* 2006; **106**: 2355.

[294] Jeon S, Fisher EL, Carroll PJ, Walsh PJ. *J. Am. Chem. Soc.* 2006; **128**: 9618.

[295] Tsukamoto H, Ueno T, Kondo Y. *J. Am. Chem. Soc.* 2006; **128**: 1406.

[296] Charve SN, Choo H, Cha JH, Pae AN, Choi KI, Cho YS. *Org. Lett.* 2006; **8**: 3617.

[297] Cho C, Krische MJ. *Org. Lett.* 2006; **8**: 891.

[298] Wang S, Tu Y, Chen P, Hu X, Zhang F, Wang A. *J. Org. Chem.* 2006; **71**: 4343.

[299] Kong JR, Ngai M, Krische MJ. *J. Am. Chem. Soc.* 2006; **128**: 718.

[300] Ngai M, Barchuk A, Krische MJ. *J. Am. Chem. Soc.* 2007; **129**: 280.

[301] Miller KM, Jamison TF. *Org. Lett.* 2005; **7**: 3077.

[302] Engel DA, Dudley GB. *Org. Lett.* 2006; **8**: 4027.

[303] Liu Y, Liu M, Guo S, Tu H, Zhou Y, Gao H. *Org. Lett.* 2006; **8**: 3445.

[304] Dai G, Larock RC. *J. Org. Chem.* 2003; **68**: 920.

[305] Dai G, Larock RC. *Org. Lett.* 2001; **3**: 4035.

[306] Huang Q, R. Larock RC. *Tetrahedron Lett.* 2002; **43**: 3557.

[307] Hung Q, Larock RC. *J. Org. Chem.* 2003; **68**: 980.

[308] Dai G, Larock RC. *Org. Lett.* 2002; **4**: 193.

[309] Dai G, Larock RC. *J. Org. Chem.* 2002; **67**: 7042.

[310] Kang J, Kim H, Lee J, Shin S. *Org. Lett.* 2006; **8**: 3537.

[311] Kusama H, Suzuki Y, Takaya J, Iwasawa N. *Org. Lett.* 2006; **8**: 895.

[312] Sergin IV, Gevorgyan V. *J. Am. Chem. Soc.* 2006; **128**: 12050.

[313] Trost BM, Machacek M, Schnaderbeck MJ. *Org. Lett.* 2000; **2**: 1761.

[314] López F, Castedo L, Mascareñas J. *J. Am. Chem. Soc.* 2002; **124**: 4218.

[315] Trost BM, Chisholm JD, Wrobleski ST, Jung M. *J. Am. Chem. Soc.* 2002; **124**: 12420.

[316] Trost BM, Papillon JPN. *J. Am. Chem. Soc.* 2004; **126**: 13618.

[317] Trost BM, Papillon JPN, Nussbaumer T. *J. Am. Chem. Soc.* 2005; **127**: 17921.

[318] Shimamoto T, Chimori M, Sogawa H, Yamamoto K. *J. Am. Chem. Soc.* 2005; **127**: 16410.

[319] Wang C, Lin P, Cheng C. *J. Am. Chem. Soc.* 2002; **124**: 9696.

[320] Yoshimatsu M, Kinoshita S, Sugimoto T. *Chem. Pharm. Bull.* 1999; **47**: 1497.

[321] Wang C, Lin P, Cheng C. *J. Am. Chem. Soc.* 2002; **124**: 9696.

[322] Kuninobu Y, Nishina Y, Takai K. *Org. Lett.* 2006; **8**: 2891.

[323] Paih JL, Rodríguesz DC, Dérien S, Dixneuf PH. *Synlett* 2000; 95.

[324] Trost BM. *Acc. Chem. Res.* 1990; **23**: 34.

[325] Buzas A, Gagosz F. *J. Am. Chem. Soc.* 2006; **128**: 12614.

[326] Wang S, Zhang L. *J. Am. Chem. Soc.* 2006; **128**: 14274.

[327] Lin MY, Das A, Liu RS. *J. Am. Chem. Soc.* 2006; **128**: 9340.

[328] Fehr C, Farris I, Sommer H. *Org. Lett.* 2006; **8**: 1839.

[329] Kim H, Lee C. *J. Am. Chem. Soc.* 2006; **128**: 6336.

[330] Shintani R, Yashio K, Nakamura T, Okamoto K, Shimada T, Hayashi T. *J. Am. Chem. Soc.* 2006; **128**: 2772.

[331] Joo JM, Yuan Y, Lee C. *J. Am. Chem. Soc.* 2006; **128**: 14818.

[332] Movassaghi M, Hill MD. *J. Am. Chem. Soc.* 2006; **128**: 4592.

[333] Menz H, Kirsch SF. *Org. Lett.* 2006; **8**: 4795.

[334] Jayanth TT, Jeganmohan M, Cheng M, Chu S, Cheng C. *J. Am. Chem. Soc.* 2006; **128**: 2232.

[335] Mori M, Uesaka N, Saitoh F, Shibasaki M. *J. Org. Chem.* 1994; **59**: 5643.

[336] Chatani N, Furukawa N, Sakurai H, Murai S. *Organometallics* 1996; **15**: 901.

[337] Sturla SJ, Kablaoui NM, Buchwald SL. *J. Am. Chem. Soc.* 1999; **121**: 1976.

[338] Cao P, Wang B, Zhang X. *J. Am. Chem. Soc.* 2000; **122**: 6490.

[339] Kim SM, Lee SI, Chung YK. *Org. Lett.* 2006; **8**: 5425.

[340] Urabe H, Suzuki D, Sasaki M, Sato F. *J. Am. Chem. Soc.* 2003; **125**: 4036.

[341] Blaszykowski C, Harrak Y, Goncalves MH, Cloarec JM, Dhimane AL, Fensterbank L, Malacria M. *Org. Lett.* 2004; **6**: 3771.

[342] Harrak Y, Blaszykowski C, Bernard M, Cariou K, Mainetti E, Mouriès V, Dhimane AL, Fensterbank L, Malacria M. *J. Am. Chem. Soc.* 2004; **126**: 8656.

[343] Staben ST, Kennedy-Smith JJ, Huang D, Corkey BK, LaLonde RL, Toste FD. *Angew. Chem. Int. Edn* 2006; **45**: 5991.

[344] Toullec PY, Genin E, Leseurre L, Genêt JP, Michelet V. *Angew. Chem. Int. Edn* 2006; **45**: 7427.

[345] Nevado C, Charruault L, Michelet V, Nieto-Oberhuber C, Muñoz MP, Méndez M, Rager MN, Genêt JP, Echavarren AM. *Eur. J. Org. Chem.* 2003; 706.

[346] Maddess ML, Mainetti E, Harrak Y, Brancour C, Devin P, Dhimane AL, Fensterbank L, Malacria M. *Chem. Commun.* 2007; 936.

[347] Chatani N, Inoue H, Kotsuma T, Murai S. *J. Am. Chem. Soc.* 2002; **124**: 10294.

[348] Chatani N, Morimoto T, Muto T, Murai S. *J. Am. Chem. Soc.* 1994; **116**: 6049.

[349] Duan X, Guo L, Bi H, Liu X, Liang Y. *Org. Lett.* 2006; **8**: 3053.

[350] Suginome M, Yamamoto A, Murakimi M. *J. Am. Chem. Soc.* 2003; **125**: 6358.

[351] Hercouet A, Berrée F, Lin CH, Toupet C, Carboni B. *Org. Lett.* 2007; **9**: 1717.

[351a] Lee SI, Kim SM, Choi MR, Kim SY, Chu YK, Han WS, Kang SO. *J. Org. Chem.* 2006; **71**: 9366.

[352] Nishizawa M, Takao H, Yadav VK, Imagawa H, Sugihara T. *Org. Lett.* 2003; **5**: 563.

[353] Pastine SJ, Youn SW, Sames D. *Org. Lett.* 2003; **5**: 1055.

[354] Tsuchimoto T, Maeda T, Shirakawa E, Kawakami Y. *Chem. Commun.* 2000; 1573.

[355] Nakao Y, Kanyiva KS, Oda S, Hiyama T. *J. Am. Chem. Soc.* 2006; **128**: 8146.

[356] Tsuchimoto T, Hatanaka K, Shirakawa E, Kawakami Y. *Chem. Commun.* 2003; 2454.

[357] Shintani R, Okamoto K, Hayashi T. *J. Am. Chem. Soc.* 2005; **127**: 2872.

[358] Shintani R, Yashio K, Nakamura T, Okamoto K, Shimada T, Hayasi T. *J. Am. Chem. Soc.* 2006; **128**: 2772.

[359] Jayanth TT, Jeganmohan M, Cheng M, Chu S, Cheng C. *J. Am. Chem. Soc.* 2006; **128**: 2232.

[360] Nakao Y, Yukawa T, Hirata Y, Oda S, Satoh J, Hiyama T. *J. Am. Chem. Soc.* 2006; **128**: 7116.

[361] Shibata T, Koga Y, Narasaka K. *Bull. Chem. Soc. Jpn.* 1995; **68**: 911.

[362] Older CM, Stryker JM. *Organometallics* 2000; **19**: 2661.

[363] Rutledge TF. *Acetylene Compounds*, Reinhold: New York, 1968; p. 245.

[364] Aschwanden P, Carreira EM. *Acetylene Chemistry* (Eds.: Diederich F, Stang PJ and Tykwinskib RR), Wiley-VCH: Weinheim, 2005; p. 101.

[365] www.organic-chemistry.org/namedreactions/glaser-coupling.shtm.

[366] www.organic-chemistry.org/namedreactions/cadiot-chodkiewicz-coupling.shtm.

[367] http//en.wikipedia.org/wiki/Cadiot-Chodkiewicz_coupling.

[368] www.organic-chemistry.org/namedreactions/eglinton-reaction.shtm.

[369] Ziessel R, Suffert J, Youinou MT. *J. Org. Chem.* 1996; **61**: 6535.

[370] Suginome M, Shirakura M, Yammoto A. *J. Am. Chem. Soc.* 2006; **128**: 14438.

[371] Chinchilla R, Nájera C. *Chem. Rev.* 2007; **107**: 874.

[372] www.organic-chemistry.org/namedreactions/sonogashira-coupling.shtm.

[373] http//en.wikipedia.org/wiki/Sonogashira_coupling.

[374] Elangovan A, Wang Y, Ho T. *Org. Lett.* 2003; **5**: 1841.

[375] Eckhardt M, Fu GC. *J. Am. Chem. Soc.* 2005; **125**: 13642.

[376] Ruiz J, Cutillas N, López F, López G, Bautista D. *Organometallics* 2006; **25**: 5768.

[377] Lu BZ, Zhao W, Wei H, Dufour M, Farina V, Senavayake CH. *Org. Lett.* 2006; **8**: 3271.

[378] Liang Y, Xie YX, Li JH. *J. Org. Chem.*, 2006; **71**: 379.

[379] Gholap AR, Venkatesan K, Pasricha R, Daniel T, Lahoti RJ, Srinivasan KV. *J. Org. Chem.* 2005; **70**: 4869.

[380] Yi C, Hua R. *J. Org. Chem.* 2006; **71**: 2535.

[381] Liang B, Dai M, Chen J, Yang Z. *J. Org. Chem.* 2005; **70**: 391.

[382] Batey RA, Shen M, Lough AJ. *Org. Lett.* 2002; 1411.

[383] Lemay AB, Vulic KS, Ogilvie WW. *J. Org. Chem.* 2006; **71**: 3615.

[384] Karpov AS, Müller TJJ. *Synthesis* 2003; 2815.

[385.] a) Larock RC. *Acetylene Chemistry* (Eds.: Diederich F, Stang PJ and Tykwinski RR), Wiley-VCH: Weinheim, 2005; p. 51; b) *Acetylene Compounds*, Reinhold: New York, 1968; p. 51.

[386] Genin E, Toullec PY, Antoniotti S, Brancour C, Genêt JP, Michelet V. *J. Am. Chem. Soc.* 2006; **128**: 3112.

[387] Zhang L, Wang S. *J. Am. Chem. Soc.* 2006; **128**: 1442.

[388] Dubé P, Toste FD. *J. Am. Chem. Soc.* 2006; **128**: 12062.

[389] Fukumoto Y, Kinashi F, Kawahara T, Chatani N. *Org. Lett.* 2006; **8**: 4641.

[390] Ambrogio I, Cacchi S, Fabrizi G. *Org. Lett.* 2006; **8**: 2083.

[391] Carballo RM, Ramírez MA, Rodríguez ML, Martím VS, Padrón JI. *Org. Lett.* 2006; **8**: 3837.

[392] Ishikawa T, Aikawa T, Watanabe S, Saito S. *Org. Lett.* 2006; **8**: 3881.

[393] Panne P, Fox JM. *J. Am. Chem. Soc.* 2007; **129**: 22.
[394] Belting V, Krause N. *Org. Lett.* 2006; **8**: 4489.
[395] Liang Y, Tang S, Zhang X, Mao L, Xie Y, Li J. *Org. Lett.* 2006; **8**: 3017.
[396] Cunha RLOR, Zukerman-Schpector J, Caracelli I, Comasseto JV. *J. Organomet. Chem.* 2006; **691**: 4807.
[397] Ueura K, Satoh T, Miura M. *J. Org. Chem.* 2007; **72**: 5362.
[398] Arcadi A, Cacchi S, Marinelli F. *Tetrahedron Lett.* 1989; **30**: 2581.
[399] Huo Z, Patil NT, Jin T, Pahadi NK, Yamamoto Y. *Adv. Synth. Catal.* 2007; **349**: 680.
[400] Asao N, Iso K, Yudha S. *Org. Lett.* 2006; **8**: 4149.
[401] Sakaguchi S, Mizuta T, Ishii Y. *Org. Lett.* 2006; **8**: 2459.
[402] Nakamura I, Yamagishi U, Song D, Konta S, Yamamoto Y. *Angew. Chem. Int. Edn* 2007; **46**: 2284.
[403] Duan X, Guo L, Bi H, Liu X, Liang Y. *Org. Lett.* 2006; **8**: 3053.
[404] Harada T, Kitano C, Mizunashi K. *Synlett*, 2007; 1130.
[405] Strat FL, Maddaluno J. *Org. Lett.* 2002; **4**: 2791.
[406] Harada T, Mizunashi K, Muramatsu K. *Chem. Commun.* 2006; 638.
[407] Nevado C, Echavarren AM. *Synthesis*, 2005; 167.
[408] Shintani R, Hayashi T. *Org. Lett.* 2005; **7**: 2071.
[409] Jung IG, Seo J, Lee SI, Choi SY, Chung YK. *Organometallics* 2006; **25**: 4240.
[410] Rhee KU, Krische MJ. *J. Am. Chem. Soc.* 2006; **128**: 10674.
[411] Field LD, Ward AJ. *J. Organomet. Chem.* 2003; **681**: 91.