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New Catalytic Performances of Ruthenium and Rhodium Complexes Directed toward Organic Synthesis with High Atom Efficiency

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Low-valent ruthenium complexes often show intriguing and characteristic catalytic activity for novel organic transformations with high atom efficiency. The design and synthesis of novel low-valent ruthenium complexes having a variety of electron-donating and/or electron-withdrawing ligands is most promising strategy. Several ruthenium catalysts achieved the construction of novel functional organic molecules through cleavage of carbon–carbon single bonds, cocyclization of alkynes, alkenes, and/or carbon monoxide, and co-oligomerization of different alkenes without formation of by-products, which meets green and sustainable requirements for organic synthesis in the 21st century. Note that many findings in ruthenium catalysis have opened the door to a new field of rhodium-catalyzed synthetic organic chemistry, represented by cocyclization of alkynes and heterocumulenes.

1. Introduction

Because of remarkable progress in the field of organic and industrial chemistry, a lot of nonnatural organic compounds represented by medicines, detergents, cosmetics, and plastics can be supplied in bulk and inexpensively, which makes our lifestyles more comfortable and convenient. However, we are now facing serious environment and resource problems. Internationally, resource/energy-consuming products and processes will no longer be viable in the near future. The objective is not to reduce the cost or satisfy legal regulations, and from a long range outlook, chemistry plays a significant role in the development of products and processes that satisfy both environmental needs and economic growth by advanced molecular transformations of carbon resources, which gives only the desired and new materials with high atom efficiency (without by-products) for the sustainable growth of society in the 21st century.[1]

We believe transition-metal catalysts to be the key to solving problems in traditional organic synthesis. Among organic reactions, addition and rearrangement reactions are highly atom-efficient, since in these reactions all the atoms of the starting materials are incorporated into the products without formation of wastes. On the other hand, substitution and elimination reactions have serious drawbacks in atom efficiency because the formation of an equimolar amount of by-products is inevitable.

Our strategy based on an addition reaction is development of new transformations of unsaturated compounds, such as alkynes and alkenes, through ruthenium- and rhodium-catalyzed cleavage and formation of carbon–carbon bonds. This is a potentially useful and important protocol for construction of novel organic molecules, since they are highly atom-economical, in contrast to cross-coupling reactions providing a significant amount of undesirable metal salts.[2]

Here, we review the results of our recent study on new catalytic capabilities of ruthenium and rhodium complexes directed toward organic synthesis with high atom efficiency.

2. Chemistry of (η^6-1,3,5-Cyclooctatriene)bis(η^2-dimethyl fumarate)ruthenium

A variety of synthetic organic reactions catalyzed by ruthenium complexes have been rapidly developed over the past three decades by taking advantage of their characteristic reactivity.[3,4] Zero-valent ruthenium complexes have an electron-rich metal center which is favorable for a metal-oxidation step such as oxidative addition and cyclization reactions. Thus, the design and synthesis of novel zero-valent ruthenium complexes are attractive in terms of high reactivity and catalytic activity, in which proper tuning and matching of the ligands are critically important, since ruthenium has many coordination sites compared to group 9 or 10 metals such as rhodium and palladium. Extensive effort has been applied to elucidate the reactivity of [Ru(η^4-cod)(η^6-cot)] (cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene).[5–10] Recently, we found that the reaction of [Ru(η^4-cod)(η^6-cot)] with dimethyl fumarate gave a novel and versatile zero-valent ruthenium complex, [Ru(η^6-cot)(η^2-dmfm)$_2$] (dmfm: dimethyl fumarate), in high yield via ligand displacement between cod and 2 equivalents of dmfm,[11] which prompted us to investigate the reactivity of this complex toward phosphines, amines, arenes, and *p*-quinones, as well as water. All ruthenium complexes

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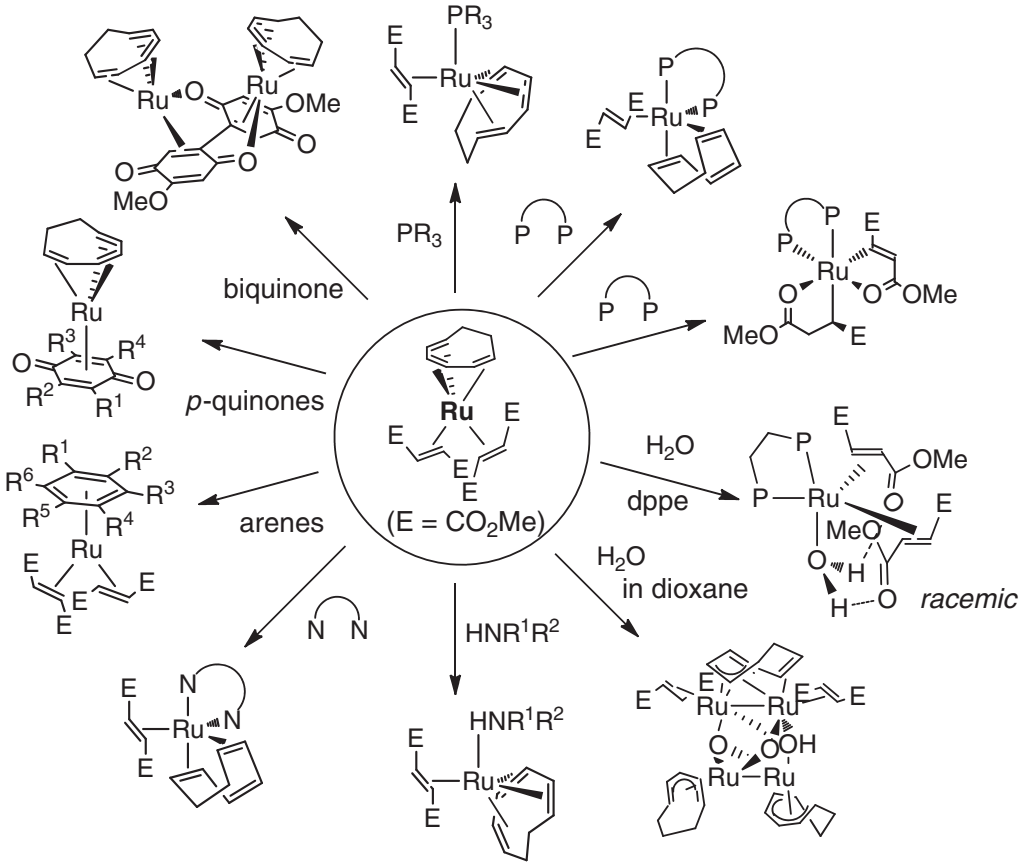


Scheme 1. Novel ruthenium complexes derived from [Ru(η^6-cot)(η^2-dmfm)$_2$].

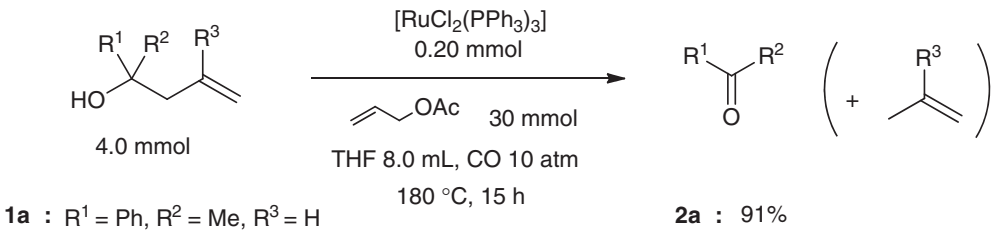
synthesized by our research group (Scheme 1)[12] can be expected to be highly efficient catalysts for novel organic transformations of unsaturated compounds such as alkynes, alkenes, carbon monoxide, and heterocumulenes to meet green and sustainable requirements in the 21st century.

3. Ruthenium- and Rhodium-Catalyzed Cleavage of Carbon–Carbon Bonds Enables Reconstructive Synthesis of Novel Functional Monomers

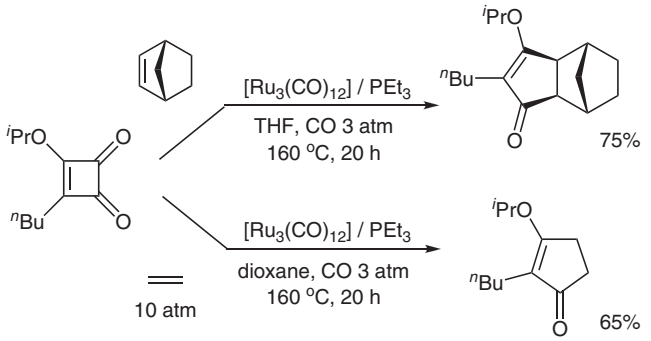
Cleavage of a carbon–carbon bond by transition-metal complexes under homogeneous conditions has recently received much scientific and technological interest, and has opened the door to a new field of synthetic organic chemistry.[4f,4h,13] Except for alkene and alkyne metatheses,[14] most catalytic carbon–carbon bond-cleaving reactions so far reported have been classified as reactions due to ring strain,[15] chelation assistance,[16] incipient aromatic stabilization,[17] skeletal rearrangement,[18,19] β-carbon elimination, or combinations of these phenomena.[20–22] In this part, we reviewed ruthenium- and rhodium-catalyzed reconstructive synthesis of novel functional organic molecules via cleavage of a carbon–carbon bond.

3.1 Ruthenium-Catalyzed Cleavage of a Carbon–Carbon Bond in Homoallyl Alcohols: Deallylation and Allyl-Transfer Reactions. In the course of our study of η^3-allylruthenium chemistry,[4e,23] a catalytic deallylation of tertiary homoallyl alcohols **1** to ketones **2** and alkenes was found, in which the key step of the present reaction is β-carbon elimination (Scheme 2).[24] The present reaction is the first example of the transition-metal-complex-catalyzed cleavage of a carbon–carbon bond without ring strain. This reaction was applicable to opening cyclic homoallyl alcohols to linear ketones, giving a new strategy for the ring-opening reaction. More recently, we developed a heterogeneous Ru/CeO_2 catalyst which has high catalytic activity for allyl-transfer from tertiary homoally alcohols to aldehydes.[25] This heterogeneous catalyst can be easily recovered and reused, and in sharp contrast to the homogeneous ruthenium catalyst,[24] neither carbon monoxide pressure nor allylic acetates are needed.

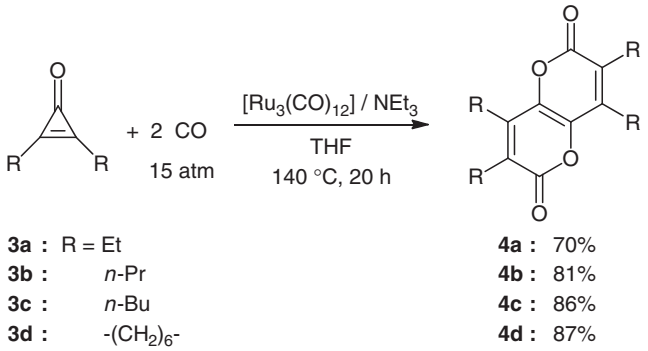
3.2 Ruthenium-Catalyzed Synthesis of Cyclopentenones by Unusual Monodecarbonylative Coupling of Cyclobutenediones with Alkenes. Cyclobutenediones have been recognized as versatile reagents for the construction of various multicyclic compounds.[26] The conversions of cyclobutenediones to quinones[27] as well as 5-alkylidene-2-cyclopentene-1,4-diones[28] using a stoichiometric amount of transition-metal complexes have been studied in detail, which proceed via (maleoyl)metal species. However, neither transition-metal-complex-catalyzed transformation of cyclobutenediones nor the synthetic reaction via metallacyclopentenedione and/or metallacyclobutenone complexes instead of (maleoyl)metal complexes has been reported. During our study of the catalytic synthesis of cyclopentenones,[29] we found a novel ruthenium-catalyzed reconstructive synthesis of cyclopentenones by unusual monodecarbonylated coupling reaction of cyclobutenediones with alkenes involving cleavage of a carbon–carbon bond at the C2–C3 bond selectively under the direction of a 3-



Scheme 2. Deallylation of tertiary homoallyl alcohols via β-carbon elimination.



Scheme 3. Ru-catalyzed selective mono-decarbonylative coupling of cyclobutenediones with alkenes to cyclopentenones.



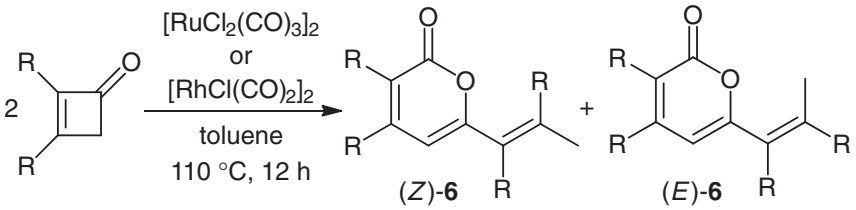
Scheme 4. Ru-catalyzed carbonylative dimerization of cyclopropenones to pyranopyrandiones.

alkoxy substituent to give a ruthenacyclopentenedione intermediate (Scheme 3).[30] Appropriate carbon monoxide pressure (3 atm) is needed to control selective *mono*-decarbonylation of a ruthenacyclopentenedione to a ruthenacyclobutenone intermediate, as well as to suppress complete decarbonylation to an (alkoxy)alkyne and carbon monoxide.

3.3 Ruthenium-Catalyzed Carbonylative Dimerization of Cyclopropenones and *cross*-Carbonylation of Cyclopropenones with Alkynes to Pyranopyrandiones. Several stoichiometric reactions of cyclopropenones with transition-metal complexes to give metallacyclobutenones,[31] (maleoyl)-metal complexes,[32] and dinuclear complexes[33] via cleavage of a carbon–carbon bond have been reported, however few transition-metal-complex-*catalyzed* reactions using cyclopropenones directed toward organic synthesis have been reported.[34] We have developed an unprecedented ruthenium-catalyzed carbonylative dimerization of cyclopropenones **3** involving cleavage of a carbon–carbon bond, which gave a novel functional monomer, pyranopyrandione **4**, in high yield (Scheme 4).[35] In addition, unsymmetrically substituted pyranopyrandiones were generally obtained in good to high yields by ruthenium-catalyzed *cross*-carbonylation of cyclopropenones with internal alkynes.

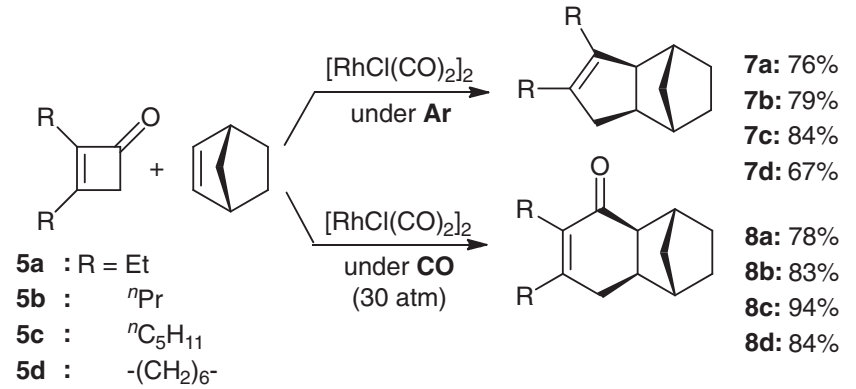
On the basis of ^{13}CO-labeled experiment, we postulated the following mechanism. The initial step in the present reaction might consist of oxidative addition of the carbon–carbon bond between a carbonyl and the α-carbon in cyclopropenone to an active ruthenium center to give a ruthenacyclobutenone intermediate. Carbonylation of ruthenacyclobutenone (or carbonylative cyclization of alkynes on the ruthenium[32,36]) would give a (maleoyl)ruthenium intermediate. Subsequent isomerization of a (maleoyl)ruthenium intermediate produces an active (η^4-bisketene)ruthenium intermediate,[37] which reacts with another molecule of cyclopropenone by oxidative addition and insertion reactions to give a (ketene)ruthenium intermediate. Rapid tautomerization would give a ruthenium carbene intermediate, and insertion of carbon monoxide into a carbene–ruthenium bond would give a new ketene intermediate.[38] Finally, insertion of a carbonyl group of a ketene moiety into an acyl–ruthenium bond and reductive elimination give the desired pyranopyrandione.

3.4 Ruthenium- and Rhodium-Catalyzed Ring-Opening Reactions of Cyclobutenones. Particular attention has been focused on the thermal reactivity of cyclobutenones bearing alkynyl, alkenyl, aryl, and allenyl substituents at the 4-position because of their potential application to the synthesis of ring-expanded compounds.[39] However, 4-nonsubstituted cyclobutenones are relatively stable, and only the pioneering work by Liebeskind and co-workers on the transition-metal-complex-catalyzed synthesis of phenols from 4-nonsubstituted cyclobutenones and alkynes has been reported.[20a,40,41] This methodology is quite attractive, since transition-metal vinylketene complexes have been postulated to be important intermediates in reactions leading to a variety of organic ring products, such as phenols, naphthols, cyclohexadienones, cyclopentenones, lactams, furans, α-pyrones, and 2-furanones.[42] As for a catalytic conversion of cyclobutenones, a novel stereoselective synthesis of 2-pyranones **6** via ring-opening dimerization of cyclobutenones **5** catalyzed by ruthenium ($[RuCl_2(CO)_3]_2$) and rhodium ($[RhCl(CO)_2]_2$) complexes has been developed (Scheme 5).[43]



		$[RuCl_2(CO)_3]_2$	$[RhCl(CO)_2]_2$
		E/Z	*E/Z*
5a	R = Et	**6a:** 79% (41/59)	**6a:** 86% (100/0)
5b	^{n}Pr	**6b:** 81% (22/78)	**6b:** 75% (100/0)
5c	$^n C_5H_{11}$	**6c:** 85% (24/76)	**6c:** 86% (100/0)
5d	$-(CH_2)_6-$	**6d:** 93% (100/0)	**6d:** 84% (100/0)

Scheme 5. Ru- and Rh-catalyzed ring-opening dimerization of cyclobutenones to 2-pyranones.



Scheme 6. Rh-catalyzed ring-opening coupling of cyclobutenones with 2-norbornene to bicyclic cyclopentenes and cyclohexenones.

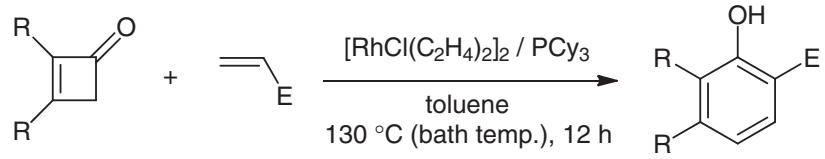
In the presence of 2-norbornene, the highly *exo*-selective coordination ability of 2-norbornene[44] leads to the formation of a rhodacyclopentenone intermediate,[20a] and subsequent stereoselective insertion of 2-norbornene into a rhodium–carbon bond would give a rhodacycloheptenone intermediate. Under an argon atmosphere, this rhodacycloheptenone is easily decarbonylated to a rhodacyclohexene intermediate, followed by reductive elimination giving the corresponding cyclopentenes **7**. On the other hand, under carbon monoxide pressure, rapid reductive elimination from the stabilized rhodacycloheptenone by carbon monoxide occurs to give the corresponding cyclohexenones **8** (Scheme 6).

3.5 Rhodium-Catalyzed Direct Synthesis of Substituted Phenols from Cyclobutenones and Electron-Deficient Alkenes. Development of ruthenium- and rhodium-catalyzed novel transformations of cyclobutenones[43] prompted us to examine the reaction of cyclobutenones with alkynes and/or other alkenes to construct phenols. Although a pioneering study by Liebeskind and co-workers revealed that rhodacyclopentenones obtained by the stoichiometric reaction of $[RhCl(PPh_3)_3]$ with cyclobutenones are unreactive toward alkynes and in no case were any phenol products detected,[20a,40a] we found that an appropriate choice of ligand enables the rhodium-catalyzed ring-opening reaction of cyclobutenones with alkynes to phenols.

However, since a nickel-catalyzed synthesis of phenols from cyclobutenones and alkynes under mild reaction conditions has already been reported,[20a] we investigated the reaction of cyclobutenones with *alkenes*.[45] Fortunately, we succeeded in developing a direct method for the synthesis of 2-substituted phenols **10** by the rhodium-catalyzed ring-opening reaction of cyclobutenones **5** with electron-deficient *alkenes* **9** via cleavage of a carbon–carbon bond, followed by dehydrogenation/isomerization reactions (Scheme 7).[46] No regioisomeric by-product was obtained at all.

4. Ruthenium- and Rhodium-Catalyzed Cocyclization of Alkynes with Heterocumulenes

4.1 Rhodium-Catalyzed Cocyclization of Alkynes with Isocyanates to 2-Pyridones or Pyrimidine-2,4-diones. Many naturally occurring and synthetic compounds containing the 2-pyridone scaffold possess interesting pharmacological properties.[47] Recent interest in the 2-pyridone ring system has led to several new procedures for its preparation.[48] A highly convergent and atom-economical approach is the transition-metal-complex-catalyzed cocyclization of two alkynes with an isocyanate.[49] Since this methodology was first reported independently by Yamazaki using cobalt catalysts[50] and by Hoberg using nickel catalysts,[51] remarkable progress has been made with these catalysts.[52,53] On the other hand, Takahashi and co-workers succeeded in preparing various 2-pyridones from two different internal alkynes and an isocyanate via the formation of an azazirconacyclopentenone intermediate, followed by transmetallation with $[Ni(PPh_3)_2Cl_2]$, however this



5a :	R = Et	**9a :**	E = COEt	**10a :** 73%
5b :	^{n}Pr	**9a :**	COEt	**10b :** 75%
5d :	-$(CH_2)_6$-	**9a :**	COEt	**10c :** 43%
5a :	Et	**9b :**	CO^{n}Pr	**10d :** 65%
5a :	Et	**9c :**	CO_2Me	**10e :** 40%

Scheme 7. Rh-catalyzed synthesis of 2-substituted phenols by dehydrogenative ring-opening coupling of cyclobutenones with alkenes.

reaction requires *stoichiometric* amounts of both Ni and Zr complexes.[54] Recently, Itoh and Yamamoto developed the first ruthenium-catalyzed synthesis of bicyclic 2-pyridones by the partial intermolecular cycloaddition of diynes with isocyanates.[55]

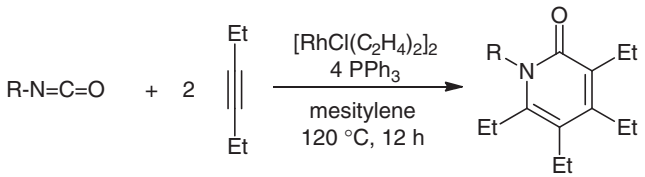
To the best of our knowledge, the rhodium-complex-catalyzed cocyclization of alkynes with isocyanates has thus far been investigated by only two research groups. Flynn reported that 1-(4-chlorophenyl)-3,5-methoxycarbonyl-4,6-dimethylpyrid-2-one was obtained in only 13% yield when a rhodacyclic complex was used as a neutral rhodium catalyst for the cocyclization of methyl tetrolate with 4-chlorophenyl isocyanate.[56] Tanaka and co-workers reported the chemo-, regio-, and enantioselective cycloaddition of diynes or terminal alkynes with isocyanates to give 2-pyridones catalyzed by a cationic rhodium complex, $[Rh(cod)_2]BF_4$, with H8-BINAP.[57] Since various neutral rhodium complexes are highly effective for cocyclization and related reactions of alkynes,[58,59] we reinvestigated the catalytic activities of several neutral rhodium complexes combined with phosphine ligands in detail.

A neutral rhodium(I) complex, $[RhCl(PPh_3)_2]$ generated by the combination of $[RhCl(C_2H_4)_2]_2$ with a 4-fold amount of PPh_3, effectively catalyzed the cocyclization of alkynes with isocyanates to give 2-pyridones and/or pyrimidine-2,4-diones, selectively, by controlling the molar ratio of alkynes and isocyanates.[60]

Both aromatic and aliphatic isocyanates **11** were readily converted into the corresponding 2-pyridones **12** (Scheme 8). No significant effect was observed for the electron-donating (4-Me) and electron-withdrawing substituents (4-Cl) on a phenyl ring in aromatic isocyanates. The reactions of *n*-hexyl isocyanate and cyclohexyl isocyanate with 3-hexyne gave the corresponding 2-pyridones, in isolated yields of 56% (**12d**) and 34% (**12e**), respectively, while more bulky aliphatic isocyanates, such as *tert*-butyl isocyanate and adamantyl isocyanate, could not be used in the present reaction.

On the other hand, treatment of alkynes with a large excess of isocyanate (**11d**, 20 equivalents) under the same catalytic reaction conditions gave pyrimidine-2,4-diones **13** in high yields, which were obtained by the cocyclization of two isocyanates with an alkyne (Scheme 9). No 2-pyridone **12** was obtained at all, as confirmed by careful GC-MS analysis.

The most plausible mechanism is as follows. An azarhodacyclopentenone derived from the oxidative cyclization of an

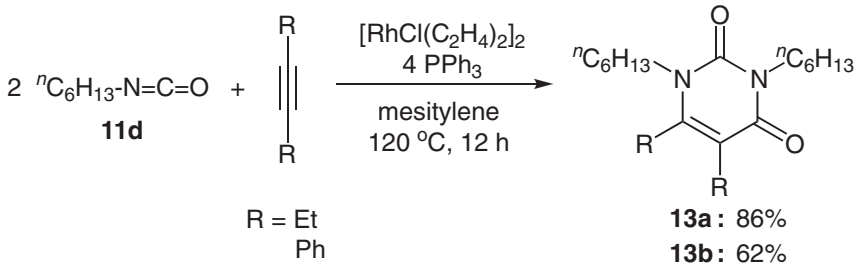


11a :	R = C_6H_5	**12a :**	50%
11b :	4-MeC_6H_4	**12b :**	59%
11c :	4-ClC_6H_4	**12c :**	63%
11d :	^{n}C$_6$H$_{13}$	**12d :**	56%
11e :	*cyclo*-C$_6$H$_{11}$	**12e :**	34%

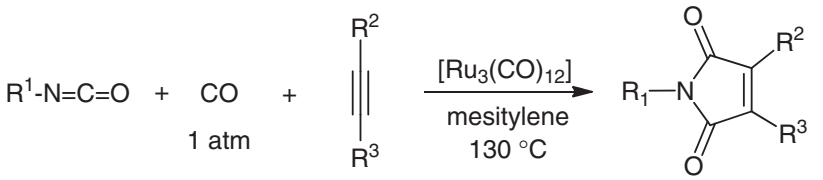
Scheme 8. Rh-catalyzed cocyclization of isocyanates with 3-hexyne to 2-pyridones.

alkyne and an isocyanate on an active neutral rhodium center is the key intermediate for the present reaction.[61] Since cocyclization of 1,6-heptadiyne and phenyl isocyanate[55a,55b] did not proceed at all by the present catalyst system, a mechanism involving a rhodacyclopentadiene derived from the oxidative cyclization of two alkynes can be ruled out. An azarhodacycloheptadienone could be formed by the selective insertion of an alkyne into the rhodium–carbon bond in an azarhodacyclopentenone, and the subsequent reductive elimination gives 2-pyridone. On the other hand, insertion of an isocyanate in place of an alkyne into the rhodium–nitrogen bond rather than the rhodium–carbon bond in an azarhodacyclopentenone proceeded, when a large excess of isocyanates was used, to give a diazarhodacycloheptenedione, and subsequent reductive elimination gives pyrimidine-2,4-diones.

4.2 Ruthenium-Catalyzed [2 + 2 + 1] Cocyclization of Alkynes, Isocyanates, and Carbon Monoxide. If heterocumulenic compounds such as carbodiimides and/or isocyanates can be used in the catalytic [2 + 2 + 1] cocyclization with alkynes and carbon monoxide, it could lead to a new approach for the construction of novel heterocyclic compounds, as a heteroatomic variant of the Pauson–Khand reaction. However, such processes are strictly limited to very recent examples of the $[Mo(CO)_6]$-mediated[62] and $[Co_2(CO)_8]$-catalyzed[63] *intramolecular* cocyclization of alkynecarbodiimides with carbon monoxide. Two other examples of the *intermolecular* [2 + 2 + 1] cocyclization of isocyanates, alkynes and carbon monoxide have required stoichiometric amounts of metal complexes such as $[Ni(cod)_2]$[51b] and $[Fe(CO)_5]$.[64] At the outset of our study on ruthenium-catalyzed



Scheme 9. Rh-catalyzed cocyclization of *n*-hexyl isocyanates with internal alkynes to pyrimidine-2,4-diones.



11a: $R^1 = C_6H_5$	**14a:** $R^2 = R^3 = {}^n$Pr	**15a:** 82% (42 h)
11a: $R^1 = C_6H_5$	**14b:** $R^2 = R^3 = C_6H_5$	**15b:** 98% (3 h)
11a: $R^1 = C_6H_5$	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15c:** 97% (3 h)
11a: $R^1 = C_6H_5$	**14d:** $R^2 = C_6H_5$, $R^3 = Me_3Si$	**15d:** 96% (6 h)
11b: R^1 = 4-MeC_6H_4	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15e:** 94% (3 h)
11f: R^1 = 4-$MeOC_6H_4$	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15f :** 95% (3 h)
11c: R^1 = 4-ClC_6H_4	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15g:** 94% (3 h)
11g: R^1 = 4-$CF_3C_6H_4$	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15h:** 98% (5 h)
11h: R^1 = Biphenyl	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15i :** 94% (3 h)
11d: $R^1 = {}^n C_6H_{13}$	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15j :** 95% (3 h)
11e: R^1 = *cyclo*-C_6H_{11}	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15k:** 96% (8 h)
11i: R^1 = Adamantyl	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15l :** 96% (12 h)
11j: $R^1 = {}^t$Butyl	**14c:** $R^2 = C_6H_5$, R^3 = Me	**15m:** 97% (18 h)

Scheme 10. Ru-catalyzed [2 + 2 + 1] cocyclization of alkynes, isocyanates, and carbon monoxide.

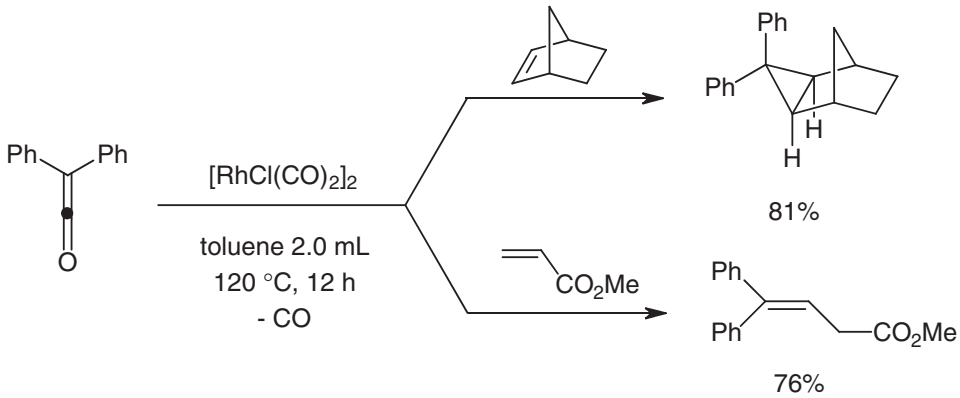
cocyclization reactions, we found a novel and rapid synthesis of polysubstituted maleimides **15** by the ruthenium-catalyzed intermolecular [2 + 2 + 1] cocyclization of alkynes **14**, isocyanates **11**, and carbon monoxide (Scheme 10).[65] A traditional industrial process for manufacturing maleimides is the reaction of amines with maleic anhydride obtained by the oxidation of benzene or C_4-hydrocarbons, which gives only unsubstituted and/or symmetrically substituted maleimides.[2b] The present reaction offers a highly efficient method for preparing novel unsymmetrically polysubstituted maleimides in excellent yields with high selectivity, which are important building blocks in materials science[66] and biological chemistry.[67]

4.3 Rhodium-Catalyzed Decarbonylative Coupling Reactions of Diphenylketene with Alkenes. Ketenes are reactive and useful synthetic intermediates in traditional organic chemistry.[68] Much attention has been focused on ketene-coordinated transition-metal complexes[42b,69] with the aim of developing new catalytic reactions using ketenes as a starting material.[70] Based on palladium-catalyzed transformations of heterocumulenic compounds developed by Mitsudo and co-workers,[71] we focused our attention on development of novel rhodium-catalyzed decarbonylative coupling reactions of diphenylketene with *alkenes*.[72]

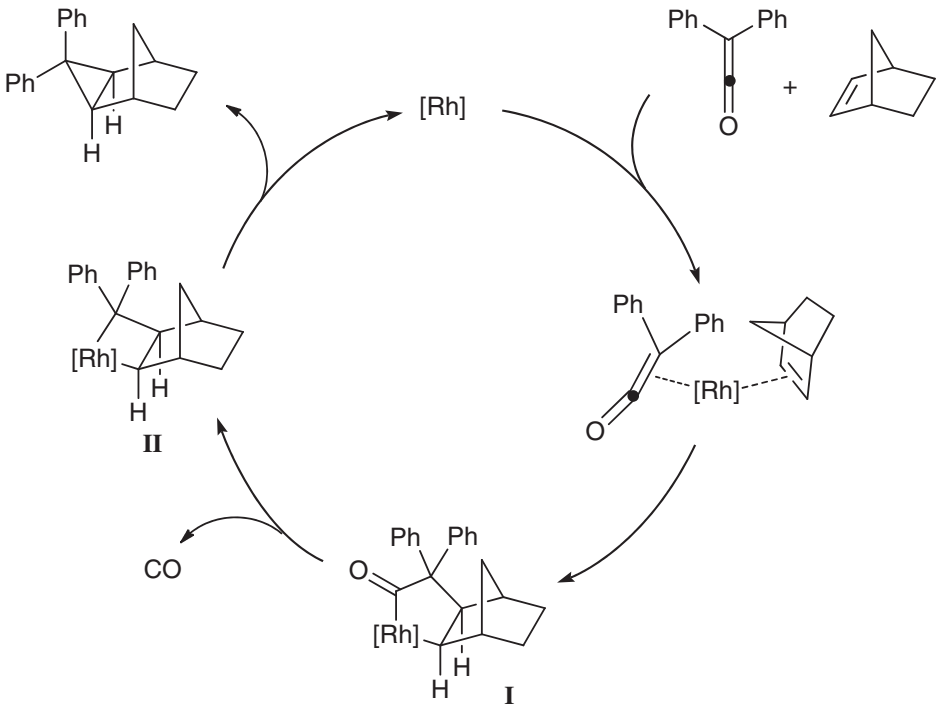
The reaction of diphenylketene with 2-norbornene gave the corresponding substituted cyclopropane via decarbonylation. On the other hand, when the reaction of diphenylketene with electron-deficient terminal alkenes such as methyl acrylate in place of 2-norbornene was carried out in the presence of $[RhCl(CO)_2]_2$ catalyst in toluene under the same reaction conditions, a decarbonylative linear coupling product, methyl 4,4-diphenyl-3-butenoate, was obtained in an isolated yield of 76% without the formation of a cyclopropane derivative (Scheme 11).

The initial step might consist of the concomitant coordination of diphenylketene and 2-norbornene to an active rhodium center. Oxidative cyclization gives a rhodacyclopentanone intermediate **I**, and subsequent decarbonylation of **I** would give a rhodacyclobutane intermediate **II**. Although **II** has a β-hydrogen, it takes a *trans*-position toward rhodium. Therefore, reductive elimination from **II** occurred predominantly to give the corresponding substituted cyclopropane without β-hydrogen elimination (Scheme 12).

Decarbonylative linear coupling reaction also proceeds via a rhodacyclobutane intermediate **IV** (Scheme 13). In contrast to **II**, **IV** generated by decarbonylation of a rhodacyclopentanone intermediate **III** has a *cis*-β-hydrogen toward rhodium, and



Scheme 11. Rh-catalyzed decarbonylative coupling of diphenylketene with alkenes.



Scheme 12. A possible mechanism for cyclopropanation of 2-norbornene with diphenylketene.

rapid β-hydrogen elimination proceeds to give a (hydrido)-(allyl)rhodium intermediate **V**, which undergoes reductive elimination to give linear coupling products (Scheme 13).

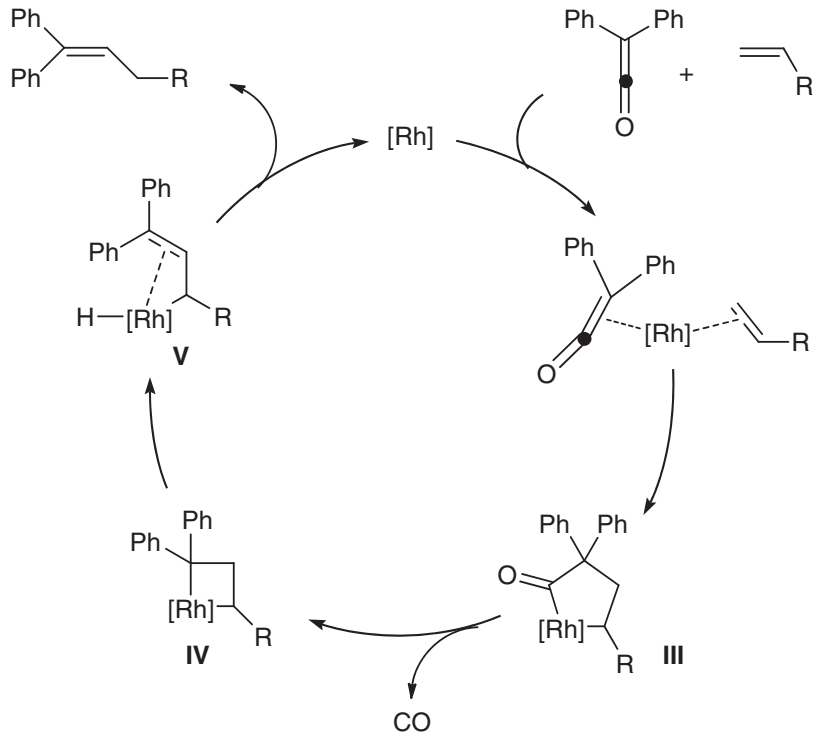
4.4 Rhodium-Catalyzed Linear Codimerization and Cycloaddition of Ketenes with Alkynes. In general, ketenes coordinate to transition-metal complexes in two ways: 1) coordination through a C=C bond in ketenes,[73] and 2) coordination through a C=O bond in ketenes.[74] If these coordination modes can be controlled through the selection of ketenes in transition-metal catalysis, completely different methods for the construction of novel organic molecules could be developed according to the structure and reactivity of ketenes using the same transition-metal catalyst.

After many trials, we developed a novel [$RhCl(PPh_3)_3$]-catalyzed linear codimerization of *alkylphenylketenes* with internal alkynes and a novel synthesis of furans by the unusual [$RhCl(PPh_3)_3$]-catalyzed cycloaddition of *diarylketenes* with internal alkynes (Scheme 14).[75] In these reactions, the catalyst is the same but the products are completely different according to the structure and reactivity of the starting ketenes.

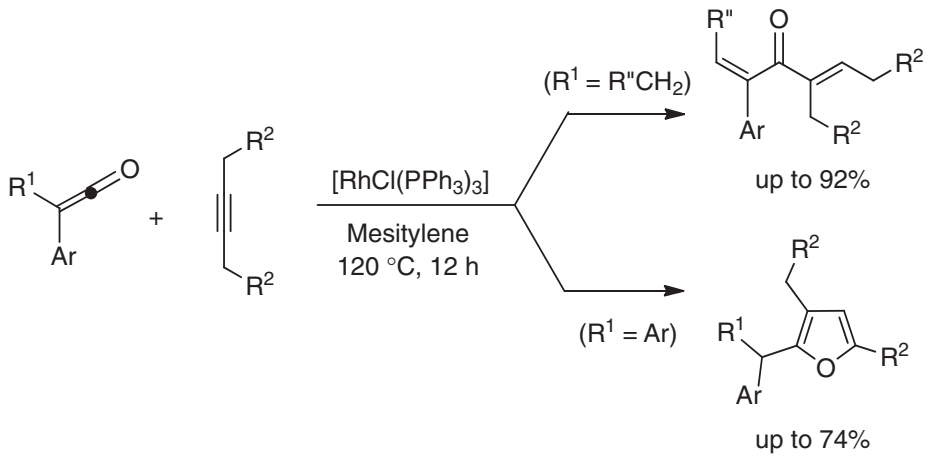
5. Ruthenium-Catalyzed Cocyclization of Alkynes, Alkenes, and Carbon Monoxide

5.1 Intramolecular Pauson–Khand Reaction of 1,6-Enynes with Carbon Monoxide. Metal-mediated cocyclization of alkynes, alkenes, and carbon monoxide (the Pauson–Khand reaction[76]) is becoming increasingly popular as a tool for selective organic synthesis.[77] This method provides an easy way to prepare a cyclopentenone skeleton from simple starting materials, i.e., alkynes, alkenes, and carbon monoxide, through a formal [2 + 2 + 1] cocyclization, and has been used successfully as the key step in the synthesis of several natural products containing a cyclopentenone skeleton.[78]

We have reported the [2 + 2] cycloaddition of alkynes with 2-norbornene catalyzed by ruthenium complexes,[4a,44b,79] in which ruthenacyclopentene is a key intermediate. If carbon



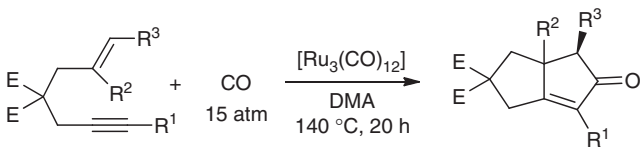
Scheme 13. A possible mechanism for linear coupling reaction of electron-deficient alkenes with diphenylketene.



Scheme 14. Rh-catalyzed decarbonylative coupling of ketenes with alkenes.

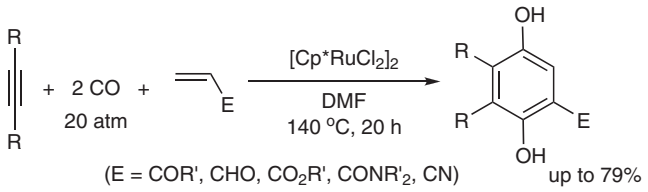
monoxide is inserted into this ruthenacyclopentene, a catalytic version of the Pauson–Khand reaction can be achieved. In the course of our continuous investigations of transition-metal-complex-catalyzed cocyclization reactions, we found the first ruthenium-catalyzed Pauson–Khand-type reaction of 1,6-enynes **16** with carbon monoxide to bicyclic cyclopentenones **17** (Scheme 15).[29a,80]

5.2 Ruthenium-Catalyzed [2 + 2 + 1 + 1] Cocyclization of 2-Norbornenes or Electron-Deficient Alkenes with Alkynes to Hydroquinones. Having one more molecule of carbon monoxide, the [2 + 2 + 1 + 1] cocyclization of an alkyne, an alkene, and two molecules of carbon monoxide would lead to substituted hydroquinones. In 1998, we first developed $[Ru_3(CO)_{12}]$-catalyzed [2 + 2 + 1 + 1] cocyclization of 2-norbornene, alkynes, and two molecules of carbon

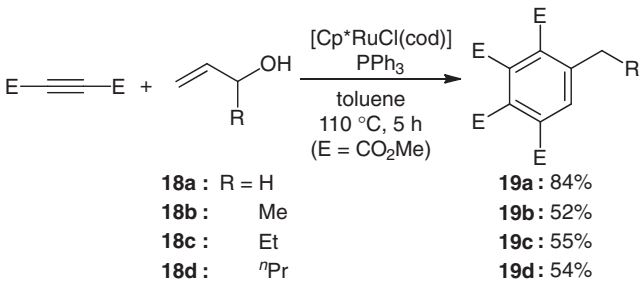


16a : R1 = Et, R^2 = H, R^3 = H, E = CO_2Me — **17a :** 75%
16b : R^1 = Et, R^2 = H, R^3 = H, E = COMe — **17b :** 74%
16c : R^1 = *n*-Bu, R^2 = H, R^3 = H, E = CO_2Me — **17c :** 84%
16d : R^1 = $SiMe_3$, R^2 = H, R^3 = H, E = CO_2Me — **17d :** 85%
16e : R^1 = Et, R^2 = H, R^3 = Me, E = CO_2Me — **17e :** 41%
16f ; R^1 = Et, R^2 = Me, R^3 = H, E = CO_2Me — **17f ;** 73%

Scheme 15. $[Ru_3(CO)_{12}]$-catalyzed intramolecular Pauson–Khand-type reaction.



Scheme 16. $[Cp^*RuCl_2]_2$-catalyzed *cross*-carbonylation of alkynes with electron-deficient alkenes to hydroquinones.



Scheme 17. Synthesis of benzenepolycarboxylates by Ru-catalyzed *cross*-benzannulation of acetylenedicarboxylates with allylic alcohols.

monoxide leading to the corresponding hydroquinone derivatives.[81] Although this reaction is unique and industrially useful, restrictions with regard to an alkene coupling partner should be overcome. Collaborative study with Prof. Ryu and Dr. Fukuyama found that the [2 + 2 + 1 + 1] cocyclization reaction can be extended to electron-deficient alkenes such as α,β-unsaturated ketones, aldehydes, esters, amides, and nitriles, in which $[Cp^*RuCl_2]_2$ is the best catalyst (Scheme 16).[82]

In both reactions, the mechanism involving the formation of a (maleoyl)ruthenium intermediate by the reaction of an alkyne with two molecules of carbon monoxide, and the subsequent insertion of alkenes to form a ruthenacycloheptenedione is postulated.

6. Ruthenium-Catalyzed Highly Selective Co-oligomerization of Alkynes and/or Alkenes

Alkynes and alkenes are key materials in the petrochemical industry.[2b] They are easily available, cheap, reactive, and readily converted into a range of valuable chemicals.[83] Catalytic dimerization, codimerization, and co-oligomerization of alkynes and/or alkenes are important methodologies in organic synthesis directed toward a green and sustainable chemistry, since in these reactions all the atoms of the starting materials are incorporated into the products without generation of wastes (100% atom-economy).[1,2a] Dimerization and codimerization have been widely used on an industrial scale, and provide a variety of biodegradable detergents, new kinds of polymers, lubricants, and many other industrially useful chemicals.[84]

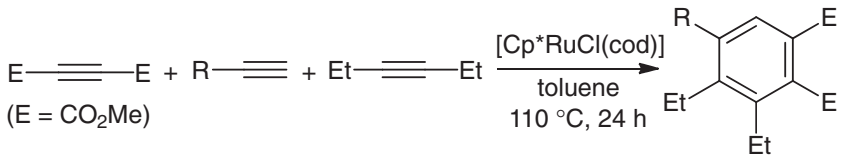
Here, discussion will be focused on the recent progress of ruthenium-catalyzed codimerization and cotrimerization of different alkenes, developed mainly by the present authors.

6.1 Synthesis of Benzenepolycarboxylates by *cross*-Benzannulation of Allylic Compounds with Acetylenedicarboxylates. The transition-metal-complex-catalyzed cyclotrimerization of alkynes has been extensively studied as a feasible method for constructing substituted aromatic nuclei.[85] The related cocyclization of two alkyne molecules with an alkene molecule can also be catalyzed by transition metals to generally give 1,3-cyclohexadiene derivatives.[86] Both processes can be rationalized by assuming metallacyclopentadiene intermediates[87] via the oxidative cyclization of two alkyne molecules on low-valent transition-metal catalysts, followed by insertion of an alkyne and/or an alkene; eg., cobalt,[85a,86a–86e] titanium,[86f,86g,88] palladium,[89] ruthenium,[86h–86j,90] and rhodium[86k–86m] catalysts. Although consecutive syntheses of benzene derivatives via 1,3-cyclohexadienes by a combination of the cocyclization reaction with dehydrogenation,[91] *retro*-Diels–Alder reaction[92] or base-assisted oxidation[93] have been developed, methods for the direct synthesis of polysubstituted benzenes by the cocyclization of alkynes with alkenes, *so-called cross-benzannulation*, are quite limited.

We attempted the reaction of alkynes with functionalized alkenes such as allylic compounds in the presence of a ruthenium catalyst. Fortunately, a novel ruthenium-catalyzed [2 + 2 + 2] *cross*-benzannulation of acetylenedicarboxylates with allylic compounds **18** proceeded to give benzenetetracarboxylates **19** directly in high yields instead of a normal cycloadduct of 1,3-cyclohexadienes (Scheme 17).[94] The present reaction may complement a previously reported palladium-catalyzed similar reaction,[95] and may be more synthetically useful since allylic alcohols can be used directly.

A mechanism involving a (η^3-allyl)ruthenium intermediate can be ruled out, since 3-buten-2-ol was suitable for the present reaction, while no reaction occurred with β-methallyl alcohol and *trans*-crotyl alcohol. When the partially intramolecular cocyclization of diynes such as 1,6-heptadiyne with allyl alcohol was examined, the product was the normal 1,3-cyclohexadiene derivative, not a benzene derivative, which clearly indicated that the present reaction does not involve a ruthenacyclopentadiene intermediate. Accordingly, we now believe that a ruthenacyclopentene, which is generated by oxidative cyclization of dimethyl acetylenedicarboxylate and allylic alcohols on an active ruthenium center, is a key intermediate in the present reaction. The alkoxycarbonyl group (an electron-withdrawing group) decreased the electron density of the ruthenium center. This facilitates the intramolecular coordination of the hydroxy group to ruthenium, which results in β-hydroxy elimination to form the intermediate.[96] Subsequent insertion of another molecule of dimethyl acetylenedicarboxylate, intramolecular insertion of a C=C bond into an alkenyl–ruthenium bond, and successive β-hydride elimination/isomerization would give the corresponding benzenepolycarboxylates in good yield with high selectivity.

6.2 Ruthenium-Catalyzed [2 + 2 + 2] Cocyclization of Three Different Alkynes. Although intensive studies have been done to date, there are few reports of the selective [2 + 2 + 2] cycloaddition of *three different alkynes*, due to difficult control of the chemo- and regioselectivity.[85b] Early transition metals such as zirconium[97] and titanium[98] are known to mediate the selective cycloaddition, in which the chemoselectivity is well regulated by stepwise addition of the different alkynes. As for catalytic reactions using late transition



20a:	R = $^{n}C_6H_{13}$	**21a:**	48%
20b:	$^{n}C_8H_{17}$	**21b:**	57%
20c:	$^{n}C_{10}H_{21}$	**21c:**	61%
20d:	Ph	**21d:**	35%
20e:	$SiMe_3$	**21e:**	32%

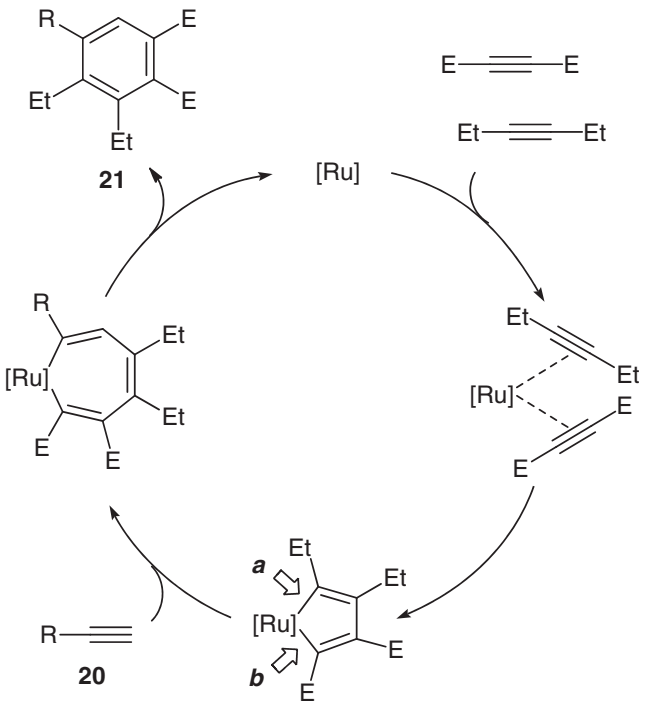
Scheme 18. Ru-catalyzed [2 + 2 + 2] cocyclization of three different alkynes.

metals, a palladium-catalyzed unique aromatic ring construction from two different alkynes and a diyne has been reported by Yamamoto and co-workers, of which the mechanism is actually not simple [2 + 2 + 2] cocyclization but dimerization of the alkynes and successive [4 + 2] benzannulation with the diyne.[99] A nickel(0)–zinc(II) phenoxide system is reported to be effective for catalytic [2 + 2 + 2] cocyclization proceeding under mild reaction conditions, while the chemo- and regioselectivity are still unsatisfactory and problematic.[100] Recently, a ruthenium-catalyzed reaction has also been reported, where in situ generation of diynes from alkynylboronates and propargyl alcohol is elegantly applied.[101]

We have recently reported the ruthenium-catalyzed highly chemoselective intermolecular [2 + 2 + 2] cocyclization of 2 equiv of terminal alkynes with dimethyl acetylenedicarboxylate to afford the corresponding *o*-phthalates in good yield.[102] In the course of our continuous investigations, we found the same ruthenium catalyst, [Cp*RuCl(cod)], could be applied to the three-component coupling reaction and successfully achieved the chemoselective [2 + 2 + 2] cocyclization of three different alkynes, by controlling the molar ratio of the substrates.[103]

The reaction of dimethyl acetylenedicarboxylate (1.0 equivalent), 1-decyne (**20b**, 6.0 equivalents), and 3-hexyne (40 equivalents) was carried out in toluene under reflux for 24 h in the presence of a catalytic amount (5.0 mol %) of [Cp*RuCl(cod)] to give a single regioisomer of three-component coupling products, dimethyl 3,4-diethyl-5-octylphthalate (**21b**) in 57% yield, together with the formation of by-products represented by tetramethyl 5,6-diethyl-1,2,3,4-benzenetetracarboxylate (>20%) (Scheme 18). The structure of dimethyl 3,4-diethyl-5-octylphthalate was confirmed by ^{13}C inadequate measurement, in addition to general spectroscopic analysis.

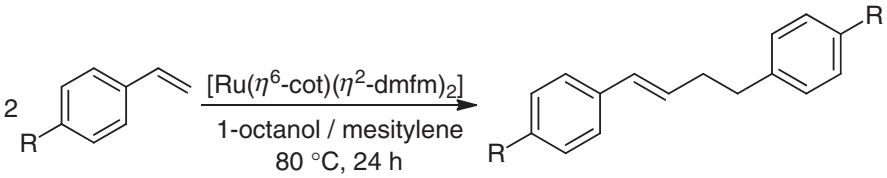
As for the mechanism, dimethyl acetylenedicarboxylate and 3-hexyne coordinate to an active ruthenium species, and oxidatively cyclize to a ruthenacyclopentadiene. There are two directions of ***a*** and ***b***, from which the terminal alkyne can insert a ruthenium carbon bond in the ruthenacyclopentadiene. Insertion from the direction of ***a*** seems to be more favorable, since the ruthenium–carbon bond bearing an ester group is made stronger by π-back donation from ruthenium to the π^* orbital of α-carbon. A ruthenacycloheptatriene is predominantly formed depending on the steric hindrance between R and Et groups. Reductive elimination gives the trialkylated *o*-phthalates along with the regeneration of the catalytically active species (Scheme 19).



Scheme 19. A possible mechanism for Ru-catalyzed [2 + 2 + 2] cocyclization of three different alkynes.

6.3 Ruthenium-Catalyzed Unusual *Head-to-Head* Dimerization of Styrenes and Linear Codimerization of Styrenes with Ethylene. The first transition-metal complexes that were shown to catalyze the homodimerization of styrenes were based on palladium.[104] Later, nickel-[105] and zirconium-based catalysts[106] were shown to be effective for this dimerization reaction, and these generally gave a head-to-tail dimer, (*E*)-1,3-diaryl-1-butenes. There has been only one previous example of *head-to-head* dimerization to give (*E*)-1,4-diaryl-1-butene, by Kretschmer and co-workers[107] using a bis(indenyl)yttrium hydride as a catalyst. However, their catalyst system is unwieldy because of the instability of the catalyst toward air and moisture.

The codimerization of styrenes with ethylene has also been extensively studied since it was first reported in 1965.[108] Many transition-metal complexes are active in this process,[109,110] and catalysts containing nickel are the most active.[111,112] The products are *head-to-tail* dimers, 3-aryl-1-butenes, and an

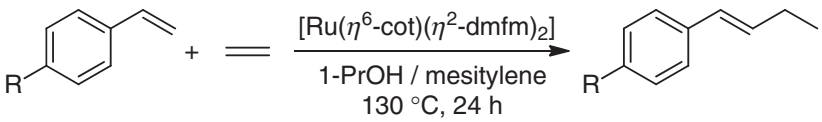


22a : R = H
22b : R = CH_3
22c : R = OCH_3
22d : R = F

23a : 80 (53)%[a] (95% *E* form)
23b : 71% (95% *E* form)
23c : 66%[b] (97% *E* form)
23d : 67 (56)%[a] (97% *E* form)

[a] Figures in the parentheses are isolated yield.
[b] 1-PrOH (6.0 mmol) at 110 °C.

Scheme 20. Ru-catalyzed *head-to-head* dimerization of styrenes.



22a : R = H
22b : R = CH_3
22c : R = OCH_3

24a : 70% (95% *E* form)
24b : 67% (97% *E* form)
24c : 81% (98% *E* form)

Scheme 21. Ru-catalyzed linear codimerization of styrenes with ethylene.

enantioselective version of the codimerization (hydrovinylation) of styrenes with ethylene has recently been developed.[112,113]

On the basis of our continuous study of the catalytic activity of a zero-valent ruthenium complex, [Ru(η^6-cot)(η^2-dmfm)$_2$], we found that it catalyzed an unusual *head-to-head* dimerization of styrenes **22** to (*E*)-1,4-diaryl-1-butenes **23**[114,115] in the presence of primary alcohols (Scheme 20).[116] No significant effect was observed for the substituents on the phenyl ring in styrenes.

In addition, the present catalyst system is effective for the regio- and stereoselective linear codimerization of styrenes with ethylene. As described previously, transition-metal-complex-catalyzed codimerization of styrenes with ethylene generally gave 3-aryl-1-butenes (hydrovinylation), while unusual codimers, (*E*)-1-aryl-1-butenes **24**, were obtained by the present catalyst system in good yields with high selectivity (Scheme 21).

We believe that both reactions involve the ruthenacyclopentane intermediate.[117] The ring opening of a ruthenacyclopentane by direct β-hydrogen elimination is not a favored process, but this could be facilitated by protonation or σ-bond metathesis[118] with the primary alcohol, which plays an important role of cocatalyst. Then, the stereoselective β-hydrogen elimination could occur to give the dimer with regeneration of the Ru(0) species and the primary alcohol cocatalyst.

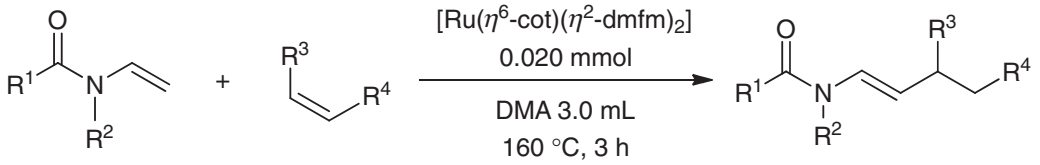
6.4 Regio- and Stereoselective Synthesis of Enamides by Ruthenium-Catalyzed Co-oligomerization of *N*-Vinylamides with Alkenes. Enamides are contained in many natural products such as salicylihalamide[119a] and lobatamide,[119b] and have recently been synthesized using transition-metal catalysts, as represented by (a) the vinylation of amides,[120] (b) the chelation-assisted coupling reaction of *N*-vinylamides with 1,3-butadiene,[121] (c) the addition of amides to alkynes,[122] (d) the oxidative amidation of alkenes,[123] and (e) the isomerization of *N*-allylamides.[124]

In considering potential new methods for the synthesis of enamides, we have focused our efforts on ruthenium-catalyzed regio- and stereoselective co-oligomerization reactions. Many examples of transition-metal-complex-catalyzed codimerization reactions of *alkenes with alkynes* have been reported.[84,125] In sharp contrast, codimerization as well as co-oligomerization reactions of *different alkenes* are still quite difficult except for hydrovinylation of styrenes,[108–113] and a challenging subject in modern organic and organometallic chemistry.[116]

We report here zero-valent ruthenium-complex-catalyzed codimerization reaction of *different alkenes*; i.e., a codimerization reaction of *N*-vinylamides with alkenes as well as a co-oligomerization reaction of *N*-vinylamides, acrylates, and ethylene, which offer novel and atom-economical methods for synthesis of enamides with high regio- and stereoselectivity in one step (Scheme 22).[126,127]

N-Vinylamides with a large excess of alkenes under the same catalytic reaction conditions followed by hydrogenation gave 1:2 co-oligomers in up to 63% yield. This means that double C–C bond-formation proceeded selectively at the β-position of a vinyl group in *N*-vinylamides. In addition, codimerization of the isolated enamide with ethyl acrylate proceeded by the present catalyst system to give the corresponding codimer in an isolated yield of 56% after hydrogenation. This strongly suggests that the present co-oligomerization proceeds stepwise and substituted *N*-vinylamides would be generally applicable to the present reaction.

We then attempted to develop a three-component coupling reaction of different alkenes. After many trials, we realized this reaction through the combination of *N*-vinylamides, ethyl

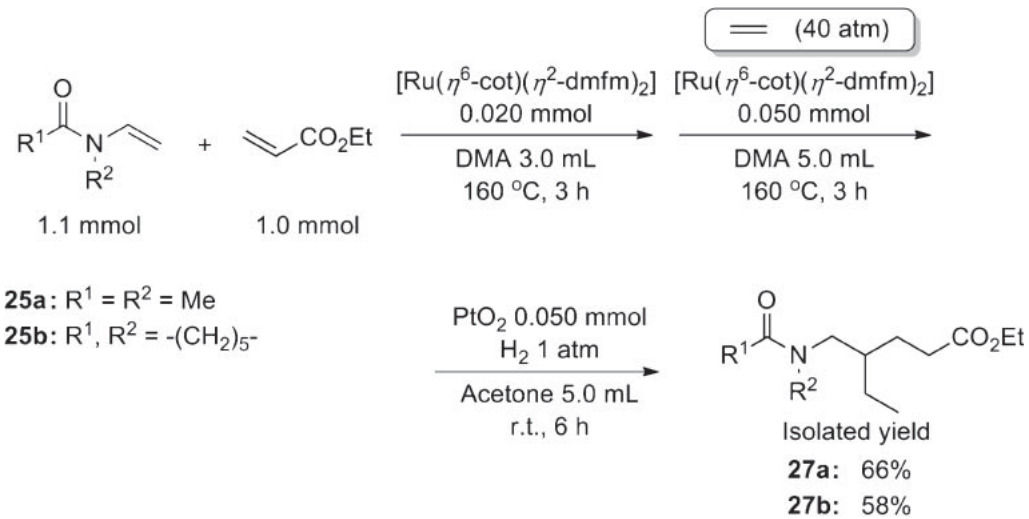


21 1.1 mmol + **22** 1.0 mmol → **23**

25a : $R^1 = R^2$ = Me	**9d :** R^3 = H, $R^4 = CO_2{}^tBu$	**26b :** 77 (61)% (88% *E* form)
25a : $R^1 = R^2$ = Me	**9a :** R^3 = H, R^4 = COEt	**26c :** 70 (48)% (94% *E* form)
25a : $R^1 = R^2$ = Me	**9c :** $R^3 = R^4 = CO_2Me$	**26d :** 76 (52)% (98% *E* form)
25a : $R^1 = R^2$ = Me	**9e :** $R^3 = R^4$ = 	**26e :** 33% (99% *E* form, and *exo* only)[a]
25a : $R^1 = R^2$ = Me	**9f :** $R^3 = R^4$ = H	**26f :** 16% (97% *E* form)[b]
25b : R^1, $R^2 = -(CH_2)_5-$	**9g :** R^3 = H, $R^4 = CO_2Et$	**26g :** 60 (50)% (88% *E* form)

Yield was determined by GLC. Figures in the parentheses are isolated yield.
[a]2-Norbornene (5.0 mmol). [b]Ethylene (10 atm).

Scheme 22. Ru-catalyzed codimerization of *N*-vinylamides with alkenes to enamides.

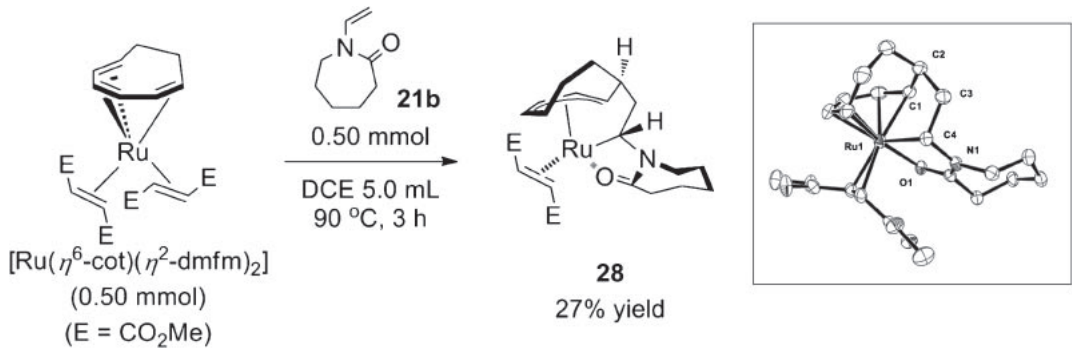


Scheme 23. Ru-catalyzed cotrimerization of *N*-vinylamides, acrylates, and ethylene.

acrylate, and ethylene (40 atm). Hydrogenation of the generated isomeric cotrimers gave a single product in up to 66% yield (**27a**, Scheme 23). *To the best of our knowledge, the selective cotrimerization reaction of two or three different alkenes had never been accomplished before.*

A stoichiometric reaction of [Ru(η^6-cot)(η^2-dmfm)$_2$] with *N*-vinylcaprolactam in 1,2-dichloroethane (DCE) at 90 °C for 3 h under an argon atmosphere gave a new complex in 27% isolated yield which could be obtained by a ligand-exchange reaction of one molecule of dmfm with *N*-vinylcaprolactam, followed by oxidative cyclization between a cot ligand with a vinyl group of *N*-vinylcaprolactam (Scheme 24). This complex also showed good catalytic activity for the present codimerization reaction of *N*-vinylacetamides with ethyl acrylate to give the codimer in 56% yield.

The reaction starts with the removal of a cot ligand in [Ru(η^6-cot)(η^2-dmfm)$_2$] by *N*-vinylamides via metallacycle formation and reductive elimination[128] to give coordinatively unsaturated zero-valent ruthenium species, which is effective for the formation of a ruthenium hydride species via activation of sp^2 C–H bonds in alkenes or a dmfm ligand.[129] Alkenes are then inserted into a Ru–H bond, followed by the successive chelation-assisted insertion of *N*-vinylamides into a Ru–C bond. Subsequent β-hydrogen elimination gives the codimer with regeneration of an active ruthenium hydride species. At this stage, a mechanism that involves oxidative cyclization of *N*-vinylamides with alkenes to give a ruthenacyclopentane intermediate could not be completely excluded, however the result of deuterium-scrambling in the reaction of *N*-vinylacetamide with diethyl acrylate-d_2 can be reasonably



Scheme 24. A stoichiometric reaction of [Ru(η^6-cot)(η^2-dmfm)$_2$] with *N*-vinylcaprolactam. Formation of a catalytically active ruthenacyclic complex, **28**.

explained by a mechanism involving a ruthenium hydride species.

Conclusion

In spite of the inertness of the carbon–carbon bonds in organic molecules, there have been growing interests in catalytic cleavage of carbon–carbon bonds which realizes rapid and reconstructive synthesis of new functional organic molecules. In this review, some of our strategies for achieving ruthenium- and rhodium-catalyzed cleavage of carbon–carbon bonds were disclosed. Note that low-valent ruthenium complexes also catalyze highly regio- and stereoselective co-oligomerization of alkenes as well as cocyclization of them with carbon monoxide and/or heterocumulenic compounds. We hope these new findings will offer new methods for synthetic organic chemistry.

On the other hand, it is high time to consider the future potential of organometallic chemistry. As one direction, we suggest the application of organometallic methodology to synthesis of new molecular probes such as MRI contrast agents. A preliminary result of the synthesis of novel chiral dendrimer amine-coordinated Gd complexes has been described in a patent.[130] The detailed functional evaluation of this new complex as a highly effective MRI contrast agent will be disclosed soon.

I would like to express to all of my co-workers my deep appreciation for their productive, energetic, and hard work. I also thank Prof. Take-aki Mitsudo for his guidance and encouragement. These studies were supported by MEXT, JSPS, and many other foundations which were acknowledged in the original paper.

References

1 a) *Green Catalysis*, ed. by P. T. Anastas, Wiley-VCH, Weinheim, **2009**, Vols. 1–3. b) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686.

2 a) B. M. Trost, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. b) H.-J. Arpe, *Industrial Organic Chemistry*, 5th ed., Wiley-VCH, Weinheim, **2010**.

3 a) *Comprehensive Organometallic Chemistry II*, ed. by E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon, Oxford, **1995**, Vol. 7. b) *Ruthenium in Organic Synthesis*, ed. by S.-I. Murahashi, Wiley-VCH, Weinheim, **2004**. c) *Ruthenium Catalysts and Fine Chemistry* in *Topics in Organometallic Chemistry*, ed. by C. Bruneau, P. H. Dixneuf, Springer, New York, **2004**, Vol. 11. doi:10.1007/b10989. For a review, see: d) T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599. e) B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067. f) Y. Wakatsuki, H. Zhaomin, M. Tokunaga, *Chem. Rec.* **2003**, *3*, 144. g) N. Chatani, *Chem. Rec.* **2008**, *8*, 201. h) R.-S. Liu, *Synlett* **2008**, 801. i) W. Tam, J. Goodreid, N. Cockburn, *Curr. Org. Synth.* **2009**, *6*, 219.

4 For a review, see: a) T. Mitsudo, Y. Hori, Y. Watanabe, *J. Organomet. Chem.* **1987**, *334*, 157. b) T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205. c) T. Mitsudo, T. Kondo, *Synlett* **2001**, 309. d) T. Kondo, T. Mitsudo, *Spec. Chem. Mag.* **2002**, *22*, 30. e) T. Kondo, T. Mitsudo, *Curr. Org. Chem.* **2002**, *6*, 1163. f) T. Kondo, T. Mitsudo, *Chem. Lett.* **2005**, *34*, 1462. g) Y. Ura, H. Tsujita, T. Mitsudo, T. Kondo, *Bull. Korean Chem. Soc.* **2007**, *28*, 2139. h) T. Kondo, *Synlett* **2008**, 629.

5 a) E. O. Fischer, J. Müller, *Chem. Ber.* **1963**, *96*, 3217. b) J. Müller, E. O. Fischer, *J. Organomet. Chem.* **1966**, *5*, 275.

6 a) P. Pertici, G. Vitulli, *Comments Inorg. Chem.* **1991**, *11*, 175, and references cited therein. b) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem.* **1981**, *20*, 2353. c) B. Chaudret, R. Poilblanc, *Organometallics* **1985**, *4*, 1722. d) F. Bouachir, B. Chaudret, F. Dahan, F. Agbossou, I. Tkatchenko, *Organometallics* **1991**, *10*, 455. e) K. A. Leñero, M. Kranenburg, Y. Guari, P. C. J. Kamer, P. W. N. M. van Leeuwen, S. Sabo-Etienne, B. Chaudret, *Inorg. Chem.* **2003**, *42*, 2859. f) R. R. Schrock, J. Lewis, *J. Am. Chem. Soc.* **1973**, *95*, 4102. g) L. J. Farrugia, J. C. Jeffery, C. Marsden, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1985**, 645. h) S. Hüffer, K. Polborn, W. Beck, *J. Organomet. Chem.* **1997**, *543*, 47. i) K.-M. Frosin, L. Dahlenburg, *Inorg. Chim. Acta* **1990**, *167*, 83. j) M. Airoldi, G. Deganello, G. Dia, G. Gennaro, *Inorg. Chim. Acta* **1983**, *68*, 179. k) D. Labroue, R. Pince, R. Quéau, *J. Organomet. Chem.* **1991**, *402*, 363. l) T. Suzuki, H. Yamada, K. Yunoki, H. Yamaguchi, *Energy Fuels* **1992**, *6*, 352. m) J. A. Wiles, S. H. Bergens, K. P. M. Vanhessche, D. A. Dobbs, V. Rautenstrauch, *Angew. Chem., Int. Ed.* **2001**, *40*, 914. n) M. Murata, K. Kawakita, T. Asana, S. Watanabe, Y. Masuda, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 825.

7 a) K. Itoh, K. Mukai, H. Nagashima, H. Nishiyama, *Chem. Lett.* **1983**, 499. b) K. Itoh, H. Nagashima, T. Ohshima, N. Oshima, H. Nishiyama, *J. Organomet. Chem.* **1984**, *272*, 179.

8 a) S. Komiya, J. G. Planas, K. Onuki, Z. Lu, M. Hirano, *Organometallics* **2000**, *19*, 4051. b) S. Komiya, M. Hirano, *Dalton Trans.* **2003**, 1439. c) M. Hirano, K. Onuki, Y. Kimura, S. Komiya, *Inorg. Chim. Acta* **2003**, *352*, 160. d) M. Hirano, R. Asakawa, C.

Nagata, T. Miyasaka, N. Komine, S. Komiya, *Organometallics* **2003**, *22*, 2378.

9 a) K. Sano, T. Yamamoto, A. Yamamoto, *Z. Naturforsch.* **1985**, *40B*, 210. b) K. Osakada, A. Grohmann, A. Yamamoto, *Organometallics* **1990**, *9*, 2092. c) Y. Maruyama, I. Shimizu, A. Yamamoto, *Chem. Lett.* **1994**, 1041.

10 a) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, J. Y. Satoh, *J. Am. Chem. Soc.* **1991**, *113*, 9604. b) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, P. S. Johar, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 987.

11 T. Mitsudo, T. Suzuki, S.-W. Zhang, D. Imai, K. Fujita, T. Manabe, M. Shiotsuki, Y. Watanabe, K. Wada, T. Kondo, *J. Am. Chem. Soc.* **1999**, *121*, 1839.

12 a) T. Mitsudo, Y. Ura, T. Kondo, *J. Organomet. Chem.* **2004**, *689*, 4530. b) T. Mitsudo, Y. Ura, T. Kondo, *Chem. Rec.* **2006**, *6*, 107. c) T. Mitsudo, Y. Ura, T. Kondo, *Proc. Jpn. Acad., Ser. B* **2007**, *83*, 65.

13 a) M. Murakami, Y. Ito, in *Activation of Unreactive Bonds and Organic Synthesis* in *Topics in Organometallic Chemistry*, ed. by S. Murai, Springer, New York, **1999**, Vol. 3, pp. 97–129. doi:10.1007/3-540-68525-1_5. For a review, see: b) K. C. Bishop, III, *Chem. Rev.* **1976**, *76*, 461. c) R. H. Crabtree, *Chem. Rev.* **1985**, *85*, 245. d) P. W. Jennings, L. L. Johnson, *Chem. Rev.* **1994**, *94*, 2241. e) B. Rybtchinski, D. Milstein, *Angew. Chem., Int. Ed.* **1999**, *38*, 870. f) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759.

14 a) *Alkene Metathesis in Organic Synthesis* in *Topics in Organometallic Chemistry*, ed. by A. Fürstner, Springer, Berlin, **1998**, Vol. 1. doi:10.1007/3-540-69708-X. b) Y. Yamamoto, K. Itoh, in *Ruthenium in Organic Synthesis*, ed. by S.-I. Murahashi, Wiley-VCH, Weinheim, **2004**, Chap. 4, pp. 95–128. For a recent review, see: c) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708. d) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746. e) A. N. Lozano-Vila, S. Monsaert, A. Bajek, F. Verpoort, *Chem. Rev.* **2010**, *110*, 4865. f) M. Mori, *Materials* **2010**, *3*, 2087.

15 a) R. Noyori, T. Odagi, H. Takaya, *J. Am. Chem. Soc.* **1970**, *92*, 5780. b) R. Noyori, Y. Kumagai, I. Umeda, H. Takaya, *J. Am. Chem. Soc.* **1972**, *94*, 4018. c) S. Aoki, T. Fujimura, E. Nakamura, I. Kuwajima, *J. Am. Chem. Soc.* **1988**, *110*, 3296. d) T. Fujimura, S. Aoki, E. Nakamura, *J. Org. Chem.* **1991**, *56*, 2809. e) C. Perthuisot, B. L. Edelbach, D. L. Zubris, W. D. Jones, *Organometallics* **1997**, *16*, 2016. f) B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc.* **1998**, *120*, 2843. g) M. Lautens, Y. Ren, *J. Am. Chem. Soc.* **1996**, *118*, 10668. h) M. Hayashi, T. Ohmatsu, Y.-P. Meng, K. Saigo, *Angew. Chem., Int. Ed.* **1998**, *37*, 837.

16 For a review, see: a) C.-H. Jun, C. W. Moon, D.-Y. Lee, *Chem.—Eur. J.* **2002**, *8*, 2422. b) C.-H. Jun, C. W. Moon, H. Lee, D.-Y. Lee, *J. Mol. Catal. A: Chem.* **2002**, *189*, 145. c) C.-H. Jun, J. H. Lee, *Pure Appl. Chem.* **2004**, *76*, 577. d) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610. e) Y. J. Park, J.-W. Park, C.-H. Jun, *Acc. Chem. Res.* **2008**, *41*, 222. For a leading reference, see: f) J. W. Suggs, C.-H. Jun, *J. Am. Chem. Soc.* **1984**, *106*, 3054. g) J. W. Suggs, C.-H. Jun, *J. Am. Chem. Soc.* **1986**, *108*, 4679. h) N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **1999**, *121*, 8645. i) M. Gandelman, M. E. van der Boom, D. Milstein, *Chem. Commun.* **2000**, 1603.

17 a) K. Kaneda, H. Azuma, M. Wayaku, S. Teranishi, *Chem. Lett.* **1974**, 215. b) S.-Y. Liou, M. E. van der Boom, D. Milstein, *Chem. Commun.* **1998**, 687.

18 a) N. Chatani, T. Morimoto, T. Muto, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 6049. b) N. Chatani, K. Kataoka, S. Murai, N. Furukawa, Y. Seki, *J. Am. Chem. Soc.* **1998**, *120*, 9104. c) N. Chatani, H. Inoue, T. Kotsuma, S. Murai, *J. Am. Chem. Soc.* **2002**, *124*, 10294. d) M. Méndez, M. P. Muñoz, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, *123*, 10511. e) C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Chem.—Eur. J.* **2003**, *9*, 2627. f) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. g) A. Fürstner, H. Szillat, B. Gabor, R. Mynott, *J. Am. Chem. Soc.* **1998**, *120*, 8305. h) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785. i) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863. j) F. Marion, J. Coulomb, C. Courillon, L. Fensterbank, M. Malacria, *Org. Lett.* **2004**, *6*, 1509. k) S. Oi, I. Tsukamoto, S. Miyano, Y. Inoue, *Organometallics* **2001**, *20*, 3704. l) R. J. Madhushaw, C.-Y. Lo, C.-W. Hwang, M.-D. Su, H.-C. Shen, S. Pal, I. R. Shaikh, R.-S. Liu, *J. Am. Chem. Soc.* **2004**, *126*, 15560. m) J.-J. Lian, A. Odedra, C.-J. Wu, R.-S. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 4186. For a review, see: n) S. I. Lee, N. Chatani, *Chem. Commun.* **2009**, 371. o) C. Nieto-Oberhuber, S. López, E. Jiménez-Núñez, A. M. Echavarren, *Chem.—Eur. J.* **2006**, *12*, 5916. p) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326. q) L. Zhang, J. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271. r) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208.

19 a) B. M. Trost, G. J. Tanoury, *J. Am. Chem. Soc.* **1988**, *110*, 1636. b) B. M. Trost, M. K. Trost, *Tetrahedron Lett.* **1991**, *32*, 3647. c) B. M. Trost, M. K. Trost, *J. Am. Chem. Soc.* **1991**, *113*, 1850. d) B. M. Trost, V. K. Chang, *Synthesis* **1993**, 824. e) B. M. Trost, M. Yanai, K. Hoogsteen, *J. Am. Chem. Soc.* **1993**, *115*, 5294. f) B. M. Trost, A. S. K. Hashmi, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085. g) B. M. Trost, C. D. Haffner, D. J. Jebaratnam, M. J. Krische, A. P. Thomas, *J. Am. Chem. Soc.* **1999**, *121*, 6183. h) B. M. Trost, A. C. Gutierrez, E. M. Ferreira, *J. Am. Chem. Soc.* **2010**, *132*, 9206.

20 a) M. A. Huffman, L. S. Liebeskind, *J. Am. Chem. Soc.* **1991**, *113*, 2771. b) M. A. Huffman, L. S. Liebeskind, *J. Am. Chem. Soc.* **1993**, *115*, 4895. c) N. Tsukada, A. Shibuya, I. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 8123. d) P. A. Wender, A. G. Correa, Y. Sato, R. Sun, *J. Am. Chem. Soc.* **2000**, *122*, 7815.

21 a) M. Murakami, H. Amii, Y. Ito, *Nature* **1994**, *370*, 540. b) M. Murakami, H. Amii, K. Shigeto, Y. Ito, *J. Am. Chem. Soc.* **1996**, *118*, 8285. c) M. Murakami, K. Takahashi, H. Amii, Y. Ito, *J. Am. Chem. Soc.* **1997**, *119*, 9307. d) M. Murakami, T. Itahashi, H. Amii, K. Takahashi, Y. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 9949. e) M. Murakami, K. Itami, M. Ubukata, I. Tsuji, Y. Ito, *J. Org. Chem.* **1998**, *63*, 4. f) M. Murakami, T. Tsuruta, Y. Ito, *Angew. Chem., Int. Ed.* **2000**, *39*, 2484. g) M. Murakami, T. Itahashi, Y. Ito, *J. Am. Chem. Soc.* **2002**, *124*, 13976. h) T. Matsuda, M. Makino, M. Murakami, *Org. Lett.* **2004**, *6*, 1257. i) T. Matsuda, M. Makino, M. Murakami, *Angew. Chem., Int. Ed.* **2005**, *44*, 4608. j) M. Murakami, S. Ashida, T. Matsuda, *J. Am. Chem. Soc.* **2005**, *127*, 6932. For a review, see: k) M. Murakami, M. Makino, S. Ashida, T. Matsuda, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1315. l) M. Murakami, *Chem. Rec.* **2010**, *10*, 326.

22 For a recent example, see: a) H. Terai, H. Takaya, S.-I. Murahashi, *Synlett* **2004**, 2185. b) Y. Nakao, S. Oda, T. Hiyama, *J. Am. Chem. Soc.* **2004**, *126*, 13904. c) S. Matsumura, Y. Maeda, T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **2003**, *125*, 8862. d) T. Nishimura, S. Uemura, *Synlett* **2004**, 201. e) T. Nishimura, Y. Nishiguchi, Y. Maeda, S. Uemura, *J. Org. Chem.* **2004**, *69*, 5342. f) P. Zhao, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 11618. g) A. I. Siriwardana, M. Kamada, I. Nakamura, Y. Yamamoto, *J. Org.*

Chem. **2005**, *70*, 5932. h) A. Funayama, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2005**, *127*, 15354. i) T. Satoh, M. Miura, *Synthesis* **2010**, 3395. In this review, we cannot refer to metal-assisted or -mediated cleavage of carbon–carbon bonds because of the space limitation. Among them, however, ruthenium-mediated activation of hydrocarbons without functional groups is highly important. See: j) H. Suzuki, Y. Takaya, T. Takemori, M. Tanaka, *J. Am. Chem. Soc.* **1994**, *116*, 10779. k) H. Suzuki, T. Kakigano, H. Fukui, M. Tanaka, Y. Moro-oka, *J. Organomet. Chem.* **1994**, *473*, 295. l) Y. Ohki, H. Suzuki, *Angew. Chem., Int. Ed.* **2000**, *39*, 3463. m) T. Takemori, A. Inagaki, H. Suzuki, *J. Am. Chem. Soc.* **2001**, *123*, 1762. n) A. Inagaki, D. G. Musaev, T. Takemori, H. Suzuki, K. Morokuma, *Organometallics* **2003**, *22*, 1718. For a review, see: o) H. Suzuki, A. Inagaki, K. Matsubara, T. Takemori, *Pure Appl. Chem.* **2001**, *73*, 315. p) H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009.

23 a) T. Kondo, H. Ono, N. Satake, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945. b) Y. Tsuji, T. Mukai, T. Kondo, Y. Watanabe, *J. Organomet. Chem.* **1989**, *369*, C51. c) T. Kondo, T. Mukai, Y. Watanabe, *J. Org. Chem.* **1991**, *56*, 487. d) T. Mitsudo, S.-W. Zhang, T. Kondo, Y. Watanabe, *Tetrahedron Lett.* **1992**, *33*, 341. e) T. Mitsudo, S.-W. Zhang, N. Satake, T. Kondo, Y. Watanabe, *Tetrahedron Lett.* **1992**, *33*, 5533. f) S.-W. Zhang, T. Mitsudo, T. Kondo, Y. Watanabe, *J. Organomet. Chem.* **1993**, *450*, 197. g) T. Mitsudo, N. Suzuki, T. Kondo, Y. Watanabe, *J. Org. Chem.* **1994**, *59*, 7759. h) S.-W. Zhang, T. Mitsudo, T. Kondo, Y. Watanabe, *J. Organomet. Chem.* **1995**, *485*, 55.

24 T. Kondo, K. Kodoi, E. Nishinaga, T. Okada, Y. Morisaki, Y. Watanabe, T. Mitsudo, *J. Am. Chem. Soc.* **1998**, *120*, 5587.

25 H. Miura, K. Wada, S. Hosokawa, M. Sai, T. Kondo, M. Inoue, *Chem. Commun.* **2009**, 4112.

26 a) A. H. Schmidt, *Synthesis* **1980**, 961. b) H. W. Moore, O. H. W. Decker, *Chem. Rev.* **1986**, *86*, 821. c) L. S. Liebeskind, R. Chidambaram, D. Mitchell, B. S. Foster, *Pure Appl. Chem.* **1988**, *60*, 27. d) L. S. Liebeskind, *Tetrahedron* **1989**, *45*, 3053. e) H. W. Moore, B. R. Yerxa, *Chemtracts: Org. Chem.* **1992**, *5*, 273. f) P. A. Tempest, R. W. Armstrong, *J. Am. Chem. Soc.* **1997**, *119*, 7607.

27 a) S. L. Baysdon, L. S. Liebeskind, *Organometallics* **1982**, *1*, 771. b) L. S. Liebeskind, J. P. Leeds, S. L. Baysdon, S. Iyer, *J. Am. Chem. Soc.* **1984**, *106*, 6451. c) L. S. Liebeskind, C. F. Jewell, Jr., *J. Organomet. Chem.* **1985**, *285*, 305.

28 L. S. Liebeskind, R. Chidambaram, *J. Am. Chem. Soc.* **1987**, *109*, 5025.

29 a) T. Kondo, N. Suzuki, T. Okada, T. Mitsudo, *J. Am. Chem. Soc.* **1997**, *119*, 6187. b) Y. Morisaki, T. Kondo, T. Mitsudo, *Org. Lett.* **2000**, *2*, 949.

30 T. Kondo, A. Nakamura, T. Okada, N. Suzuki, K. Wada, T. Mitsudo, *J. Am. Chem. Soc.* **2000**, *122*, 6319.

31 a) W. Wong, S. J. Singer, W. D. Pitts, S. F. Watkins, W. H. Baddley, *J. Chem. Soc., Chem. Commun.* **1972**, 672. b) J. P. Visser, J. E. Ramakers-Blom, *J. Organomet. Chem.* **1972**, *44*, C63. c) J. Foerstner, A. Kakoschke, R. Wartchow, H. Butenschön, *Organometallics* **2000**, *19*, 2108. See also: d) C. W. Bird, E. M. Briggs, J. Hudec, *J. Chem. Soc. C* **1967**, 1862. e) W. L. Fichteman, P. Schmidt, M. Orchin, *J. Organomet. Chem.* **1968**, *12*, 249. f) C. W. Bird, E. M. Briggs, *J. Organomet. Chem.* **1974**, *69*, 311.

32 a) L. S. Liebeskind, S. L. Baysdon, M. S. South, S. Iyer, J. P. Leeds, *Tetrahedron* **1985**, *41*, 5839. b) H. Hoberg, A. Herrera, *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 876. c) L. Song, A. M. Arif, P. J. Stang, *Organometallics* **1990**, *9*, 2792. d) L. H. Gade, H. Memmler, U. Kauper, A. Schneider, S. Fabre, I. Bezougli, M. Lutz, C. Galka, I. J. Scowen, M. McPartlin, *Chem.—Eur. J.* **2000**, *6*, 692.

33 W. E. Carroll, M. Green, J. A. K. Howard, M. Pfeffer, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1978**, 1472.

34 a) R. Noyori, I. Umeda, H. Takaya, *Chem. Lett.* **1972**, 1189. b) A. Baba, Y. Ohshiro, T. Agawa, *J. Organomet. Chem.* **1976**, *110*, 121. c) A. Baba, Y. Ohshiro, T. Agawa, *Chem. Lett.* **1976**, 11. d) Y. Ohshiro, H. Nanimoto, H. Tanaka, M. Komatsu, T. Agawa, N. Yasuoka, Y. Kai, N. Kasai, *Tetrahedron Lett.* **1985**, *26*, 3015. e) N. Chatani, T. Hanafusa, *J. Org. Chem.* **1987**, *52*, 4408.

35 T. Kondo, Y. Kaneko, Y. Taguchi, A. Nakamura, T. Okada, M. Shiotsuki, Y. Ura, K. Wada, T. Mitsudo, *J. Am. Chem. Soc.* **2002**, *124*, 6824.

36 M. Barrow, N. L. Cromhout, A. R. Manning, J. F. Gallagher, *J. Chem. Soc., Dalton Trans.* **2001**, 1352.

37 C. F. Jewell, Jr., L. S. Liebeskind, M. Williamson, *J. Am. Chem. Soc.* **1985**, *107*, 6715.

38 L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed., University Science Books, Sausalito, **1999**, Chap. 6, pp. 143–186.

39 For a review, see: a) *Advances in Strain in Organic Chemistry*, ed. by B. Halton, JAI Press, London, **1995**, Vol. 4. b) T. K. M. Shing, in *Houben-Weyl Methods in Organic Chemistry*, 4th ed., ed. by A. de Meijere, Thieme, Stuttgart, **1997**, Vol. E17f, Chap. 8B, pp. 898–913.

40 a) M. A. Huffman, L. S. Liebeskind, W. T. Pennington, Jr., *Organometallics* **1990**, *9*, 2194. b) M. A. Huffman, L. S. Liebeskind, *J. Am. Chem. Soc.* **1990**, *112*, 8617. c) M. A. Huffman, L. S. Liebeskind, W. T. Pennington, *Organometallics* **1992**, *11*, 255.

41 A thermal reaction of cyclobutenones with activated alkynes to phenols via a vinylketene intermediate has also been reported. a) R. L. Danheiser, S. K. Gee, *J. Org. Chem.* **1984**, *49*, 1672. b) R. L. Danheiser, A. Nishida, S. Savariar, M. P. Trova, *Tetrahedron Lett.* **1988**, *29*, 4917.

42 a) M. F. Semmelhack, R. Tamura, W. Schnatter, J. Park, M. Steigerwald, S. Ho, *Stud. Org. Chem.* **1986**, *25*, 21. b) S. E. Gibson, M. A. Peplow, *Adv. Organomet. Chem.* **1999**, *44*, 275, and references therein.

43 T. Kondo, Y. Taguchi, Y. Kaneko, M. Niimi, T. Mitsudo, *Angew. Chem., Int. Ed.* **2004**, *43*, 5369.

44 a) S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* **1976**, *98*, 4054. b) T. Mitsudo, H. Naruse, T. Kondo, Y. Ozaki, Y. Watanabe, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580. c) T. Kondo, S. Uenoyama, K. Fujita, T. Mitsudo, *J. Am. Chem. Soc.* **1999**, *121*, 482.

45 A related construction of phenols by the thermolysis of 4-alkenylcyclobutenones, which were prepared by palladium-catalyzed cross-coupling of 4-chlorocyclobutenones with alkenylstannyl and/or zinc reagents, has been reported. D. J. Krysan, A. Gurski, L. S. Liebeskind, *J. Am. Chem. Soc.* **1992**, *114*, 1412.

46 T. Kondo, M. Niimi, M. Nomura, K. Wada, T. Mitsudo, *Tetrahedron Lett.* **2007**, *48*, 2837.

47 For a review, see: J. H. Rigby, *Synlett* **2000**, 1.

48 a) M. Torres, S. Gil, M. Parra, *Curr. Org. Chem.* **2005**, *9*, 1757. b) N. Y. Gorobets, B. H. Yousefi, F. Belaj, C. O. Kappe, *Tetrahedron* **2004**, *60*, 8633.

49 J. A. Varela, C. Saá, *Chem. Rev.* **2003**, *103*, 3787.

50 a) P. Hong, H. Yamazaki, *Synthesis* **1977**, 50. b) P. Hong, H. Yamazaki, *Tetrahedron Lett.* **1977**, *18*, 1333.

51 a) H. Hoberg, B. W. Oster, *Synthesis* **1982**, 324. b) H. Hoberg, B. W. Oster, *J. Organomet. Chem.* **1982**, *234*, C35. c) H. Hoberg, B. W. Oster, *J. Organomet. Chem.* **1983**, *252*, 359.

52 For cobalt catalysts, see: a) R. A. Earl, K. P. C. Vollhardt,

J. Am. Chem. Soc. **1983**, *105*, 6991. b) R. A. Earl, K. P. C. Vollhardt, *J. Org. Chem.* **1984**, *49*, 4786. c) P. Diversi, G. Ingrosso, A. Lucherini, S. Malquori, *J. Mol. Catal.* **1987**, *40*, 267. For a review, see: d) K. P. C. Vollhardt, *Acc. Chem. Res.* **1977**, *10*, 1.

53 For nickel catalysts, see: H. A. Duong, M. J. Cross, J. Louie, *J. Am. Chem. Soc.* **2004**, *126*, 11438, and references therein.

54 a) T. Takahashi, F.-Y. Tsai, Y. Li, H. Wang, Y. Kondo, M. Yamanaka, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **2002**, *124*, 5059. b) Y. Li, H. Matsumura, M. Yamanaka, T. Takahashi, *Tetrahedron* **2004**, *60*, 1393.

55 a) Y. Yamamoto, H. Takagishi, K. Itoh, *Org. Lett.* **2001**, *3*, 2117. b) Y. Yamamoto, K. Kinpara, T. Saigoku, H. Takagishi, S. Okuda, H. Nishiyama, K. Itoh, *J. Am. Chem. Soc.* **2005**, *127*, 605. A theoretical study was also reported. See: c) R. Schmid, K. Kirchner, *J. Org. Chem.* **2003**, *68*, 8339.

56 S. T. Flynn, S. E. Hasso-Henderson, A. W. Parkins, *J. Mol. Catal.* **1985**, *32*, 101.

57 K. Tanaka, *Synlett* **2007**, 1977, and references therein.

58 M. Fujiwara, I. Ojima, in *Modern Rhodium-Catalyzed Organic Reaction*, ed. by P. A. Evans, Wiley-VCH, Weinheim, **2005**, pp. 129–149.

59 The unusual [2 + 2 + 2] cocyclization of alkenylisocyanates and alkynes via CO migration has been reported. See: R. T. Yu, T. Rovis, *J. Am. Chem. Soc.* **2006**, *128*, 2782.

60 T. Kondo, M. Nomura, Y. Ura, K. Wada, T. Mitsudo, *Tetrahedron Lett.* **2006**, *47*, 7107.

61 In the present reaction, decarbonylation of isocyanates occurred to some extent. The generated carbon monoxide may coordinate to an active rhodium species leading to deactivation of the rhodium catalyst, which good accords with the low catalytic activity of $[RhCl(CO)(PPh_3)_2]$.

62 T. Saito, M. Shiotani, T. Otani, S. Hasaba, *Heterocycles* **2003**, *60*, 1045.

63 C. Mukai, T. Yoshida, M. Sorimachi, A. Odani, *Org. Lett.* **2006**, *8*, 83.

64 Y. Ohshiro, K. Kinugasa, T. Minami, T. Agawa, *J. Org. Chem.* **1970**, *35*, 2136.

65 T. Kondo, M. Nomura, Y. Ura, K. Wada, T. Mitsudo, *J. Am. Chem. Soc.* **2006**, *128*, 14816.

66 a) J. K. Pontrello, M. J. Allen, E. S. Underbakke, L. L. Kiessling, *J. Am. Chem. Soc.* **2005**, *127*, 14536. b) X. Zhang, Z.-C. Li, Z.-M. Wang, H.-L. Sun, Z. He, K.-B. Li, L.-H. Wei, S. Lin, F.-S. Du, F.-M. Li, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 304.

67 a) A. S. Kalgutkar, B. C. Crews, L. J. Marnett, *J. Med. Chem.* **1996**, *39*, 1692. b) W. Yang, O. Auciello, J. E. Butler, W. Cai, J. A. Carlisle, J. E. Gerbi, D. M. Gruen, T. Knickerbocker, T. L. Lasseter, J. N. Russell, Jr., L. M. Smith, R. J. Hamers, *Nat. Mater.* **2002**, *1*, 253.

68 For a review, see: a) *The Chemistry of Functional Groups: The Chemistry of Ketenes, Allenes, and Related Compounds Part 1 and Part 2*, ed. by S. Patai, John Wiley & Sons, New York, **1980**. b) T. T. Tidwell, *Science of Synthesis* **2006**, *23*, 15; T. T. Tidwell, *Science of Synthesis* **2006**, *23*, 391; T. T. Tidwell, *Science of Synthesis* **2006**, *23*, 569. c) A. R. Far, *Angew. Chem., Int. Ed.* **2003**, *42*, 2340.

69 For example, see: a) E. O. Fischer, A. C. Filippou, H. G. Alt, K. Ackermann, *J. Organomet. Chem.* **1983**, *254*, C21. b) M. Wiederhold, U. Behrens, *J. Organomet. Chem.* **1994**, *476*, 101. For a review, see: c) G. L. Geoffroy, S. L. Bassner, *Adv. Organomet. Chem.* **1988**, *28*, 1.

70 H. Okumoto, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, John Wiley & Sons, New York, **2002**, pp. 2655–2662.

71 a) T. Mitsudo, M. Kadokura, Y. Watanabe, *Tetrahedron Lett.* **1985**, *26*, 3697. b) T. Mitsudo, M. Kadokura, Y. Watanabe, *J. Org. Chem.* **1987**, *52*, 1695. c) T. Mitsudo, M. Kadokura, Y. Watanabe, *J. Org. Chem.* **1987**, *52*, 3186.

72 a) T. Kondo, Y. Tokoro, Y. Ura, K. Wada, T. Mitsudo, *ChemCatChem* **2009**, *1*, 82. Independently, palladium-catalyzed C–C coupling reactions of 2-norbornenes with diphenylketene have been reported. b) J. M. Goll, E. Fillion, *Organometallics* **2008**, *27*, 3622.

73 Y. C. Xu, C. A. Challener, V. Dragisich, T. A. Brandvold, G. A. Peterson, W. D. Wulff, P. G. Williard, *J. Am. Chem. Soc.* **1989**, *111*, 7269.

74 a) D. B. Grotjahn, H. C. Lo, *Organometallics* **1995**, *14*, 5463. b) H. C. Lo, D. B. Grotjahn, *J. Am. Chem. Soc.* **1997**, *119*, 2958. c) D. B. Grotjahn, G. A. Bikzhanova, J. L. Hubbard, *Organometallics* **1999**, *18*, 5614. d) D. B. Grotjahn, L. S. B. Collins, M. Wolpert, G. A. Bikzhanova, H. C. Lo, D. Combs, J. L. Hubbard, *J. Am. Chem. Soc.* **2001**, *123*, 8260. e) D. B. Grotjahn, J. M. Hoerter, J. L. Hubbard, *J. Am. Chem. Soc.* **2004**, *126*, 8866.

75 T. Kondo, M. Niimi, Y. Yoshida, K. Wada, T. Mitsudo, Y. Kimura, A. Toshimitsu, *Molecules* **2010**, *15*, 4189.

76 a) I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc. D* **1971**, 36a. b) I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

77 a) D. Strübing, M. Beller, in *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed., ed. by M. Beller, C. Bolm, Wiley-VCH, Weinheim, **2004**, Vol. 1, Chap. 3.13, pp. 619–632. For a recent review, see: b) B. E. Hanson, *Comments Inorg. Chem.* **2002**, *23*, 289. c) S. E. Gibson (née Thomas), A. Stevenazzi, *Angew. Chem., Int. Ed.* **2003**, *42*, 1800. d) L. V. R. Boñaga, M. E. Krafft, *Tetrahedron* **2004**, *60*, 9795. e) S. E. Gibson, S. E. Lewis, N. Mainolfi, *J. Organomet. Chem.* **2004**, *689*, 3873. f) K. H. Park, Y. K. Chung, *Synlett* **2005**, 545. g) S. Laschat, A. Becheanu, T. Bell, A. Baro, *Synlett* **2005**, 2547. h) I. Omae, *Appl. Organomet. Chem.* **2009**, *23*, 91. i) M. P. Croatt, P. A. Wender, *Eur. J. Org. Chem.* **2010**, 19.

78 J. G. Donkervoort, A. R. Gordon, C. Johnstone, W. J. Kerr, U. Lange, *Tetrahedron* **1996**, *52*, 7391.

79 a) T. Mitsudo, K. Kokuryo, Y. Takegami, *J. Chem. Soc., Chem. Commun.* **1976**, 722. b) T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, Y. Takegami, *J. Org. Chem.* **1979**, *44*, 4492.

80 Independently, a similar ruthenium-catalyzed Pauson–Khand reaction of 1,6-enynes. T. Morimoto, N. Chatani, Y. Fukumoto, S. Murai, *J. Org. Chem.* **1997**, *62*, 3762.

81 N. Suzuki, T. Kondo, T. Mitsudo, *Organometallics* **1998**, *17*, 766.

82 T. Fukuyama, R. Yamaura, Y. Higashibeppu, T. Okamura, I. Ryu, T. Kondo, T. Mitsudo, *Org. Lett.* **2005**, *7*, 5781.

83 *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed., ed. by M. Beller, C. Bolm, Wiley-VCH, Weinheim, **2004**, Vols. 1–2.

84 a) *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed., ed. by B. Cornils, W. A. Herrmann, Wiley-VCH, Weinheim, **2002**, Vols. 1–3. b) G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed., Wiley-VCH, Weinheim, **2002**. c) J. Christoffers, R. G. Bergman, *J. Am. Chem. Soc.* **1996**, *118*, 4715. d) Y. Liang, G. P. A. Yap,

A. L. Rheingold, K. H. Theopold, *Organometallics* **1996**, *15*, 5284. e) S. Hajela, J. E. Bercaw, *Organometallics* **1994**, *13*, 1147. f) A. M. Al-Jarallah, J. A. Anabtawi, M. A. B. Siddiqui, A. M. Aitani, A. W. Al-Sa'doun, *Catal. Today* **1992**, *14*, 1. g) J. Skupinska, *Chem. Rev.* **1991**, *91*, 613. h) W. E. Piers, P. J. Shapiro, E. E. Bunel, J. E. Bercaw, *Synlett* **1990**, 74. i) S. M. Pillai, M. Ravindranathan, S. Sivaram, *Chem. Rev.* **1986**, *86*, 353.

85 a) N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081. b) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49. c) I. Ojima, M. Tzamarioudaki, Z. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635. d) H.-W. Frühauf, *Chem. Rev.* **1997**, *97*, 523. e) K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. f) E. Negishi, C. Copéret, S. Ma, S.-Y. Liou, F. Liu, *Chem. Rev.* **1996**, *96*, 365. g) S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901.

86 For Co: a) D. W. Macomber, A. G. Verma, R. D. Rogers, *Organometallics* **1988**, *7*, 1241. b) Z. Zhou, L. P. Battaglia, G. P. Chiusoli, M. Costa, M. Nardelli, C. Pelizzi, G. Predieri, *J. Chem. Soc., Chem. Commun.* **1990**, 1632. c) G. P. Chiusoli, M. Costa, Z. Zhou, *J. Chem. Soc., Perkin Trans. 1* **1992**, 1399. d) V. Gandon, N. Agenet, K. P. C. Vollhardt, M. Malacria, C. Aubert, *J. Am. Chem. Soc.* **2006**, *128*, 8509. e) A. Geny, D. Lebœuf, G. Rouquié, K. P. C. Vollhardt, M. Malacria, V. Gandon, C. Aubert, *Chem.—Eur. J.* **2007**, *13*, 5408. For Ti: f) G. J. Balaich, I. P. Rothwell, *J. Am. Chem. Soc.* **1993**, *115*, 1581. g) E. S. Johnson, G. J. Balaich, I. P. Rothwell, *J. Am. Chem. Soc.* **1997**, *119*, 7685. For Ru: h) Y. Yamamoto, H. Kitahara, R. Ogawa, K. Itoh, *J. Org. Chem.* **1998**, *63*, 9610. i) Y. Yamamoto, H. Kitahara, R. Hattori, K. Itoh, *Organometallics* **1998**, *17*, 1910. j) Y. Yamamoto, H. Kitahara, R. Ogawa, H. Kawaguchi, K. Tatsumi, K. Itoh, *J. Am. Chem. Soc.* **2000**, *122*, 4310. For Rh: k) R. Grigg, R. Scott, P. Stevenson, *J. Chem. Soc., Perkin Trans. 1* **1988**, 1365. For Ni: l) A. J. Chalk, *J. Am. Chem. Soc.* **1972**, *94*, 5928. m) T. Tsuda, H. Mizuno, A. Takeda, A. Tobisawa, *Organometallics* **1997**, *16*, 932.

87 For direct observation of cobaltacyclopentadienes and their related reactions in terms of the reaction mechanism for alkyne cyclotrimerization, see: a) R. Diercks, B. E. Eaton, S. Gürtzgen, S. Jalisatgi, A. J. Matzger, R. H. Radde, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1998**, *120*, 8247. The pathways involving cascades of metathesis steps in ruthenium-catalyzed conversion of triynes to benzene derivatives have been described. b) J.-U. Peters, *Chem. Commun.* **1997**, 1983. c) B. Witulski, T. Stengel, J. M. Fernández-Hernández, *Chem. Commun.* **2000**, 1965.

88 a) O. V. Ozerov, F. T. Ladipo, B. O. Patrick, *J. Am. Chem. Soc.* **1999**, *121*, 7941. b) O. V. Ozerov, B. O. Patrick, F. T. Ladipo, *J. Am. Chem. Soc.* **2000**, *122*, 6423.

89 a) H. Suzuki, K. Itoh, Y. Ishii, K. Simon, J. A. Ibers, *J. Am. Chem. Soc.* **1976**, *98*, 8494. b) L. D. Brown, K. Itoh, H. Suzuki, K. Hirai, J. A. Ibers, *J. Am. Chem. Soc.* **1978**, *100*, 8232.

90 a) Y. Yamamoto, R. Ogawa, K. Itoh, *Chem. Commun.* **2000**, 549. b) Y. Yamamoto, H. Takagishi, K. Itoh, *J. Am. Chem. Soc.* **2002**, *124*, 28.

91 D. M. Singleton, *Tetrahedron Lett.* **1973**, *14*, 1245.

92 A. Carbonaro, A. Greco, G. Dall'Asta, *Tetrahedron Lett.* **1968**, *9*, 5129.

93 a) S. Ikeda, N. Mori, Y. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 4779. b) S. Ikeda, H. Watanabe, Y. Sato, *J. Org. Chem.* **1998**, *63*, 7026. c) N. Mori, S. Ikeda, Y. Sato, *J. Am. Chem. Soc.* **1999**, *121*, 2722.

94 T. Kondo, Y. Kaneko, F. Tsunawaki, T. Okada, M. Shiotsuki, Y. Morisaki, T. Mitsudo, *Organometallics* **2002**, *21*, 4564.

95 a) C. Munz, C. Stephan, H. tom Dieck, *J. Organomet. Chem.* **1991**, *407*, 413. b) N. Tsukada, S. Sugawara, Y. Inoue, *Org. Lett.* **2000**, *2*, 655.

96 a) Y. Matsushima, H. Kikuchi, M. Uno, S. Takahashi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2475. b) Y. Sorek, H. Cohen, D. Meyerstein, *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3431. c) Y. Sorek, H. Cohen, D. Meyerstein, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1169.

97 a) T. Takahashi, M. Kotora, Z. Xi, *J. Chem. Soc., Chem. Commun.* **1995**, 361. b) T. Takahashi, Z. Xi, A. Yamazaki, Y. Liu, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **1998**, *120*, 1672. c) T. Takahashi, F.-Y. Tsai, Y. Li, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **1999**, *121*, 11093.

98 a) D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 7925. b) R. Tanaka, Y. Nakano, D. Suzuki, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2002**, *124*, 9682.

99 V. Gevorgyan, U. Radhakrishnan, A. Takeda, M. Rubina, M. Rubin, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 2835.

100 N. Mori, S. Ikeda, K. Odashima, *Chem. Commun.* **2001**, 181.

101 Y. Yamamoto, J. Ishii, H. Nishiyama, K. Itoh, *J. Am. Chem. Soc.* **2004**, *126*, 3712.

102 Y. Ura, Y. Sato, M. Shiotsuki, T. Kondo, T. Mitsudo, *J. Mol. Catal. A: Chem.* **2004**, *209*, 35.

103 Y. Ura, Y. Sato, H. Tsujita, T. Kondo, M. Imachi, T. Mitsudo, *J. Mol. Catal. A: Chem.* **2005**, *239*, 166.

104 a) M. G. Barlow, M. J. Bryant, R. N. Haszeldine, A. G. Mackie, *J. Organomet. Chem.* **1970**, *21*, 215. b) K. Kawamoto, A. Tatani, T. Imanaka, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1239. c) P. Grenouillet, D. Neibecker, I. Tkatchenko, *Organometallics* **1984**, *3*, 1130. d) A. Sen, T.-W. Lai, *Organometallics* **1983**, *2*, 1059. e) G. Wu, A. L. Rheingold, R. F. Heck, *Organometallics* **1987**, *6*, 2386. f) K. Kaneda, T. Kiriyama, T. Hiraoka, T. Imanaka, *J. Mol. Catal.* **1988**, *48*, 343. g) Z. Jiang, A. Sen, *J. Am. Chem. Soc.* **1990**, *112*, 9655. h) Z. Jiang, A. Sen, *Organometallics* **1993**, *12*, 1406. i) T. Tsuchimoto, S. Kamiyama, R. Negoro, E. Shirakawa, Y. Kawakami, *Chem. Commun.* **2003**, 852. j) G. W. Kabalka, G. Dong, B. Venkataiah, *Tetrahedron Lett.* **2004**, *45*, 2775. k) J. Peng, J. Li, H. Qiu, J. Jiang, K. Jiang, J. Mao, G. Lai, *J. Mol. Catal. A: Chem.* **2006**, *255*, 16. l) C. Sui-Seng, L. F. Groux, D. Zargarian, *Organometallics* **2006**, *25*, 571. m) C. Sui-Seng, A. Castonguay, Y. Chen, D. Gareau, L. F. Groux, D. Zargarian, *Top. Catal.* **2006**, *37*, 81.

105 a) F. Dawans, *Tetrahedron Lett.* **1971**, *12*, 1943. b) G. Henrici-Olivé, S. Olivé, E. Schmidt, *J. Organomet. Chem.* **1972**, *39*, 201. c) P. Barthelemy, A. Deffieux, P. Sigwalt, *Nouv. J. Chim.* **1985**, 173.

106 N. Galdi, C. D. Monica, A. Spinella, L. Oliva, *J. Mol. Catal. A: Chem.* **2006**, *243*, 106.

107 W. P. Kretschmer, S. I. Troyanov, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* **1998**, *17*, 284.

108 T. Alderson, E. L. Jenner, R. V. Lindsey, Jr., *J. Am. Chem. Soc.* **1965**, *87*, 5638.

109 For palladium-catalyzed reactions, see: a) G. J. P. Britovsek, W. Keim, S. Mecking, D. Sainz, T. Wagner, *J. Chem. Soc., Chem. Commun.* **1993**, 1632. b) G. J. P. Britovsek, K. J. Cavell, W. Keim, *J. Mol. Catal. A: Chem.* **1996**, *110*, 77. c) R. Bayersdörfer, B. Ganter, U. Englert, W. Keim, D. Vogt, *J. Organomet. Chem.* **1998**, *552*, 187. d) N. J. Hovestad, E. B. Eggeling, H. J. Heidbüchel, J. T. B. H. Jastrzebski, U. Kragl, W. Keim, D. Vogt, G. van Koten, *Angew. Chem., Int. Ed.* **1999**, *38*, 1655. e) E. B. Eggeling, N. J. Hovestad, J. T. B. H. Jastrzebski, D. Vogt, G. van Koten, *J. Org. Chem.* **2000**, *65*, 8857.

110 For cobalt-catalyzed reactions, see: a) S. M. Pillai, G. L. Tembe, M. Ravindranathan, *J. Mol. Catal.* **1993**, *84*, 77. b) H. Umezaki, Y. Fujiwara, K. Sawara, S. Teranishi, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2230. c) C. S. Yi, Z. He, D. W. Lee, *Organometallics* **2001**, *20*, 802.

111 a) G. Wilke, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. b) N. Kawata, K. Maruya, T. Mizoroki, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 413. c) B. Bogdanovlć, *Adv. Organomet. Chem.* **1979**, *17*, 105. d) R. Ceder, G. Muller, J. I. Ordinas, *J. Mol. Catal.* **1994**, *92*, 127. e) A. L. Monteiro, M. Seferin, J. Dupont, R. F. de Souza, *Tetrahedron Lett.* **1996**, *37*, 1157. f) G. Muller, J. I. Ordinas, *J. Mol. Catal. A: Chem.* **1997**, *125*, 97. g) V. Fassina, C. Ramminger, M. Seferin, A. L. Monteiro, *Tetrahedron* **2000**, *56*, 7403.

112 a) N. Nomura, J. Jin, H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.* **1998**, *120*, 459. b) M. Nandi, J. Jin, T. V. RajanBabu, *J. Am. Chem. Soc.* **1999**, *121*, 9899. c) T. V. RajanBabu, N. Nomura, J. Jin, B. Radetich, H. Park, M. Nandi, *Chem.—Eur. J.* **1999**, *5*, 1963. d) J. Jin, T. V. RajanBabu, *Tetrahedron* **2000**, *56*, 2145. e) A. Bösmann, G. Franciò, E. Janssen, M. Solinas, W. Leitner, P. Wasserscheid, *Angew. Chem., Int. Ed.* **2001**, *40*, 2697. f) H. Park, T. V. RajanBabu, *J. Am. Chem. Soc.* **2002**, *124*, 734. g) G. Franciò, F. Faraone, W. Leitner, *J. Am. Chem. Soc.* **2002**, *124*, 736.

113 a) T. V. RajanBabu, *Chem. Rev.* **2003**, *103*, 2845. b) R. B. Bedford, M. Betham, M. E. Blake, A. Garcés, S. L. Millar, S. Prashar, *Tetrahedron* **2005**, *61*, 9799. c) M. M. P. Grutters, C. Müller, D. Vogt, *J. Am. Chem. Soc.* **2006**, *128*, 7414.

114 Ruthenium-catalyzed *head-to-tail* dimerization of styrenes to 1,3-diaryl-1-butenes has been reported. M. Higashimura, K. Imamura, Y. Yokogawa, T. Sakakibara, *Chem. Lett.* **2004**, *33*, 728.

115 1,4-Diaryl-1-butenes are an important starting material for the synthesis of aryltetralins, as well as a key intermediate for the construction of eight-membered-ring systems, such as 2,2′-cyclolignans. a) S. Hajra, B. Maji, A. Karmakar, *Tetrahedron Lett.* **2005**, *46*, 8599. b) B. Kramer, A. Averhoff, S. R. Waldvogel, *Angew. Chem., Int. Ed.* **2002**, *41*, 2981.

116 T. Kondo, D. Takagi, H. Tsujita, Y. Ura, K. Wada, T. Mitsudo, *Angew. Chem., Int. Ed.* **2007**, *46*, 5958.

117 The formation of ruthenacyclopentane was proposed in ruthenium-catalyzed cyclization of 1,6-dienes. Y. Yamamoto, Y. Nakagai, N. Ohkoshi, K. Itoh, *J. Am. Chem. Soc.* **2001**, *123*, 6372.

118 A theoretical study of σ-bond metathesis of Pd(II)–CH_3 with CH_3OH has been reported. A. Milet, A. Dedieu, G. Kapteijn, G. van Koten, *Inorg. Chem.* **1997**, *36*, 3223.

119 a) L. Yet, *Chem. Rev.* **2003**, *103*, 4283. b) R. Shen, C. T. Lin, E. J. Bowman, B. J. Bowman, Jr., J. A. Porco, *J. Am. Chem. Soc.* **2003**, *125*, 7889.

120 J. R. Dehli, J. Legros, C. Bolm, *Chem. Commun.* **2005**, 973.

121 M. Catellani, G. P. Chiusoli, M. Costa, *J. Organomet. Chem.* **1995**, *500*, 69.

122 a) T. Kondo, A. Tanaka, S. Kotachi, Y. Watanabe, *J. Chem. Soc., Chem. Commun.* **1995**, 413. b) L. J. Gooßen, J. E. Rauhaus, G. Deng, *Angew. Chem., Int. Ed.* **2005**, *44*, 4042.

123 a) T. Hosokawa, M. Takano, Y. Kuroki, S.-I. Murahashi, *Tetrahedron Lett.* **1992**, *33*, 6643. b) V. I. Timokhin, S. S. Stahl, *J. Am. Chem. Soc.* **2005**, *127*, 17888. c) J. M. Lee, D.-S. Ahn, D. Y. Jung, J. Lee, Y. Do, S. K. Kim, S. Chang, *J. Am. Chem. Soc.* **2006**, *128*, 12954.

124 a) J. K. Stille, Y. Becker, *J. Org. Chem.* **1980**, *45*, 2139. b) S. Krompiec, M. Pigulla, M. Krompiec, S. Baj, J. Mrowiec-Białoń, J. Kasperczyk, *Tetrahedron Lett.* **2004**, *45*, 5257.

125 a) Y. Ura, H. Tsujita, K. Wada, T. Kondo, T. Mitsudo, *J. Org. Chem.* **2005**, *70*, 6623. b) H. Tsujita, Y. Ura, K. Wada, T. Kondo, T. Mitsudo, *Chem. Commun.* **2005**, 5100.

126 H. Tsujita, Y. Ura, S. Matsuki, K. Wada, T. Mitsudo, T. Kondo, *Angew. Chem., Int. Ed.* **2007**, *46*, 5160.

127 Intramolecular photocyclization of enamides of α,β-unsaturated acids as well as intramolecular electrocyclization of them by flash vacuum thermolysis have been reported. a) I. Ninomiya, Y. Tada, T. Kiguchi, O. Yamamoto, T. Naito, *J. Chem. Soc., Perkin Trans. 1* **1984**, 2035. b) I. Ninomiya, C. Hashimoto, T. Kiguchi, T. Naito, *J. Chem. Soc., Perkin Trans. 1* **1984**, 2911. c) S. Lesniak, B. Pasternak, *Synth. Commun.* **2002**, *32*, 875.

128 We have reported the formation of divalent ruthenacycles via the oxidative cyclization of 1,3,5-cyclooctatriene with maleic anhydride or maleimides and reductive elimination from these metallacyclic complexes. Y. Ura, T. Utsumi, H. Tsujita, K. Wada, T. Kondo, T. Mitsudo, *Organometallics* **2006**, *25*, 2934.

129 M. Shiotsuki, T. Suzuki, T. Kondo, K. Wada, T. Mitsudo, *Organometallics* **2000**, *19*, 5733.

130 T. Kondo, H. Tsujita, Z. A. Siddique, S. Matsuki, H. Miura, H. Tochio, T. Matsuda, M. Narazaki, H. Tsuzuki, K. Kuge, Y. Tomida, K. Yoshimura, T. Yano, PCT WO 2009/069833 A1.

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