Bull. Chem. Soc. Jpn., 72, 2591—2602 (1999) 2591

Accounts

Carbon–Carbon Bond Cleavage and Selective Transformation of Zirconacycles

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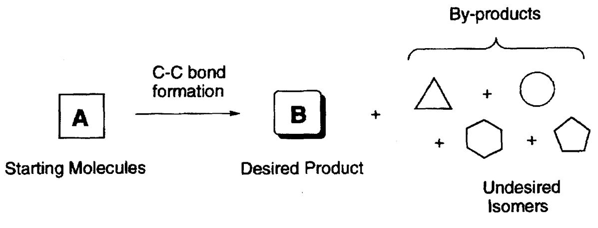
(Received May 17, 1999)

This account describes recent development in carbon–carbon bond cleavage reactions and selective transformation of 5-membered zirconacycles, including zirconacyclopentanes, zirconacyclopentenes, and zirconacyclopentadienes. These zirconacycles can be prepared by coupling of unsaturated compounds such as alkenes and/or alkynes, but the zirconacycles also undergo β,β'-C–C bond cleavage, which has been further applied to organic transformation reactions. Combination of the β,β'-C–C bond cleavage and the C–C bond formation on zirconocene provided a highly selective and novel transformation. Vinylzirconation of alkynes, regioselective allylzirconation of alkynes, and coupling of alkynes with nitriles or ketones were achieved by this method. Zirconacyclopentadienes prepared symmetrically or unsymmetrically were converted into naphthalene, diene, and benzene derivatives. Preparation of benzene derivatives from three different alkynes was performed by combination of C–C bond cleavage and C–C bond formation on zirconocene in one-pot in high yield with excellent selectivity.

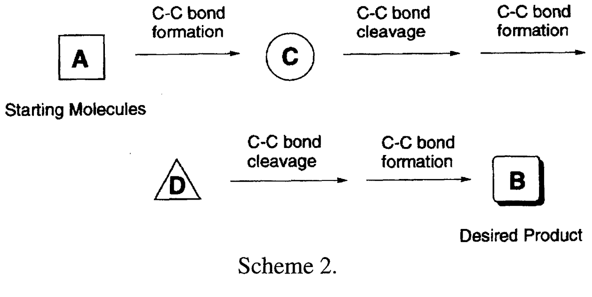
It is generally accepted that once a carbon–carbon bond is formed, it is impossible to cleave the bond again; this is usually true. Therefore, when a new reagent for carbon–carbon bond formation is developed, several selectivities such as chemoselectivity, regioselectivity, stereoselectivity, and enantioselectivity should be simultaneously achieved. Otherwise, after the carbon–carbon bond is formed, these selectivities can not be improved. Undesired products are obtained as by-products as shown in Scheme 1. This is the major reason why development of highly selective reactions is difficult.

However, if we can cleave the carbon–carbon bond even after the bond is formed, the situation is completely changed. Selective transformation via carbon–carbon bond activation is therefore a very attractive area in organic chemistry. Several carbon–carbon bond cleavage reactions have been well known for a long time in organic chemistry.[1] One of our goal is to develop a novel type of organic synthesis which consists of the combination of selective C–C bond cleavage and selective C–C bond formation as shown in Scheme 2. Very recently we have developed a novel preparative method of benzene derivatives from three different alkynes by repeating the combination of C–C bond cleavage and C–C bond formation on zirconocene (vide infra).



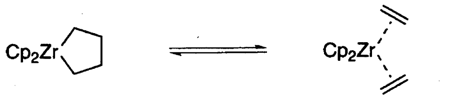
Scheme 1.

In this paper, we show our recent results on novel type of organic synthesis by the combination of selective C–C bond cleavage and selective C–C bond formation using zirconacycles which are formally in equilibrium with their reduced structures as shown in Eqs. 1, 2, and 3.[2]

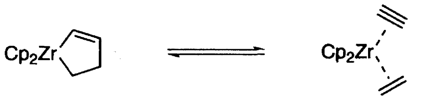


Scheme 2.

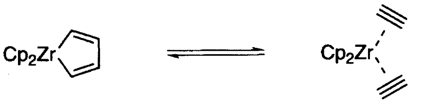
[#] CREST, Science and Technology Corporation (JST), Sapporo 060-0811.



1 **2** (1)



3 **4** (2)

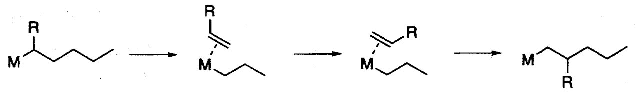


5 **6** (3)

Regioselective Substituent Transfer

Several examples of selective transformation via carbon-carbon bond cleavage are shown in Scheme 3.

As one example, the regioselective substituent transfer is discussed here. Substituent transfer involves not only the carbon–carbon bond cleavage but also a new carbon–carbon bond formation. One method is to cleave the carbon–carbon bond between the R group and the main skeleton. But this is not convenient for the substituent transfer, since the new position should also be activated for the new carbon–carbon bond formation. A possible strategy is shown in Eq. 4. Cleavage of the β,β'-carbon–carbon bond provides an alkyl-olefin-metal compound (**7** → **8**). The R group might rotate due to the sterical requirement caused by a ligand of the metal (**8** → **9**). Insertion of the rotated olefin into the metal–alkyl bond provides the product with the substituent at the next carbon (**9** → **10**).

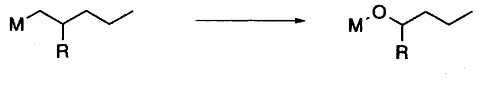


7 **8** **9** **10** (4)

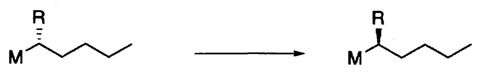
Along this line, we found a novel type of methyl group transfer reaction. Starting from 2,4-dibromohexane, 2,3-dimethyl-1,4-dibromobutane was obtained regioselectively and stereoselectively as shown in Eq. 5.[3] This selective transfer reaction proceeded via β,β'-carbon–carbon bond cleavage of zirconacyclopentanes (vide infra).

(i) Regioselective substituent transfer

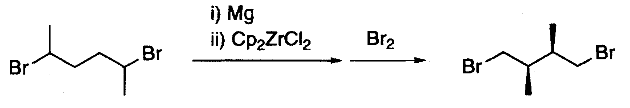
(ii) Replacement of a carbon in the skeleton by other atoms



(iii) Stereoselective recombination of a substituent



Scheme 3. Novel transformations via C–C bond cleavage.



11 **12** (5)

β,β'-C–C Bond Cleavage of Zirconacyclopentanes

Zirconacyclopentanes are prepared by coupling of two olefins or a diene on 'Cp$_2$Zr' or by the reaction of Cp_2ZrCl_2 with 1,4-dimetallobutane derivatives.[4—6] The simplest zirconacyclopentane is $Cp_2Zr(C_4H_8)$ (**1**) which is prepared from 'Cp$_2$Zr' and two ethylene molecules or from Cp_2ZrCl_2 and $BrMg(CH_2)_4MgBr$ (Chart 1). The formation of this zirconacyclopentane was observed when a reduced zirconocene was treated with ethylene gas. Because of its unstability, isolation and full characterization have not been done yet.[4b,d] One major question regarding the zirconacyclopentanes prepared from two olefins or a diene on zirconocene is whether the β,β'-carbon–carbon bond is actually formed or not. In order to verify the structure of the simplest but still useful zirconacyclopentane, we tried to isolate it. For stabilizing the zirconacyclopentane, two *t*-Bu groups were introduced to each cyclopentadiene ligand.[4j,m,5e] And, successfully, we were able to isolate crystals suitable for X-ray analysis.[5e] Into a reaction mixture of $(1,3\text{-}t\text{-}Bu_2\text{-}C_5H_3)_2ZrCl_2$ and 2 equiv of *n*-BuLi was bubbled ethylene gas; then, under ethylene atmosphere, $(1,3\text{-}t\text{-}Bu_2\text{-}C_5H_3)_2Zr(C_4H_8)$ (**13**) gradually crystallized to afford single crystals. X-ray analysis ($R = 4.1\%$, $R_w = 4.7\%$) shows that the bond lengths of C(1)–C(2), C(2)–C(3), and C(3)–C(4) are 1.542(5), 1.502(5), and 1.547(4) Å, respectively. The structure of zirconacyclopentane clearly reveals that there is a σ-bond between two ethylene moieties on zirconium as shown in Fig. 1. When this complex was treated with one equiv of diphenylacetylene at 65 °C for 72 h, the β,β'-carbon–carbon bond cleavage occurred to afford a zirconacyclopentene.[5e]

Zirconacyclopentane with usual Cp ligands is also prepared from $BrMg(CH_2)_4MgBr$ and Cp_2ZrCl_2 as mentioned above. Addition of PMe_3 to the zirconacyclopentane thus prepared gave a zirconocene-ethylene complex **14** in 84% yield.[5a] This clearly showed that the carbon–carbon bond cleavage on zirconacyclopentane proceeded since there was a carbon–carbon bond in the starting di-Grignard reagent. The use of an aldehyde instead of PMe_3 showed a similar carbon–carbon bond cleavage reaction which produced

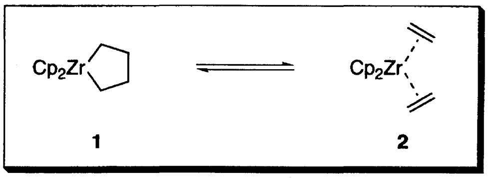


Chart 1.

an oxazirconacyclopentane **15**.[7] After hydrolysis, the corresponding alcohol **16** was obtained in 53% yield as shown in the following Scheme 4.

Methyl transfer reaction of 2,5-dibromohexane described in the previous section proceeds via β,β'-carbon–carbon bond cleavage of zirconacyclopentanes, as shown in Eq. 6.[3] In the case of zirconium, it was difficult to follow the reaction by NMR since the reaction was fast. At room temperature, the reaction was complete within 1 h. However, in the case of Hf, the same transfer proceeded slowly at 50 °C. Therefore, this reaction was monitored by NMR. The result is shown in Fig. 2. Hafnacyclopentane with two methyl groups at the α-position was formed cleanly. The Cp signal of the hafnacyclopentane gradually decreased. A new Cp signal assigned to a hafnacyclopentane with two methyl groups at the β-position appeared and gradually increased with decrease of the starting complex. At the end of the reaction, only the methyl transferred hafnacyclopentane was observed in the reaction mixture.

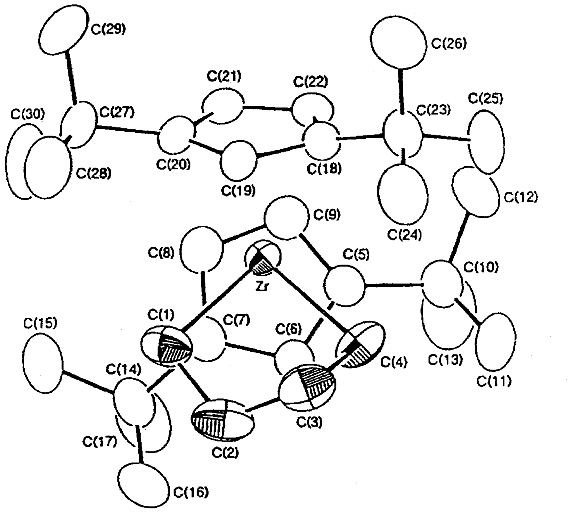


Fig. 1. Crystal structure of zirconacyclopentane **13**.

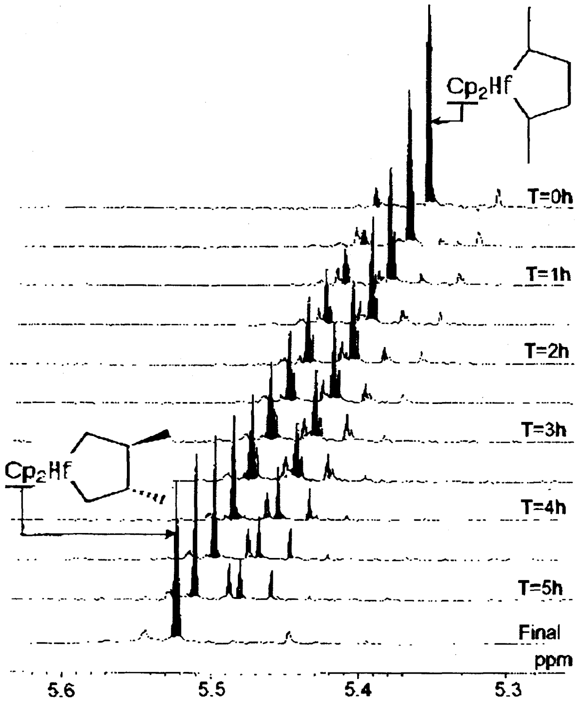
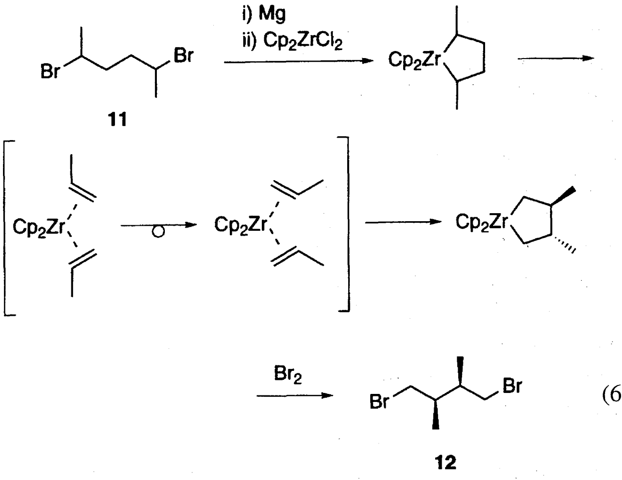
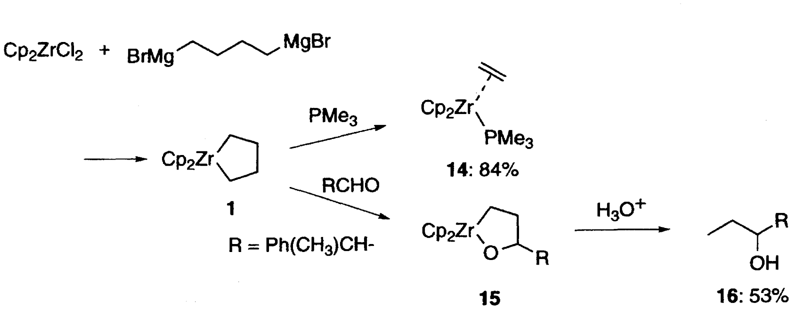


Fig. 2. Rearrangement of 2,5-dimethylhafnacyclopentane.



(6)

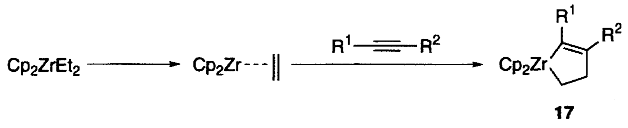
During this reaction there exist one intermediate, which has one methyl group at the α-position and the other methyl group at the β-position. The formation of a bis-olefin complex was not observed. So far, there is no report of the observation of such a zirconocene–bis(olefin) complex. However, the equilibrium between a zirconacyclopentane and a zirconocene–bis(olefin) complex can explain most of the carbon–carbon bond cleavage reactions of zirconacyclopentanes.



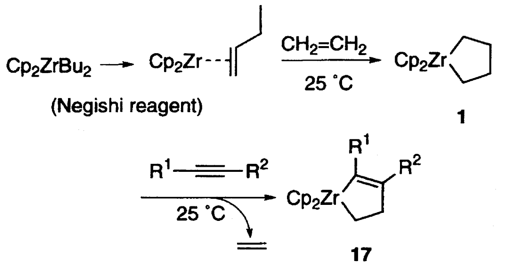
Scheme 4.

β,*β*′-C–C Bond Cleavage of Zirconacyclopentenes

Zirconacyclopentenes were prepared by the reaction of Cp_2ZrEt_2 with an alkyne (Eq. 7)[8] or by the carbon–carbon bond cleavage of zirconacyclopentane (Eq. 8)[5e]



(7)



(8)

The structure of zirconacyclopentene **17a** ($R^1 = R^2 = Ph$) was determined by X-ray crystallography.[9] Its hafnium analogue, a hafnacyclopentene, has been prepared from hafnacyclopentane and characterized by X-ray analysis by Erker.[10] The structure of zirconacyclopentene determined here was almost the same as that for the hafnium case. Single crystals of **17a** were obtained here from the reaction of diphenylacetylene with zirconacyclopentane **1** under ethylene atmosphere. X-Ray analysis ($R = 4.8\%$, $R_w = 4.5\%$) shows the bond lengths of C(1)–C(2), C(2)–C(3), and C(3)–C(4) is 1.336(5), 1.507(7), and 1.443(7) Å, respectively (Fig. 3). The length of the *β*,*β*′-carbon–carbon bond in **4a** falls in the region of normal single C–C bonds (Chart 2). This also clearly showed that there is a σ-bond between the *β* and *β*′-carbons of the zirconacyclopentene.

The reagent Cp_2ZrEt_2,[11] which we used here, showed a quite different reactivity from the Negishi reagent which acts as 'Cp_2Zr' equivalent.[12] The Negishi reagent, Cp_2ZrBu_2, is converted into a zirconocene–butene complex. Study on the formation of the butene complex revealed that the mechanism is rather complicated.[13] But the butene ligand is very labile; when it is treated with alkynes, the butene ligand is liberated and does not incorporate in the product. However, the Cp_2ZrEt_2 we reported is converted into a zirconocene–ethylene complex and the ethylene ligand is not labile. It reacts with various unsaturated compounds and the ethylene incorporates in the products. In this sense, our reagent, Cp_2ZrEt_2 is quite different from Cp_2ZrBu_2 (Negishi reagent).

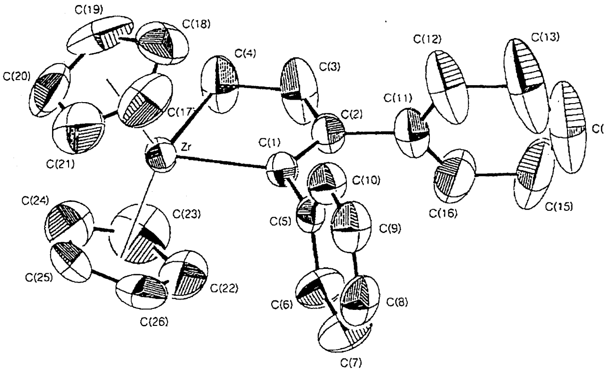


Fig. 3. Crystal structure of zirconacyclopentene **17a**.

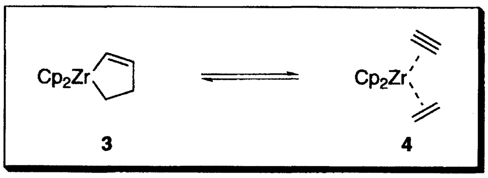
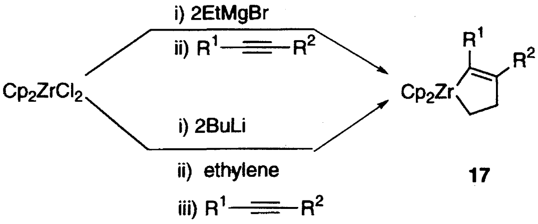


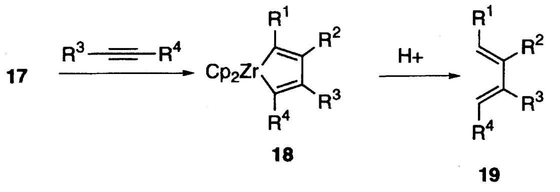
Chart 2.

Preparation of Unsymmetrical Zirconacyclopentadienes

As for the unsymmetrical zirconacyclopentadienes, the basic strategy is a reaction of a different alkyne with zirconocene–alkyne complexes stabilized with phosphine or pyridine derivatives. The most general method to prepare the zirconocene–alkyne complex consists of hydrozirconation of alkynes using Cp_2ZrHCl, followed by methylation of the resulting alkenylzirconocene chloride.[14]

We found that zirconacyclopentenes prepared from one equiv of alkynes and Cp_2ZrEt_2 reacted with a different alkyne at 50 °C to give unsymmetrically substituted zirconacyclopentadienes in high yields. Very interestingly, the once-formed *β*,*β*′-C–C bond in **4** was cleaved and the ethylene moiety was replaced by the second alkyne. This method is very convenient, but sometimes 3—5% of homo-coupling products are formed as by-products. In such cases, the use of ethylene is recommended. The unsymmetrical zirconacyclopentadienes were formed with excellent selectivities.





(9)

In this procedure, the zirconacyclopentadienes were prepared from zirconacyclopentanes via zirconacyclopentenes. This means that the once-formed *β*,*β*′-C–C bonds in **1** and **17** were cleaved and the two ethylene moieties were replaced one by one by the first alkyne and the second alkyne. Ethylene plays a very important role in this procedure.

Formation of zirconacyclopentadienes by the reaction of zirconacyclopentenes (Fig. 4) with an alkyne was applied to a novel-type rearrangement of dialkynylsilane, as shown in Eq. 10.[15]

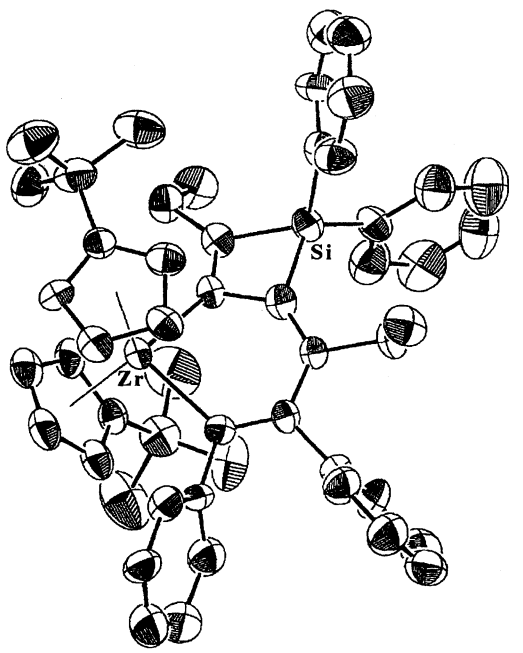
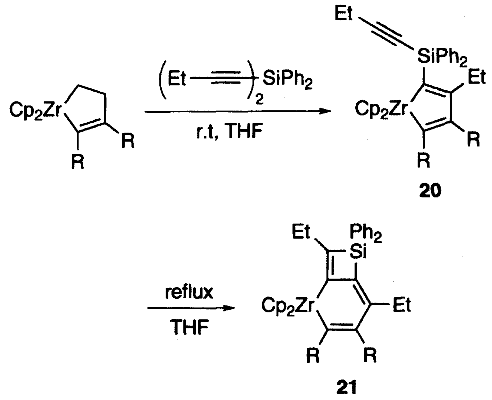


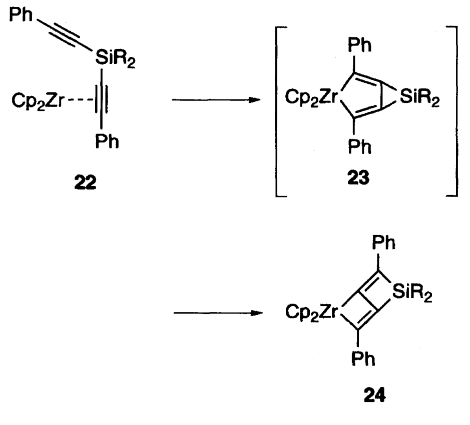
Fig. 4. Crystal structure of zirconacyclohexadiene **21a**.



(10)

R = Ph, 89%; R = Et, 82%

A similar rearrangement of dialkynylsilane was observed in the reaction with Cp_2ZrEt_2 which gave new 4-4 fused ring compounds **24** (Fig. 5) containing zirconium and silicon in each ring.[16] Both structures were determined by X-ray analysis. This type of rearrangement is not limited only to dialkynylsilane. Alkynylphosphine also showed a similar rearrangement in the reaction with a zirconocene complex.[17]



(11)

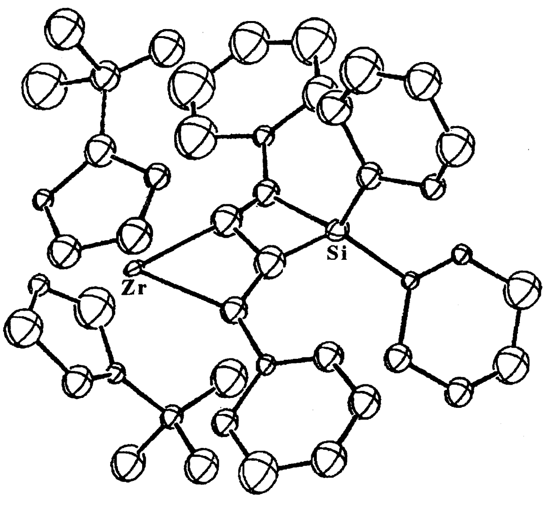
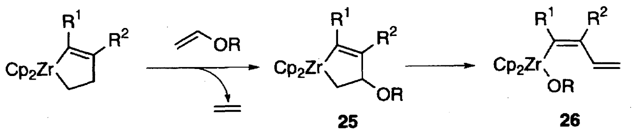


Fig. 5. Crystal structure of **24**.

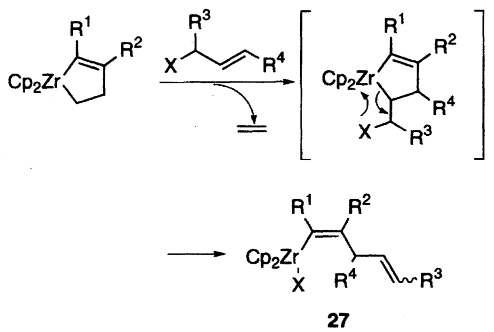
Carbozirconation of Alkynes via Zirconacyclopentenes

The carbon–carbon bond cleavage of zirconacyclopentenes provides various types of novel reactions of alkynes, since the rest of the ethylene molecule is replaced by this reaction. For example, vinylmetalation of alkynes using conventional methods has been difficult. In the reaction of zirconacyclopentenes with vinyl ethers the ethylene molecule is replaced and the double bond of vinyl ether couples with an alkyne moiety. The resulting β-alkoxyzirconacyclopentenes **25** undergoes the β-alkoxy elimination to afford vinylzirconation of alkynes as shown in Eq. 12. This is the first example of vinylmetalation of unactivated alkynes.[18]



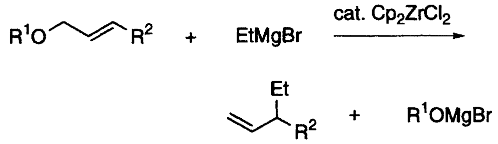
(12)

Zirconacyclopentenes also react with allylic compounds, forming allylzirconation products (Eq. 13).[19—21] Usually, allylmetalation of alkynes gives a mixture of two products, since the carbon–carbon bond formation occurs at both the α and γ positions of allyl compounds via 4-membered or 6-membered intermediates. The reaction of zirconacyclopentenes with allyl compounds is quite different from the usual allylation reactions. Replacement of the ethylene moiety with the double bond of allyllic compounds proceeds in two ways. Carbon-carbon bond formation might occur at the α-carbon and β-carbon to give two isomers. However, only one isomer is converted into allylmetalation of alkynes and the other isomer is in equilibrium with the first isomer. Therefore, both isomers give the same allylation product. The carbon-carbon bond formation occurred at only the γ-position of allyl compounds with perfect selectivity as shown in the following equation.

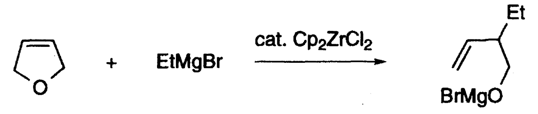


(13)

This type reaction of allyl ether on zirconocene was applied to a catalytic reaction as shown below.[21] This reaction proceeds via zirconacyclopentanes.

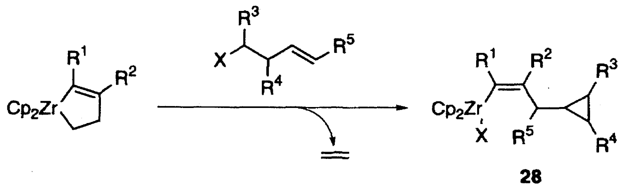


(14)



(15)

Treatment of zirconacyclopentenes with homoallyl bromides afforded allylcyclopropane derivatives as carbozirconation products (Eq. 16).[22] Such cyclopropane ring formation from zirconacycles has been reported by Whitby and his co-workers.[23]

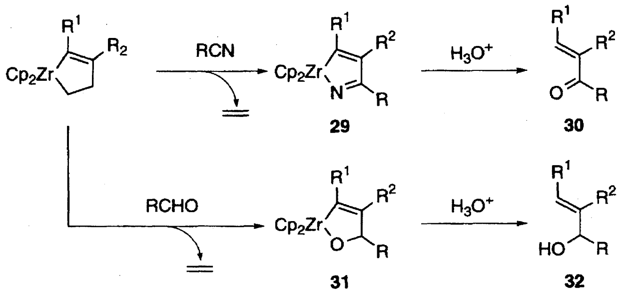


(16)

The coupling reaction of alkynes with nitriles or ketones can be achieved by this method very conveniently.[8,9] These reactions also proceed via β,β'-C–C bond cleavage of zirconacyclopentenes (Scheme 5).

The β,β'-C–C Bond Cleavage Reaction of Zirconacyclopentadienes

Zirconacyclopentadienes (Chart 3) are relatively more stable than zirconacyclopentanes and zirconacyclopentenes.



Scheme 5.

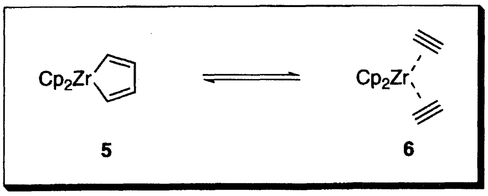
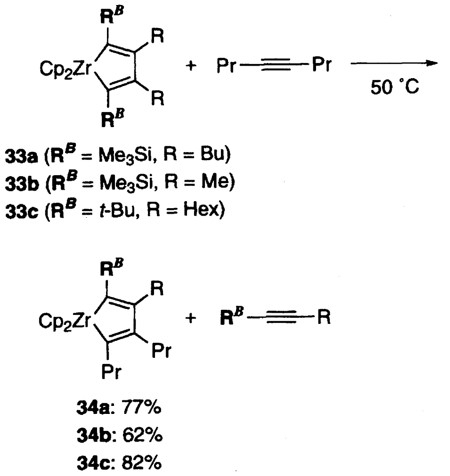


Chart 3.

They do not readily undergo the β,β'-C–C bond cleavage. Isomerization of silylated zirconacyclopentadienes has been known.[14b] And the β,β'-carbon–carbon bond cleavage reaction has been reported in the case of tantalum.[24] However, the use of the β,β'-C–C bond cleavage of zirconacyclopentadienes for organic synthesis was not known yet, when we started our investigations.[25]

After investigations, we found that, when zirconacyclopentadienes have two bulky substituents at its α and α' positions (R^B = $SiMe_3$, or *t*-Bu), one of the alkynes with the bulky substituent is replaced by a different alkyne such as 4-octyne (Eq. 17).[25]

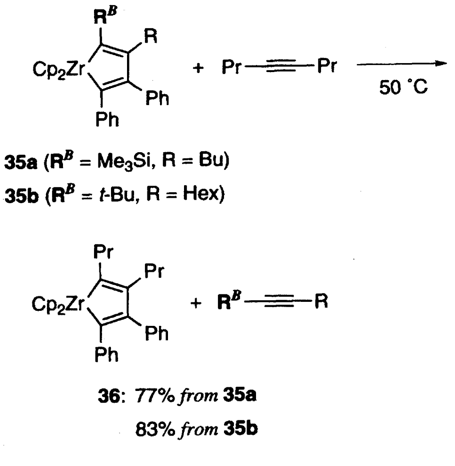


33a (R^B = Me_3Si, R = Bu)
33b (R^B = Me_3Si, R = Me)
33c (R^B = *t*-Bu, R = Hex)

34a: 77%
34b: 62%
34c: 82%

(17)

In the case of unsymmetrically substituted zirconacyclopentadiene **35a** or **35b**, having a bulky substituent at its α position and a phenyl group at its α' position, the alkyne with a bulky substituent was replaced when it was treated with 4-octyne. The cross-coupling product **36** between 4-octyne and diphenylacetylene was selectively formed (Eq. 18).



35a (R^B = Me_3Si, R = Bu)
35b (R^B = *t*-Bu, R = Hex)

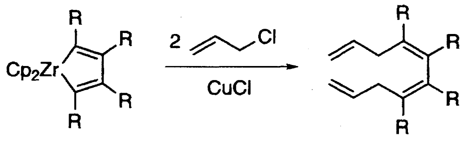
36: 77% *from* **35a**
83% *from* **35b**

(18)

The β,β'-C–C bond cleavage reaction of zirconacyclopentadienes takes place not only with alkynes but also when various unsaturated organic substrates are used. As shown in Scheme 6, for example, treatment of **33a** with acetonitrile generates azazirconacyclopentadiene **37** which, upon hydrolysis, affords α,β-unsaturated ketone **38** in 97% yield. Reaction of **33a** with a ketone such as 3-pentanone forms oxazirconacyclopentadiene **39**, which gives an allyl alcohol **40** in 85% yield after hydrolysis. When **33a** was treated with allylsilyl ether, allylzirconation product **41** discussed above was formed.

Reactions of Zirconacyclopentadienes

Zirconacyclopentadienes are now very conveniently prepared either symmetrically or unsymmetrically from alkynes by various methods. This means the development of novel reactions of zirconacyclopentadienes is very useful and attractive in organic synthesis. As one application, we developed copper-mediated double allylation of zirconacyclopentadienes which produces 1,4,6,9-tetraenes stereoselectively.[26,27]



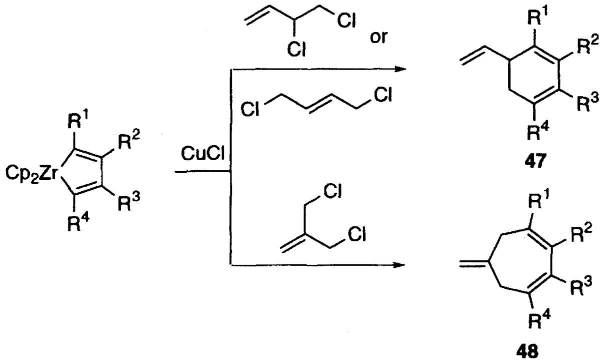
43

(19)

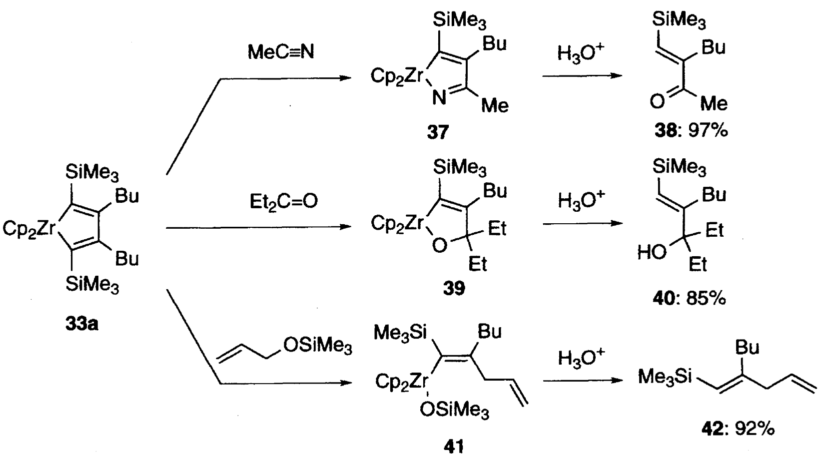
The tetraenes were cyclized with Cp_2ZrBu_2 to afford eight-five membered fused ketones in high yields after CO insertion reaction as shown in the following Scheme 7. This indicates that such eight-five membered fused ketones can be conveniently prepared from two alkynes, two allyl chloride and carbon monoxide in one-pot.

When two allyl chloride moieties exist in the same molecule, the cyclized compounds were formed by the reaction with zirconacyclopentadienes, as shown below (Scheme 8).[28]

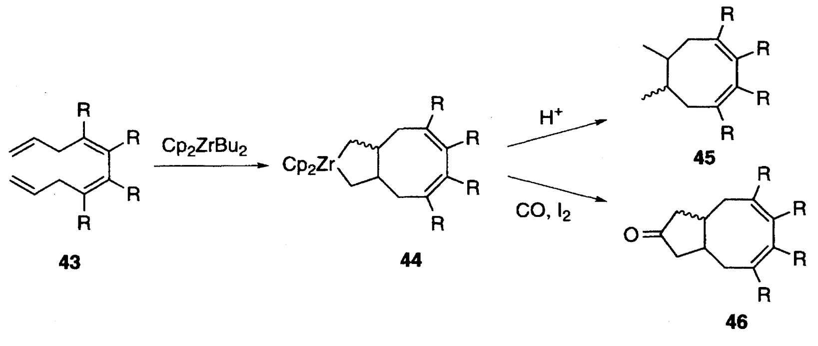
Recently, we have reported copper-mediated coupling of zirconacyclopentadienes with dihalo aromatic compounds, which represents the first example of such intermolecular coupling of two alkynes with dihaloarenes.[29] Polycyclic



Scheme 8.

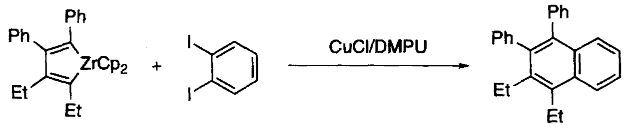


Scheme 6.



Scheme 7.

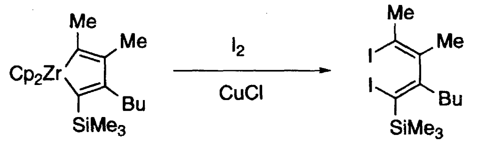
arenes with different substituents could be prepared in high yields from the reaction of dihalo aromatic compounds with unsymmetrically substituted zirconacyclopentadienes in a one-pot process (Eq. 20). In the case of dihalothiophene, benzothiophene is formed.



49: 53%

(20)

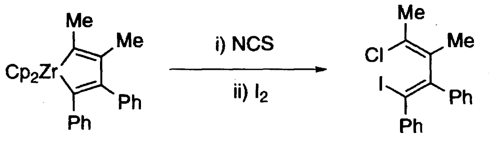
1,4-Dihalo-1,3-diene derivatives are important synthetic intermediates. Synthesis of such type dienes with different substituents is difficult. Reaction of unsymmetrically substituted zirconacyclopentadienes, prepared in situ via the above-described repeated C–C bond cleaving and C–C bond forming process, with I_2 in the presence of CuCl generated cleanly 1,4-diiodo-1,3-diene derivatives in high yields (Eq. 21).[30]



(21)

50: 73%

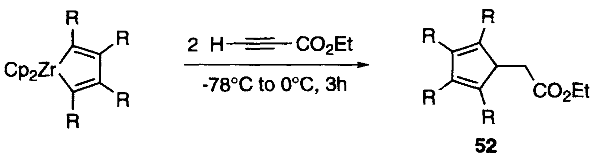
Similarly, mixed-dihalogenated 1,3-diene derivatives **51** with various substituents were obtained in one-pot in good to high yields with high selectivities when unsymmetrically substituted zirconacyclopentadienes were treated with halogenation reagents such as NCS, NBS, or I_2 (Eq. 22).[31]



(22)

51: 90%

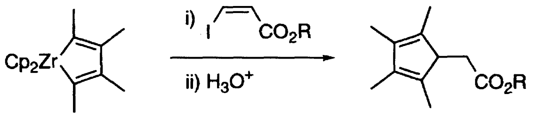
Five-membered ring compounds such as cyclopentadienes and cyclopentenones can be prepared by 1,1-cycloaddition of zirconacyclopentadienes to alkynes,[32] coupling/Michael addition reaction with 3-iodopropenoates in the presence of CuCl,[33] or the unusual reaction of zirconacyclopentadienes with carbon monoxide in the presence of *n*-BuLi,[34] as shown below.



52

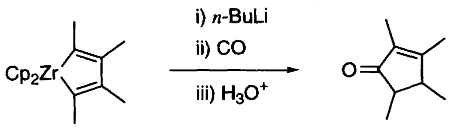
R = Me, 93%; R = Pr, 96%

(23)



53

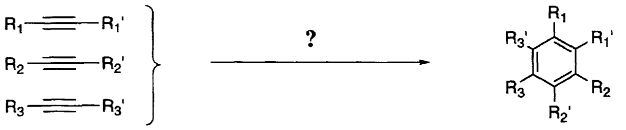
(24)



54

(25)

One-Pot Preparation of Benzene Derivatives from Three Different Alkynes

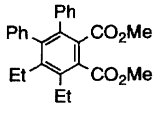
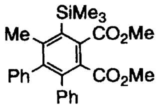
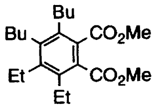
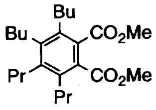
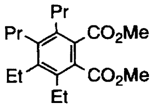
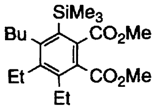
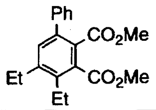


(26)

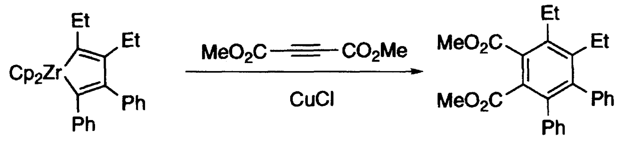
Development of a selective preparative method of multisubstituted benzene derivatives from three different alkynes using transition-metal complexes is of great interest both in practical application and in synthetic chemistry. When two or three different alkynes are used, a mixture of different benzene derivatives is generally formed. It is obvious that the best approach for the selective cyclotrimerization of three different alkynes is to control the selectivity of the intermediate; in other words, to prepare cleanly unsymmetrically substituted metallacyclopentadienes by intermolecular cross-coupling of two different alkynes. Wakatsuki and Yamazaki et al. first demonstrated the formation of benzene derivatives from three different alkynes using cobalt–alkyne complexes.[35] However, the overall yield was less than 15% and the column separation of isomers was required according to the literature. In this sense, high yield and a selective preparative method of benzene derivatives in high yield from three different alkynes remains to be found.

As we described above, through twice-cleavage of the β,β'-C–C bond of zirconacyclopentane and zirconacyclopentene, we developed a practical procedure for the preparation of unsymmetrically substituted zirconacyclopentadienes.[5d] When thus in situ formed zirconacyclopentadienes were treated with a third alkyne, which has electron-withdrawing groups in the presence of CuCl, multisubstituted benzene derivatives were formed very selectively from three different alkynes in high yields.[36] This reaction can be done in one-pot from the beginning. Some results are shown in Table 1. This whole process involves two cleavage reactions of theβ,β'-C–C bond and four new C–C bond formations.

Table 1. Formation of Benzene Derivatives from Three Different Alkynes by One-Pot Reaction

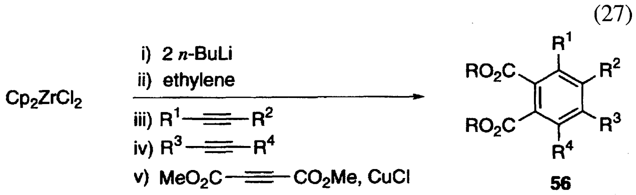
1st Alkyne	2nd Alkyne	DMAD	Product	Yield/%	By-products A/%	B/%
Et—≡—Et	Ph—≡—Ph	2 eq		95 (63)	0	Tr
Me_3Si—≡—Me	Ph—≡—Ph	2		(56)	< 2	< 2
Bu—≡—Bu	Et—≡—Et	2		90 (71)	3	Tr
Bu—≡—Bu	Pr—≡—Pr	2		87 (62)	Tr	4
Pr—≡—Pr	Et—≡—Et	2		91 (60)	0	2
Et—≡—Et	Me_3Si—≡—Bu	2		83 (74)	0	Tr
Et—≡—Et	Ph—≡—H	2		85 (66)	2	0

DMAD: dimethyl acetylenedicarboxylate. By-product **A** and **B**: Benzene derivative containing two molecules of 1 st alkyne and 2nd alkyne, respectively. Tr = trace.



55: 95%

(27)



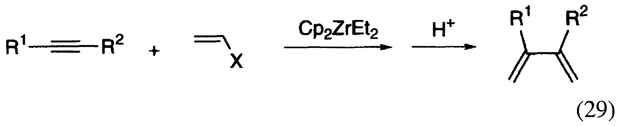
56

(28)

Conclusion

The mechanistic investigation into the β,β′-carbon–carbon bond cleavage of the above zirconacycles has not been completed yet. We must await further study on this matter. However, it is clear that the combination of carbon–carbon bond cleavage of zirconacycles, the replacement of the unsaturated molecules, and the highly selective new carbon–carbon bond formation on zirconocene can provide novel-type synthetic methods with excellent selectivities. This area will be more attractive in organic synthesis. A similar type of process is also expected for other early transition metal compounds such as Ti, Hf, Nb, and Ta. These metals will be used for such carbon–carbon cleavage reactions.

In the near future, organic synthesis using carbon–carbon bond activation will be more important and development of many useful transformations is expected. As described in the Introduction Section, such carbon–carbon bond activation has a chance to open up a quite novel concept in organic synthesis. We expect that novel-type carbon–carbon bond cleavage methods will appear. Recently we found a different type of carbon–carbon bond cleavage reaction in the coupling of alkynes with vinyl halides which was not included in this Account, since this is not the β,β′-C–C cleavage of zirconacycles as shown below.[37]



(29)

Mechanistic studies on the carbon–carbon bond cleavage reactions provide useful information and play an important role in the progress of this area. Not just speculation but some experimental results on the mechanism will help its development.

We would like to thank Prof. Kiyohiko Nakajima of Aichi University of Education for supporting our research by X-ray studies. We also thank Prof. Ei-ichi Negishi for his useful discussion and encouragement in the area of organozirconium chemistry. Finally, we thank all co-workers in our group whose names are cited in the references.

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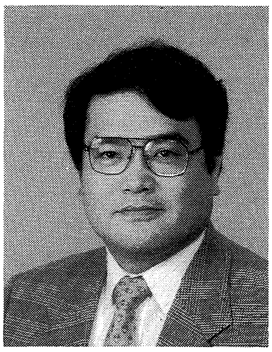

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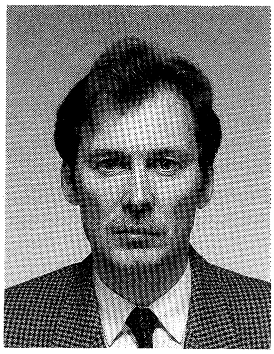
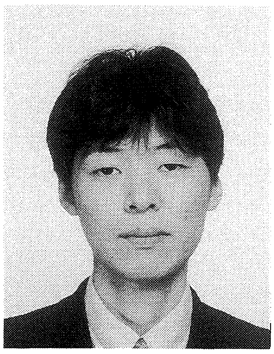
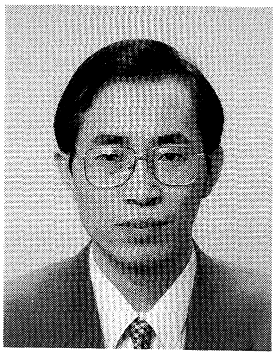
Professor Tamotsu Takahashi received the bachelor's and Ph.D. degrees from the University of Tokyo in 1978 and 1983, respectively. He became a research associate at the same university in 1983. From 1984 to 1986, he worked at Purdue University as a postdoctorate. In 1991, he moved to Institute for Molecular Science as Associate Professor. In 1995, he moved to Hokkaido University as Professor. He received the Progress Award in Synthetic Organic Chemistry, Japan in 1993 and Divisional Award (Organic Chemistry) of Chemical Society of Japan in 1998. He is now a project leader in the CREST program of Science and Technology (JST) (1998—2003).



Martin Kotora (Catalysis Research Center, Hokkaido University, Japan)
Prof. Martin Kotora received his first degree from Charles University (Prague, Czech Republic) in 1986 and his Ph.D. degree from Institute of Chemical Process Fundamentals (Prague, Czech Republic) in 1991. He worked in Prof. Takahashi's group at Institute for Molecular Science as a JSPS postdoctoral fellow from 1993—1995 and in Prof. Negishi's group at Purdue University in 1995—1996. He moved to Catalysis Research Center, Hokkaido University in 1996 as Associate Professor.



Ryuichiro Hara (Catalysis Research Center, Hokkaido University, Japan)
Dr. Ryuichiro Hara graduated from the University of Tokyo in 1990. He received his Ph.D. degree from the Graduate School of Advanced Studies in 1998. He joined Prof. Takahashi's group as a Ph.D. student in 1992 and as a technical staff in 1994 at Institute for Molecular Science. In 1996, he moved to Hokkaido University as Research Associate.



Zhenfeng Xi (Department of Chemistry, Peking University, China)
Prof. Zhenfeng Xi graduated from Xiamen University, China in 1983 and received his Ph.D. degree in 1996 from the Graduate University for Advanced Studies, Japan under the supervision of Prof. Takahashi. After his postdoctorate work (1996—1997) in Prof. Takahashi's group, he became Research Associate at Catalysis Research Center, Hokkaido University in 1997. In 1998, he moved to Peking University in China as Associate Professor and he was promoted to Professor of Peking University in 1999.