Copper-Catalyzed or Mediated Carbon-Carbon Bond Formation
Reactions of Zirconacycles and Alkenylzirconocenes

Martin Kotora, Zhenfeng Xi and Tamotsu Takahashi *
Catalysis Research Center and Graduate School of Pharmaceutical Sciences,
Hokkaido University.

Abstract: In this account we would like to present our recent developments in copper
catalyzed or mediated carbon-carbon bond formation reactions of zirconacycles as well as
reactions of related alkenylzirconocene compounds.

1. Introduction

One of the most attractive reactions of transition metal compounds is coupling (or dimerization)
of alkenes and/or alkynes to give metallacycles. Formally, during this process the metal is oxidized and
unsaturated bonds are reduced (Scheme 1). Therefore, in some cases it is called "oxidative coupling",
but in other cases it is also called "reductive coupling". This is sometimes confusing. Thus-formed
metallacycles such as metallacyclopentanes, metallaarylacylenes and metallaarylacylenenes can
participate in a number of further reactions or transformations (ref. 1). Metallacycles prepared from low-
valent early transition metal compounds (Zr, Hf, Ti, Nb, Ta etc.) (ref. 2) are very useful since the metal-
carbon bonds are easily hydrolyzed by simple acids such as 1N of hydrochloric acid. Organic
compounds are readily obtained after hydrolysis. Intramolecular cyclization of diynes, enynes or dienes
are known for almost all early transition metals (ref. 1). However, as for selective intermolecular
coupling of two different alkynes or alkenes, zirconocene chemistry has a big advantage in this respect
(ref. 3). Furthermore, zirconacycles can participate in the catalytic reactions using transmetallation from
zirconium to magnesium (ref. 4).

Scheme 1

Zirconacyclopentadienes, which can be cleanly prepared from two different alkynes, have long
been believed to be very inert for further carbon-carbon bond formation (ref. 5). We have recently
found various carbon-carbon bond formation reactions of zirconacyclopentadienes with the assistance of
a copper reagent. The copper-mediated or catalyzed reactions could be expanded to
zirconacyclopentanes, zirconacyclopentenes and alkenylzirconocenes.

In this paper we would like to present our results on copper-catalyzed or mediated C-C bond
formation reactions of zirconacycles and alkenylzirconocenes. Other types of regioselective or
chemoselective reactions of zirconacycles or the carbon-carbon bond activation via zirconacycles without
copper developed in our group are omitted in this paper (ref. 6).

2. Allylation of Organozirconocenes

Reaction of alkenylzirconium compounds with CuCl was reported as early as 1977 by Schwartz,
Yoshifuji et al. (ref. 7). However, the formed organocopper compound proved to be very unstable and
quickly decomposed, affording a dimer and metallic copper. Nonetheless, we have recently found that the presence of Li or Mg salts in the reaction mixture of alkenylzirconocenes and CuCl or CuCN slows the dimerization of organocopper compounds to such extent that they may preferentially participate in C-C bond-forming reactions.

For example, the reaction of alkenylzirconocene compound 1 with allyl chloride in the presence of CuCN (1 equiv) affords only the dimer 2 with concomitant precipitation of metallic copper. On the other hand, when LiCl (2 equiv.) is present, the allylation product 3 is formed in 59% yield along with 27% of the dimer 2 (Scheme 2). When a catalytic amount of CuCN (10% mol) was used, the allylation product 3 was formed in 75% yield and the dimer 2 was formed in 4% yield. These results unambiguously show the positive effect of Li salts for C-C bond formation reaction. Only Mg salts exhibit the same effect (ref. 8).

These results prompted us to test this reaction for allylation of trisubstituted alkenylzirconocenes 5 prepared from zirconocyclopentenes 4 by reaction with allylic substrates (ref. 6c). Simple addition of allyl chloride and a catalytic amount of the copper(I) salt (10 mol %) to the reaction mixture afforded diallylated alkynes 6 in high yield. No addition of Li or Mg salts to the reaction mixture was necessary, because they were already formed during the reaction (Scheme 3) (ref. 8).

Combination of allylzirconation of alkynes via zirconacyclopentene, which produces an alkenylzirconium compound, and copper(I)-catalyzed reaction with allyl chlorides afforded the 1,4,7-trienes 6. Alkyl, aryl, and trimethylsilyl groups are tolerated in the starting alkyne. Moreover, the use of variously substituted allylic substrates in the first and the second step enables preparation of the trienes with various substitution patterns. Some examples are given in Table 1.

The 1,4,7-trienes 6 are good starting materials for zirconocene-catalyzed or mediated reactions. When the triene is treated with Cp₂ZrCl₂ (Negishi reagent) (ref. 9) a cyclization proceeds to give stereoselectively cis-zircona[3.4.0]bicyclononenes 7. After hydrolysis, cis-4,5-dimethylcyclohexenes 8 are obtained as the sole products (Scheme 4). This cyclization reaction can be also carried out catalytically using 10% of Cp₂ZrCl₂ and an excess of n-BuMgX. The yields of the stoichiometric and the catalytic cyclization are given in Table 2 (ref. 10).

Table 1. Preparation of 1,4,7-Trienes by Double Allylation of Alkynes

<table>
<thead>
<tr>
<th>Alkyne</th>
<th>1. Allyl compd</th>
<th>2. Allyl compd</th>
<th>Product</th>
<th>Yield/ %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu—Bu</td>
<td>OTMS</td>
<td>Cl</td>
<td>Bu—Bu</td>
<td>87 (79)</td>
</tr>
<tr>
<td>Ph—Me</td>
<td>OTMS</td>
<td>Cl</td>
<td>Ph—Me</td>
<td>87 (81)</td>
</tr>
</tbody>
</table>
Zirconacyclopentenes containing both alkenyl- and alkylzirconium moieties are ideal substrates for chemoselective C-C bond formation via transmetallation. Indeed, we found that the alkenylzirconium bond is selectively transmetallated with CuCl at 0 °C. Under the same conditions it is possible to conduct selective allylation of sp²-C with a catalytic amount of copper chloride to obtain 9.
which, after hydrolysis, gives 10 (Scheme 5 path A). The alkylzirconium under these conditions is not transmetallated and remains unreactive. Nonetheless, double allylated product 11 can be obtained, when the reaction temperature is increased and excess of allyl chloride is used (ref. 11). The selective transmetallation of the alkenyl zirconium bond can be used for selective allylation of the alkyl zirconium bond as well. Thus, zirconacyclopentene ring cleavage with a stoichiometric amount of CuCl followed by quenching with 1 equiv of MeOH affords alkylzirconium intermediate 12. The reaction of the Zr-C(sp³) bond with allyl chloride provides selectively sp³-C allylated product 13 (Scheme 5 path B) (ref. 12).

Scheme 5

Successful results with the above-mentioned alkenylzirconocenes prompted us to try allylation of zirconacyclopentadienes 14, which have long been considered to be an unreactive species unable to participate in C-C bond formation reactions. The zirconacyclopentadienes 14 reacted smoothly with 2 equiv of allyl chloride in the presence of a catalytic or stoichiometric amount of CuCl to give 15 (Scheme 6). The diallylation reaction proceeded for various substituents such as alkyl, aryl, and trimethylsilyl groups in high yields. Bicyclic zirconacyclopentadienes and zirconaindene could be allylated as well (ref. 13).

Surprisingly, the diallylated products 15 (1,4,6,9-tetraenes) proved to be good substrates for further zirconium-mediated cyclization. The treatment of the tetraenes 15 with Cp₂ZrBu₂ (Negishi reagent) resulted in the formation of zirconacycles containing 8-membered rings. Hydrolysis afforded dimethyloctadiene derivatives 16 and carbonylation gave 8-5-membered fused ring ketones 17 (Scheme 6). Some examples of diallylation and preparation of the 8-5-ring ketones are given in Table 3.

Scheme 6
3. Acylation of Zirconacycles

Chemoselective and regioselective cleavage of zirconacycles is very interesting. One of our initial studies included regioselective transmellation of one Zr-C bond in zirconacyclopentanes and further C-C bond formation reaction. We have found that copper-catalyzed reaction of zirconacyclopentane 18 with acyl chloride proceeded selectively only with one Zr-C at -10 °C. Moreover, if the reaction mixture is quenched with an excess of iodine a doubly functionalized cyclopentane ring 19a was obtained (Scheme 7). Surprisingly, the scope of this reaction proved to be very wide and fruitful. When the reaction mixture, after monoacylation, was warmed to room temperature, stirred for 24 h, and treated with acid, a bicyclized compound with a 5-membered ring 19b was obtained (ref. 14). Some examples are given in Table 4. Products of double acylation were not obtained. The formation of the five-membered ring compound indicates that at room temperature nucleophilic addition of the second alkyl metal bond to the keto group proceeds (Scheme 7). Whether it is attack of the Zr-C or Cu-C bond

Table 3. Diallylation of Zirconacyclopentadienes and Formation of 8-5 Fused-Ring Compounds

| Zirconacyclo- | Tetraene | Yield/%$^a$ | Cyclization | Yield/%$^{a,b}$ | Trans/Cis |
|pentadiene | | | product | | |
|Et | Et | Et | | | |
|Ph | Ph | Ph | | | |
|Me$_3$Si | Me$_3$Si | Me$_3$Si | | | |
|Ph | Ph | Ph | | | |
|Me | Me | Me | | | |
|Bu | Bu | Bu | | | |
|Et | Et | Et | | | |

$^a$ GC yields. $^b$ Isolated yields in parentheses.
remains to be clarified. Nonetheless, this simple reaction sequence enables effective synthesis of the five-membered ring compounds from zirconacyclopentanes.

![Scheme 7](image)

This one-step ring formation reaction from zirconacyclopentane to the cyclopentenes prompted us to check this procedure in the reaction with zirconacyclopentenes. As might be expected, it was supposed that the product of the reaction of zirconacyclopentene 20 with acyl chlorides catalyzed by CuCl would be a cyclopentadiene 21. Indeed, our assumption was correct and the 1,2,3-trisubstituted cyclopentadienes were obtained under the identical conditions as above (ref. 15). Bicyclic cyclopentadienes 23 were also obtained from bicyclic zirconacyclopentenes 22 as well (Scheme 8). Some examples are given in Table 5.

![Scheme 8](image)

### Table 4. Reaction of Zirconacyclopentane with RCOCl in the Presence of CuCl.

<table>
<thead>
<tr>
<th>Zirconacyclopentane</th>
<th>RCOCl</th>
<th>Iodination product 19a yield%&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Cyclized product 19b yield%&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂ZrEt</td>
<td>PhCOCl</td>
<td>95 (63)</td>
<td>75 (54)</td>
</tr>
<tr>
<td>Cp₂ZrEt</td>
<td>i-PrCOCl</td>
<td>64 (56)</td>
<td>76 (55)</td>
</tr>
<tr>
<td>Cp₂ZrEt&lt;sup&gt;a&lt;/sup&gt;</td>
<td>EtCOCl</td>
<td>55 (48)</td>
<td>68 (56)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Cis:trans = 5:1.  <sup>b</sup> GC yields. Isolated yields are in parentheses.

### Table 5. Formation of Cyclopentadienes from Zirconacyclopentanes.

<table>
<thead>
<tr>
<th>Zirconacyclopentene</th>
<th>R¹</th>
<th>R²</th>
<th>RCOCl</th>
<th>Product</th>
<th>Yield%&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>Et</td>
<td>Et</td>
<td>PhCOCl</td>
<td>21a</td>
<td>72 (51)</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>20a</td>
<td>p-MeC₆H₄COCl</td>
<td>21b</td>
<td>71</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>20a</td>
<td>2,4-C₆H₄Cl₂COCl</td>
<td>21c</td>
<td>91 (62)</td>
</tr>
<tr>
<td>Pr</td>
<td>Pr</td>
<td>20b</td>
<td>BuCOCl</td>
<td>21d</td>
<td>75 (54)</td>
</tr>
<tr>
<td>Ph</td>
<td>Me</td>
<td>20c</td>
<td>PhCOCl</td>
<td>21e</td>
<td>66 (35)</td>
</tr>
<tr>
<td>Ph</td>
<td>22a</td>
<td>PhCOCl</td>
<td>23a</td>
<td>63 (54)</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>22a</td>
<td>BuCOCl</td>
<td>23b</td>
<td>79 (56)</td>
<td></td>
</tr>
<tr>
<td>Bu</td>
<td>22b</td>
<td>PhCOCl</td>
<td>23c</td>
<td>98 (65)</td>
<td></td>
</tr>
<tr>
<td>Bu</td>
<td>22b</td>
<td>BuCOCl</td>
<td>23d</td>
<td>68 (59)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> GC yields. Isolated yields are in parentheses.
4. Formation of Benzene Derivatives

The formation of benzene derivatives by cyclotrimerization of alkynes in the presence of transition metal complexes has been extensively and intensively studied (ref. 16). Nonetheless, this chemistry is currently still of great interest, since there are some crucial problems concerning regio- and chemoselectivity of the cycloaddition reaction of different alkynes. When two or three different alkynes are employed, a mixture of different benzene derivatives is generally formed. Wakatsuki and Yamazaki et al. (ref. 17) reported formation of a benzene derivative from three different alkynes using a cyclopentadienyl cobalt diphenylacetylene complex. Though a good example, separation of the intermediates was needed and the benzene derivative from three different alkynes was obtained in ca. 15% yield based on the cobalt alkyne complex. The intermediacy of metallacyclopentadienes has been widely accepted for cyclotrimerization of alkynes. It is obvious that the best approach for the selective cyclotrimerization of three different alkynes is to control the selectivity at the intermediate stage, that is, to prepare cleanly unsymmetric metallacyclopentadienes via an intermolecular cross-coupling of two different alkynes. Recently, a variety of unsymmetrically substituted zirconacyclopentadienes have been prepared by several procedures (ref. 3a-d). A general, practical, and convenient procedure has been developed in our lab (ref. 3e). Using this procedure, unsymmetrically substituted zirconacyclopentadienes 24 could be prepared in high yields with high selectivity; homo-coupling products of either the first alkyne 25 or the second alkyne 26 were negligible (Scheme 9).

Scheme 9

\[
\text{Cp}_2\text{ZrCl}_2 \xrightarrow{1. n-BuLi, 2. Ethylene, 3. R^1-\equiv-\equiv-R^2} \text{Cp}_2\text{Zr} \xrightarrow{R^3-\equiv-\equiv-R^4} \begin{array}{c}
\text{Cp}_2\text{Zr} \\
\text{Cp}_2\text{Zr}
\end{array}
\]

However, there has not been developed a procedure for reaction of zirconacyclopentadienes with the third alkynes (ref. 5a). Nonetheless, we have found that the zirconacyclopentadienes 24 react with acetylene dicarboxylates in the presence of CuCl affording benzene derivatives 27 (Scheme 10) with concomitant deposition of copper mirror on the wall of the reaction vessel. The best yields of 27 were obtained when a stoichiometric amount of CuCl (2 equiv) and two equiv of dimethyl acetylenedicarboxylate (DMAD) were used (ref. 18).

Scheme 10

\[
\text{Cp}_2\text{Zr} \xrightarrow{\text{MeO}_2\text{O}-\equiv-\equiv-CO_2\text{Me}} \xrightarrow{\text{CuCl}} \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{MeO}_2\text{C}
\end{array} \xrightarrow{\text{MeO}_2\text{C}} \begin{array}{c}
\text{MeO}_2\text{C} \\
\text{MeO}_2\text{C}
\end{array}
\]

Results for the reaction of unsymmetrically substituted zirconacyclopentadienes are given in Table 6. Both the monocyclic and bicyclic zirconacyclopentadienes 24 reacted with DMAD to afford the benzene derivatives 27.

The use of unsymmetrically substituted zirconacyclopentadienes resulted in the formation of unsymmetrically substituted benzene compounds. Thus were prepared benzene rings containing alkyl, aryl, trimethylsilyl and ester groups. The side-products formed from homocoupled zirconacyclopentadienes 28 and 29 were not detected. The structure of 27d was confirmed by X-ray analysis which clearly shows the benzene ring formed from three different alkynes. Also, the regiochemistry of substituents present in the zirconacyclopentadiene is retained during the reaction. As far as the reaction mechanism of the benzene ring formation is concerned, several pathways can be considered.
5. Formation of Polycyclic Arenes

A similar reaction to the above-mentioned process is the pathway for the synthesis of polycyclic arenes. Starting materials are once again the zirconacyclopentadienes 24, which in the presence of 2 equiv of CuCl, DMPU or HMPA reacts with 1,2-iodobenzene providing as product, naphthalene derivatives 31 (Scheme 11). The reaction strongly depends on the amount of the additive (DMPU or HMPA). The coupling with diiodobenzene does not proceed when no additive is used. The best yields of the naphthalene derivatives are obtained with 2.5-3 equiv of DMPU. It is supposed that the first step is, as usual, transmetallation of Zr-C bonds to Cu-C bonds resulting in the formation of a diorganocopper compound. This assumption is supported by the fact that after addition of CuCl a yellow precipitate 30 is formed, but it does not react with aryl halides. Upon addition of DMPU this precipitate is dissolved, and only then the coupling with aryl halides proceeds (ref. 19).

The zirconacyclopentadienes with alkyl or aryl groups can be used as starting material. As far as dihalo arenes are concerned, the best results are obtained with diiodo derivatives, but iodo bromo gives similar results. The use of 1,2,4,5-tetraiodobenzene affords an anthracene derivative. Also, heteroaryl dihalide was used; however, the yield of the product was rather modest. Some examples are given in Table 7.

Table 6. One-Pot Formation of Benzene Derivatives from Alkynes

<table>
<thead>
<tr>
<th>1st Alkyne</th>
<th>2nd Alkyne</th>
<th>3rd Alkyne</th>
<th>Product</th>
<th>Yield/%a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et—Et—Et</td>
<td>Et—Et—Et</td>
<td>DMAD</td>
<td><img src="image" alt="Et—Et—Et DMAD" /></td>
<td>27a 84 (59)</td>
</tr>
<tr>
<td>Bu—Bu—Bu</td>
<td>Et—Et—Et</td>
<td>DMAD</td>
<td><img src="image" alt="Bu—Bu—Bu DMAD" /></td>
<td>27b 90 (71)</td>
</tr>
<tr>
<td>Et—Et—Et</td>
<td>Ph—Ph—Ph</td>
<td>DMAD</td>
<td><img src="image" alt="Et—Et—Et DMAD" /></td>
<td>27c 95 (63)</td>
</tr>
<tr>
<td>Me—SiMe3</td>
<td>Ph—Ph—Ph</td>
<td>DMAD</td>
<td><img src="image" alt="Me—SiMe3 DMAD" /></td>
<td>27d (56)</td>
</tr>
<tr>
<td>Et—Et</td>
<td>DMAD</td>
<td><img src="image" alt="Et—Et DMAD" /></td>
<td>27e 93 (64)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="b)" /></td>
<td>Et—Et—Et</td>
<td>DMAD</td>
<td><img src="image" alt="b) Et—Et—Et DMAD" /></td>
<td>27f 80 (54)</td>
</tr>
</tbody>
</table>

a GC yields. Isolated yields are in parentheses.

b Zirconocene-benzylene complex.
6. Oxidative Addition

Alkenylzirconocene compounds, which are easily prepared by the hydrozirconation of alkynes, are very useful intermediates in organic synthesis. Hydrozirconation of terminal alkynes regio- and stereoselectively affords alkenylzirconocene compounds 32 (Scheme 12). Even if compound 33 is formed in situ, it immediately isomerizes to 32 in the presence of Cp₂ZrCl (ref. 20). Consequently, the alkenylzirconocene compounds 33 can not be obtained by hydrozirconation.

Scheme 12

Table 7. Reaction of Zirconacyclopentadienes with Aryl Halides

<table>
<thead>
<tr>
<th>Zirconacyclopentadiene</th>
<th>Aryl halide</th>
<th>Product</th>
<th>Yield%a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp₂ZrEt₂Et</td>
<td>Ph</td>
<td>Ph</td>
<td>53</td>
</tr>
<tr>
<td>Cp₂ZrPhEt₂</td>
<td>Ph</td>
<td>Ph</td>
<td>89 (70)b</td>
</tr>
<tr>
<td>Cp₂ZrEtPh</td>
<td>Ph</td>
<td>Ph</td>
<td>61 (48)</td>
</tr>
<tr>
<td>Cp₂ZrC₈H₁₅</td>
<td>Ph</td>
<td>Ph</td>
<td>32 (29)</td>
</tr>
<tr>
<td>Cp₂ZrEt₂Et</td>
<td>SPh</td>
<td>Et</td>
<td>- (62)</td>
</tr>
</tbody>
</table>

a GC yields. Isolated yields are in parentheses. b Reaction with 1-ido-2-bromobenzene gave the product in the same yield.
To prepare the compound 33, we investigated a novel oxidative addition reaction of 2-haloalkenes to Zr(II) (ref. 21). In comparison with late transition metal chemistry, only a few examples of intermolecular oxidative addition reactions are known for zirconocene using alkyl halide (ref. 22), arenes (ref. 22b), phosphorus compounds (ref. 23), silanes (ref. 24), and allyl ethers (ref. 25). In some cases, further synthetic applications were reported, but the oxidative addition intermediates were not structurally characterized. Furthermore, there is no report of oxidative addition for alkenyl halides to reduced zirconocene.

Treatment of 2-chloropropene with Cp2ZrBu2 (Negishi reagent) gave the oxidative addition product in 80% yield at room temperature. Results for other 2-haloalkenes are given in Table 8.

Table 8. Oxidative Addition of 2-Haloalkenes to Negishi reagent

<table>
<thead>
<tr>
<th>2-Haloalkene</th>
<th>Product</th>
<th>Yield %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-Ph</td>
<td>Cp2ZrPh</td>
<td>98</td>
</tr>
<tr>
<td>Cl-CH3</td>
<td>Cp2ZrCl CH3</td>
<td>80 (54)</td>
</tr>
<tr>
<td>Br-CH3</td>
<td>Cp2ZrBr CH3</td>
<td>93 (73)</td>
</tr>
<tr>
<td>Cl-C5H11</td>
<td>Cp2ZrCl C5H11</td>
<td>70</td>
</tr>
<tr>
<td>Cl-N</td>
<td>Cp2ZrCl N</td>
<td>92 (61)</td>
</tr>
</tbody>
</table>

* NMR yields. Isolated yields are in parentheses.

To obtain good crystals for X-ray analysis, a t-Bu-substituted cyclopentadienyl ligand was used. The treatment of (t-BuC5H4)2ZrBu2 with haloalkene in ether afforded the product in 83% NMR yield. Recrystallization from hexane gave yellow crystals in 62% yield.

Also, several C-C bond formation reactions of the oxidative addition products were studied. Palladium-catalyzed coupling and copper-catalyzed allylation gave satisfactory results. It is noteworthy that the overall reaction sequence could be carried out in one-pot without isolation of the intermediate. A few results are presented in Table 9.

Table 9. One-Pot catalytic C-C Bond Formation Reaction of Haloalkenes via Oxidative Addition of 2-Haloalkenes to Zirconocene

<table>
<thead>
<tr>
<th>2-Haloalkene</th>
<th>Catalyst</th>
<th>Reagent</th>
<th>Product</th>
<th>Yield %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp2ZrCl-Ph</td>
<td>CuCl</td>
<td></td>
<td>Cl-Cl</td>
<td>83</td>
</tr>
<tr>
<td>Cp2ZrCl-CH3</td>
<td>Pd0/ZnCl2</td>
<td>Phl</td>
<td>Ph-CH3</td>
<td>78</td>
</tr>
<tr>
<td>Cp2ZrBr-C5H11</td>
<td>Pd0/ZnCl2</td>
<td>PhCOCl</td>
<td>O-C5H11</td>
<td>63</td>
</tr>
</tbody>
</table>

* GC yields.

7. Latest Developments

Recent progress in copper-assisted reactions of zirconacycles includes a) development of effective diiodination of zirconacyclopentadiene forming 1,4-diiododienes (ref. 26), b) coupling of trisubstituted alkenylzirconium compounds with aryl, alkenyl halides (ref. 27) or alkynyl halides (ref. 28) resulting in the stereoselective formation of substituted tetraenes and enynes, respectively, and c) highly regio- and diastereoselective carbon-carbon bond formation of unsymmetrically substituted zirconacyclopentanes (ref. 29).

8. Conclusion

We can conclude that zirconacycles are versatile organometallic intermediates, which can serve as building-blocks for the construction of a number of linear or cyclic compounds. The discussed reaction pathways are summarized in Scheme 13. Although the reaction patterns of zirconacycles display a wide
range of C-C bond formations, we assume that this area is not fully exploited yet and many new interesting reactions are expected to be discovered.

9. Acknowledgment

We are deeply indebted to a number of past and present co-workers who have worked on the chemistry of Zr-species. Their names are indicated in our papers cited herein.

References


(Received June 9, 1997)