Coupling reactions of zirconocene complexes and heterosubstituted alkenes

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This *tutorial review* surveys recent advances in the field of zirconium promoted coupling reactions of unsaturated molecules (and/or organolithium compounds) and heterosubstituted alkenes. This reaction has recently emerged as a powerful tool in organic chemistry to access a variety of synthetically useful building blocks not easily available by other methods. In particular, three different reaction pathways are discussed: i) the reaction involving alkyne–zirconocene and aryne–zirconocene complexes which allows access to dienyl and aryl zirconocene complexes; ii) the reaction of alkene–zirconocene complexes and enol ethers which has shown to be highly dependent on the structure of the enol ether used, allowing the synthesis of simple vinyl zirconocenes or multicomponent coupling products, and; iii) the reaction involving imine–zirconocene complexes which supposes a new entry to allylic amines.

Introduction

The great majority of organozirconium compounds used in organic and organometallic chemistry are zirconocene complexes (Cp_2Zr derivatives).[1,2] Before Wailes and Weigold discovered the hydrozirconation reaction,[3] the zirconocene complexes had only found application as catalyst in polymerization reactions. However, the extensive work developed by Schwartz,[4–7] in the mid-1970s, about the hydrozirconation reaction can be considered as the first synthetically useful application of the zirconocene complexes in organic chemistry. Systematic investigations in the late-1970s and 1980s developed by Negishi further expanded the synthetic scope of these complexes.[8] Since then, the interest in organozirconium chemistry has been widely increased due to the unique ability of these complexes to promote uncommon transformations.

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José Barluenga was born in 1940 in Tardienta, Spain. He studied chemistry at the University of Zaragoza and received his doctorate in 1966 under the guidance of Professor Gómez Aranda. He spent three and a half years as a postdoctoral research fellow of the Max Planck Gesellschaft at the Max Planck Institut für Kohlenforschung (Mülheim a.d. Ruhr, Germany) in the group of Professor H. Hoberg working on aluminium chemistry. In 1970 he became Research Associate at the University of Zaragoza where he was promoted to Associate Professor in 1972. In 1975 he moved to the University of Oviedo as Professor in Organic Chemistry, where he is currently Director of the Instituto Universitario de Química Organometálica "Enrique Moles". Professor Barluenga is a recipient of the Research Award of the Foundation Alexander von Humboldt (1989), Solvay Award from Spanish CEOE (1990), the First DuPOnt Award (1991), the Iberdrola Award (1996), the Gold Medal of the Real Sociedad Española de Química (1999), First Ciencia y Tecnología Química "Enrique Moles" Award (2001), Fundación García Cobrizo Award (2002), and the Hermanos Elhuyar-Hans Goldschmidt Vorlesung Award (2005). Professor Barluenga has also received the DSc Honoris Causa from the University of Alcalá de Henares, Spain (2001). His major research interest is focused on developing new synthetic methodologies in organic chemistry by means of organometallic reagents as well as iodine-based systems.

Félix Rodríguez was born in Jarrio (Asturias, Spain). After his undergraduate education in chemistry at the University of Oviedo he joined the research group of Professor Barluenga where he worked in the field of organometallic chemistry using Fischer carbene complexes. In 1998 he received his PhD and then moved to the University of Cambridge for a postdoctoral stay (1999–2001) as a Marie Curie fellow under the supervision of Professor Steven V. Ley. During this time he was involved in several projects including the development of synthetic methodologies in the field of butane 2,3-diacetal (BDA) chemistry, the total synthesis of a number of natural products, and the development of new strategies for the parallel synthesis of small-molecule libraries by immobilization of key intermediates. In 2002 he returned to the University of Oviedo, and currently he is supported by a Ramón y Cajal contract. His research interest is focused on the use of transition metal complexes in organic synthesis (particularly group 4 and 6 organometallic compounds) and the design of new metal-catalysed processes.

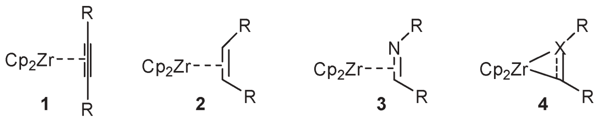
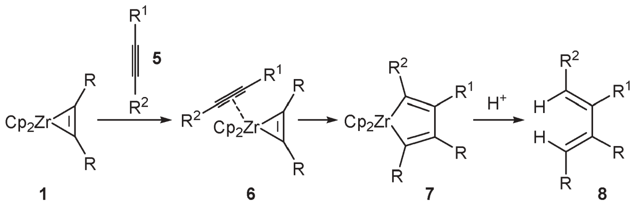


Fig. 1 Unsaturated molecule–zirconocene complexes.

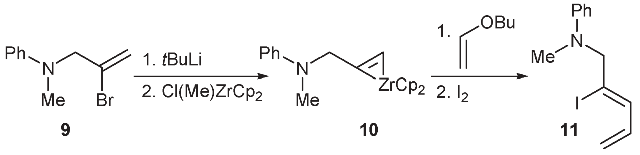
The zirconocene unit (Cp_2Zr) is an unstable 14-electron species which is generated *in situ* in most cases from Cp_2ZrCl_2 by reduction with Mg and $HgCl_2$[9] or by treatment with two equivalents of an organolithium or Grignard reagent (Negishi's procedure).[10] The reaction of zirconocene with unsaturated molecules gives rise to the corresponding 16-electron unsaturated molecule–zirconocene complex. As shown in Fig. 1 the most common complexes of this kind are the alkyne– (**1**), alkene– (**2**), and imine–zirconocene complexes **3**. These complexes **1–3** may be best viewed as resonance hybrids between these species **1–3** and the corresponding zirconacyclopropane species **4** (Fig. 1).

The most typical reactivity of the zirconocene complexes **1–3** is shown in the example of Scheme 1. Thus, the 16-electron alkyne–zirconocene complex **1** (represented as its zirconacyclopropene resonance form) tends to react with another unsaturated molecule such as the new alkyne **5** to give the 18-electron complex **6**. The subsequent cyclometalation reaction furnishes the corresponding zirconacyclopentadiene derivative **7**. Although these complexes may react with many electrophiles, the simplest reaction is their hydrolysis to give the corresponding butadiene derivative **8**. Following the same strategy zirconocene complexes **1–3** react with unsaturated molecules (not only alkynes as **5** but also alkenes, allenes, *etc.*) to give the corresponding zirconacyclopentane derivative analogous to **7** which can be further transformed into an organic molecule by treatment with electrophiles.

In this review article we will focus on recent reports about the reaction of zirconocene complexes **1–3** and heterosubstituted alkenes (mainly enol ethers and alkenyl bromides). As we will discuss, in general these processes initiate following reaction pathways analogous to that described in Scheme 1. However, the presence of a heteroatom in the alkene moiety, confers particular features to the mechanisms of the reactions and then, interesting and in many cases unexpected products are obtained.



Scheme 1 Synthesis of 1,3-butadienes by insertion of alkynes on alkynezirconocene complexes.



Scheme 2 Synthesis of a 2,4-pentadienyl amine from a 2-bromoallylamine by insertion of a enol ether on a propargylaminezirconocene complex.

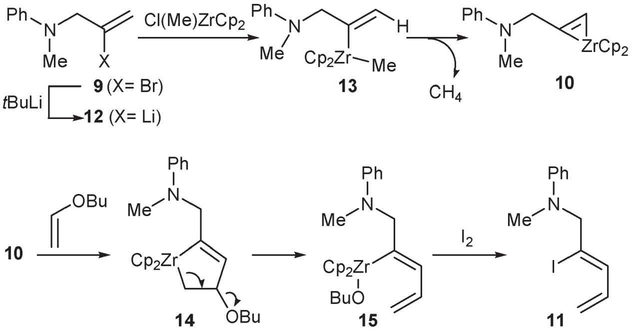
Reaction of alkynezirconocene complexes and heterosubstituted alkenes

Reaction with enol ethers

The first reported example about the reaction of a zirconocene complex and a heterosubstituted olefin was published in 1995.[11] As shown in Scheme 2, this reaction is initiated by treatment of *N*-(2-bromoallyl)-*N*-methylaniline **9** with *tert*-butyllithium followed by reaction with zirconocene methyl chloride to give the zirconacyclopropene (or alkynezirconocene complex) **10**. This complex reacts with butyl vinyl ether to give, after treatment with iodine, the 1,3-butadiene **11**.

Lucía Álvarez-Rodrigo was born in Oviedo (Spain) in 1980. She did her undergraduate studies in organic chemistry at the University of Oviedo (1998–2002) and is currently a PhD student working under the supervision of Professor Barluenga at the Instituto Universitario de Química Organometálica Enrique Moles (Universidad de Oviedo, Spain). Lucia's research is concerned with the use of organozirconium compounds for the development of new synthetic methods and the design of new zirconium-catalysed reactions.

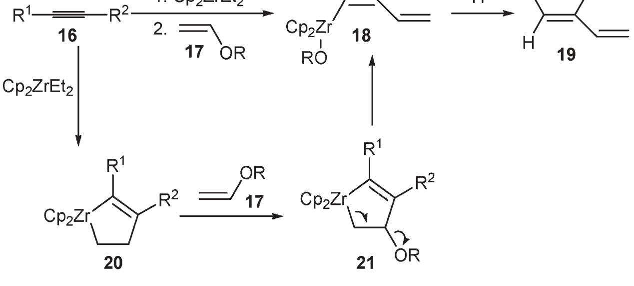
Francisco J. Fañanás was born in 1952 in Huesca, Spain. He received his BS degree from the University of Zaragoza in 1974 and his PhD in chemistry in 1979 from the University of Oviedo under the supervision of Professor Barluenga and Professor Yus. He was a post-doctoral fellow at Professor H. Hoberg's laboratory at the Max Planck Institut für Kohlenforschung, Mülheim a.d. Ruhr, Germany, from 1982–1984 working on nickel chemistry. In 1985 he joined the Instituto Nacional del Carbón in Oviedo as a Research Assistant. Thereafter, in 1987, he joined the Organic Department at the University of Oviedo as an Associate Professor. Professor Fañanás is co-author of more than 80 scientific articles, monographs and book chapters. His research interest is focused in organic synthesis mediated by transition metals of groups 4 and 6.



Scheme 3 Mechanism for the formation of a 2,4-pentadienyl amine from a 2-bromoallylamine mediated by zirconium complexes.

The mechanism of this process is depicted in Scheme 3. The reaction of the bromide **9** with *tert*-butyllithium generates the corresponding organolithium derivative **12**. This compound reacts with zirconocene methyl chloride to give the methyl-(vinyl)zirconocene complex **13**. Subsequent β-abstraction of hydrogen leads to the zirconacyclopropene derivative **10** releasing a molecule of methane. The insertion of the double bond of the vinyl ether takes place regioselectively at the less hindered zirconium–carbon bond of **10** leading to intermediate **14**. Moreover, this reaction is also regioselective with respect to the enol ether: the double bond is oriented during the insertion step so that the oxygen atom is far away from the zirconocene moiety. Elimination of the alkoxy group in **14** results in the formation of the dienylzirconocene derivative **15**. Finally, the reaction with the electrophile (iodine in this case) leads to the product **11** (Scheme 3).

Soon after this pioneering work appeared, T. Takahashi *et al.* published a similar reaction which differed only in the method used for the generation of the alkynezirconocene complex.[12] As shown in Scheme 4, the reaction of Cp_2ZrEt_2, which is *in situ* converted into $Cp_2Zr(CH_2{=}CH_2)$, with alkynes **16** gives the zirconacyclopentene derivatives **20**. The ethylene moiety of **20** is easily replaced by unsaturated compounds such as enol ethers **17** to give the new zirconacyclopentene derivatives **21** which are analogous to **14** in Scheme 3, and evolves in the same way to give the dienylzirconocene **18** and finally the corresponding 1,3-butadiene derivatives **19** (Scheme 4).



Scheme 4 Synthesis of butadiene derivatives from alkynes and enol ethers mediated by zirconium complexes.

Perspectives, scope, and limitations of these methodologies

From a synthetic point of view, the reactions shown in Schemes 2 and 4 suppose an easy way for the synthesis of functionalized 1,3-butadienes as very simple starting materials are required. These processes can be considered as zirconium promoted three-component coupling reactions (an alkyne or alkenyl bromide, an enol ether, and an electrophile).

The reactions with zirconocene complex **10** (which formally can be considered as derived from a terminal alkyne) are completely regioselective. Similarly, when symmetrical internal alkynes **16** are used, the final butadiene derivatives **19** are obtained as single isomers. However, when the reaction is performed with unsymmetrical alkynes **16** ($R^1 \neq R^2$), compounds **19** are formed as mixtures of regioisomers. The methodology shown in Scheme 4 has also a second structural limitation as terminal alkynes **16** can not be used. However, when butadiene derivatives **19** derived from a terminal alkyne are required, the methodology shown in Scheme 2 offers a good alternative.

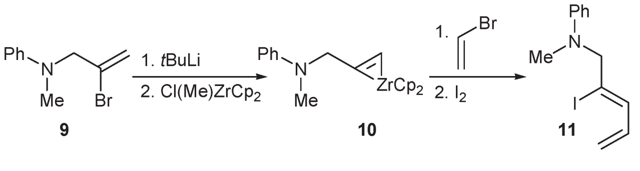
At present, these reactions are limited to the use of unsubstituted vinyl ethers and so, compounds such as **11** and **19** contain a terminal unsubstituted double bond.

Therefore, although these procedures are a very valuable option for the synthesis of functionalized 1,3-butadiene, further studies on these methodologies are still required in order to overcome some of the limitations discussed.

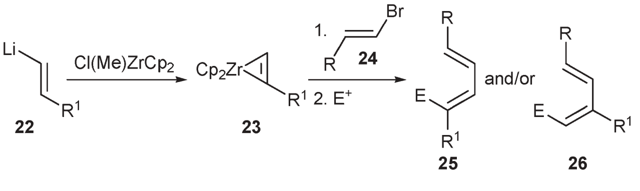
Reaction with alkenyl bromides

The reaction of an alkynezirconocene complex and vinyl bromide was described for the first time in Barluenga's previously mentioned pioneering work.[11] Thus, in a similar process to that described for enol ethers (see Scheme 2), the reaction of alkynezirconocene complex **10** and vinyl bromide also leads, after treatment with iodine, to the 1,3-butadiene derivative **11** (Scheme 5).

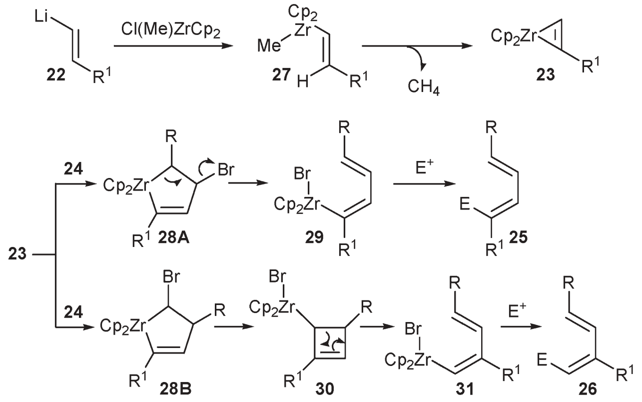
Deeper investigations on this field showed a more complex process.[13,14] Thus it was shown that the reaction of alkynezirconocene complexes **23**, which are obtained by reaction of



Scheme 5 Synthesis of a 2,4-pentadienylamine from a 2-bromoallylamine by insertion of vinyl bromide on a propargylamine–zirconocene complex.



Scheme 6 Regioselective synthesis of different 1,3-butadiene derivatives from alkenyllithium compounds and alkenyl bromides mediated by zirconium complexes.



Scheme 7 Mechanism for the zirconium mediated regioselective synthesis of different 1,3-butadiene derivatives from alkenyllithium compounds and alkenyl bromides.

alkenyllithium compounds **22** and zirconocene methyl chloride with alkenyl bromides **24**, gives dienes **25** and/or **26** depending on the structure of both the starting alkenyllithium derivative **22** and the alkenyl bromide **24** (Scheme 6).[11,13] Interestingly, when alkyl-substituted vinyl bromides are used, the reaction exclusively leads to dienes **26**.

The formation of these dienes **25** and **26** can be explained by the mechanism shown in Scheme 7. Firstly, the reaction of organolithium compound **22** with zirconocene methyl chloride generates the methyl(vinyl)zirconocene complex **27** which evolves by β-abstraction of hydrogen to furnish the zirconacyclopropene complex **23**. Insertion of the double bond of the alkenyl bromide takes place regioselectively at the less hindered zirconium–carbon bond of **23**. However, depending on the orientation of the vinyl bromide during the insertion step, two different zirconacyclopentene derivatives, **28A** or **28B**, can be obtained. Intermediate **28A** evolves through β-elimination of the bromine to give the dienylzirconocene complex **29**, which gives diene **25** after reaction with an electrophile. This mechanism is analogous to that described for the reaction with enol ethers (see Schemes 3 and 4). On the other hand, formation of dienes **26** can be understood from intermediate **28B** through an intramolecular migratory insertion process to afford cyclobutene–zirconocene complex **30**. Thermal cleavage of cyclobutene complex gives dienylzirconocene complex **31** which after reaction with an electrophile furnishes diene **26**. Experimental support for this mechanism was found by the isolation, under appropriate reaction conditions, of several cyclobutenes derived from complex **30**.[13]

Perspectives, scope, and limitations of these methodologies

The reaction of alkyne–zirconocene complexes and alkenyl bromides constitutes an alternative to the reaction of enol ethers previously discussed. By choosing the appropriate conditions, different 1,3-butadiene derivatives **25** or **26** can be obtained. In addition, some of the limitations of the reaction with enol ethers have been surpassed. For example, as commented before, by the use of vinyl ethers, only unsubstituted terminal double bonds could be obtained. In contrast, substituted alkenyl bromides **24** allow the synthesis of 1,3-butadiene derivatives which contain a terminal substituted double bond.

Moreover, the reaction of alkynezirconocene complexes and alkenyl bromides can be directed to the synthesis of cyclobutenes derived from **30**. It should be remarked that this methodology constitutes a powerful tool to access to this kind of compounds which are not easily available by other methods, and it could find application in many synthetic organic programs.

Reaction of arynezirconocene complexes and enol ethers

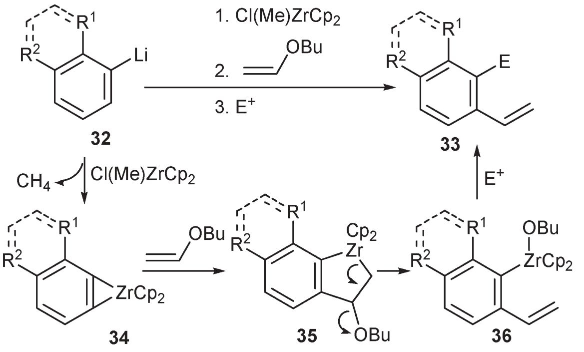
Arynezirconocene complexes could be considered as a particular class of alkynezirconocene complexes.[15] These complexes are very interesting compounds as they allow an easy functionalization of an aromatic ring.[16]

Particularly interesting is the reaction of the aryne zirconocene complexes and enol ethers. Thus, the reaction of organolithium compounds **32** and zirconocene methyl chloride followed by treatment with butyl vinyl ether and an electrophile leads to the formation of functionalized styrene derivatives **33** as single regioisomers (Scheme 8).[17]

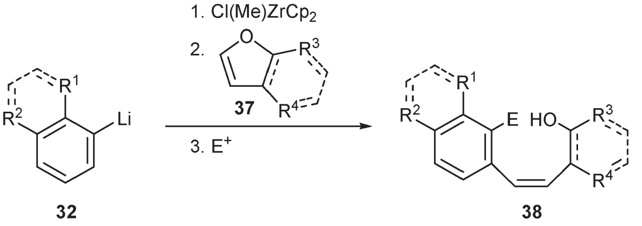
The process proceeds through the formation of the aryne–zirconocene complex **34** by the reaction of the initial organolithium compound **32** and the zirconocene methyl chloride. Insertion of the double bond of the butyl vinyl ether takes place regioselectively at the zirconium–carbon bond of **34** which is far away from the R^1 group, leading to intermediate **35**. Moreover, this reaction is also regioselective with respect to the enol ether: the double bond is oriented during the insertion step so that the oxygen atom is also far away from the zirconocene moiety. Elimination of the alkoxy group in **35** results in the formation of the new zirconocene complex **36** which by treatment with the corresponding electrophile furnishes final products **33**.

In a similar process, when the reaction is performed with cyclic enol ethers **37**, interesting *Z*-alkene derivatives **38** are obtained.[17]

In summary, the reaction of aryllithium compounds and enol ethers constitutes an easy methodology for the functionalization of an aromatic ring by the selective introduction of a vinyl moiety and an electrophile in two adjacent positions of the initial aromatic ring. As the starting materials are very simple and easily available, the protocol supposes a powerful alternative to the known methods for the functionalization of aromatic rings.



Scheme 8 Synthesis of substituted styrene derivatives by insertion of butyl vinyl ether on arynezirconocene complexes.



Scheme 9 Synthesis of *Z*-alkene derivatives by insertion of cyclic enol ethers on arynezirconocene complexes.

Reaction of alkenezirconocene complexes and heterosubstituted alkenes

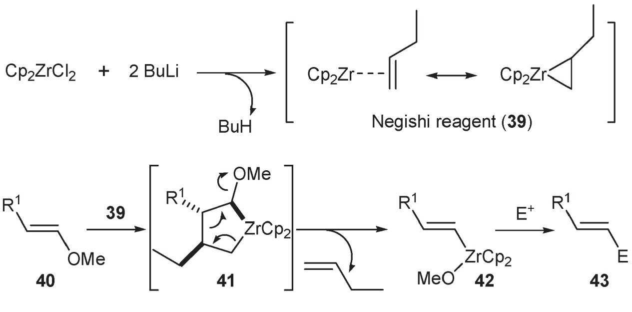
Reaction with enol ethers

Acyclic enol ethers **40** react with the Negishi reagent **39**, generated from zirconocene dichloride and two equivalents of butyllithium, to give the vinylzirconocene complexes **42** (Scheme 10).[18] These complexes react with electrophiles to afford the new functionalized alkenes **43** in a reaction which formally supposes a substitution reaction of the alkoxide of the starting enol ether **40** by the corresponding electrophile.[19]

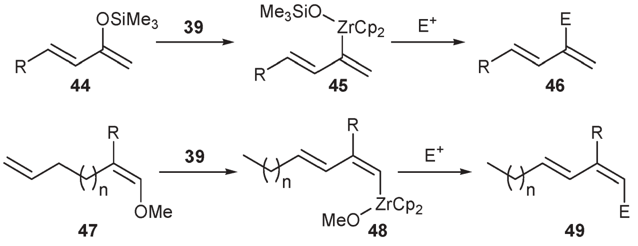
Initially, this interesting transformation was thought to proceed through a formal exchange of the olefinic ligand to generate a new alkene–zirconocene complex, followed by β-elimination of the alkoxide.[18,20] Further investigations in this field seem to indicate that this reaction occurs through a carbometallative ring expansion which generates the intermediate **41** followed by an elimination reaction (Scheme 10).[21]

When the above referred reaction is performed with 2-silyloxy-1,3-butadienes **44**, the corresponding dienylzirconocene complexes **45** are obtained (Scheme 11).[22] Further reaction of this complexes with electrophiles leads to functionalized 1,3-butadienes **46**. Interestingly, when non-conjugated dienes such as **47** are treated with the Negishi reagent **39**, a regioisomerization of the less substituted double bond occurs and formation of the conjugated dienylzirconocene complexes **48** is observed (Scheme 11).[23,24] As in previous examples, reaction of these complexes with electrophiles leads to functionalized dienes **49**.

Totally different reaction pathways are found when cyclic enol ethers are used. Thus, the reaction of alkenezirconocene complexes **51**, generated by reaction of zirconocene dichloride and two equivalents of alkyllithium compounds **50**, with five-membered cyclic enol ethers **52** and further reaction with an electrophile furnishes the new alcohol derivatives **53** in high yields.[25] When the same reaction is performed using the six-membered carbocycles **54**, cyclobutane derivatives **55** are isolated (Scheme 12).

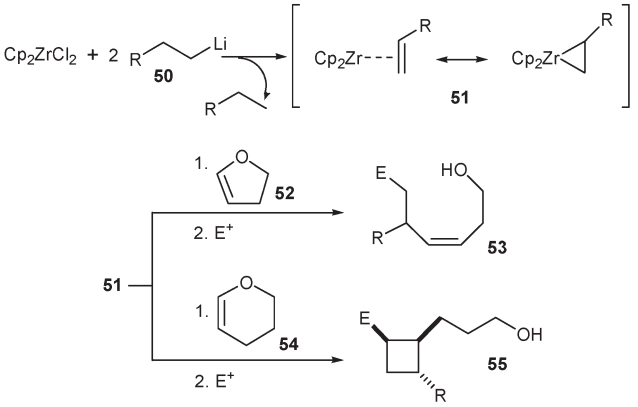


Scheme 10 Vinylzirconocene complexes from the reaction of Negishi reagent and acyclic enol ethers.

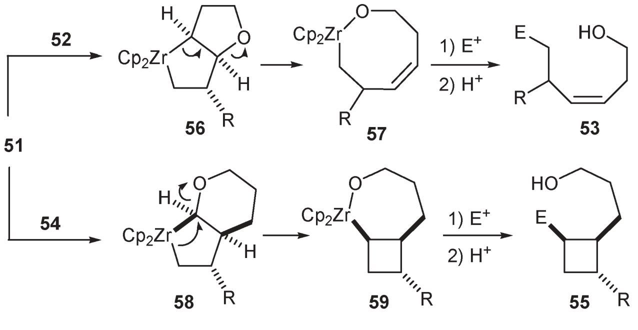


Scheme 11 Dienylzirconocene complexes from the reaction of Negishi reagent and alkoxydienes.

The mechanism that explains the formation of compounds **53** and **55** is shown in Scheme 13. In the first place, we consider the insertion of the double bond of enol ether **52** into the zirconium-secondary carbon of zirconacyclopropane **51** to generate the bicyclic intermediate **56** which evolves through a β-elimination of the alkoxy group to form the oxazirconacyclooctene derivative **57**. The final addition of the electrophile leads, after the hydrolysis step, to the *Z*-alkene derivatives **53**. It is important to remark that this process is doubly regioselective. On one hand, the insertion only occurs at the Zr–C bond of **51** which implies the more substituted carbon is attacked, while conversely, the reaction is also regioselective



Scheme 12 *Z*-Alkenol or cyclobutane derivatives from the reaction of cyclic enol ethers and alkenezirconocene complexes.



Scheme 13 Mechanism of the insertion reaction of cyclic enol ethers on alkene zirconocene complexes.

with respect to the enol ether **52**: the double bond is orientated during the insertion step placing the oxygen atom far away from the zirconocene moiety. Moreover, the generation of cyclobutane derivatives **55** from the six-membered enol ether **54** can be explained by an insertion of the double bond of this enol ether into **51** to produce the bicyclic intermediate **58**. An intramolecular migratory insertion process generates intermediate **59**, which after reaction with an electrophile and hydrolysis affords cyclobutane derivatives **55**. This insertion process is also regioselective with respect to the zirconacyclopropane **51** with the reaction occurring at the more substituted Zr–C bond. The reaction is also regioselective with respect to the enol ether **54** since the double bond of this enol ether is orientated so that the oxygen atom is close to the zirconocene moiety (Scheme 13).

Reaction with vinyl sulfides, sulfoxides, and sulfones

Marek *et al.* have widely studied the reaction of sufur-substituted alkenes and alkenezirconocene complexes both from the synthetic and mechanistic point of view. Thus, the reaction of the Negishi reagent **39** with vinyl sulfides (**60**), sulfoxides (**61**) or sulfones (**62**) supposes a straightforward method for the preparation of alkenylzirconocene complexes such as **64** (Scheme 14).[26]

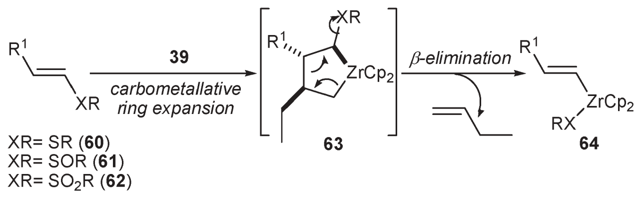
The reactivity of this vinylic organometallic **64** can be increased by transmetalation reaction into organocopper, organozinc or organopalladium species and therefore new carbon–carbon bonds are easily achieved. Moreover, mechanistic studies performed with these sulfur-substituted alkenes demonstrated that the reaction occurs through a carbometallative ring expansion process which generates intermediate **63** followed by a β-elimination process (Scheme 14).[21,27]

Reaction with vinyl halides

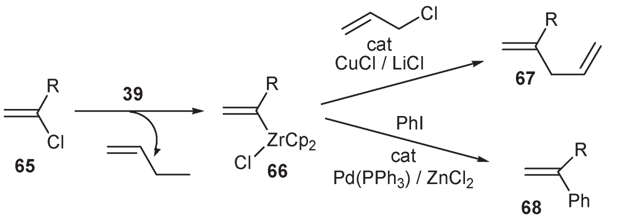
In a reaction similar to those described in previous sections, 2-chloroalkenes **65** react with alkenezirconocene complex **39** to afford the corresponding alkenylzirconocene complex **66**.[28] *In situ* copper- or palladium-catalyzed coupling reactions allow the synthesis of alkenes such as **67** and **68** (Scheme 15).

Perspectives, scope, and limitations of these methodologies

Although numerous methods for the preparation of sp^2 organometallic derivatives are known, the conceptually simple transformation of enol ethers or sulfur-substituted alkenes into vinyl organometallic species was unknown. However, as shown in previous sections, the reaction of the Negishi reagent **39** and enol ethers **40**, sulfur substituted alkenes **60**, **61**, **62**, or even vinyl halides **65** leads to the formation of the corresponding alkenylzirconocene complex. Moreover, the reactivity of the latter can be increased by a transmetalation reaction (into copper or palladium) and several types of carbon–carbon bonds are easily created in a single-pot operation.



Scheme 14 Vinylzirconocene complexes from the reaction of Negishi reagent and sulfur substituted alkenes.



Scheme 15 Vinylzirconocene complexes from the reaction of Negishi reagent and alkenyl chlorides. Coupling reactions.

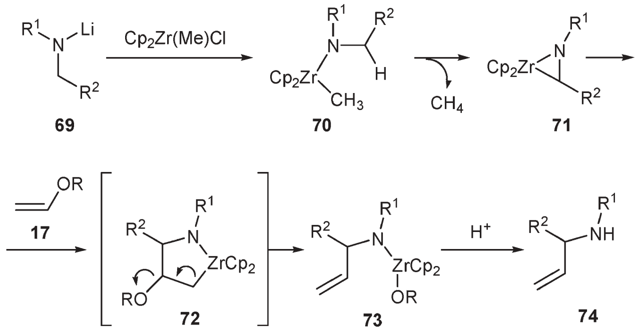
This conceptually new reaction has been applied to the synthesis of dienyl zirconocene derivatives. Particularly interesting are those reactions based on tandem double bond isomerisation–elimination sequences. In addition, the transmetallation reaction (zirconium into copper) allows further reaction with a great variety of electrophiles. These processes suppose a competitive method for the synthesis of 1,3-butadiene derivatives.

Also remarkable is the reaction of alkenezirconocene complexes and cyclic enol ethers shown in Scheme 12. The process can be considered as a zirconium mediated three-component cross coupling reaction (an alkyllithium compound, a cyclic enol ether, and an electrophile). From a synthetic point of view, the reaction should find application in organic synthesis as compounds **53** and **55** are useful building blocks which are obtained as single isomers in a very simple way and which are difficult to get following traditional synthetic procedures. At present, these reactions are limited to the use of unsubstituted five, and six membered cyclic enol ethers. Further studies directed to the use of substituted and chiral non-racemic cyclic enol ethers are still required. Also interesting should be the investigation of the behaviour of cyclic enol ethers of different size.

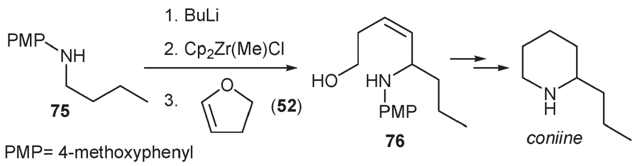
Reaction of iminezirconocene complexes and enol ethers

Iminezirconocene complexes **71** are easily obtained from the reaction of lithium amidures **69** and zirconocene methyl chloride (Scheme 16).[29] This process affords the methylzirconocene amide **70** which evolves through β-abstraction of hydrogen to give iminezirconocene complexes **71** and a molecule of methane.[30] Reaction of these complexes with enol ethers **17** leads, after hydrolysis, to the formation of the new allylamines **74**.[31] This reaction is thought to proceed through the regioselective insertion of the double bond of the enol ether **17** on the zirconium–carbon bond of **71**. Moreover, the insertion of enol ether **17** occurs with the appropriate orientation to furnish the zirconaazacyclopentane **72**. β-Elimination of the alkoxy group leads to the zirconocene complex **73** which after hydrolysis afford allylamines **74**.

This strategy allows the synthesis of amino alcohol derivatives containing a *Z*-double bond in their structure



Scheme 16 Allyl amines from iminezirconocene complexes and acyclic enol ethers.



Scheme 17 Insertion of 2,3-dihydrofuran on a iminezirconocene complex as key step in the synthesis of coniine.

when 2,3-dihydrofuran **52** is used as starting enol ether. Simple conventional modification of these amino alcohols leads to 2-substituted piperidines. By applying this approach, a formal total synthesis of the alkaloid coniine is easily achieved from the protected butylamine **75** (Scheme 17).[31]

Final remarks

As shown along this article, the reaction of zirconocene complexes and heterosubstituted olefins constitutes a recent and interesting field that deserves further attention. In general, these reactions are straightforwardly performed from simple starting materials allowing the synthesis of building blocks not easily available by other methodologies. Undoubtedly, future work in this field should be directed to the developing of catalytic processes which would avoid the use of stoichiometric amounts of zirconium complexes.

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