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Metal complex catalysis in the synthesis of organomagnesium compounds

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Abstract. The published data on the synthesis of organomagnesium compounds assisted by metal complex catalysts are generalised and described systematically for the first time. Hydro-, carbo- and cyclomagnesiation reactions of unsaturated compounds with R^1MgR^2 (R^1 = Alk, Ar; R^2 = H, Hal; $R^1 = R^2$ = Alk) catalysed by Ti, Zr and other transition metal salts and complexes are considered. Selected examples of applications of organomagnesium reagents to organic synthesis are given. The bibliography includes 206 references.

I. Introduction

The first organomagnesium compounds (hereinafter, OMC) were synthesised by Grignard [1] in 1900 by a reaction of organic halides with metallic magnesium. This simple and efficient method for the synthesis of OMC is still widely employed in synthetic practice. The Grignard reagents are used to create new C–C bonds for the syntheses of various classes of organic compounds. The preparation of OMC by this method and their applications have been subjects of numerous publications. The results reported have been summarised in a number of monographs.[2–10] It is evident that further progress regarding this classical method for the synthesis of OMC should primarily rely on the involvement of more complex halide-containing systems in the reaction with metallic magnesium.

The elaboration of a novel non-traditional approach to the synthesis of organomagnesium reagents from unsaturated compounds and ordinary Grignard reagents under conditions of metal complex catalysis is a sound achievement of modern organometallic chemistry. These include catalytic hydro-, carbo- and cyclomagnesiation with R^1MgR^2 (R^1 = Alk, Ar: R^2 = H, Hal; $R^1 = R^2$ = Alk). Owing to the high reactivity and availability of starting magnesium-containing reagents, the applicability to the synthesis of organomagnesium compounds with diverse structures and the mild conditions of these catalytic reactions, they hold much promise in organic and organometallic synthesis.

Presently, a large body of information on the formation of OMC in the presence of metal complex catalysts and various types of promoters has been collected (for instance, see reviews [11–15]). The authors of the present review have also contributed to the emergence and maturation of the chemistry of organometallic compounds. The aim of the present review is to summarise the published results concerning catalytic synthesis of OMC and analyse the most promising avenues in the further development of this field of research. Applications of OMC to organic synthesis are illustrated with selected examples only. Furthemore, numerous publications on the use of organomagnesium derivatives as co-catalysts in the oligo- and polymerisation of unsaturated compounds are also beyond the scope of the review.

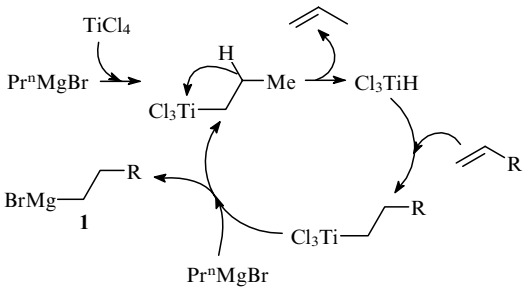
II. Hydromagnesiation of α-alkenes

The interaction of magnesium hydrides or alkylmagnesium halides with unsaturated compounds (alkenes, dienes or alkynes) catalysed by Ti, Zr and other transition metal salts and complexes is a convenient synthetic route to diverse OMC. The diversity of unsaturated compounds and the availability of starting reagents make it possible to prepare various uncommon OMC, which can be hard to synthesise by the traditional Grignard method.

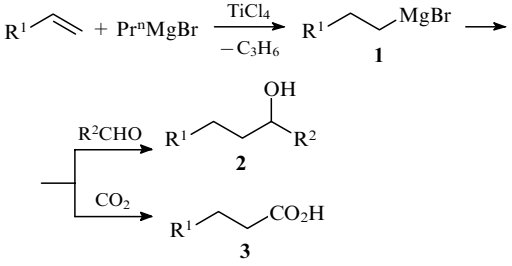
Catalytic hydromagnesiation of α-alkenes with Pr^nMgBr in the presence of titanium compounds was first reported by Finkbeiner and Cooper in 1961.[16] They found that different terminal alkenes could be converted into the respective organomagnesium derivatives **1** in the presence of 3 mol.% $TiCl_4$ in yields of 20% – 50% with evolution of an equimolar amount of propylene. The latter is indirect evidence of the generation, under the reaction conditions, of titanium hydrides, which are responsible for the subsequent hydrometallation of the starting alkenes.

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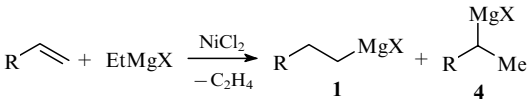


The thus prepared organomagnesium compounds **1** react with aldehydes or carbon dioxide to yield the respective alcohols **2** or carboxylic acids **3**.



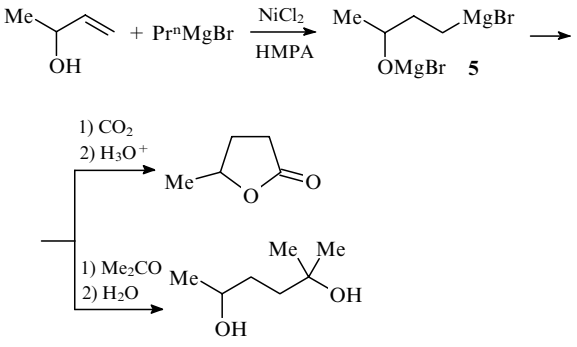
R^1 = Alk, cyclo-C_6H_{11} (Cy), Bn; R^2 = H, Me.

In addition to $TiCl_4$, such compounds as $Ti(OPr^i)_4$, Cp_2TiCl_2 (Cp is cyclopentadienyl), $ZrCl_4$, VCl_4 (see Refs 17, 18) can also be used as catalysts for this reaction. In contrast to Ti-containing catalytic systems, nickel complexes are less selective in the reaction of α-alkenes with RMgX. In particular, both primary (compounds **1**) and secondary (compounds **4**) OMC are formed in the presence of a catalytic amount of $NiCl_2$, their ratio being dependent on the structures of the starting alkenes and the nature of the hydrometallation agents.[19, 20]

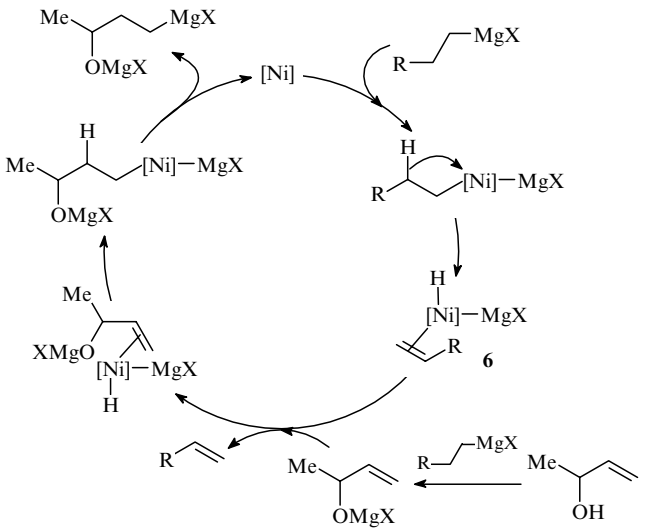


R = Alk; X = Br, Cl.

Meanwhile, $NiCl_2$-catalysed hydromagnesiation of allylic alcohols with n-propylmagnesium bromide yields the primary products selectively. An organomagnesium compound **5** prepared by this method further reacted with CO_2 and acetone.[21]

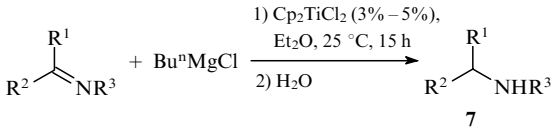


Presumably, the generation of nickel hydride complexes **6**, responsible for the hydrometallation of the starting allylic alcohols, is the key step in the synthesis of the OMC **5**. The catalytic cycle can be represented as follows.



Cp_2TiCl_2-catalysed hydromagnesiation reactions of α-alkenes were studied[22] using a variety of organomagnesium reagents (EtMgCl, EtMgBr, Pr^nMgCl, Pr^iMgBr, Bu^nMgCl, Bu^sMgCl, Bu^iMgCl, Bu^iMgBr, Bu^iMgI, Et_2Mg, Pr^n_2Mg, Pr^i_2Mg, Bu^n_2Mg, Bu^s_2Mg, Bu^t_2Mg). Higher homologues of the OMC were obtained in satisfactory yields.

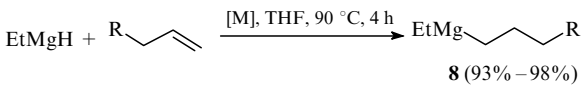
In addition to alkenes,[22] hydrometallation of imines was accomplished under the action of Bu^nMgCl (1.2 equiv.) and a catalytic amount of Cp_2TiCl_2 under mild conditions (Et_2O, 25 °C, 15 h). Magnesium amides are formed in this reaction, and their subsequent hydrolysis yielded the corresponding secondary amines **7**.[23]



R^1 = H, Me, Et, Pr^i; R^2 = Et, Pr^i, Ph; R^3 = Pr^n, Pr^i, Bu^t, Bn.

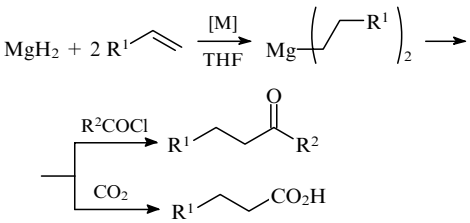
An efficient method for the hydrogenation of alkenes with hydrogen (p = 1 atm) using a two-component catalyst Cp_2TiCl_2–Pr^iMgBr ([Ti] : [Mg] : [alkene] = 1 : 6 : 50, 20 °C, 5 h), which afforded the corresponding alkanes in a nearly quantitative yield, was proposed.[24]

Organomagnesium hydrides RMgH (R = H, Hal, Alk) are employed in the hydromagnesiation of alkenes. Magnesium hydride generated *in situ* from Mg and H_2 adds to ethylene, isobutylene and oct-1-ene to afford the corresponding dialkylmagnesium compounds in yields 4%–13%. Meanwhile, the reaction of terminal and 1,1(or 1,2)-disubstituted alkenes with MgH_2 in the presence of a catalytic amount of Cp_2TiCl_2 in THF at a molar ratio alkene : MgH_2 : [Ti] of 2 : 1 : 0.05 under mild conditions (from 20 to 60 °C) affords the alkylmagnesium derivatives in high yields.[25] A system $CrCl_3$–[Mg–anthracene] (1 : 1) in THF has been recommended as a promoter for the synthesis of magnesium hydride complexes ($HMgCl \cdot MgH_2$ or $2\,HMgCl \cdot MgH_2$).[26, 27] Organomagnesium compounds **8** are prepared in nearly quantitative yield upon hydromagnesiation of α-alkenes with EtMgH in the presence of Ni- or Zr-containing catalysts.[28]



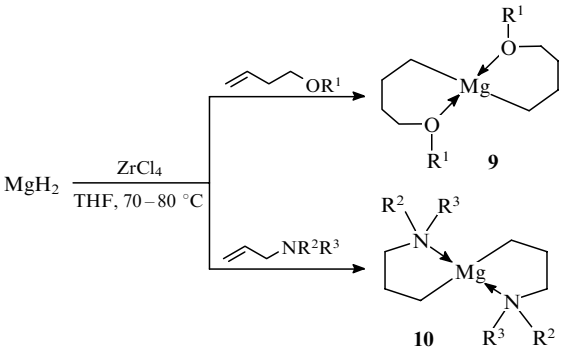
R = Alk; [M] = $NiCl_2$, Cp_2ZrCl_2.

Bogdanović *et al.*[29–31] have employed catalysts based on Zr, Ti, Hf, Cr and Fe halides for the hydromagnesiation of alkenes with magnesium hydride. The OMC obtained were further converted into the corresponding ketones and carboxylic acids.



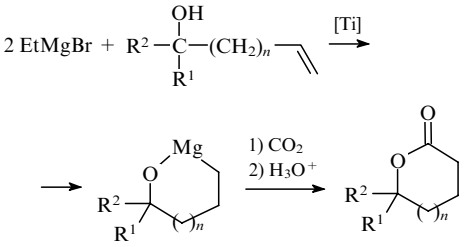
R^1 = H, Alk, cyclo-Alkenyl; [M] = ZrI_4, $ZrCl_4$, $ZrBr_4$, $TiCl_4$, Cp_2TiCl_2, $HfCl_4$, $CrCl_3$, $FeCl_2$; R^2 = Alk.

Hydromagnesiation of ω-N(or O)-substituted α-alkenes with MgH_2 in the presence of $ZrCl_4$ yields magnesium-containing compounds **9** and **10** stabilised by intramolecular coordination of the nitrogen or oxygen atoms to the central magnesium atoms.[32]

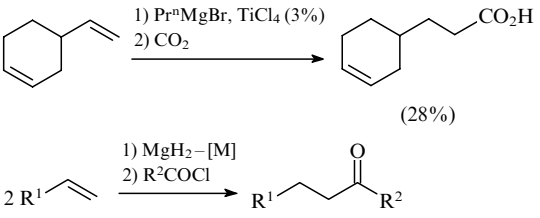


R^1, R^2, R^3 = Alk.

Catalytic hydromagnesiation of α-alkenes followed by functionalisation of the resulting OMC involving the reactive Mg–C bond has been successfully used in the synthesis of steroids,[33] alcohols,[16,18,21] γ- and δ-lactones,[34] ketones, carboxylic acids[16,31] and other classes of organic compounds. Selected examples of these reactions are given below.



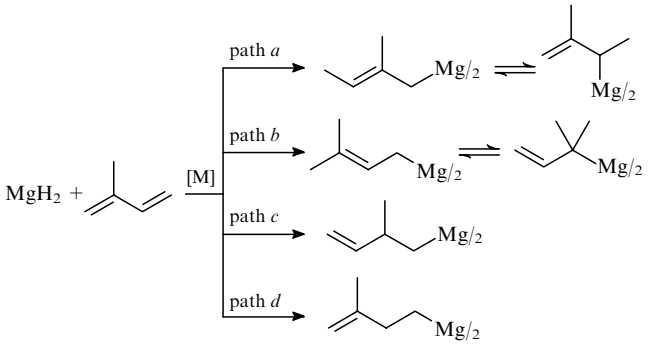
R^1, R^2 = Alk; R^1–R^2 = cyclo-Alk; n = 1, 2; [Ti] = Cp_2TiCl_2.



R^1 = H, Alk, Alkenyl; R^2 = Alk; [M] = $TiCl_4$, $ZrCl_4$, ZrI_4.

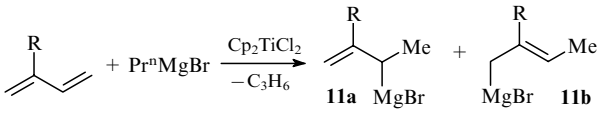
III. Hydromagnesiation of 1,3-dienes

Hydromagnesiation of 1,3-dienes with magnesium hydrides is an efficient method for the synthesis of unsaturated OMC.[35,36] As in the case of alkenes, Ti-containing catalysts, *viz.*, Cp_2TiCl_2 and $TiCl_4$, demonstrated the highest catalytic activities in this reaction. With these catalysts, the conversion of the starting dienes is typically ~75%. On the other hand, the conversion of the diene did not exceed 30% and the process proceeded non-selectively with Cp_2ZrCl_2, $ZrCl_4$, $HfCl_4$ and $CrCl_3$ as catalysts. This can be illustrated by catalytic reactions of isoprene with magnesium hydride, which can follow four alternative reaction pathways: 1,4-addition to form either the Mg–C(1) (path *a*) or Mg–C(4) (path *b*) bond, 1,2-addition to form either the Mg–C(1) (path *c*) or Mg–C(4) (path *d*) bond. The hydromagnesiation in the presence of Cp_2TiCl_2, Cp_2ZrCl_2, $TiCl_4$ or $ZrCl_4$ proceeds as the 1,4-addition of magnesium hydride to isoprene.[35]



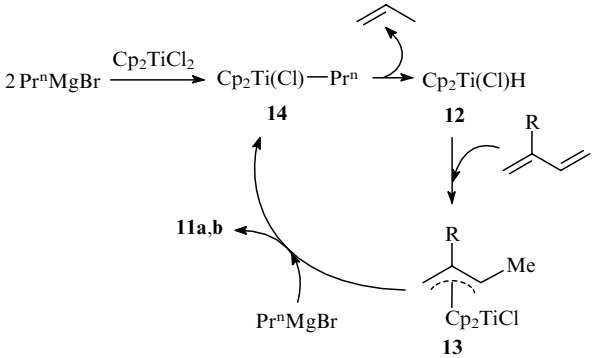
[M] = Cp_2TiCl_2, Cp_2ZrCl_2, $TiCl_4$, $ZrCl_4$.

Hydromagnesiation of 1,3-dienes (butadiene, isoprene or myrcene) or styrene with Pr^nMgBr in the presence of a catalytic amount of Cp_2TiCl_2 is the simplest and the most convenient method for the synthesis of unsaturated OMC.[37] These studies were preceded by investigations into the hydromagnesiation of α-alkenes with propylmagnesium bromide in the presence of $TiCl_4$.[16–18] The attempted use of $TiCl_4$ as a catalyst for the hydromagnesiation of 1,3-dienes failed, whereas, in the presence of Cp_2TiCl_2, regioisomeric allylic OMC **11a**,**b** were successfully prepared from 2-substituted 1,3-dienes.[37] It is of note that such a reaction is unknown for 1-substituted 1,3-dienes.



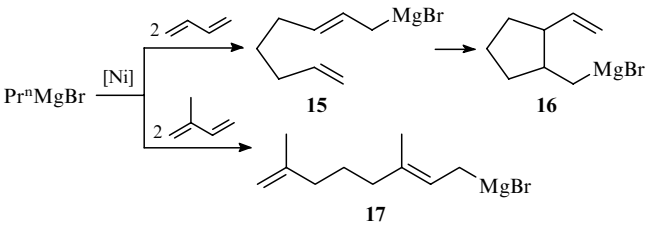
R = H, Me, $(CH_2)_2CH$ = CMe_2.

Sato *et al.* proposed [37] a mechanism of catalytic hydromagnesiation of 1,3-dienes, which implies that it is titanium organic hydrides **12** generated as a result of the reaction of Cp_2TiCl_2 with Pr^nMgBr that act as active hydrometallation intermediates in these reactions. They add to 1,3-dienes giving rise to allylic bis(cyclopentadienyl)titanium complexes **13**.[38] The latter undergo transmetallation by an excess of Pr^nMgBr and are converted into regioisomeric allylmagnesium bromides **11a**,**b** with regeneration of catalytically active n-propyltitanium complexes **14**.



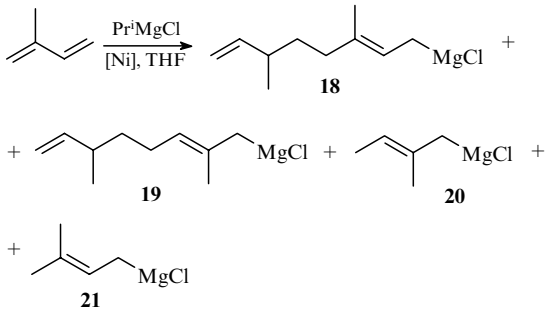
The hydromagnesiation pathway depends on both the nature of the catalyst and the structure of the starting 1,3-dienes. For instance, butadiene reacts with Pr^nMgBr in the presence of a catalytic amount of $Ni(PPh_3)_2Cl_2$ to form octa-2,7-dienylmagne-

sium bromide (**15**), which undergoes intramolecular cyclisation into an organomagnesium compound **16**.[39] Isoprene reacts with Pr^nMgBr (an ethereal solution) to yield 3,7-dimethylocta-2,7-dienylmagnesium bromide (**17**).[40]



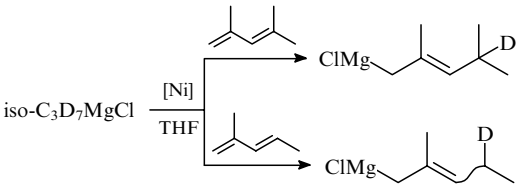
[Ni] = $Ni(PPh_3)_2Cl_2$.

Hydromagnesiation of 2-alkyl-1,3-dienes (isoprene, myrcene, 2-isopropylbuta-1,3-diene, 2-*tert*-butylbuta-1,3-diene) with RMgX (R = Et, Pr^n, Pr^i, Bu^i, Bu^s; X = Cl, Br, I) in the presence of nickel catalysts with phosphine oxide or nitrogen-containing ligands is less selective.[41,42] In this case, allylic-type isomers of monomeric organomagnesium compounds (**20** and **21**) are formed in addition to the regioisomeric dimeric hydromagnesiation products **18** and **19**.



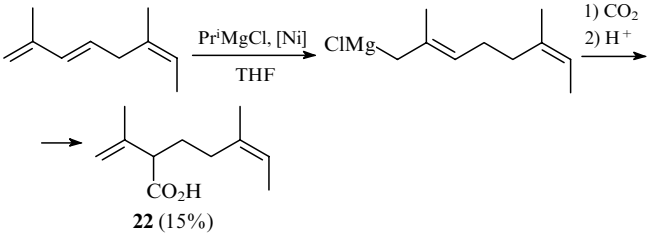
[Ni] = $NiPy_4Cl_2$.

The use of pyridine nickel complexes as catalysts enabled the hydromagnesiation of 2-alkoxy- (see Ref. 43), 1-alkylbuta-1,3-dienes[44,45] and of di- and poly-alkylbuta-1,3-dienes,[46] which could not be effected using Cp_2TiCl_2.[37]



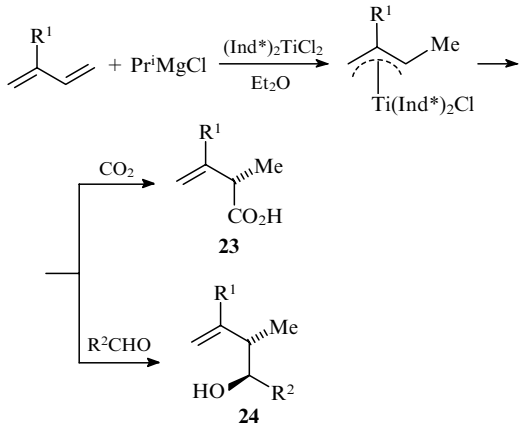
[Ni] = $NiPy_4Cl_2$.

An efficient method for the synthesis of isoprenoid carboxylic acids **22** using Grignard reagents was developed.[46–48] It is based on the reaction of allylic OMC, generated *in situ* by the hydromagnesiation of substituted 1,3-dienes, with CO_2. If carbonyl compounds are used instead of carbon dioxide, the corresponding isoprenoid alcohols are formed.[46–48]

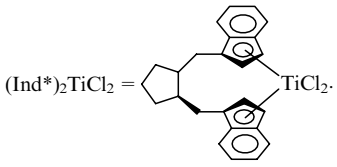


[Ni] = $NiPy_4Cl_2$.

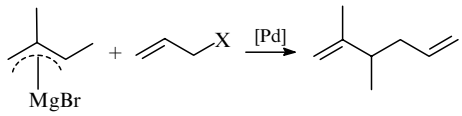
Hydrometallation of 2-alkylbutadienes with Pr^iMgCl catalysed by a chiral indenyl titanium complex afforded allylic titanium complexes; their treatment with CO_2 or aldehydes represents a convenient method for the synthesis of optically active β,γ-unsaturated carboxylic acids **23** or *threo*-homoallylic alcohols **24** with high enantiomeric purity (96%).[49]



R^1 = n-C_9H_{19}, $Me_2C=CH(CH_2)_3$; R^2 = Et, Pr^i, Bu^t, Ph;

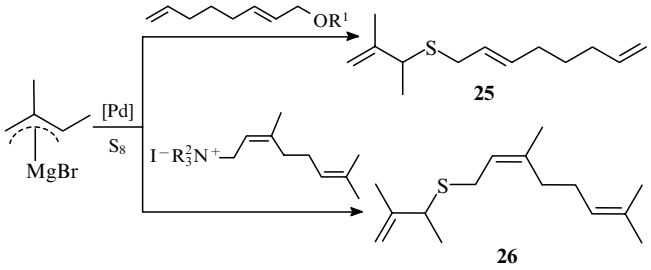


Cross-coupling of N-, O- and S-functionalised allylic compounds with dienylmagnesium reagents catalysed by transition metal complexes results in unsaturated hydrocarbons with the isoprenoid structure in high yields.[50]



X = OAlk, OAr, OAc, SAlk, SO_2Alk, $Alk_3N^+Hal^-$.

An analogous scheme was used for the synthesis of polyene sulfides **25** and **26**.[51] In this case, a sulfur atom (from the S_8 molecule) is inserted at the Mg–C bond simultaneously with the interaction of the 'isoprenemagnesium' reagent with the allylic electrophiles.



R^1 = Me, Et, Ph; R^2 = Me, Et.

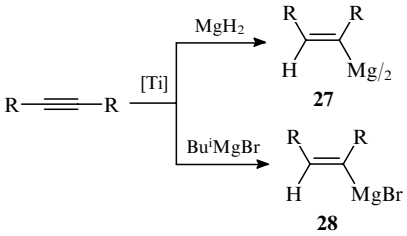
The corresponding thioesters are formed if CS_2 is used in this reaction.[51]

Synthesis and transformations of such OMC of the non-Grignard type prepared from 1,3-dienes and highly active metallic Mg are reviewed in more detail elsewhere.[13]

IV. Hydromagnesiation of alkynes

The catalytic hydromagnesiation of alkynes with magnesium hydrides or alkylmagnesium halides in the presence of Ti complexes affords vinylic organomagnesium compounds. The direction and selectivity of this reaction depend on the nature of the

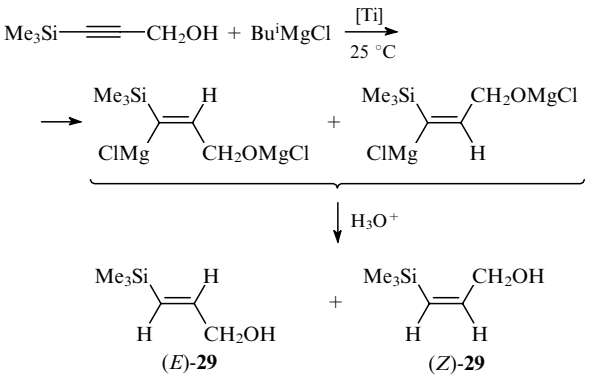
catalyst, the structure of the starting alkyne and the hydromagnesiation reagent used. Hydromagnesiation of symmetrical disubstituted acetylenes with MgH_2,[25] $MgH_2 \cdot CuI$, $MgH_2 \cdot CuOBu^t$ (see Ref. 52) or Bu^iMgHal (Hal = Cl, Br) [11,53] in the presence of a catalytic amount of Cp_2TiCl_2 yields alkenylmagnesium compounds **27** or **28** with *E*-double bonds.



R = Alk, Ph; [Ti] = Cp_2TiCl_2.

Hydromagnesiation of non-symmetrical dialkylacetylenes affords two regioisomeric alkenylmagnesium halides in nearly equal proportions. The hydromagnesiation of alkylarylacetylenes [53] and alkyl(trimethylsilyl)acetylenes [54–59] is more selective. In ether at 20 °C, the magnesium atom is preferably (>95%) attached to the carbon atom bearing the phenyl or silyl substituents.[60]

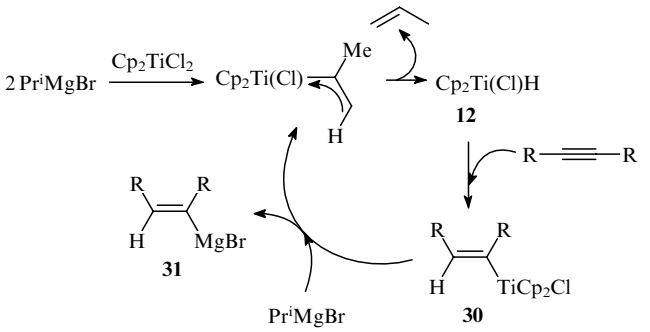
Hydromagnesiation of 3-trimethylsilylprop-2-yn-1-ol with Bu^iMgCl in the presence of Cp_2TiCl_2 (the ratio [alkyne]:[Mg]:[Ti] = 1:2.4:0.08; 25 °C, 6 h) followed by hydrolysis of the reaction mixture affords stereoisomeric alcohols **29** in a total yield of 98%, *E*:*Z* = 95:5.[61]



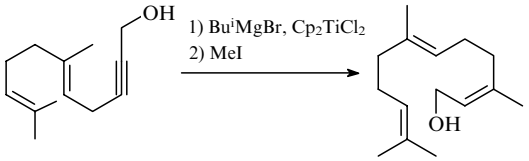
[Ti] = Cp_2TiCl_2.

Cp_2TiCl_2-catalysed hydromagnesiation of disubstituted acetylenes with organomagnesium compounds of the type R^1MgR^2 was studied by Dzhemilev *et al.*[62] It was shown that reagents containing cyclic and allylic substituents are less reactive than Alk_2Mg, whereas OMC with tertiary and vinylic substituents are virtually inert in this reaction.

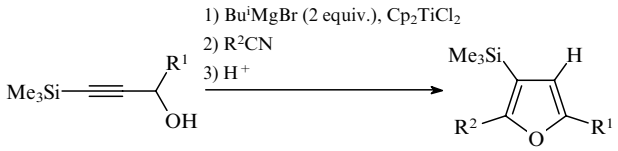
The mechanism of the hydromagnesiation of disubstituted acetylenes with Grignard reagents in the presence of Ti complexes implies the generation of reactive titanium hydrides **12** under the reaction conditions. These intermediates hydrometallate the starting alkynes to form alkenyltitanium complexes **30**. This step determines the regio- and stereoselectivities of the formation of the target products: in the case of symmetrical alkynes, the transmetallation of complexes **30** with AlkMgX yields *E*-alkenylmagnesium halides **31**.[60] The regioselectivity of the addition of the titanium hydride complex **12** to non-symmetrical disubstituted acetylenes is governed by the nature of substituents that determine the electron density on the carbon atoms of the C≡C bond.



Vinylic organomagnesium compounds synthesised by the hydromagnesiation of disubstituted acetylenes are used in the selective synthesis of *Z*- (see Refs 25, 62, 63) and *E*-alkenes,[64] terpenoids,[65] *E*-allylic alcohols,[66] *Z*-α,β-unsaturated ketones,[67] substituted furans,[68,69] different biologically active compounds and fragrances.[55,70–73] Selected examples of the use of this reaction for the preparation of compounds with valuable properties are given below.

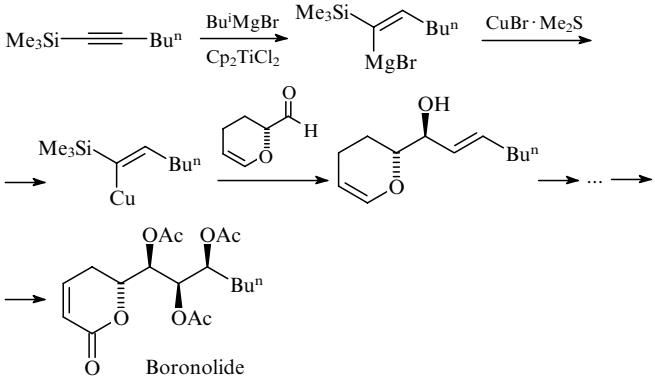


Farnesol (98%)

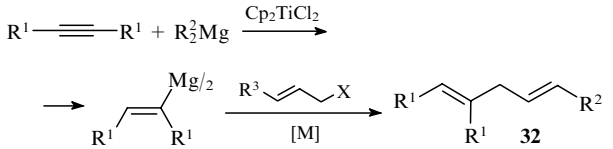


(38%–88%)

R^1 = H, Pr^n; R^2 = Me, Et, Pr^i, Ph.

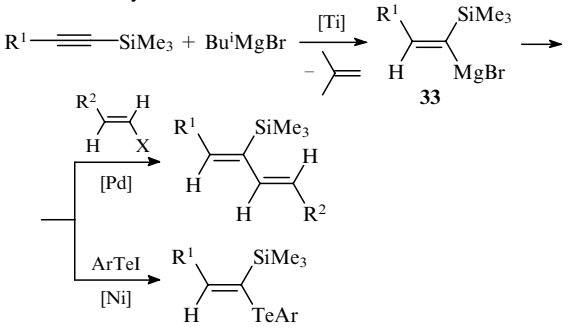


Cross-coupling of vinylic OMC with allylic ethers, sulfones, sulfides and quaternary ammonium salts catalysed by Pd, Ni and Cu complexes yields 1,4-dienes **32** with a trisubstituted double bond in the *E* configuration.[74]



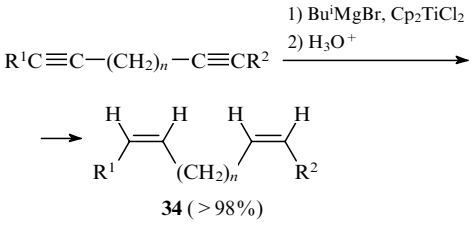
R^1 = Et, Pr^n; R^2 = Pr^n, Pr^i, Bu^n, Bu^i; R^3 = H, $(CH_2)_3CH=CH_2$; X = OR^4, SR^4, SO_2R^4 (R^4 = Et, All, Ph), Et_3N^+; [M] = Pd, Ni, Cu.

Hydromagnesiation of alkynylsilanes with Bu^iMgBr catalysed by Cp_2TiCl_2 (5 mol.%) followed by cross-coupling of the vinylic organomagnesium compounds **33** generated *in situ* with vinyl-, aryltellurenyl or trialkylstannyl halides represents a method for the stereoselective synthesis of 1,3-dienylsilanes,[75] (*E*)-α-aryltellurenylvinylsilanes,[76] (*E*)-α-silylvinylstannanes[77] and (*E*)-1,2-disubstituted vinylstannanes.[78]



R^1, R^2 = Alk; X = Br, I; Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4; [Ti] = Cp_2TiCl_2, [Pd] = $Pd(PPh_3)_4$; [Ni] = $Ni(PPh_3)_2Cl_2$.

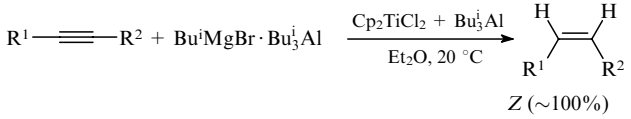
Diynes with the triple bonds separated by hydrocarbon bridges react with Bu^iMgBr with high regio- and stereoselectivities to yield *Z*-alkenes **34**.[79]



34 (> 98%)

R^1, R^2 = Alk; n = 1–4.

A mixed reagent $Bu^iMgBr \cdot Bu^i_3Al$ also provides highly stereoselective hydromagnesiation of alkynes.[79]



Z (~100%)

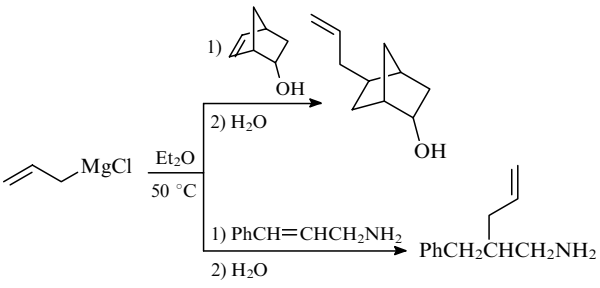
R^1, R^2 = Alk.

Thus, the hydromagnesiation of disubstituted acetylenes with magnesium hydrides and alkylmagnesium halides catalysed by titanium complexes represents an efficient method for the stereoselective conversion of alkynes into *Z*-alkenes.

V. Carbomagnesiation of alkenes

In 1978, Negishi *et al.*[80] suggested the term 'carbometallation' for the reaction of 1,2-addition of organometallic reagents to unsaturated compounds; later on, this term became commonly adopted.[81–84]

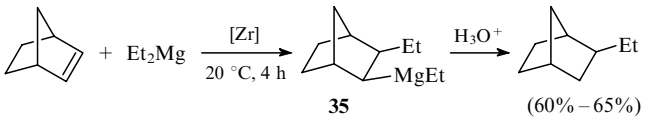
It is known[81,85,86] that only alkenes with activated double bonds, such as bicyclo[2.2.1]hept-5-en-2-ol or (*E*)-3-phenylallylamine, can be involved in the reaction of thermal carbomagnesiation with allylmagnesium halides.



Catalysts based on titanium and other transition metal chlorides ($NiCl_2$ or $CoCl_2$) enabled catalytic carbomagnesiation of α-alkenes devoid of activated double bonds with Grignard reagents.[19,20,87] However, due to low regio- and stereselectivities, these catalysts have not found wide application.

In 1983, the authors of the present review accomplished for the first time regioselective carbomagnesiation of α-alkenes with non-activated double bonds. High yields of products were obtained with Et_2Mg or EtMgBr in the presence of a catalytic amount of Cp_2ZrCl_2.[88] This reaction, referred to as 'catalytic ethylmagnesiation', is applicable to diverse alkenes.[88–91]

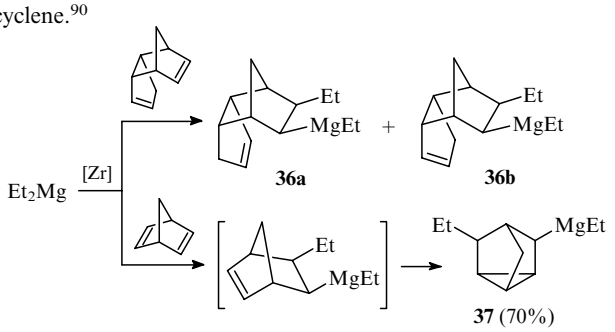
In particular, bicyclo[2.2.1]hept-2-ene reacts with an equimolar amount of Et_2Mg in the presence of a catalytic amount of Cp_2ZrCl_2 (Et_2O, 20 °C, 4 h) to form compound **35**, which was further hydrolysed to yield 2-*exo*-ethylbicyclo[2.2.1]heptane.



35 (60% – 65%)

[Zr] = Cp_2ZrCl_2.

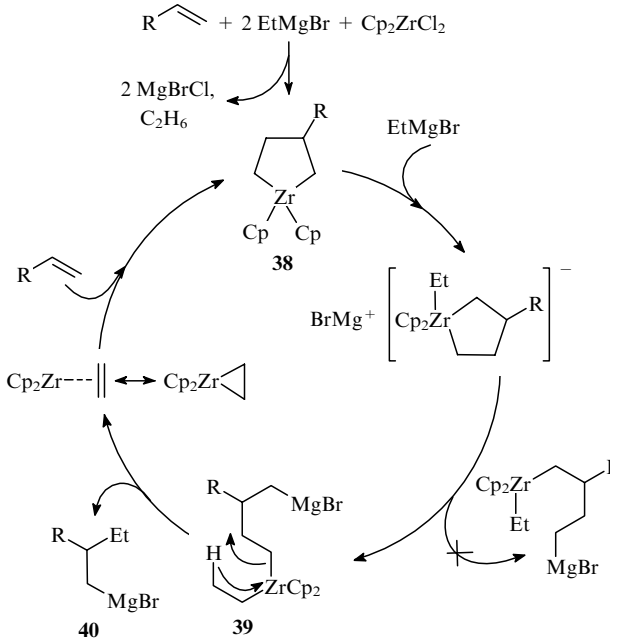
The reaction of Et_2Mg with *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (Et_2O, 20 °C, Cp_2ZrCl_2 as a catalyst) affords a mixture of regioisomeric OMC **36a**,**b** differing in the position of the ethyl group relative to the double bond in a total yield 60%, the ratio of the isomers being ~1 : 1. Under the same conditions, the organomagnesium compound **37** is obtained from bicyclo[2.2.1]hepta-2,5-diene and Et_2Mg, and its hydrolysis resulted in 3-ethylnortricyclene.[90]



37 (70%)

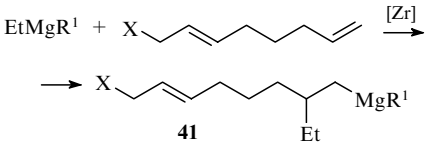
[Zr] = Cp_2ZrCl_2.

A tentative mechanism of the ethylmagnesiation reaction of alkenes with EtMgBr in the presence of Cp_2ZrCl_2 as a catalyst proposed by Negishi and Takahashi implies consecutive forma-



tion of a zirconacyclopentadiene intermediate **38** and a bimetallic complex **39**, which is finally converted into the target OMC **40**.[92–95]

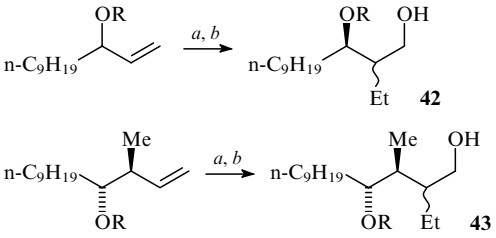
Various N-, O- and S-containing alkenes served as the substrates in the ethylmagnesiation reaction.[91,96–121] Ethylmagnesiation of octa-2,7-dienyl ethers and octa-2,7-dienylamines with EtMgR (R = Br, Et) catalysed by Cp_2ZrCl_2 involves the terminal double bond to yield the corresponding O- and N-functionalised OMC **41**.



R^1 = Br, Et; X = OR^2, SR^2 (R^2 = Me, Et, Bu^n), NEt_2; [Zr] = Cp_2ZrCl_2.

Reagents of the type EtMgOR, EtMgSR, EtMgOC(O)R, and EtMgC≡CR (R = Alk) appeared inert in ethylmagnesiation of α-alkenes catalysed by Cp_2ZrCl_2.[91]

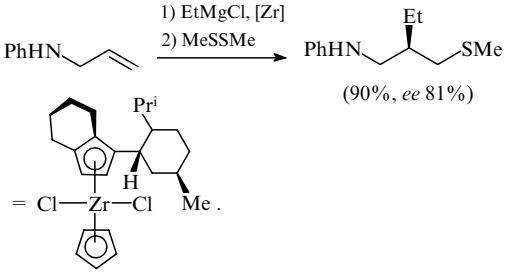
Ethylmagnesiation of allylic and homoallylic alcohols and ethers with an excess of EtMgCl in the presence of Cp_2ZrCl_2 has been studied by Hoveyda *et al.*[96–99] This reaction was highly stereoselective and afforded β-ethyl-substituted organomagnesium compounds in high yields. The structures of these OMC were established by an analysis of their oxidation products, **42** and **43**. Presumably, the high stereoselectivity of ethylmagnesiation is due to the coordination of the heteroatom of the starting unsaturated compound to the central metal atom of the catalyst.

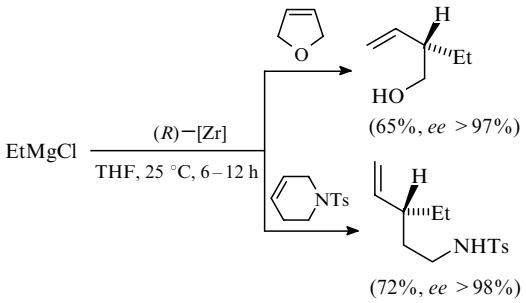


(*a*) EtMgCl (4 equiv.), Cp_2ZrCl_2 (5%), Et_2O, 25 °C, 12 h;
(*b*) $B(OMe)_3$, H_2O_2, −78 °C.

R	The ratio *anti : syn*		Yield (%)	
	42	**43**	**42**	**43**
H	5 : 95	> 99 : 1	70	75
Me	89 : 11	97 : 3	80	65

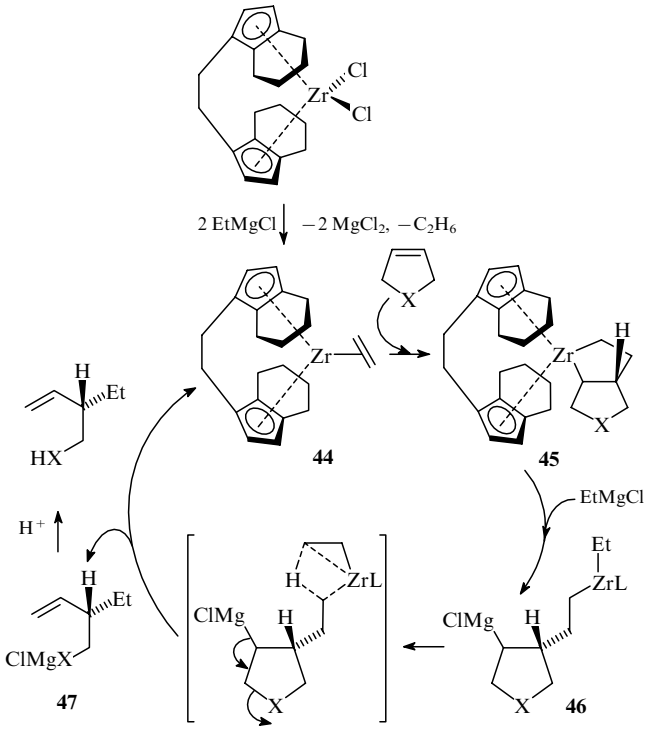
Asymmetric ethylmagnesiation of α-alkenes, non-cyclic and cyclic allylic alcohols, ethers and amines [100–117] in the presence of Zr-containing catalysts is highly diastereo- and enantioselective. The enantioselective formation of C–C bonds catalysed by chiral Zr and Ti complexes has been reviewed elsewhere.[110–113] Selected representative examples of such asymmetric syntheses are given below.





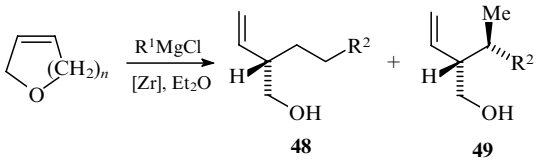
[Zr] is ethylene-1,2-bis(η5-4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

A tentative mechanism of the catalytic reaction of EtMgCl with cyclic allylic ethers and amines involves the enantioselective addition of the starting unsaturated compound to the complex **44** to form a zirconacyclopentadiene intermediate **45**.[104] The regiocontrolled opening of the zirconacyclopentadiene fragment with EtMgCl results in a sterically less hindered complex **46**, intramolecular rearrangement of which results in a γ-ethyl-substituted α-alkene **47**.



X = O, NC_9H_{19}-n; L is 1,2-bis(η5-4,5,6,7-tetrahydro-1-indenyl)ethylene.

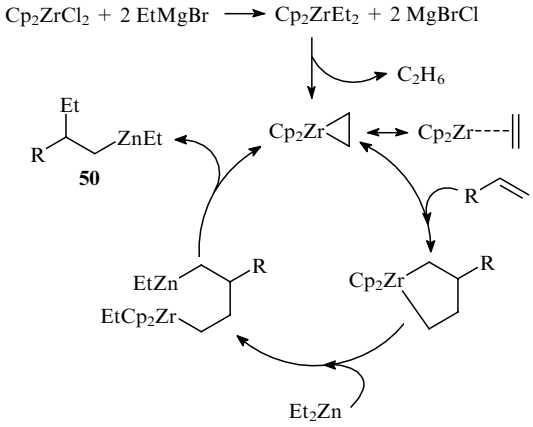
The enantioselective alkylation of cyclic allylic ethers or acyclic homoallylic alcohols (or ethers) with Pr^nMgCl or Bu^nMgCl in the presence of a catalytic amount of Cp_2ZrCl_2 affords γ-substituted terminal alkenes as isomers with primary (compounds **48**) and secondary (compounds **49**) alkyl groups. The regioselectivity of the reaction depends on the structure of the starting reagents and temperature.[121,122] Typically, ether is used as a solvent, since tetrahydrofuran provides lower selectivities and yields of the products.



[Zr] = Cp_2ZrCl_2.

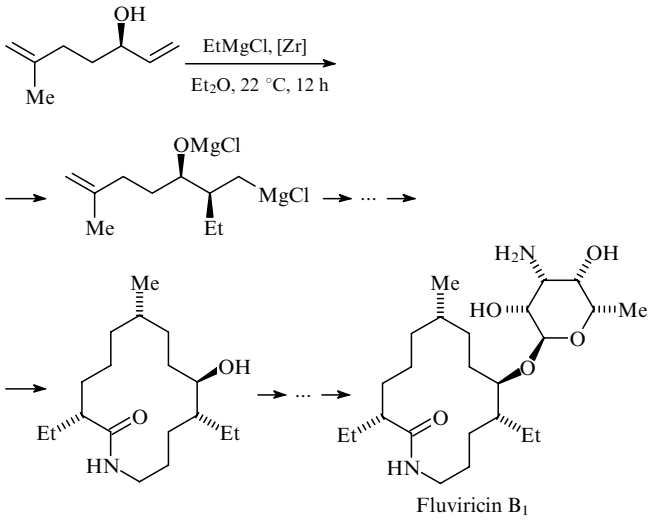
n	R^1	R^2	Temperature /°C	Ratio **49** : **48**	*ee* (%)
1	Pr^n	Me	22	2 : 1	99
1	Bu^n	Et	20	2 : 1	> 99
			70	15 : 1	> 90
2	Pr^n	Me	22	> 25 : 1	98

In analogy with ethylmagnesiation,[88] α-alkenes were successfully ethylzincated[123] with Et_2Zn catalysed by Et_2ZrCp_2. The latter was generated from Cp_2ZrCl_2 and EtMgBr. As a result, a series of organozinc compounds **50** have been obtained.



R = Alk.

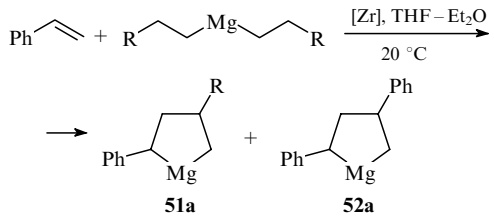
Ethylmagnesiation reaction of alkenes catalysed by Zr complexes is widely applied in the synthesis of biologically active compounds,[109, 118–120, 124] such as the natural antibiotic fluviricin B_1 (see Ref. 118).



VI. Cyclomagnesiation of alkenes and allenes

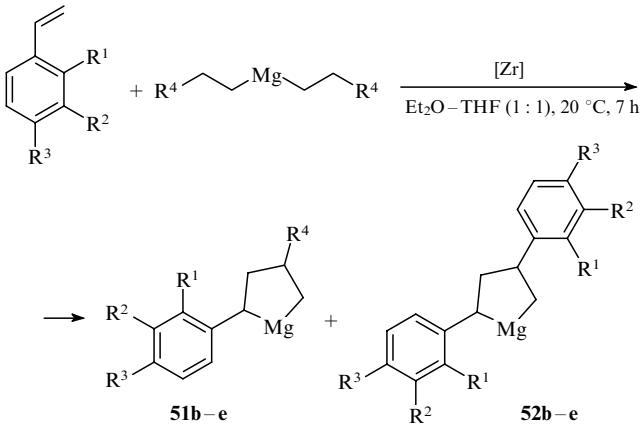
Based on the results of investigations[125, 126] into the catalytic cycloalumination of alkenes with trialkyl- or alkylhaloalanes to give aluminacyclopentanes, the first cyclomagnesiation of alkenes with R_2Mg and Cp_2ZrCl_2 as a catalyst was accomplished in 1989.[127] It was found that the reaction of styrene with Alk_2Mg (Alk = Pr^n, Bu^n, n-C_6H_{13}) in the presence of a catalytic amount of Cp_2ZrCl_2 in a mixture THF – Et_2O afforded a mixture of 2,4-disubstituted magnesacyclopentanes **51a** and **52a** in a ratio ~ 1 : 3 (the total yield is ~ 80% †).[127, 128]

† Hereinafter, the yields of OMC are calculated based on the hydrolysis products of the reaction mixture.



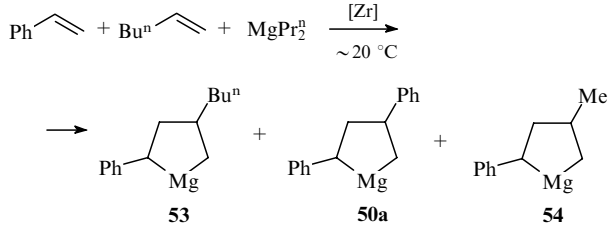
R = Me, Et, Bu^n; [Zr] = Cp_2ZrCl_2.

Ring-substituted styrenes (2-, 3- and 4-methyl-, 3-*tert*-butyl-) can also be cyclomagnesiated with R_2Mg catalysed by Cp_2ZrCl_2 to magnesacyclopentanes **51b**–**e** and **52b**–**e** (in a ratio of ~ 1 : 1) in yields of > 70%.[129–131]

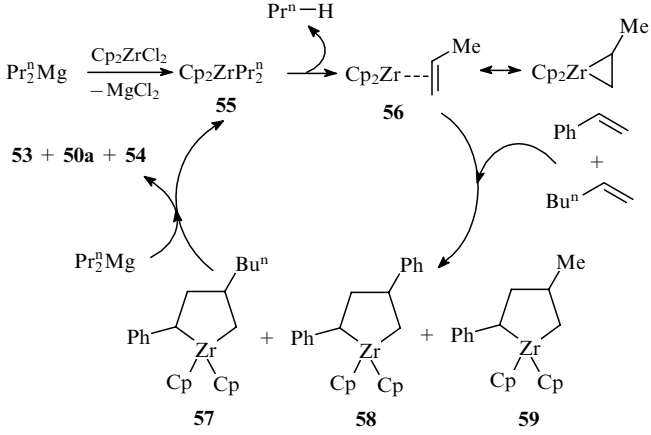


R^1 = Me, R^2 = R^3 = H (**b**); R^2 = Me, R^1 = R^3 = H (**c**);
R^3 = Me, R^1 = R^2 = H (**d**); R^3 = Bu^t, R^1 = R^2 = H (**e**); R^4 = Me, Et.

Cyclomagnesiation of a mixture of styrene and hex-1-ene with Pr^n_2Mg in the presence of Cp_2ZrCl_2 as a catalyst in a mixture THF – Et_2O resulted in 2,4-disubstituted magnesacyclopentanes **53** : **50a** : **54** in a ratio of ~ 35 : 35 : 30 in a total yield of 85%.[132]

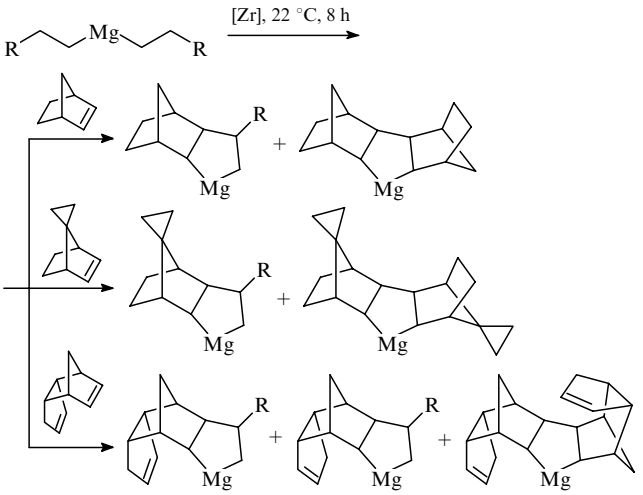


Based on the results obtained, a tentative mechanism of cyclomagnesiation of alkenes with di(n-propyl)magnesium catalysed by Cp_2ZrCl_2 has been proposed.[131] It involved alkylation of Cp_2ZrCl_2 to di(n-propyl)zirconocene **55**, intramolecular β-hydride transfer[133] with elimination of propane and formation



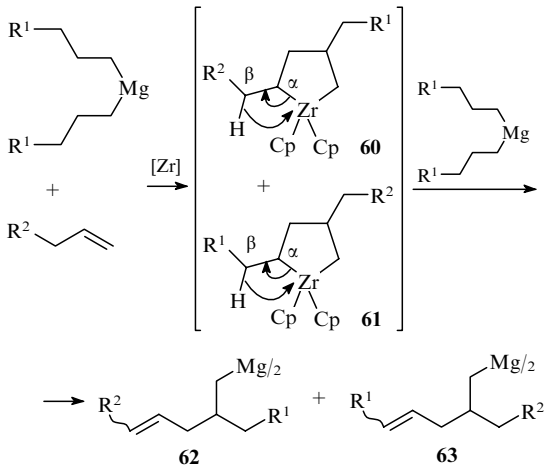
of a propylene–zirconocene intermediate **56**. The latter reacts with a mixture of alkenes affording 2,4-disubstituted zirconacyclopentanes **57**–**59**,[134] which react with the starting reagent (Pr^n_2Mg) to give the corresponding 2,4-disubstituted magnesacyclopentanes **50a**, **53** and **54**.

Cyclomagnesiation of norbornenes with Pr^n_2Mg or Bu^n_2Mg catalysed by Cp_2ZrCl_2 (3 mol.%) in THF–Et_2O resulted in mixtures of polycyclic OMC in yields of 80%–95%.[135]



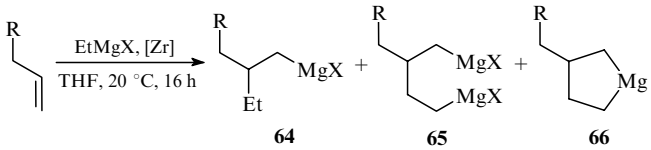
R = Me, Et.

Aliphatic α-alkenes react with Alk_2Mg (Alk = Pr^n, n-C_6H_{13}, n-C_8H_{17}) in the presence of Cp_2ZrCl_2 to give predominantly acyclic unsaturated organomagnesium compounds.[131,136] Presumably, intermediate 2,4-dialkyl-substituted zirconacyclopentanes **60** and **61** are formed under the reaction conditions, which undergo intramolecular β-hydride transfer under the action of the starting magnesium reagent and are converted into the isomeric acyclic unsaturated OMC **62** and **63**. It is of note that 2-arylzirconacyclopentanes **57**–**59** have no hydrogen atoms at the β-carbon atom and thus no transformations of this type with opening of the metallacycle take place.



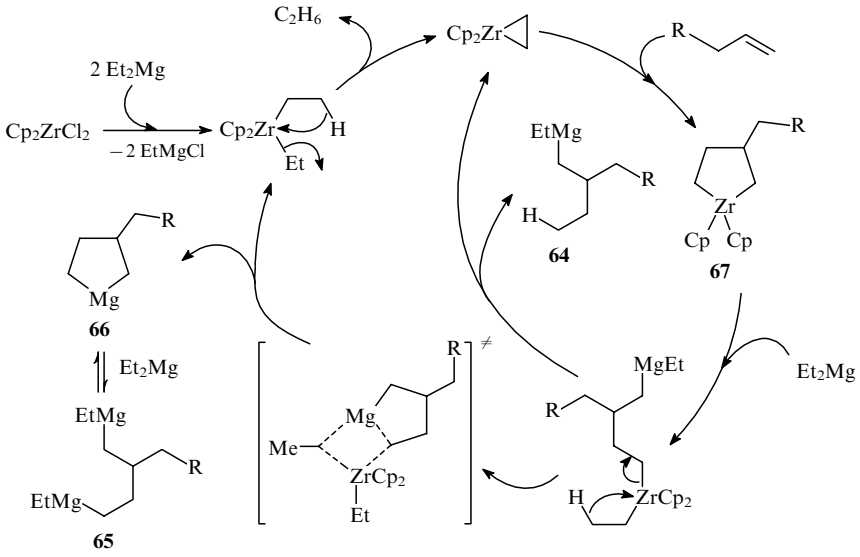
R^1 = H, Pr^n, n-C_5H_{11}; R^2 = Alk.

Unlike Alk_2Mg (Alk = Pr^n, Bu^n, n-C_6H_{13} or n-C_8H_{17}), such magnesium reagents as EtMgX (X = Cl, Br) or Et_2Mg react with α-alkenes in the presence of a catalytic amount of Cp_2ZrCl_2 to yield ethylmagnesiation (**64**) or cyclomagnesiation products **65** and/or **66**, respectively (Scheme 1). The reaction pathway depends on the reaction conditions, *viz*., the nature of the solvent, the temperature and the ratio of the starting reagents. For instance, ethylmagnesiation products are formed with high selectivity [the ratio **64**:(**65** + **66**) is 95:5] in THF (2 equiv. of EtMgHal, ~20 °C, 16 h), whereas 1,4-dimagnesium compounds are predominantly formed [the ratio **64**:(**65** + **66**) is 15:85] in Et_2O with 4 equiv. of Et_2Mg (0 °C, 16 h).[137]



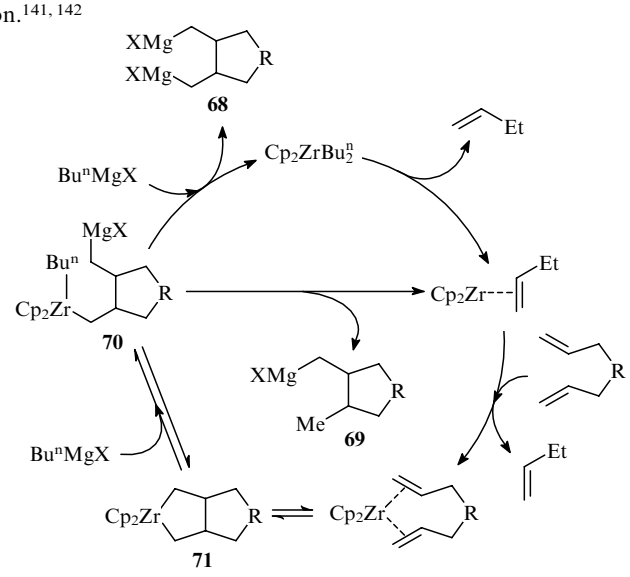
R = n-C_5H_{11} (70%),  (65%),  (75%),  (65%),  (75%), BnO (54%), $BnOCH_2$ (56%), $BnO(CH_2)_2$ (65%), $Bu^tMe_2SiO(CH_2)_2$ (70%), PhS (80%), Me_3Si (63%); X = Cl, Et.

Scheme 1



A tentative mechanism was proposed in order to rationalise the experimental results, which is shown in Scheme 1. In the first step, diethylmagnesium alkylates Cp_2ZrCl_2 to yield zirconacyclopentane intermediates **67**. Depending on the reaction conditions, the latter react with Et_2Mg to give either ethylmagnesiation (**64**) or cyclomagnesiation (**65**, **66**) products.[137, 138]

The reactions of non-conjugated α,ω-dienes with Bu^nMgX or $Bu^n{}_2Mg$ catalysed by Cp_2ZrCl_2 (1 mol.% – 10 mol.%) in ether-type solvents afford 1,2-bis(magnesiomethyl)carbocycles **68** or 1-(magnesiomethyl)-2-methylcarbocycles **69**[139–142] *via* zirconacyclopentane intermediates that are formed under these conditions.[143, 144] The rates of formation and yields of the target products, the selectivity and stereochemistry of the process depend on the structure of the starting α,ω-diene (this can be hepta-1,6-diene, octa-1,7-diene or 9,9-diallylfluorene), the organomagnesium compound used (*e.g.*, Bu^nMgHal or Bu^n_2Mg), reaction temperature (from 0 to 120 °C), solvent (Et_2O, THF, Pr^i_2O, Bu^n_2O) and the ratio of the reagents. For instance, with Bu^n_2Mg in Et_2O at 20 °C, 1,2-bis(n-butylmagnesiomethyl)cycloalkanes **68** are predominantly formed. In contrast, the reaction of α,ω-dialkenes with Bu^nMgHal in THF yields mainly 1-(halomagnesiomethyl)-2-methylcarbocycles **69**. It is of note that the total yield of organomagnesium compounds **68** and **69** in Et_2O is higher than that in THF. The ratio between *trans* and *cis* isomers in the products **68** and **69** increases with an increase in temperature. The transmetallation of bimetallic complexes **70** with the starting organomagnesium reagents is the key step of the catalytic cycle, which determines the overall chemoselectivity of the reaction.[141, 142]

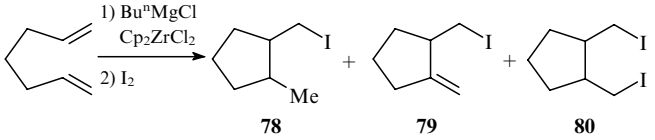


R = CH_2, $(CH_2)_2$, fluorenyl; X = Cl, Br, Bu^n.

Negishi *et al.*[145] investigated the reactions of Bu^nMgCl and $Bu^n{}_2Mg$ with 3-bis(η^5-cyclopentadienyl)zirconabicyclo[3.3.0]octane **71** (R = CH_2) in two solvents, *viz.*, THF and Et_2O (Scheme 2) to get an insight into the mechanism of the above transformations. The complex **71** (R = CH_2) is a possible intermediate in the reaction of hepta-1,6-diene with Bu^nMgX (X = Cl, Bu^n) catalysed by Cp_2ZrCl_2.

It was found that the monomagnesium derivative **72** is formed only in the case of Bu^nMgCl in THF. In all other cases (Bu^nMgCl in Et_2O and Bu^n_2Mg in any of the two solvents), the 1,4-dimagnesium derivative **73** was the major product. This fact can be explained as follows. It is known that the Grignard reagents AlkMgHal exist as monomers in tetrahydrofuran and as dimers in diethyl ether.[146] In the case of dimeric structures (Bu^nMgCl in Et_2O or Bu^n_2Mg), an intramolecular transfer of the butyl group from the magnesium to the zirconium atom occurs in the complexes **74** and **75** resulting in the 1,4-dimagnesium compound **73**. No similar process is possible for monomeric structures (Bu^nMgCl in THF) or at a molar ratio complex **71** : Bu^n_2Mg other than 1 : 1 or 1 : 2. If the reaction is performed with Bu^n_2Mg, the magnesium-containing bicyclic compound **76** is formed in addition to **73** in both solvents.

Unsaturated monomagnesium compounds **77** are obtained only in the reaction of Bu^nMgCl with hepta-1,6-diene in THF or Et_2O in the presence of a catalytic amount of Cp_2ZrCl_2 in a yield of ~10%. This conclusion was drawn from the analysis of subsequent iodination products, **78**–**80**.

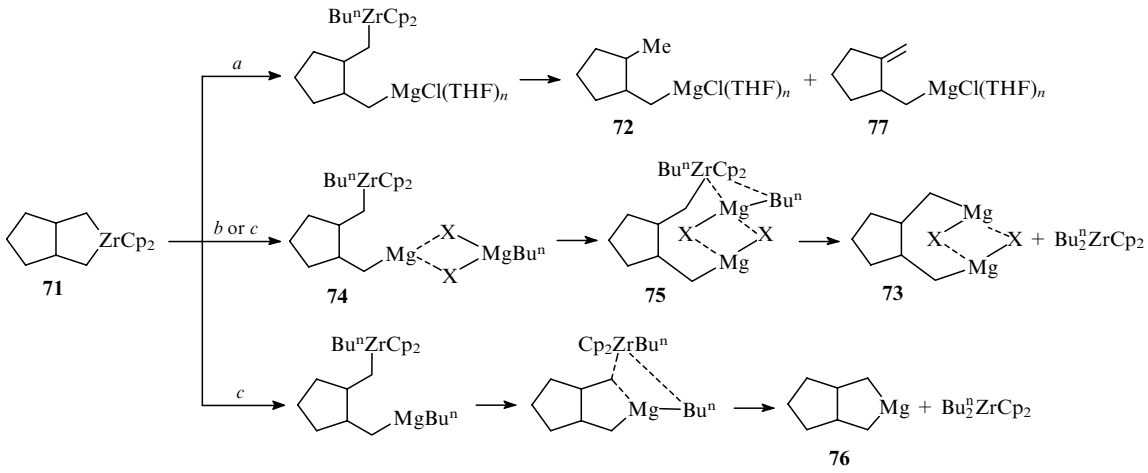


Solvent	Yield (%)		
	78	**79**	**80**
THF	45	10	traces
Et_2O	10	10	40

The stereochemistry of the carbomagnesiation and cyclomagnesiation of α-alkenes or non-conjugated dienes with Alk_2Mg or AlkMgHal catalysed by chiral zirconium complexes was discussed elsewhere.[147–149] Under the reaction conditions, intermediate *cis*- (**81**) and *trans*-zirconacyclopentanes **82** are selectively formed, which are further converted into the corresponding *cis*- and *trans*-dimagnesium compounds **83** and **84** (Scheme 3).[149]

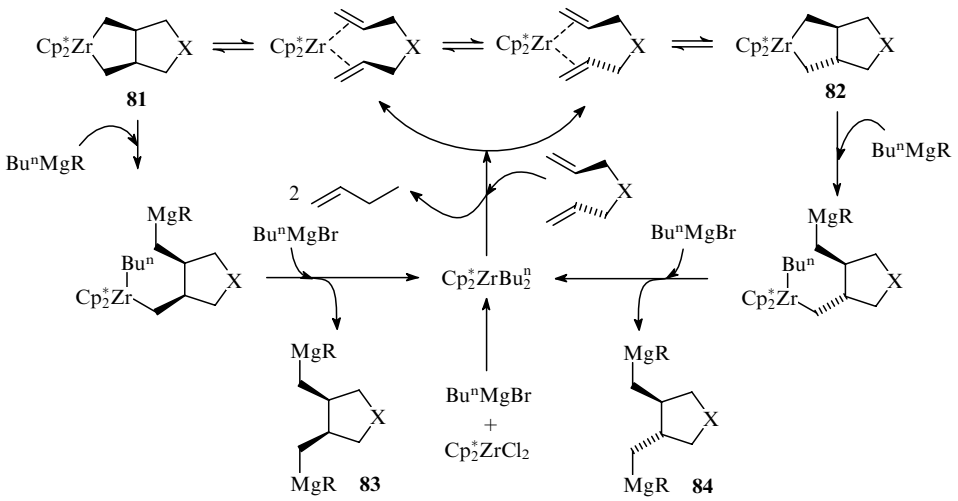
Carbocyclisation of unsaturated compounds using OMC and Zr-containing catalysts is applied to the synthesis of hydrogenated indane derivatives, including optically active ones.[150–160] The

Scheme 2



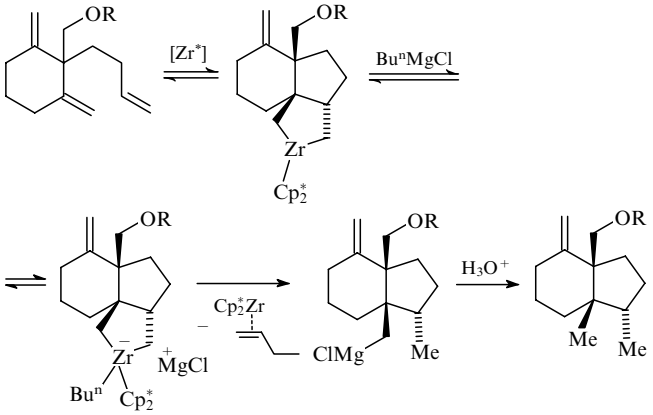
(*a*) Bu^nMgCl, THF; (*b*) Bu^nMgCl, Et_2O; (*c*) Bu^n_2Mg, Et_2O (THF); *n* = 1 or 2; X = Cl (for *b*) and Bu^n (for *c*).

Scheme 3



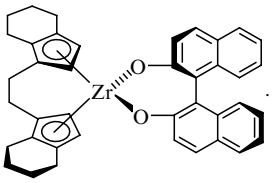
X = $(CH_2)_n$ (n = 1, 2), NBu^t, $SiMe_2$; R = Bu^n, Cl; $Cp^*_2ZrCl_2$ is 2,2′-biphenyl-bis(3,4,-dimethylcyclopentadienyl)zirconium dichloride.

multistep synthesis shown below has been accomplished by Mori *et al.*[153]

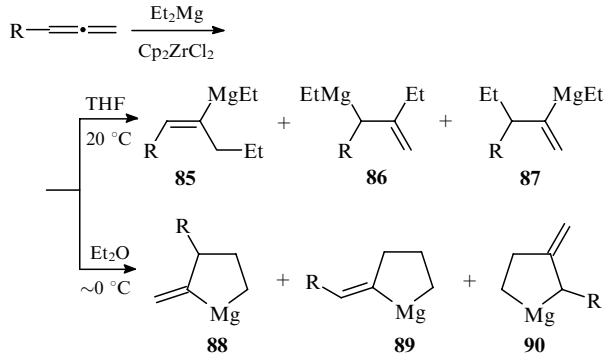


R = H, Bu^tMe_2Si;

[Zr*] = Cp^*_2Zr(BINOL) =

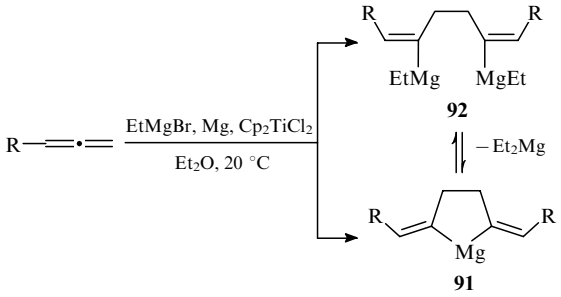


Allenes react with Et_2Mg in the presence of Cp_2ZrCl_2. Depending on the conditions, either carbomagnesiation (**85**–**87**) or cyclomagnesiation products **88**–**90** can be obtained.[161]



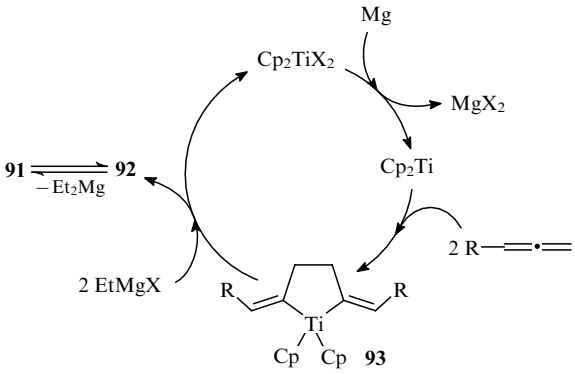
R = n-C_5H_{11}, n-C_7H_{15}, Bn.

2,5-Dialkylidenemagnesacyclopentanes **91** and 1,4-dimagnesium compounds **92** (in a ratio of ~1 : 1) were obtained[161] by Cp_2TiCl_2-catalysed cyclomagnesiation of substituted allenes with EtMgX (X = Cl, Br) and activated magnesium (see also Ref. 162).



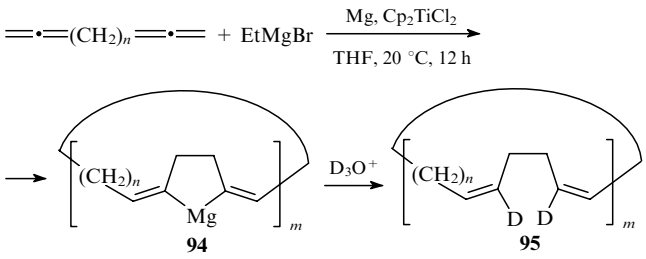
R = n-C_5H_{11}, n-C_7H_{15}, Bn.

The formal reduction of Cp_2TiCl_2 to 'Cp_2Ti', selective formation of intermediate 2,5-dialkylidenetitanacyclopentanes **93** followed by their transmetallation with EtMgX are the most probable intermediate steps, which explain the formation of the unsaturated OMC **91** and **92**.



X = Cl, Br.

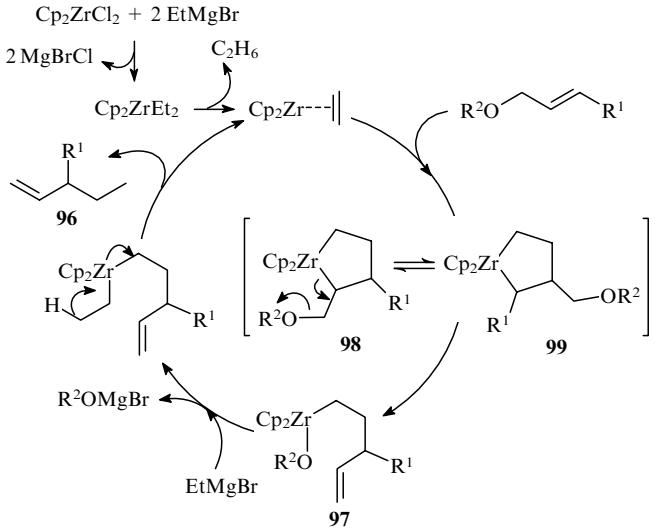
Intermolecular cyclomagnesiation of α,ω-diallenes with EtMgX and activated magnesium catalysed by Cp_2TiCl_2 (10 mol.%) has led to Mg-containing macrocycles **94** under mild conditions and in high yields (> 90%).[161] Subsequent treatment of the OMC **94** with a deuterated acid affords macrocyclic compound **95** with alternating *cis*-double bonds.



$n = 4-6$, $m = 5$.

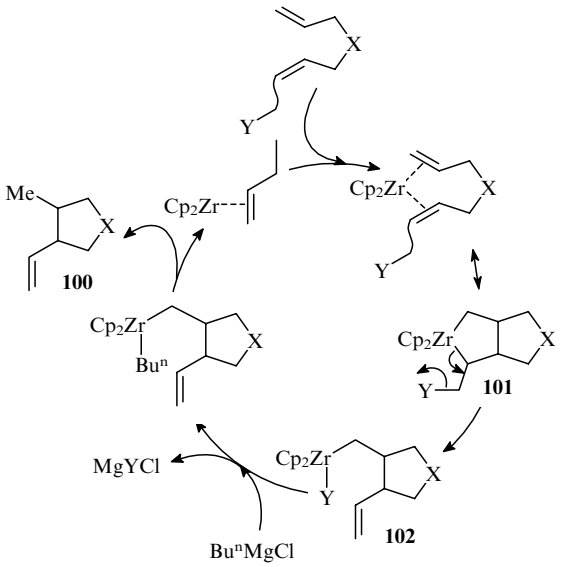
The idea of generation of zirconacyclopentane intermediates in the reaction of allylic ethers with EtMgBr in the presence of a catalytic amount of Cp_2ZrCl_2 is exploited in an efficient method for the formation of C–C bonds. In contrast to the cyclo- and carbomagnesiation reactions (see Section V), it is unsaturated compounds rather than organomagnesium compounds that are the target products of these reactions. In particular, the reaction of allylic ethers containing a disubstituted double bond with EtMgBr catalysed by Cp_2ZrCl_2 (THF, 20 °C, 6 h) results in the regioselective formation of a C–C bond involving the γ-carbon atom of the allylic ether, *i.e.*, affords an unsaturated compound **96**.[163] The high regioselectivity of the reaction is due to the formation of zirconium alkoxide **97** from regioisomeric[164] zirconacyclopentane intermediates **98** and **99**.

In addition to Cp_2ZrCl_2, Cp_2HfCl_2 can be used as a catalyst for these reactions. However, in this case, a satisfactory yield can be obtained only for a longer reaction time (65 h). No target products **96** are formed if MeMgBr devoid of the β-hydrogen atoms is used instead of EtMgBr.



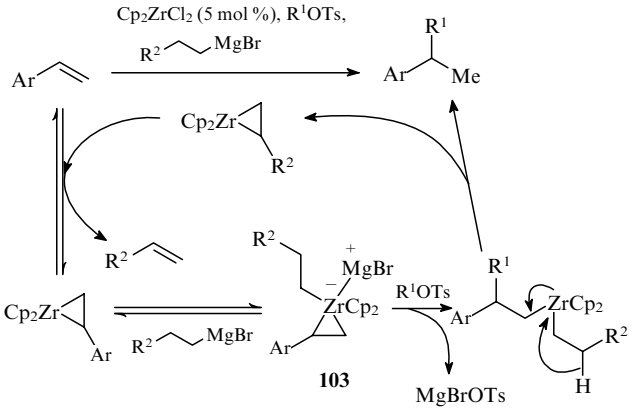
$R^1 = Pr^n$; R^2 = Me, Bn, Ph.

2-Bromo-α,ω-diene,[165] dienic ethers and amines with allylic double bonds[166, 167] cyclised into unsaturated carbo- and heterocyclic compounds **100** with high selectivities using Bu^nMgCl and Cp_2ZrCl_2 as a catalyst. The formation of zirconacyclopentane intermediates **101** is the key step of this reaction. Subsequent intramolecular rearrangement proceeds through zirconium alkoxide complexes **102**, which are further transmetallated with the starting reagent Bu^nMgCl. The catalytic cycle is closed by elimination of the unsaturated cyclic product **100**.



X = CH_2, NPr^n, NPh; Y = OMe, OPh.

Electrophilic alkylation of alkenes, indenes and chromenes with alkyl *p*-toluenesulfonates, sulfates or bromides has been realised[168–170] *via* intermediate zirconamagnesium complexes of the type **103** (see Ref. 168).

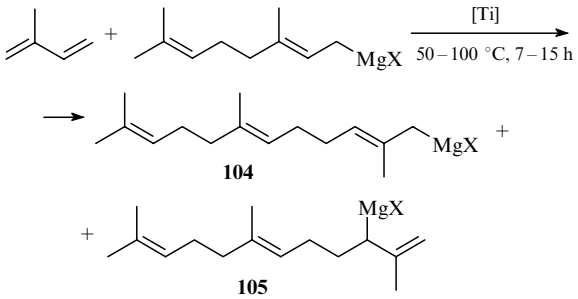


R^1, R^2 = Alk.

VII. Carbomagnesiation of 1,3-dienes

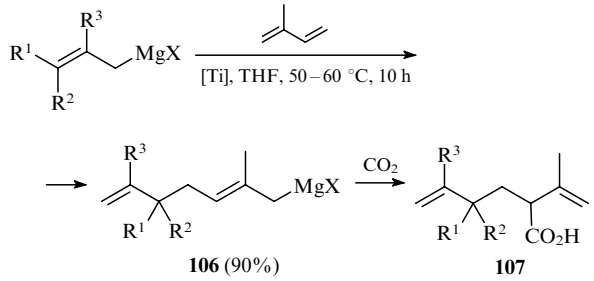
Thermal carbomagnesiation of conjugated dienes can only be performed with allylic OMC.[171, 172] Alkyl- and arylmagnesium halides do not react with 1,3-dienes under these conditions.

It was demonstrated[173] that isoprene undergoes carbomagnesiation with geranylmagnesium halides under relatively mild conditions in the presence of Ti-containing catalysts. The OMC **104** and **105** synthesised in this way were further converted into the corresponding isoprenoid alcohols.



[Ti] = Ph_2TiCl_2, $(RO)_2TiCl_2$ (R = Alk, Ar).

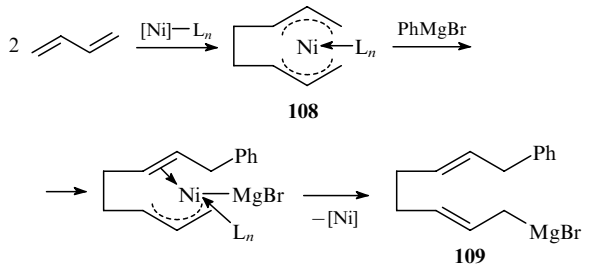
Carbomagnesiation of isoprene with allylic OMC catalysed by Cp_2TiCl_2 proceeds in THF with heating.[174, 175] The OMC **106** formed can be converted into the corresponding alcohols or carboxylic acids **107** by oxidation or reaction with CO_2.



106 (90%) **107**

R^1 = Me, R^2 = R^3 = H (25%); R^1 = R^2 = Me, R^3 = H (20%); [Ti] = Cp_2TiCl_2

The addition of PhMgBr to butadiene in the presence of low-valent nickel complexes activated by $P(OPh)_3$ [176] is the earliest example of carbomagnesiation of dienes with arylmagnesium halides. The formation of intermediate bis-π-allyl nickel complexes **108** is the key step of this reaction. This is followed by the oxidative addition of PhMgBr to this intermediate and reductive elimination of Ni^0, which yields (*E*,*E*)-octa-2,7-dienylmagnesium bromide **109** selectively.

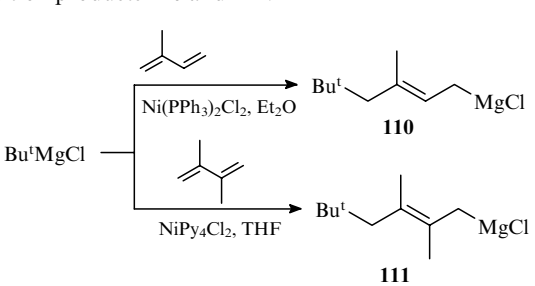


108 **109**

L_n = $P(OPh)_3$.

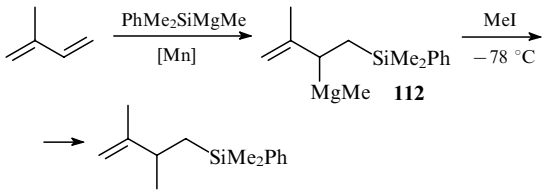
Phosphines and acetylacetone can be used as ligands in the nickel complexes. The activity of the Ni-containing catalysts in the reaction of arylmagnesium halides with butadiene decreases in the series: $Ni(PPh_3)_2Cl_2$ > $Ni(Ph_2PCH_2CH_2PPh_2)Cl_2$ > $Ni(Ph_2PCH_2CH_2PPh_2)(acac)_2$ > $Ni(acac)_2$.[177] In the case of phenylmagnesium bromide, a number of salts and complexes of various transition metals, including Pd, Cu, Rh, Ni, Co, Cr and Fe, in different oxidation states with different types of metal atom coordination, ligands and counterions were assayed as catalysts. In the presence of Fe(III) salts and complexes, the reactions of alka-1,3-dienes with arylmagnesium halides yield 1-arylalka-1,3-dienes. This reaction catalysed by phosphine Ni(II) complexes affords telomeric 1-arylalka-2,7- and 1-arylalka-2,6-dienes.[178, 179]

In contrast to arylmagnesium halides, Bu^tMgCl reacts with 1,3-dienes in the presence of nickel complexes yielding 1,4-addition products **110** and **111**.[40, 46]



110 **111**

By analogy with the carbomagnesiation reaction, silylmagnesiation of 1,3-dienes leading to unsaturated Si-containing OMC **112** in the presence of manganese catalysts was carried out.[180]



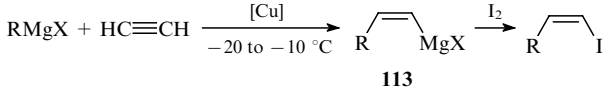
112

Carbomagnesiation of 1,3-dienes with alkyl-, aryl- and allyl-type OMC catalysed by metal complexes affords unsaturated organomagnesium reagents that are difficult to obtain by conventional methods.

VIII. Carbomagnesiation of alkynes

Regio- and stereoselective carbomagnesiation of alkynes is used in synthetic practice for the preparation of substituted alkenes with *Z*-configuration of the double bond.[181]

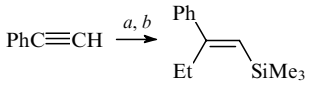
As a rule, non-catalytic carbomagnesiation of alkynes requires drastic conditions and long reaction time.[182] The use of metal complex catalysts makes it possible to decrease the temperature, reduce the duration and increase the yields of the target products. For instance, carbomagnesiation of acetylene with Grignard reagents in the presence of Cu(I) compounds takes 1–2 h at low temperature to give organomagnesium compounds **113** containing *Z*-double bonds.[183]



113

R = Alk; X = Cl, Br; [Cu] = CuBr, CuCN, PhSCu, Bu^tOCu, MeCu.

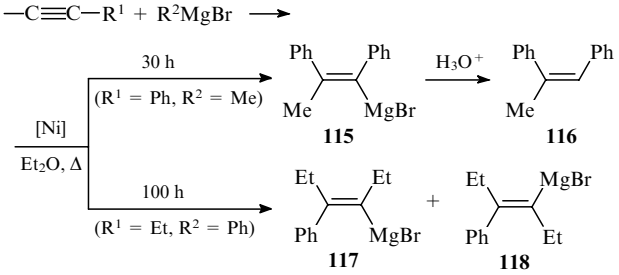
Carbomagnesiation of monosubstituted alkynes in the presence of copper salts involves the addition of the magnesium atom to the non-substituted α-carbon atom of the original alkyne. Subsequent functionalisation of the OMC formed with chlorosilanes is of interest as a method for the synthesis of unsaturated silanes of the type **114** with a *Z*(or *E*)-trisubstituted double bond.[184]



114 (85%)

(*a*) EtMgCl, CuI, LiBr, THF, –60 °C, 14 h;
(*b*) Me_3SiCl, HMPA, –60 to 20 °C, 5 h.

Carbomagnesiation of disubstituted acetylenes results in OMC containing *E*- and *Z*-double bonds. In particular, prolonged boiling of diphenylacetylene in ether with a twofold excess of MeMgBr in the presence of $Ni(PPh_3)_2Cl_2$ (10 mol.%) yields the unsaturated OMC **115**, which is hydrolysed to the individual trisubstituted alkene **116** with *cis*-arrangement of the phenyl substituents.[185] The reaction of hex-3-yne with PhMgBr under similar conditions affords *cis*- (**117**) and *trans*-isomers (**118**) in a ratio of 9 : 1. Duboudin *et al.*[185] proposed that the *cis*–*trans*-isomerisation of organomagnesium compounds in the latter case

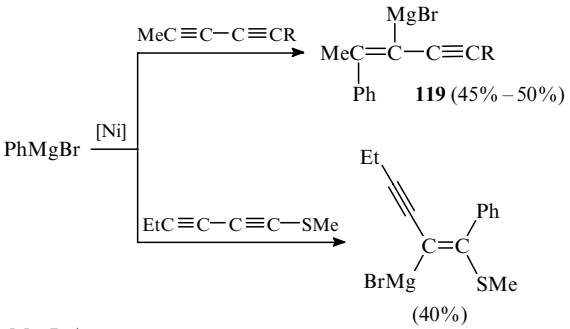


115 **116** **117** **118**

[Ni] = $Ni(PPh_3)_2Cl_2$.

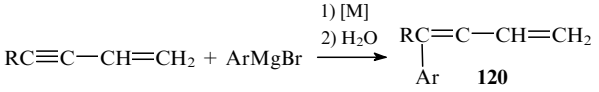
is due to the formation of intermediate π-allyl nickel complexes.[186, 187]

Diacetylenes undergo carbomagnesiation in the presence of $NiCl_2$, which results in OMC **119** with an enyne fragment.[188] Functionalised alkadiynes, such as alkyl(alkylthio)diacetylenes, have also been carbomagnesiated in the presence of Ni-containing catalysts.[189]



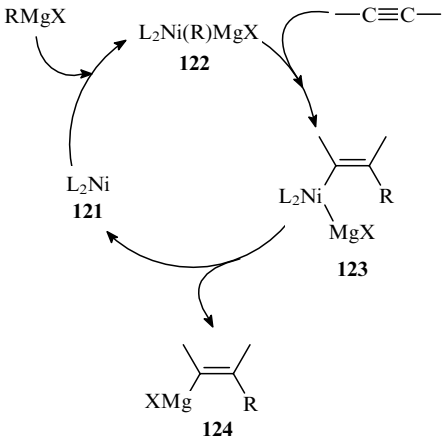
R = Me, Bu^t.

Carbomagnesiation of conjugated enynes yields alkadienylmagnesium halides, and their hydrolysis offers a convenient route to 1,3-dienic hydrocarbons.[190] Pd, Fe, Ni and Co complexes can be used as catalysts in the carbomagnesiation of 1-en-4-ynes with arylmagnesium bromides to a mixture of *Z*- and *E*-isomers of aryl-substituted 1,3-dienes **120**.[191]



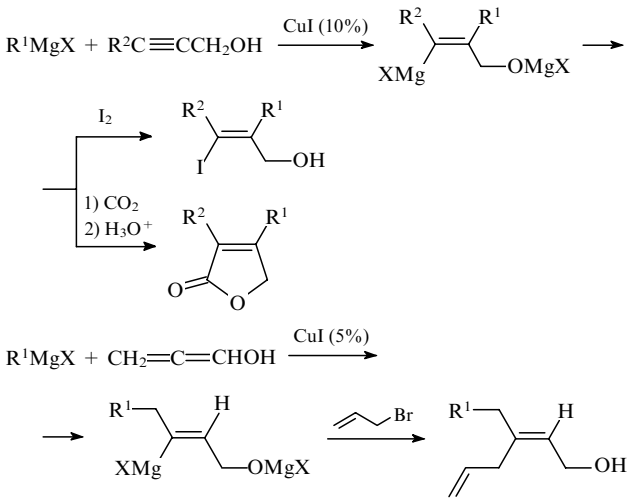
R = Me, Et; Ar = Ph, 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$; [M] = Pd, Fe, Ni, Co.

A proposed mechanism of carbomagnesiation of alkynes with the Grignard reagents in the presence of Ni-containing catalysts involves the oxidative addition of RMgHal to the low-valent nickel complex **121** to form the alkylnickel complex **122**, which induces carbomagnesiation of the original alkyne to give the alkenylnickel complex **123**.[192] Subsequent reductive elimination of a low-valent Ni complex yields the target alkenyl OMC **124**.



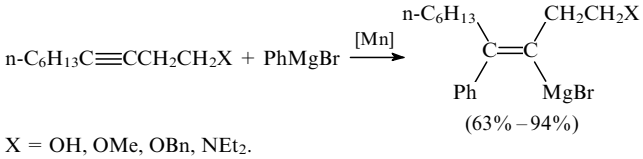
Carbomagnesiation of silylacetylenes with a fourfold excess of MeMgBr in the presence of a two-component catalyst $Ni(acac)_2$ – Me_3Al (1 : 1) is rather highly regioselective. The Grignard reagent adds predominantly (~90%) to the carbon atom bearing the silyl group.[193] The use of EtMgBr and a system $Ni(acac)_2$ – Bu^i_2AlH as a catalyst affords alkenyl- (~50%) and alkadienylmagnesium bromides (~30%). The latter are formed upon carbomagnesiation of of the original alkyne with alkenylmagnesium halide generated *in situ*.[194]

Cu(I) salts are more active catalysts in the carbomagnesiation of propargylic and allenic alcohols in contrast to the corresponding reactions with alkyl-, aryl- and silylacetylenes.[195–197]



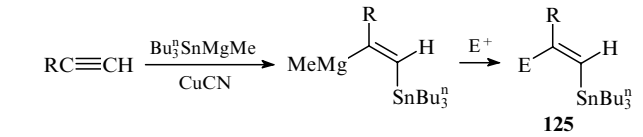
R^1 = Me, Et, Pr^i, Bu^t, All, Bn, Ph; R^2 = H, Me, Ph, Bu^n, Me_3Si; X = Cl, Br.

Propargylic ethers readily react with Grignard reagents (~20 °C, ether, 10 mol.% of CuBr) to afford carbomagnesiation products in 70% – 80% yields. [198] In the presence of $MnCl_2$ as a catalyst, carbomagnesiation [199] as well as silylmagnesiation [180] of disubstituted acetylenes, including those containing functional groups, can successfully be carried out.



X = OH, OMe, OBn, NEt_2.

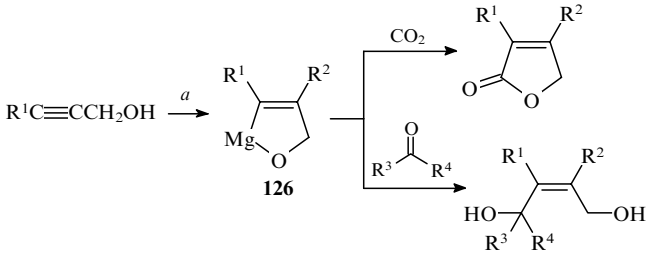
Stannylmagnesiation of terminal alkynes, like carbomagnesiation, is performed in the presence of CuCN. This reaction with various electrophilic reagents yields vinylstannanes **125** with high regio- and stereoselectivities.[200]



R = Alk, cyclo-Alk, Ph, $BnO(CH_2)_2$; E = H, D, Me, Et, All, PhCH(OH).

Carbomagnesiation of alkynes with the Grignard reagents is widely applied to the synthesis of unsaturated halides,[201] $\Delta^{\alpha,\beta}$-butenolides, alk-2-ene-1,4-diols,[202] cyclopentenones,[203] vinyl sulfones [204] and various biologically active compounds.[205] Furthermore, it is useful in the cross-coupling reactions.[206]

In particular, Duboudin and Jousseaume [202] reported the synthesis of a number of unsaturated diols and lactones exploiting organomagnesium compounds **126** prepared from the respective alkyne.



(*a*) R^{2}MgBr, CuI (10%); R^1, R^2 = H, Me, Et, Ph, Bz, All; $R^3C(O)R^4$ = EtCH(O), $Me_2C(O)$, PhC(O)Me, $(CH_2)_5C(O)$.

The above results demonstrate that the carbomagnesiation of alkynes with Grignard reagents in the presence of transition metal-based catalysts represents a convenient method for the synthesis of alkenylic, alkadienylic and enynic organomagnesium compounds. Functionalisation of such derivatives offers new potential in synthetic practice.

IX. Conclusion

The application of metal complex catalysis to the chemistry of OMC has led to the discovery of new reactions, development of efficient methods of synthesis of various types of compounds and development of novel highly reactive reagents to meet the needs of modern organic and organometallic chemistry. Non-traditional 'non-Grignard' organomagnesium compounds with different structures that became available due to advances in the metal complex catalysis, have solidly taken their places in the arsenal of common reagents. Investigations into hydro- and carbomagnesiation of alkenes, dienes and alkynes with magnesium hydride and alkylmagnesium compounds in the presence of transition metal-based catalysts are currently in progress, which unveils new avenues in the preparation of non-trivial magnesium-containing systems. Catalytic cyclomagnesiation of unsaturated compounds with AlkMgHal (or Alk_2Mg) has led to new classes of cyclic OMC.

According to the above analysis of the published data, one can expect, in the very near future, further progress in several promising directions, in particular, selective functionalisation of unsaturated compounds through the intermediate formation of Mg–C bonds; chiral synthesis of organomagnesium reagents and their conversion into optically active compounds. Hopefully, the catalytic hydro-, carbo- and cyclomagnesiation of α,ω-dialkenes, diallenes or dialkynes will be demanded by chemists for the synthesis of metal-containing and polyfunctional macrocycles required for the preparation of new reagents and materials.

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