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Review

SYNTHESIS AND TRANSFORMATIONS OF "NON-GRIGNARD" ORGANOMAGNESIUM REAGENTS OBTAINED FROM 1,3-DIENES

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TABLE OF CONTENTS

1. Introduction	1
2. Synthesis of dienylmagnesium reagents by direct metallation or hydrometal- lation of 1,3-dienes with metallic magnesium or its hydride or alkyl derivatives	2
3. Organomagnesium compounds based on cyclic 1,3-dienes and polyenes	26
4. Conclusion	37

SUMMARY

This paper is the first attempt to systematize available published data on the synthesis and transformations of unsaturated organomagnesium compounds obtained from 1,3-dienes by nontraditional methods. Direct metallation of 1,3-dienes and polyenes by chemically activated highly active magnesium is reviewed. Some results of hydro- and carbo-magnesiumation of unsaturated compounds by hydride and alkyl magnesium derivatives are cited including those obtained with homogeneous metal complex catalysts. Attention is focused also on metallation of cyclic 1,3-dienes by highly active magnesium or Grignard reagents and some of their analogues. The structure and chemistry of non-trivial organomagnesium compounds are also discussed.

INTRODUCTION

The reaction of organic halides with metallic magnesium in etheral solvents represents a well-known and widely accepted approach to organomagnesium (Grignard) compounds. An immense bulk of literature covering the synthesis and use of organomagnesium compounds (OMC) obtained by this routine procedure has been summarized in classical monographs and reviews [1-3]. Progress in OMC synthesis can be associated primarily with the availability of novel complex halides which can react with metallic magnesium. One of the most important achievements in OMC chemistry during the last two decades is a non-traditional approach to OMC based on the direct metallation of conjugated di-

enes with chemically activated or highly active Mg as well as on catalytic hydromagnesiation of 1,3-dienes by hydride or alkyl magnesium derivatives. This approach affords novel types of unsaturated OMC constituting a new class of highly active reagents. Their ready availability enhances their importance in organometallic chemistry and organic synthesis.

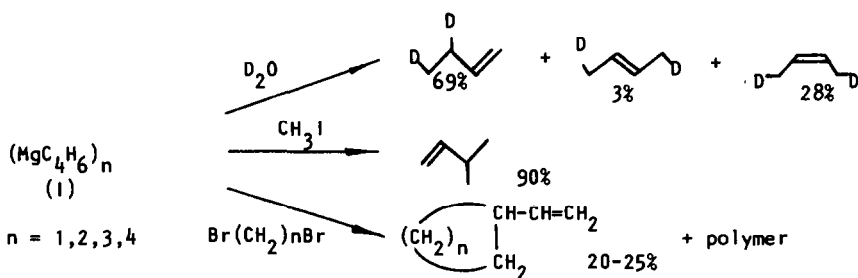
Only incomplete and fragmented accounts of the synthesis and chemistry of unsaturated OMC based on 1,3-dienes have been published (e.g. [4,5]). The notable advances in the preparation of unsaturated OMC obtained by non-routine procedures in the last decade, and the absence of any general studies, have prompted the authors to review this field, in which they themselves have been active.

SYNTHESIS OF DIENEMAGNESIUM REAGENTS BY DIRECT METALLATION OR HYDROMETALLATION OF 1,3-DIENES WITH METALLIC MAGNESIUM OR ITS HYDRIDE OR ALKYL DERIVATIVES

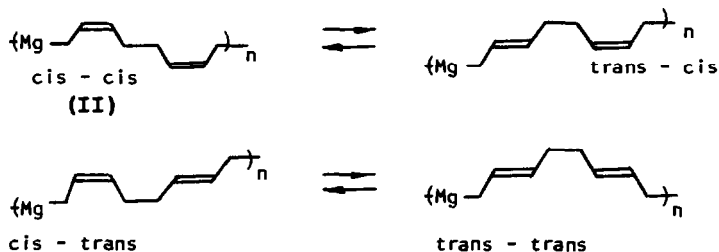
1. Organomagnesium compounds based on butadiene

Publications [6-8] on the reactions of 1,3-dienes and alkali metals have obviously promoted research on the synthesis of dienemagnesium reagents. The original work on the direct metallation of conjugated dienes by metallic Mg has been patented [9-12], and the first representative of the dienemagnesium reagents, butadienemagnesium, was obtained in 1968 [11]. OMCs of the general structure $(\text{MgC}_4\text{H}_6)_n$ (I) have been synthesized by the reaction of metallic Mg activated by catalytic amounts of I_2 , CH_3I , PhI , or $\text{C}_2\text{H}_5\text{Br}$, and an equimolar amount of butadiene in THF [13].

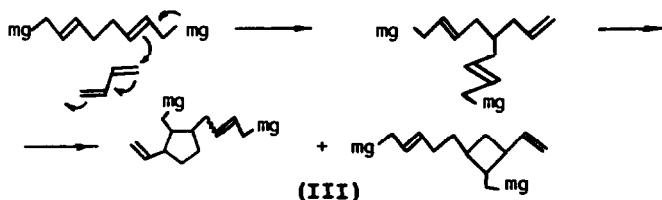
On changing the Mg/butadiene ratio from 1:1 to 3:1, $(\text{MgC}_8\text{H}_{12})_n$ (II) and $(\text{MgC}_{12}\text{H}_{18})_n$ (III) can be obtained as the main products. The structures (I)-(III) were established [13] by a number of chemical transformations. Deuterolysis of (I) and (II) affords dideuteriobutenes and dideuteriooctadienes [13]. Unlike (I) and (II), deuterolysis of (III) gives a mixture of dideuteriocyclododecatrienes. On interaction between $(\text{MgC}_4\text{H}_6)_n$ and CH_3I , 3-methyl-1-pentene is formed while alkyl dihalides lead to cyclic hydrocarbons.



The PMR spectra and the curve of the protolysis and also chemical transformations of OMCs (I) and (II) have been interpreted to imply those butadienemagnesium reagents, e.g. (II), exist in a mobile equilibrium as is shown :

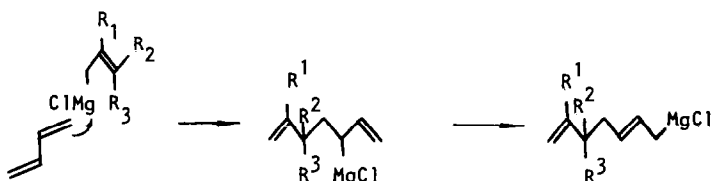


The oligomeric chain length depends on the starting ratio Mg:butadiene. It has been assumed that $(\text{MgC}_{12}\text{H}_{18})_n$ is formed from $(\text{MgC}_8\text{H}_{12})_n$ via sequential insertion of a butadiene molecule into the C-Mg bond, while $(\text{MgC}_8\text{H}_{12})_n$ in turn originates from $(\text{MgC}_4\text{H}_6)_n$. Unlike $(\text{MgC}_4\text{H}_6)_n$ and $(\text{MgC}_8\text{H}_{12})_n$, $(\text{MgC}_{12}\text{H}_{18})_n$ does not react with butadiene even when a five-fold excess of the latter is used. The low reactivity of (III) towards diene may be explained by peculiarities of the carbon skeleton structure of the OMC. Hydrolysis of $(\text{MgC}_{12}\text{H}_{18})_n$ really gives cyclic hydrocarbons the formation of which can be represented by a scheme including a step of intramolecular carbomagnesation [14,15] :

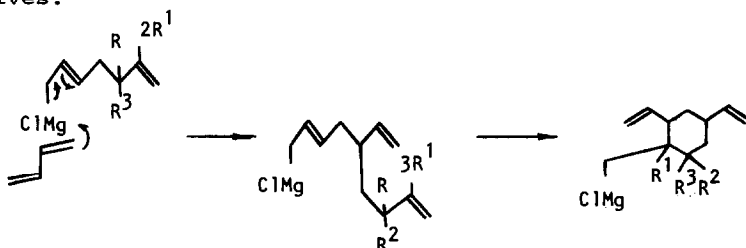


However, $(\text{MgC}_{12}\text{H}_{18})_n$ can react with an excess of butadiene at elevated temperature (120°C) to give an OMC represented by the formula $(\text{MgC}_{16}\text{H}_{24})_n$. This compound may undergo hydrolysis leading to a mixture of butadiene tetramers containing but two olefin bonds. Further, no reactive allylic Mg-C bonds are present in $(\text{MgC}_{16}\text{H}_{24})_n$, which shows no reactivity towards butadiene even at high temperature. This result supports the conclusions about the high reactivity of allylic Mg-C bonds towards olefins and 1,3-dienes, and the low reactivity of alkyl ones [15-17].

The possibility of 1,3-diene insertion into the metal-carbon bond suggests a convenient approach to unsaturated OMCs [15-17] :

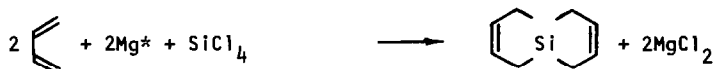


Alkyl derivatives of Mg can react with butadiene at $45\text{--}60^\circ\text{C}$ in ether during 48-96 hrs [18]. The Mg-addition is mainly directed at the C2-atom of the diene, the amount of C1-addition being minor. The unsaturated OMC formed can react further with 1,3-dienes and is followed by cyclization into cyclohexane derivatives.

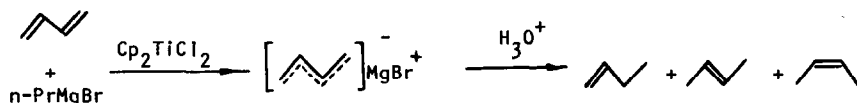


The introduction of highly active Mg in 1972 made it possible to avoid chemical activation of the Mg for 1,3-diene metalation. Highly active Mg is obtained by reduction of magnesium dihalide with alkaline metals in ethereal solvents [19-23].

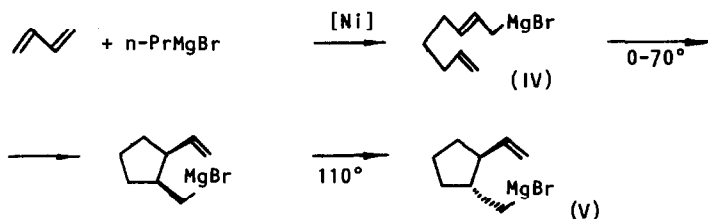
Even at ambient temperature, butadiene easily reacts with highly active Mg affording an OMC of the composition $(\text{MgC}_4\text{H}_6)_n$. On simple mixing the latter with SiCl_4 , 5-silaspiro-4,4-nona-2,7-diene is formed [24].



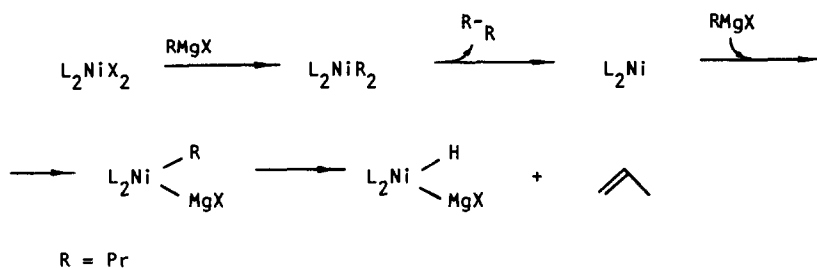
A promising synthesis of allylic OMC is represented by hydromagnesiation of conjugate dienes with propylmagnesium bromide in the presence of Cp_2TiCl_2 catalyst ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). This method was the consequence of extensive research in catalytic hydromagnesiation of olefins by Grignard reagents in the presence of TiCl_4 [25-27] and NiCl_2 [28,29]. With Cp_2TiCl_2 instead of TiCl_4 , butadiene and $n\text{-PrMgBr}$ react at ambient temperature to give an OMC hydrolyzable into an isomeric butene mixture [30].



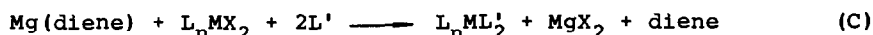
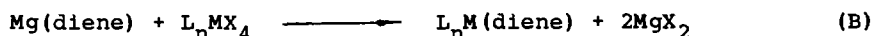
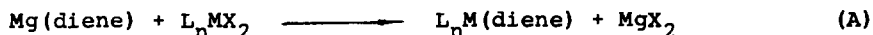
The OMC composition and yield have been found to be catalyst-dependent, the $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ complex leading exclusively to 2,7-octadienylmagnesium bromide (IV) [31]. The latter undergoes easy cyclization at room temperature into *cis*-(2-vinylcyclopentyl)methylenemagnesium bromide which on heating passes into the more stable *trans*-isomer (V).



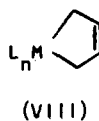
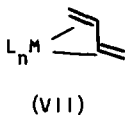
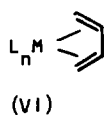
This reaction may be regarded as telomerization of butadiene with magnesium hydride which is formed from hydride complexes of nickel [32].



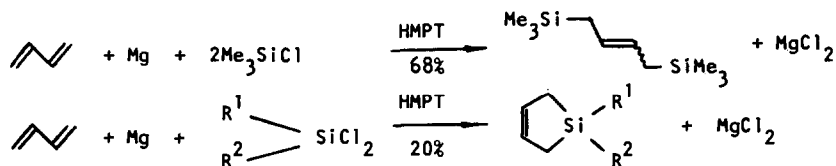
The successful synthesis of dienemagnesium reagents via direct 1,3-diene metallation promoted investigations into their use for preparing transition metal diene complexes [33]. The butadiene magnesium reagent, for example, can be used as a source of the butadiene dianion in non-transition metal complex synthesis. Ligand exchange takes place as follows [5] :



Reactions (A) and (B) make various novel diene complexes with transition metals (VI)-(VIII) easily available (Table 1) :

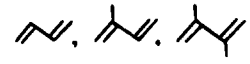
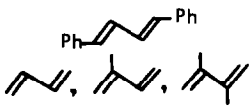











Butadienemagnesium reagents (BMR) provided original approaches to organosilicon and organophosphorus compounds. On mixing trimethylchlorosilane with butadiene and metallic Mg in HMPTA, for example, isomeric 1,4-bis(trimethylsilyl)-2-butenes are formed as a result of 1,4-addition. Similarly, dichlorosilanes lead to 1-sila-3-cyclopentenes [38-40].

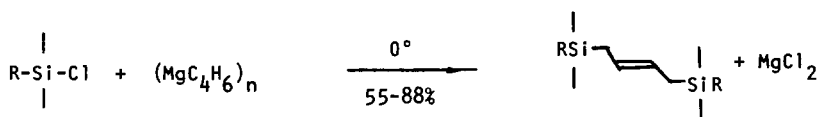


The reaction of butadiene, metallic Mg and dialkyldichlorosilane in HMPTA requires several days of heating to give only

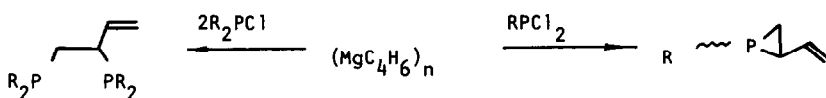
TABLE 1
DIENE COMPLEXES SYNTHESIZED BY ROUTES (B) OR (C)

No	Complex	Structure Type	Diene	Ref.
1	$\text{Cp}_2\text{Zr}(\text{diene})$	(VI)/(VII)		[34,35]
2	$\text{Cp}_2\text{Hf}(\text{diene})$	(VIII)		[34,35]
3	$(\text{COT})\text{Ti}(\text{diene})$	(VI)		[36]
4	$(\text{COT})\text{Zr}(\text{diene})$	(VI)		[36]
5	$(\text{COT})\text{Hf}(\text{diene})$	(VIII)		[36]
6	$(\text{R}_3\text{P})\text{Fe}(\text{diene})_2$	(VI)		[33]
7	$(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{Ti}(\text{diene})_2$	(VI)		[33]
8	$(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{Zr}(\text{diene})_2$	(VI)		[33]
9	$(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)\text{Hf}(\text{diene})_2$	(VI)/(VIII)		[33]
10	$\text{W}(\text{diene})_3$	(VI)		[33]
11	$(\text{allyl})(\text{diene})(\text{Cp})\text{Zr}$	(VI)		[37]

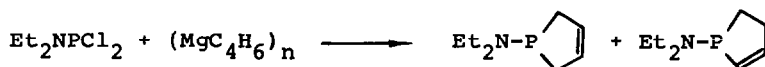
20% of silacyclopentene, but with a ready-made BMR this reaction may be conducted in toluene at 0-20°C over several hours [41]. When dimethyl- or diphenyl-silanes are used the yield of corresponding silacyclopentenes reaches 75-80%. Fully acceptable yields have been reported for poorly available 1,4-bis-(dimethylorganosilyl)-2-butenes from BMR [42]. The formation of the Z-isomer depends on the structure and nature of substituents in the starting chlorosilanes.



BMR and chlorophosphines react via 1,2-addition to give vinylphosphiranes [43] or Δ -vinyl-P,P'-ethylene-bis(diorganophosphines) [44] in a single step.



A mixture of 1-(diethylamino)-3-phospholene and 1-(diethylamino)-2-phospholene, 9:1, has been obtained from dichloroethylaminophosphine and BMR [43].

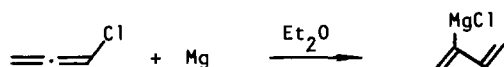


The example given above indicates the synthetic potential of BMRs, which are highly promising reagents for organic and organometallic chemistry and as polymerization co-catalysts.

2. Synthesis and chemistry of 2-(1,3-butadienyl)magnesium chloride

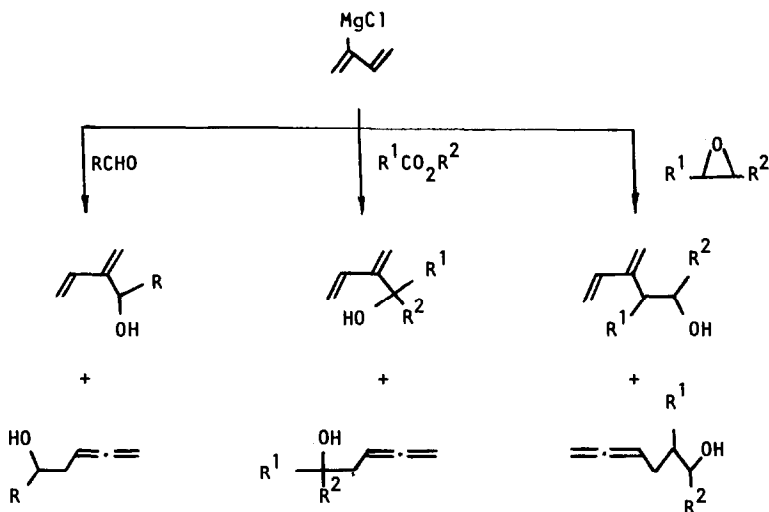
OMCs containing the 1,3-diene moiety have been successfully used in nucleophilic substitution reactions to obtain hydrocarbons with conjugated double bonds. The traditional appro-

ach to 2-(1,3-butadienyl)magnesium chloride (BMC), the simplest representative of the type, starting from chloroprene and metallic Mg is not effective. For the first time BMC has been prepared by a reaction between 4-chloro-1,2-butadiene and metallic Mg in diethyl ether in ca. 95% yield [45]. Similarly, 4-bromo-3-methyl-1,2-butadiene gives rise to 3-methyl-2-(1,3-butadienyl)-magnesium bromide [46].



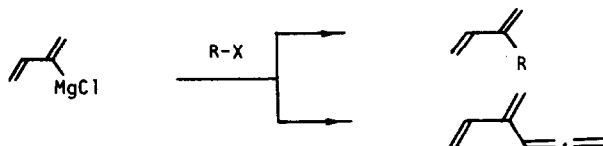
In 1970 a satisfactory route to BMC was proposed from chloroprene and metallic Mg in THF solution and in the presence of ZnCl_2 catalyst [47]. Later Zn, Cd, and Hg halides or alkyl halides were used to activate Mg in these reactions [48]. Good results are also achieved when highly active Mg is used [49].

Now that basic BMC is easily prepared, this reagent is widely used making diene alcohols by reactions with carbonyl compounds and epoxides [50-52]. Allenes accompany the diene alcohols in these reactions particularly in weakly-basic solvents and from sterically hindered aldehydes and ketones.

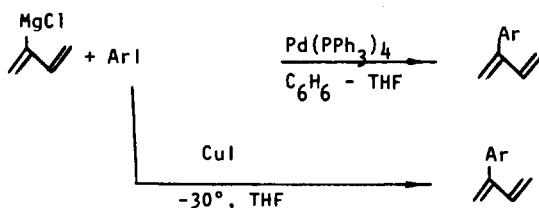


The reactions between BMC and allyl, benzyl, cinnamyl, 3-chlorocrotyl, γ,γ -dimethylallyl, and 1-ethoxyalkyl halides catalyzed by CuCl give diene compounds correspondingly

functionalized. In the case of propargyl bromide and ethyl furfuryl chloride, the the corresponding allenes have been obtained together with 2-substituted 1,3-dienes [45,53].

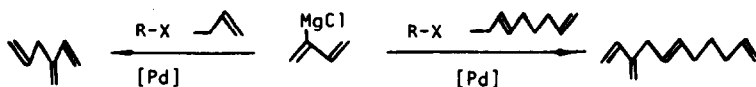


CuI And $\text{Pd}(\text{PPh}_3)_4$ are active catalysts for cross-coupling of BMC and alkyl or aryl iodides [54, 55]. This procedure affords satisfactory yields of 2-substituted 1,3-butadienes.



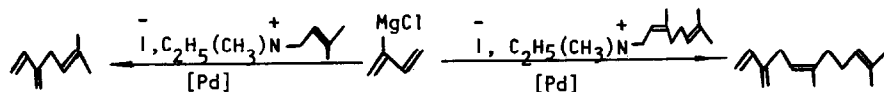
Further research has revealed the higher catalytic efficiency of Li_2CuCl_4 for the cross-coupling between 2-(1,3-butadienyl)magnesium chloride and halides [56]. Despite certain lengthening of the reaction duration, Li_2CuCl_4 has the advantages, compared to CuI, of milder reaction conditions, less catalyst consumption, and higher yield of the coupling products. The BMC coupling with variously structured halides has been accomplished in the presence of catalytic amounts of Li_2CuCl_4 .

Meanwhile, BMC reacts with allyl ethers, sulfones, and sulfides, only when phosphine Pd complexes are present, to form 3-methylene-1,5-hexadiene and 3-methylene-1,5,10-decatriene with high regioselectivity [57-59].

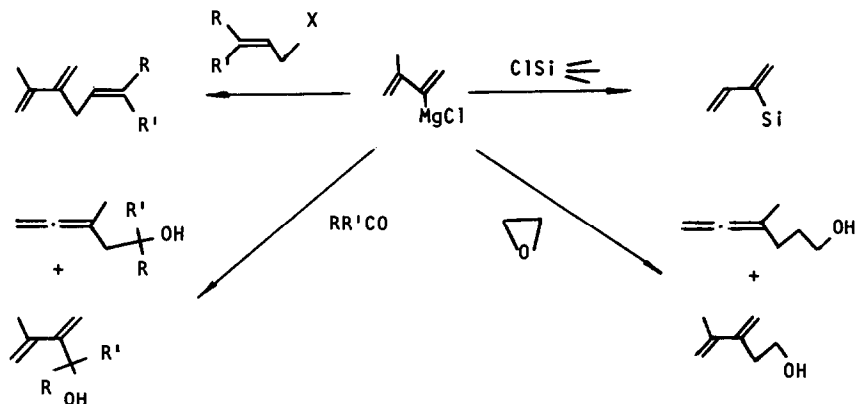


R = alkyl, Ph, Ac, X = O, S, SO_2

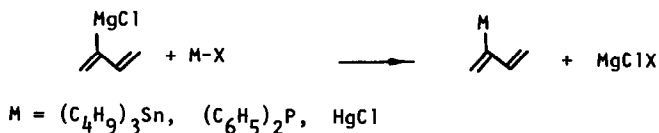
Under these conditions chosen 2-(1,3-butadienyl)magnesium chloride fails to give good yields of the cross-coupling with allyl amines. However, quaternization of the starting allyl amines affords much more reactive allylic electrophiles. Isoprenoid structure hydrocarbons, for example, have been synthesized by a reaction between quaternary ammonium salts of neryl and prenyl amines and BMC [60].



The BMC reaction with various electrophiles is attractive for obtaining unsaturated compounds containing the isoprenoid fragments [61].



The BMC cross-coupling with tin, phosphorus, or mercury halides provides a synthetic route to obtain organometallic compounds containing the 1,3-diene moiety, suitable on a preparative scale [45].

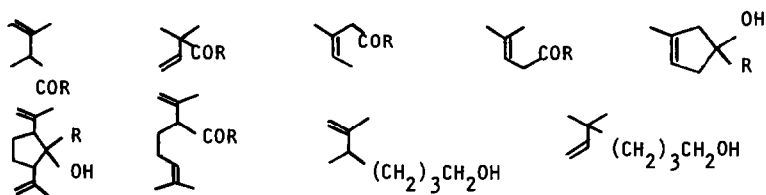


The ready availability and high reactivity of butadienemagnesium reagents make them promising reagents for organic synthesis.

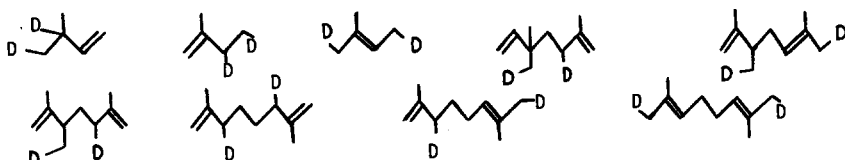
3. Metallation of isoprene, myrcene, ocymene, farnesene, and piperylene by metallic magnesium

The systematic synthetic studies of butadienemagnesium reagents stimulated advances in the direct metallation of various other 1,3-dienes by activated Mg. Alkyl halides [62], anthracene [63], $ZnCl_2$ in catalytic amounts [64], nickel complexes [65], and iron or copper halides [66] can be used to activate metallic Mg for these reactions. It has been assumed that the magnesium acts as a Lewis acid and transfers a pair of electrons to the LOMO of the 1,3-diene [67].

The metallation of isoprene by chemically activated Mg gives an isoprenylmagnesium complex. Hydrolysis of the latter affords a set of products which imply the formation of a poly-component mixture of Mg adducts with isoprene and its linear di- and trimers [68]. However, at a Mg:isoprene ratio of 1.5:1, an adduct of Mg with one isoprene molecule is predominantly formed. This OMC reacts with aliphatic aldehydes and ketones to form the corresponding tertiary alcohols. The carbonyl compounds add both to C-2 and C-3 atoms of isoprene, and also to the C-3 and C-4 atoms though to a less extent. On interaction of isoprenemagnesium reagents with aliphatic esters (ethyl formate or methyl isobutyrate), C-2 and C-3 adducts to isoprene are again the principal products; some 3-cyclopentene-1-ol derivatives have also been isolated along with certain addition products of THF solvent to the Mg-C bond. The reaction between isoprenemagnesium reagent (I) and ethyl formate, methylisobutyrate and THF gives the products:



The regio- and stereo-selectivity of 1,3-diene metallation depend on the type and structure of the activating component [69]. The deuteryolysis of isoprenemagnesium reagents obtained by the isoprene and Mg (2:1) interaction reveals unsaturated hydrocarbons containing two deuterium atoms strictly positioned in the carbon skeleton, if alkyl halides have been used as an activating component. The structure of hydrocarbons partially deuteriated and formed in the effect of D₂O on the (I) and (II) can be seen as follows.



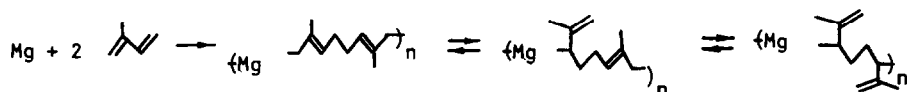
The reaction between isoprene and metallic Mg in the presence of an activating component gives a complex mixture of Mg/isoprene adducts, the composition of which depends on the starting Mg:isoprene ratio. The synthesis of individual isoprenemagnesium reagents in reference [70] is noteworthy (Table 2).

TABLE 2
CHARACTERISTICS OF ISOPRENEMAGNESIUM REAGENTS

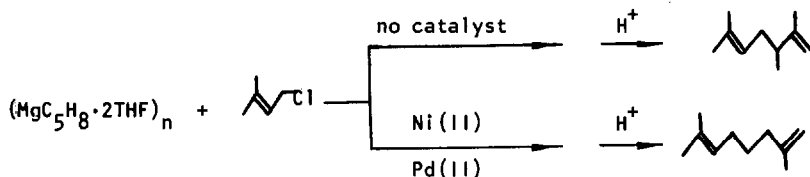
Organomagnesium compounds		Mg, % (calc.)	MW* (calc.)
(MgC ₅ H ₈ · 2THF) _n	(IX)	10.3 (10.3)	1195 ^a (236)
(MgC ₁₀ H ₁₆ · 2THF) _n	(X)	7.9 (8.0)	1205 ^b (304) 915 ^a
(MgC ₁₅ H ₂₄ · 2THF) _n	(XI)	6.5 (6.5)	562 ^a (372) 739 ^b
(MgC ₂₀ H ₃₂ · 2THF) _n	(XII)	5.4 (5.5)	450 ^a (440) 480 ^b

* Calculated for n=1; a) ebullioscopic determination in THF;
b) cryoscopic determination in benzene.

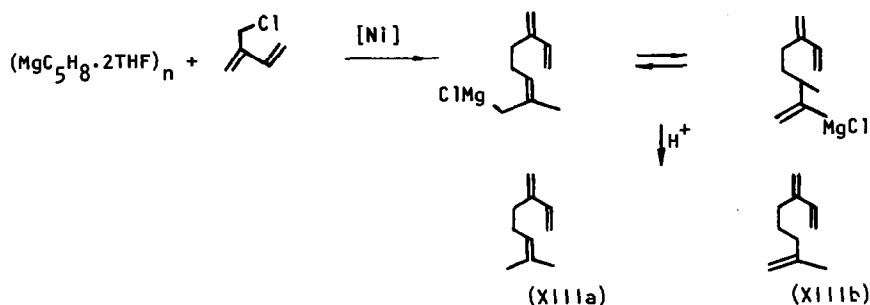
Table 2 shows that two molecules of THF coordinate to each Mg atom. The MW of OMC (IX) determined by ebullioscopy in THF corresponds to a pentamer and that of (X) to a trimer; the MW of (IX) is a mean between a dimer and a monomer while (XII) evidently has a monomeric structure. Hydrolysis of $(\text{MgC}_5\text{H}_8 \cdot 2\text{THF})_n$ gives 3-methyl-1-butene (6%), 2-methyl-1-butene (33%), and 2-methyl-2-butene (61%). $(\text{MgC}_{10}\text{H}_{16} \cdot 2\text{THF})_n$ Gives 2,7-dimethyl-1,7-octadiene (35%), 2,7-dimethyl-1,6-octadiene (46%), and 2,7-dimethyl-2,6-octadiene (19%), while hydrolysis of $(\text{MgC}_{15}\text{H}_{24} \cdot 2\text{THF})_n$ results in 2,9-dimethyl-5-isoprenyl-1,9-decadiene (85%) and 2,9-dimethyl-5-isopropenyl-1,8-decadiene (9%). These ratios of the hydrolysis products may imply that $(\text{MgC}_{10}\text{H}_{16} \cdot 2\text{THF})_n$ exists in the form of an equilibrated allylic isomer mixture.



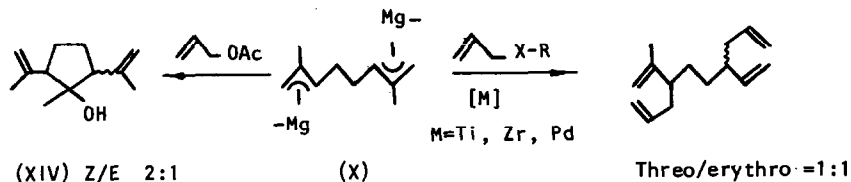
The preparation of OMCs via the direct metallation of isoprene by metallic Mg in the presence of activating components opens up new routes to important isoprenoid hydrocarbons. For example, 2,3,6-trimethyl-1,5-heptadiene (78%) and 2,7-dimethyl-1,6-octadiene (22%) have been obtained from the reaction between the isoprene magnesium reagent (IX) and 1-chloro-3-methyl-2-butene [71]. When this reaction is catalyzed by Ni(II) or Pd(II) complexes, 2,7-dimethyl-1,6-octadiene is the sole product [71].



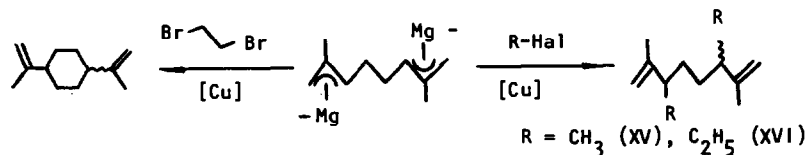
The reaction of OMC (IX) and 2-chloromethyl-1,3-butadiene in the presence of Ni(II) complexes represents a single and convenient synthetic path to myrcene (XIII) the yield reaching 75-78% and the selectivity amounting to 93-95% [71]. The ratio of α -/ β -myrcene (XIIIa/XIIIb) is 8:2.



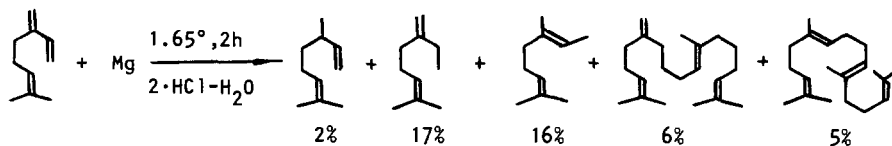
OMCs (IX) and (X) cross-couple with functionalized N-, O-, S-containing allylic electrophiles (diallyl ether, diallyl sulfide, phenyl allyl sulfone, quaternary ammonium salts of allyl amines) catalyzed by Ti, Zr, or Pd complexes with excellent regioselectivity [72-74]. Two allylic substituents add simultaneously to C-3 and C-6 atoms in OMC (X) whatever the ratio of reagents. Without catalyst, $(\text{MgC}_{16}\text{H}_{16} \cdot 2\text{THF})_n$ condenses with allyl acetate to give (XIV).



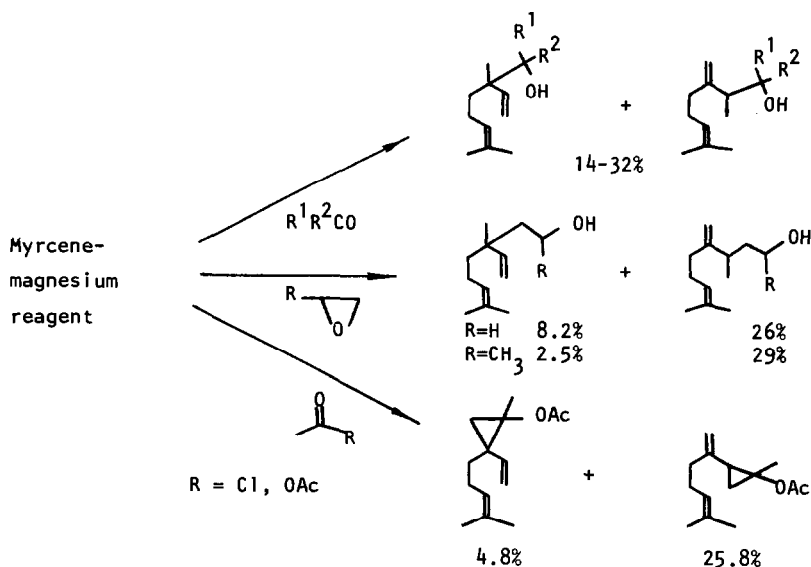
The OMC (X) couples with CH_3I or $\text{C}_2\text{H}_5\text{Br}$ in THF in a highly regioselective manner to give diastereomeric (1:1) 2,3,6,7-tetramethyl-3,6-diethyl-1,7-octadienes (XV, XVI, respectively), while the reaction with dibromoethane yields 49% of cis- and trans-1,4-diisopropenylcyclohexane in the ratio of 1:4 [75].



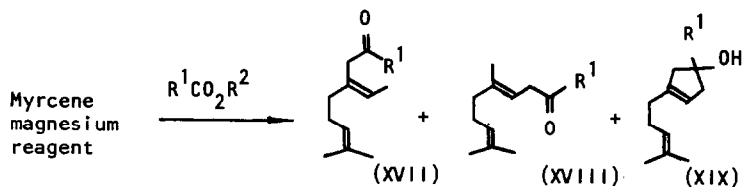
Like isoprene, myrcene reacts with metallic Mg. The reaction can be catalyzed by EtBr, transition metal halides (FeCl_3 , CuCl_2 , NiBr_2 , PdCl_2) [76, 77], or Lewis acids [$\text{BF}_3 \cdot \text{OEt}_2$, $\text{Al}(\text{OPr}^1)_3$, ZnCl_2] [78]. When transition metal halides are used a magnesium complex containing one myrcene molecule is accompanied by a dimeric myrcene magnesium reagent, as is proven by the hydrolysis products.



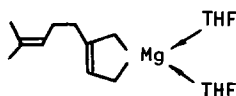
If the duration of the isoprene metallation is prolonged for 2-6 h, the yield of OMCs containing two or more myrcene molecules increased. Aldehydes, ketones, and acetyl chloride add to the C-2 and C-3 atoms of the 1,3-diene system in a myrcene magnesium reagent. The ratio of reaction products is determined by the structure of starting aldehyde. Acetaldehyde, for example, directs the addition mainly to the C-2 atom, while butyraldehyde attaches predominantly the C-3 atom of the diene.



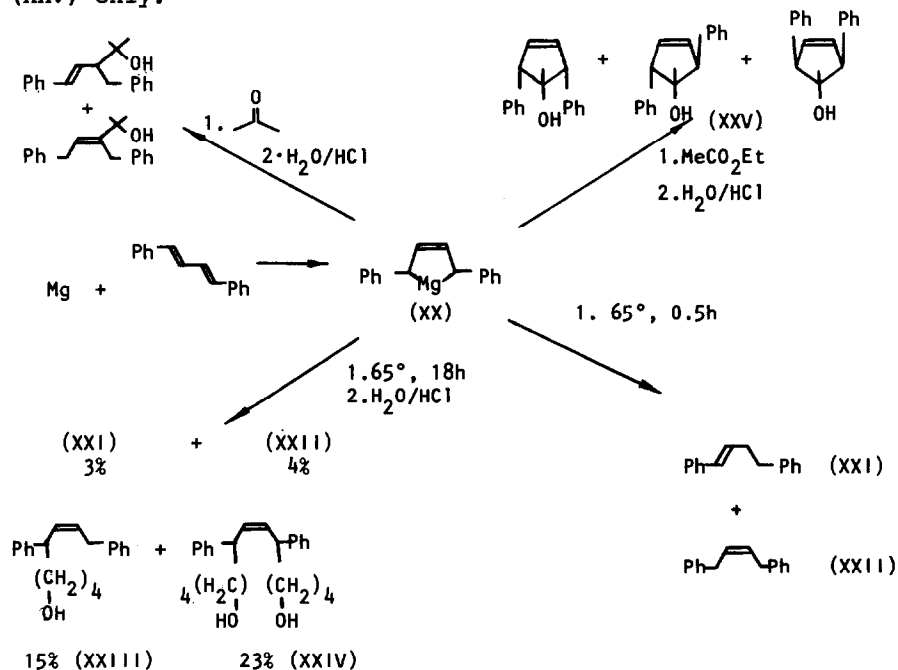
On the other hand, esters react with the myrcenemagnesium reagent via 1,4-addition followed by intramolecular cyclization to give mostly ketones (XVII) and (XVIII) in a ratio varying from 1:3 for ethyl acetate to 1:4 for ethyl butyrate. Above 65°C the formation of product (XIX) is observed.



These transformations suggest that the myrcenemagnesium reagent has the following scheme [76, 77]:

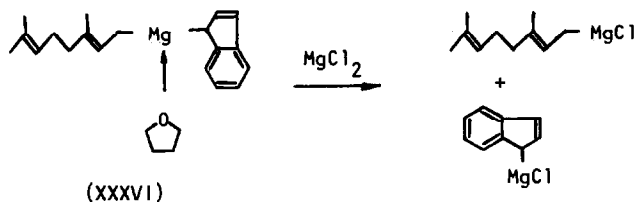


OMC (XX) Prepared from 1,4-diphenyl-1,3-butadiene and metallic Mg in the presence of catalytic amounts of $FeCl_3$ has a similar structure [76, 77]. Monomeric products, 1,4-diphenyl-1-butene (XXI) and 1,4-diphenyl-2-butene (XXII) are formed on the hydrolysis. A large reaction time (18 h, 65°C) results in the formation of dienemagnesium reagent (XX) and THF interaction products (XXIII) and (XXIV) along with (XXI) and (XXII). The reaction of OMC (XX) and ethyl acetate gives 1,4-adducts (XXV) only.



Unfortunately, all the conclusions concerning a cyclic structure of OMCs are based exclusively on chemical transformations. Noone has yet isolated a five-membering OMC and reliably proven their formation. The same is for aluminium cyclopentanes which are supposed to form on hydroalumination of 1,3-dienes [79, 80] or 1,4-pentadienes [81]: the metallocycles have not been isolated and identified in a pure state. The authors of the present paper have been the first to obtain 3- and 3,4-substituted aluminium cyclopentanes and to propose a highly selective synthesis of a novel class of organoaluminium compounds based on a reaction of trialkylalanes and Δ -olefins in the presence of zirconium complexes [82-84].

The first paper [78] to review a general method of converting a dienemagnesium complex into a higher allylicmagnesium halide discussed the reaction of myrcene magnesium complex with indene to give OMC (XXXVI) which is hydrolyzed into equimolar amounts of indene and 2,6-dimethyl-2,6-octadiene. The interaction between (XXXVI) and $MgCl_2$ leads to 3,7-dimethyl-2,6-octadienyl-magnesium chloride and indenyl-magnesium chloride.

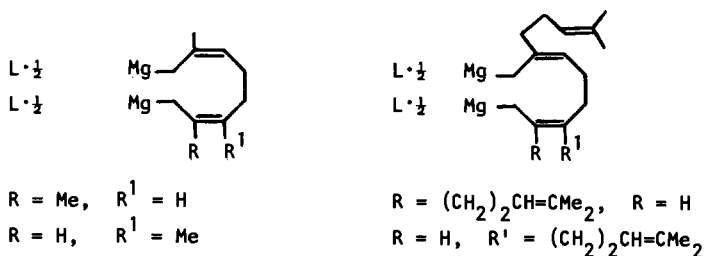


The oxidation of isoprenyl magnesium chloride by O_2 represents a simple one-step synthesis of practically important alcohols such as geraniol, linalool, and farnesol [85-87].

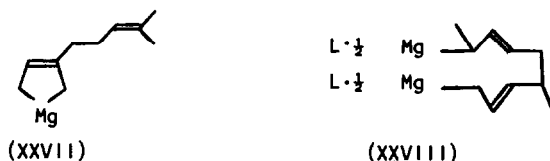
The preparation of dienemagnesium reagents using chemically activated Mg is applicable to a limited series of 1,3-dienes including butadiene, isoprene, 2,3-dimethylbutadiene, myrcene, and 1,4-diphenylbutadiene. Regretfully, this method cannot involve 1,4-disubstituted 1,3-dienes (except for trans,trans-1,4-diphenyl-1,3-butadiene).

This limitation may be overcome if highly active (finely dispersed) Mg (HAM) is used as the metallating reagent, prepared by the reduction of Mg dihalides with alkaline metals [19-

23]. The reaction of HAM and isoprene, myrcene, ocymene, or piperylene in the presence of $B(OBu)_3$ followed by the treatment of the reaction mixture in the alkaline H_2O_2 may serve an example [88, 89]. Under these conditions, all the 1,3-dienes except ocymene are converted into dimeric alcohols. The reaction between isoprene or myrcene and HAM proceeds to give dimeric isoprene or myrcene magnesium complexes of the "tail-to-tail" and "head-to-tail" types.



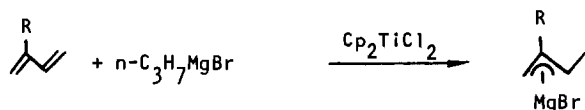
Myrcene metallation by HAM gives mainly the dimeric complex. In the case of metallic Mg activated by transition metal halides, the monomeric myrcene magnesium reagent is obtained along with a minor amount of the dimeric one [76, 77]. Ocymene reacts with HAM to give a mixture of nerol and linalool (approx. 1:1) via an intermediate monomeric ocymenemagnesium complex (XXVII) [89]. The reaction of piperylene may involve the formation of a dimeric piperylene magnesium "head-to-tail" complex (XXVIII).



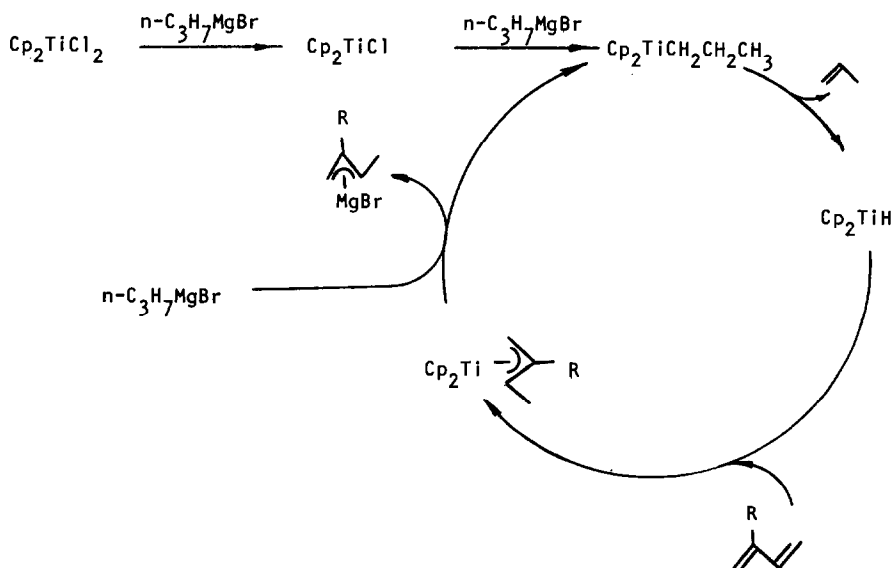
The corresponding dienemagnesium reagents have been prepared by metallation of 1,4-diphenyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene with HAM [90,91].

A simple and effective path to allylic OMCs is offered by 1,3-diene hydromagnesiation by alkyl Grignard reagents containing an active hydrogen atom β -positioned to the Mg atom,

in the presence of Cp_2TiCl_2 catalyst [4, 30]. Development of this method has been stimulated by the studies into α -olefin hydromagnesiation by $n\text{-C}_3\text{H}_7\text{MgBr}$ in the presence of TiCl_4 [26, 92, 93]. It is impossible to accomplish the 1,3-diene hydromagnesiation by the same Grignard reagent in the presence of TiCl_4 . However, by substituting Cp_2TiCl_2 for TiCl_4 , 2-substituted 1,3-dienes can be quantitatively hydromagnesiated by $n\text{-C}_3\text{H}_7\text{MgBr}$ into allylic OMCs. Under the same conditions, 1-substituted 1,3-dienes are completely inactive.

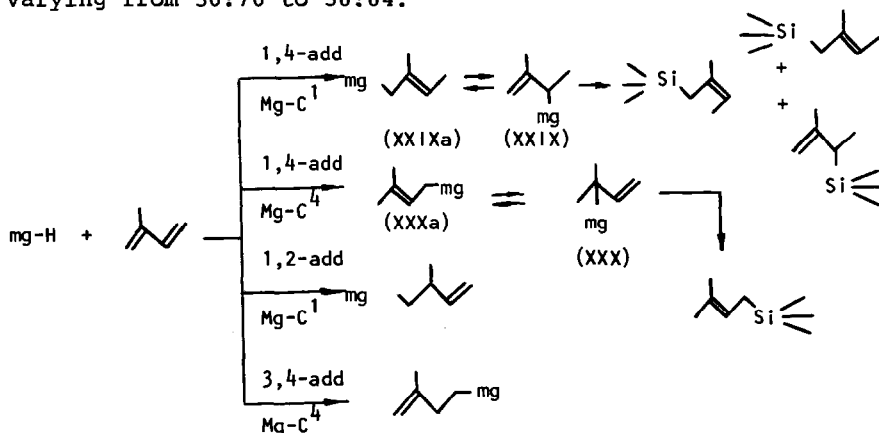


In accordance with a well-known reaction of isoprene hydro-titanation assisted by Cp_2TiH , a following mechanism has been proposed for the regioselective 1,3-diene hydromagnesiation. This mechanism involves Ti hydrides formed due to the interaction between Cp_2TiCl_2 and $n\text{-C}_3\text{H}_7\text{MgBr}$ as the key hydrometallating reagents [94].



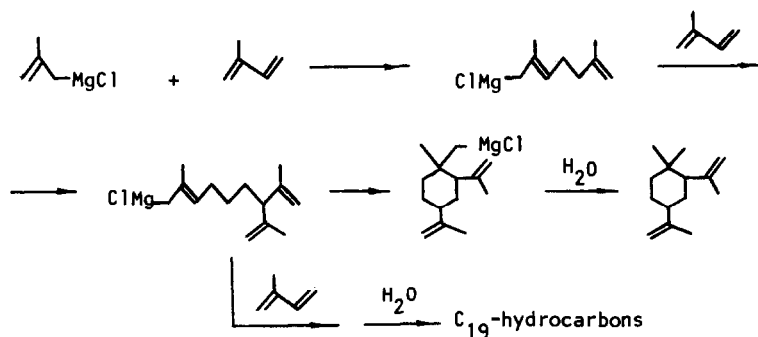
Direct hydromagnesiation of 1,3-dienes by Mg hydrides prepared by metallic Mg reduction by Bogdanovitch's method [95,96] is quite an effective way to synthesize allylic OMCs. Cp_2TiCl_2 and TiCl_4 complexes are the most active catalysts in this reaction, allowing 75% conversion of the starting diene, while Cp_2ZrCl_2 , ZrCl_4 , HfCl_4 , or CrCl_3 as catalysts never lead to the conversion surpassing 30%.

The structure and composition of hydromagnesiation products have been established by hydrolysis and silylation of the corresponding OMCs. Thus on isoprene hydromagnesiation using mg-H ($\text{mg} = \frac{1}{2}\text{Mg}$) 1,2-, 2,3-, 3,4-, and 1,4-adducts of Mg hydrides can be formed. It has been shown that on hydromagnesiation in the presence of Cp_2ZrCl_2 only 1,4-addition of Mg hydride to the 1,3-diene takes place giving (XXIX) and (XXX) mixture, in a ratio varying from 30:70 to 36:64.

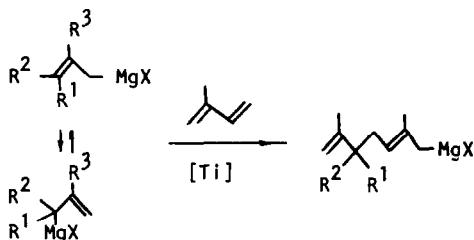


Publications [97-108] concerning olefin and acetylene hydromagnesiation are not discussed in the present paper.

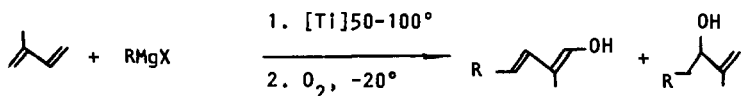
Another promising trend in the "non-Grignard" OMC synthesis is presented by the carbomagnesiation of 1,3-dienes paving the way to good yields of higher OMCs from the simplest allylic organomagnesium reagents and conjugated dienes. The carbomagnesiation of isoprene by methallylmagnesium chloride affords linear and cyclic OMCs as shown [15,18,109] :



In the presence of Cp_2TiCl_2 or $\text{TiCl}_2(\text{OEt})_2$ in catalytic amounts, this reaction involves regiospecific inclusion of an isoprene molecule into the metal-carbon bond of the starting allylic OMC to form linear unsaturated OMCs [110].

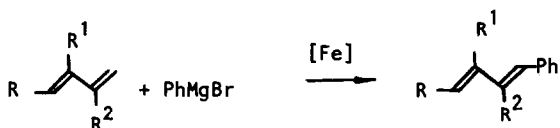


It is noteworthy that metal complex catalysts make it possible to use the allylic OMCs alongside with other OMCs in carbomagnesiation [111-113]. Mixed Ti chlorides [Cp_2TiCl_2 , $\text{TiCl}_2(\text{OEt})_2$, Ph_2TiCl_2] turned out to be the most effective catalysts for the carbomagnesiation of isoprene by Grignard reagents. The oxidation of OMCs formed, by oxygen of air, gives allylic alcohols.



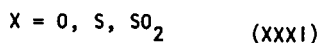
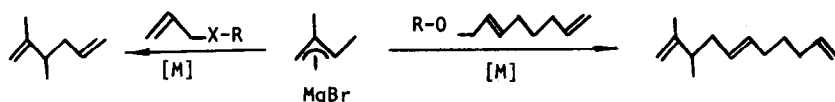
R = alkyl, aryl; [Ti] = Ph_2TiCl_2

The carbomagnesiation of 1,3-dienes by arylmagnesium halides can be realized in the presence of iron and nickel complexes [114, 115].

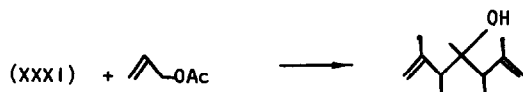


Now that preparative scale synthetic routes to allylic OMCs have been realized, the problem of the usage of "non-Grignard" reagents for organic synthesis is receiving great attention. We believe that work on the reaction between allylic OMCs and carbonyl compounds [116, 117] or allylic electrophiles [75] catalyzed by transition metal complexes is of special value.

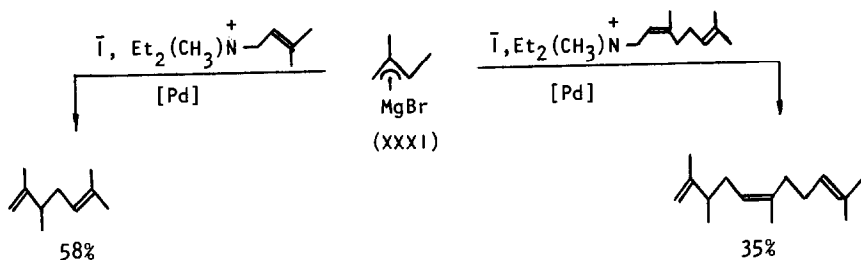
For example, the cross-coupling of OMC (XXXI) and diallyl or 2,7-octadienyl ethers, allyl sulfone, or diallyl sulfide in the presence of homogeneous metal complex catalyst leads to 2,3-dimethyl-1,5-hexadiene and 2,3-dimethyl-1,5E,10-undecatriene, the regioselectivity being high [75].



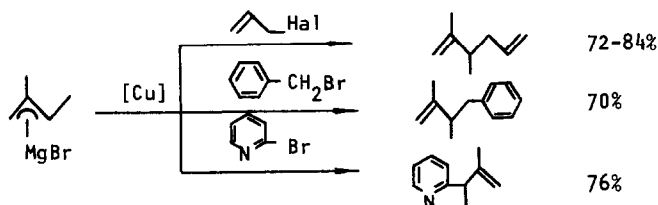
The reaction between OMC (XXXI) and allyl acetate gives a diastereomeric tertiary alcohol of threo- and erythroconfiguration (ca. ~ 1:1).



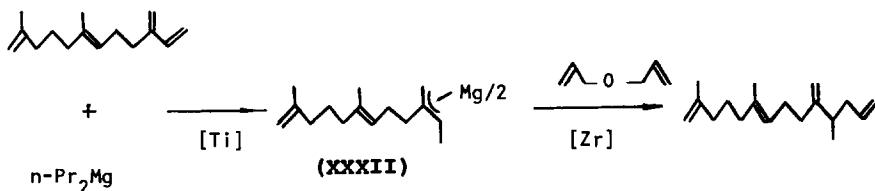
The application of organomagnesium reagents obtained by isoprene hydromagnesiation with $n\text{-C}_3\text{H}_7\text{MgBr}$ or $(n\text{-C}_3\text{H}_7)_2\text{Mg}$ [30, 118] provides a convenient approach to hydrocarbons comprising isoprenoid fragments. The synthesis of 2,3,6-trimethyl-1,5-hexadiene and 2,3,6,10-tetramethyl-1,5Z,9-undecatriene by cross-coupling of OMC (XXXI) and quaternized prenyl or neryl amines may serve as an example [57-59].



In the presence of monovalent Cu salts, OMC (XXXI) shows high regioselectivity in the reaction with alkyl or aryl halides, the addition of the alkyl or aryl substituents occurring exclusively at the C-3 atom of isoprene molecule [60].

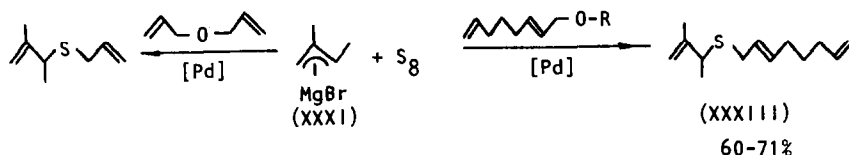


The high regioselectivity of the reaction is also observed in cross-coupling of OMC (XXXII) (obtained by farnesene hydro-magnesiation with $n\text{-Pr}_2\text{Mg}$ in the presence of Cp_2TiCl_2 catalyst), with diallyl ether, which yields ca. 35% of 2,6,11-trimethyl-10-nethylene-1,6E,13-tetradecadiene. Bulky alkyl substituents and additional double bonds in the hydrocarbon part of the OMC tend to lower target product yield, but they hardly alter the direction or selectivity of the reaction [75].

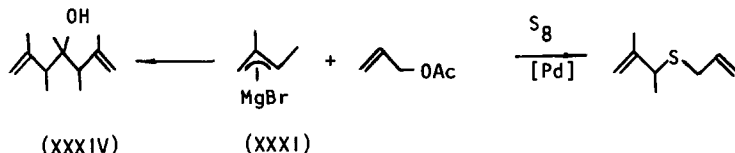


The authors have been the first to observe the reaction of OMC (XXXI) and allyl ethers in the presence of Pd phosphine complexes with simultaneous insertion of sulfur into the metal-

carbon bond [119].

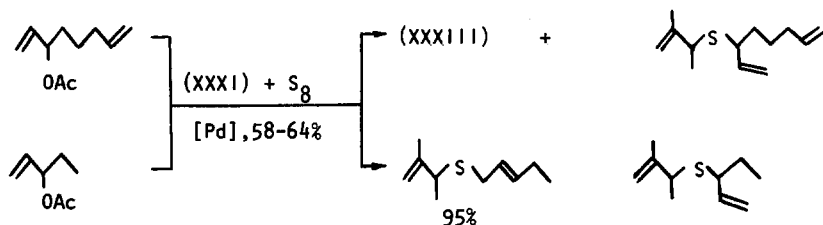


Thus, OMC (XXXI) reacts with allyl acetate in the presence of a stoichiometric amount of powdered cyclooctasulfane (S_8) in Et_2O in the presence of $\text{Pd}(\text{acac})_2\text{-2PPh}_3$ to give 4-thia-2,3-dimethyl-1,6-heptadiene in ca. 65% yield. Only 2,3,4,5,6-pentamethyl-1,6-heptadiene-4-ol (of threo/erythro configuration) is formed from the OMC and allyl acetate in the absence of sulfur [120, 121].

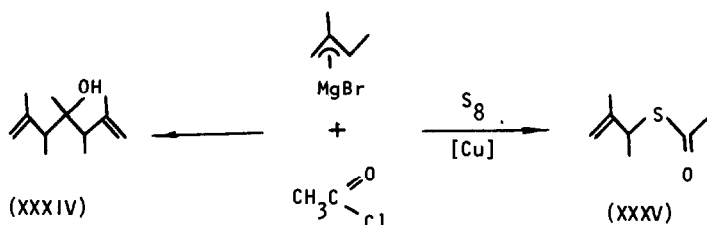


The reaction is highly stereoselective and affords unsaturated sulfides constructed by the addition of an allylic fragment, generating from allyl acetate, and a sulfur atom, to the C-3 atom of the organomagnesium reagent. On oxidation of OMCs (XXXI) by oxygen followed by acylation of products formed with acetic anhydride, 1-acetoxy-2-methyl-2-butene and 3-acetoxy-2-methyl-1-butene are obtained. The latter are produced by oxygen insertion into the magnesium-carbon bond products, either at C-1 or C-3 atom of the starting OMC [118, 122].

Linear sulfides are mainly formed from 3-acetoxy-1,7-octadiene or 3-acetoxy-1-pentene and (XXXI) in the presence of sulfur. The amount of branched regioisomer usually does not exceed 5% [120].



OMC (XXXI) And acetyl chloride under mild conditions react with simultaneous insertion of sulfur (S_8) into metal-carbon bond with catalysis by Cu complexes and yield ca. 80% of thioether (XXXI). In the absence of S_8 , alcohol (XXXIV) is formed.



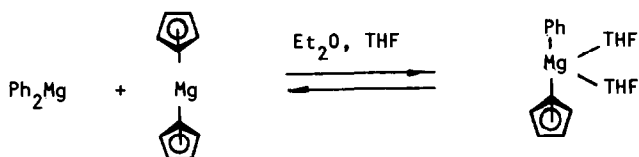
If the cyclooctasulfane is replaced by CS_2 , these reactions provide a single step synthetic approach to dithiocarboxylic esters in reasonable yields [60]. The CS_2 insertion into the Mg-C bond and the subsequent reaction between the OMC and allylic electrophiles proceeds in a regiospecific manner at the C-3 atom of the starting OMC (XXXI).

ORGANOMAGNESIUM COMPOUNDS BASED ON CYCLIC 1,3-DIENES AND POLYENES

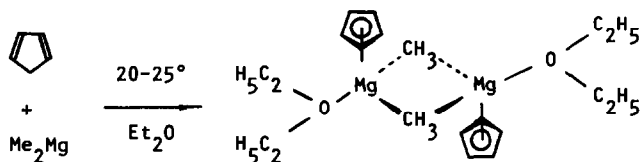
1. Magnesium cyclopentadienyl derivatives

Cyclopentadienylmagnesium derivatives were first obtained in 1914-1915 by the reaction of cyclopentadiene (CPD) with Grignard reagents [3]. It was established later [123-126] that the thermal decomposition of $CpMgBr$ under high vacuum afforded dicyclopentadienyl magnesium (Cp_2Mg) in 40% yield. The same yield of Cp_2Mg is observed from the reaction of metallic Mg with CPD at 500-600°C [126,127]. If the latter reaction is catalyzed by Cp_2TiCl_2 , it proceeds under much milder conditions

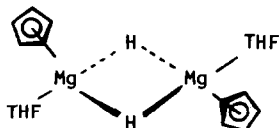
[128]. The authors assume that the titanium-magnesium complex $\text{Cp}_2\text{TiMg}_2\text{Cl}_2 \cdot 2\text{THF}$, which has been isolated and identified spectrally is the active intermediate in the formation of Cp_2Mg . Titanium compounds such as Cp_2TiCl_2 , TiCl_4 , $\text{Ti}(\text{OBU})_4$, and CpTiCl_3 have been found to be the most effective catalysts for the reaction of CPD and metallic Mg [129]. Cp_2Mg is prepared from CPD and metallic Mg in the presence, for example, of Cp_2TiCl_2 (250°C, 48 h) in nearly quantitative yield. An exchange reaction between Cp_2Mg and R_2Mg may lead to mixed cyclopentadienylalkyl (aryl) magnesium compounds CpMgR ; for example Ph_2Mg and Cp_2Mg afford PhMgCp [130].



On metallation of CPD with Me_2Mg in ether, methylcyclopentadienylmagnesium etherate is formed as a binuclear complex [131].

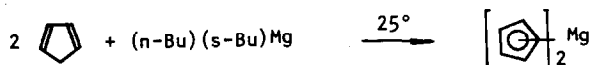


Cyclopentadienylmagnesium hydride obtained either via CPD metallation by MgH_2 [132] or by interaction between Cp_2Mg and MgH_2 in THF [133] has a similar structure.

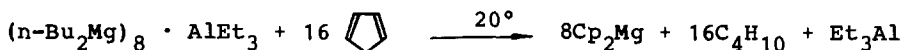


The binuclear hydride complex smoothly reacts with CPD, HCl , KOH , or HNR_2 leading to Cp_2Mg , CpMgCl , CpMgOR , or CpMgNR_2 , respectively.

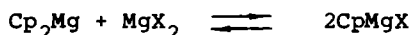
CPD metallation by n-butyl(sec-butyl)magnesium in hexane or other hydrocarbon solvent is accomplished more easily than by Grignard reagents in etheral solvents [134].



CPD Metallation can be carried out by magnesium-aluminium complexes $[n\text{-Bu}_2\text{Mg}]_n \cdot \text{AlEt}_3$ ($n=1-20$) [135]. The yield of dicyclopentadienylmagnesium is ca. $\sim 85\%$.



Studies of the properties, the structure, and the nature of the metal-carbon bond in CpMgX and Cp_2Mg are important. In THF cyclopentadienylmagnesium halides represent equilibrium Schlenk mixtures where CpMgX prevails [136].



Crystalline Cp_2Mg is built as a pentagonal antiprism where the Mg atom is enclosed between two parallel cyclopentadienyl rings [137]. X-Ray measurements have shown that all the carbon atoms in Cp_2Mg are equally distanced from the Mg atom by 2.304 Å [138]. The coplanar carbon atoms in the cyclopentadienyl rings are equally spaced at 1.390 Å, the distance between cyclopentadienyl rings being 3.960 Å. Electron diffraction shows the preference for the prismatic structure in gaseous Cp_2Mg [139-141].

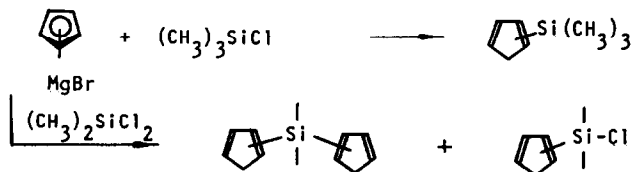
A series of Cp_2Mg properties such as ease of interaction with FeCl_2 , the susceptibility to aqueous hydrolysis, the conductivity of solutions in liquid ammonia [123], and the dipole moment increase when the benzene solvent is replaced by 1,4-dioxane [142, 143], indicate a considerable degree of Mg-Cp bond polarization. Mass-spectra also support the concept of ionic bond in Cp_2Mg [144, 145]. The coincidence of absorption bands in UV, IR, and PMR spectra of CpMgCl , CpMgBr , and Cp_2Mg recor-

ded in THF solutions with those of CpLi and CpNa also support the existence of the ionic bond in Mg cyclopentadienyl derivatives [146]. The use of ^{25}Mg NMR spectroscopy affords further information concerning the character of the Mg-Cp bond [147,148], and the authors believe that the predominantly ionic nature of this bond is common for complexes of Mg-Cp and Lewis bases. Measurements of the electrical conductivity by Cp_2Mg solutions in diethyl ether, THF or DME [149, 150] lead to the same conclusions.

The good solubility of Cp_2Mg in non-polar solvents [145] and its high volatility in vacuo [130] suggest that the covalent bond co-exists in compounds with the ionic one of this type. The IR and PMR spectra of Cp_2Mg have been analyzed by analogy with the spectra of Cp_2Fe and Cp_2Ni [151]. This has been justified by the presence of a covalent Mg-Cp bond. Besides, the energy of the Mg-Cp bond (54.5 kcal/mole) in Cp_2Mg is comparable to that of Ni-Cp in Cp_2Ni (53 kcal/mole), which leads to a conclusion that these molecules are similar not only in structure but also in the nature of the metal-Cp bond [152].

From this review of published data we conclude that both ionic and covalent bonds are present in Cp_2Mg .

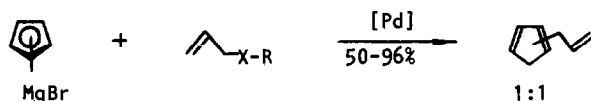
Cyclopentadienyl Mg derivatives turn out to be very convenient starting reagents in the synthesis of substituted cyclopentadienes by exchange reaction with organic halides. For example, the interaction between CpMgBr and alkyl- or aryl-halosilanes leads to CPD silyl derivatives $\text{Cp}_m\text{SiX}_n\text{R}_{4-m-n}$ where $X = \text{Br}$, $R = \text{Me}$, Et , or Ph [153,154].



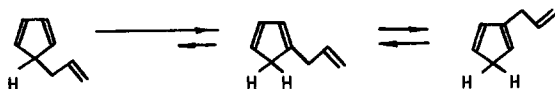
In these reaction, the yield of coupled product never surpasses 40% [155].

Recently, the authors of the present paper elaborated an effective method to synthesize an equilibrated mixture of 1- and 2-allylcyclopentadienes via a CpMgBr reaction with allyl

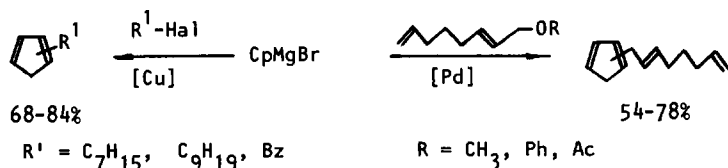
ethers, allyl sulfones, allyl sulfides, or quaternary ammonium salts of allyl amines in the presence of Pd phosphine complexes [156-159].



It is to be noted that cyclopentadienyl Mg derivatives exist as thermodynamically equilibrated mixtures of isomers which have differently positioned internal double bonds. This follows from the analysis of CpMgBr deuteration products [160]. Under cross-coupling conditions [156] 5-allylcyclopentadiene with a mobile proton at C-5 is formed initially [161] due presumably to the equality of the carbon atoms in the cyclopentadienyl anion. The following migration of the mobile proton to a neighbouring carbon atom results in the redistribution of the cyclopentadienyl ring double bonds to give 1-allylcyclopentadiene. The isomerization of the latter into 2-allylcyclopentadiene is favoured by a subsequent shift of hydride [161-164]. According to [165-167], the amount of the 5-substituted isomer in the isomeric mixture does not surpass 5%.

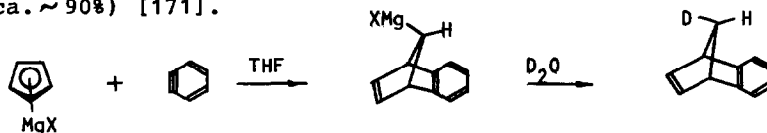


Cross-coupling of CpMgBr and 2,7-octadienyl ethers, or alkyl halides in the presence of complex palladium, or copper containing catalysts has given equilibrium mixtures of 1- and 2-substituted cyclopentadienes in high yields [156].

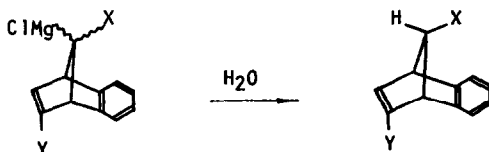


According to [168], Cp₂Mg prepared by direct CPD metallation [169] by highly active Mg [19-22] readily enters into catalyzed cross-coupling with allyl ethers, and allyl and propargyl halides.

However, CpMgBr addition to dehydrobenzene proceeds according to quite another mechanism [170]. Here the cyclopentadienyl anion plays the role of a diene, and anti-9-benzonorbornadienylmagnesium bromide is formed in a highly selective mode (ca. ~ 90%) [171].



Cycloaddition of dehydrobenzene to substituted cyclopentadienylmagnesium halides leads to 2-substituted benzenorbornadienes [172], which hydrolyze to give products which are C-9 substituted and in the syn-configuration. This proves the high degree of stereoselectivity in protolysis of this type of OMC.

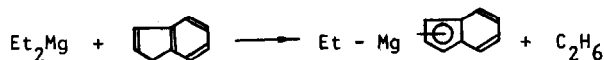


a) X = CH₃, Y = H; b) X = CH₃, Y = CH₃; c) X = Si(CH₃)₃, Y = H

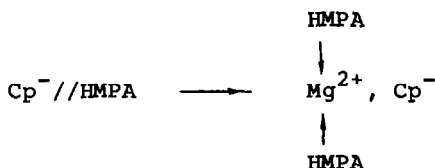
2. Preparation and transformations of OMCs based on indene and fluorene

The principle of substitution of the mobile hydrogen atom in cyclopentadiene for an organometallic moiety provides the basis for the synthesis of indenyl- and fluorenyl-magnesium halides [3]. The reactivity of indene towards Grignard reagents may be arranged as follows: $i\text{-BuMgX} > \text{MeMgX} > n\text{-BuMgX} > \text{sec-BuMgX} > n\text{-PrMgX} > \text{EtMgX} > i\text{-PrMgX}$.

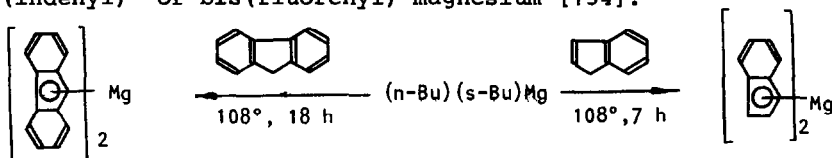
Fluorenylmagnesium bromide has been obtained similarly to indenylmagnesium bromide in xylene at 135-140°C the reaction lasting for 12 h. Unlike CPD, indene and fluorene form mixed OMCs on interaction with dialkyl Mg derivatives [173-175].



Metallation of fluorene with Et_2Mg proceeds more effectively in the presence of HMPA (hexamethylphosphoramide) [174, 175] and gives ethylfluorenylmagnesium in high yield. The PMR spectra points to a predominantly ionic nature of the Mg-C bond in HMPA solution. The fact that the chemical shift value for the fluorenyl ring protons becomes constant at a HMPA/Mg ratio > 3 indicates the formation of an ionic compound where 3 HMPA molecules are coordinated at the Mg atom.

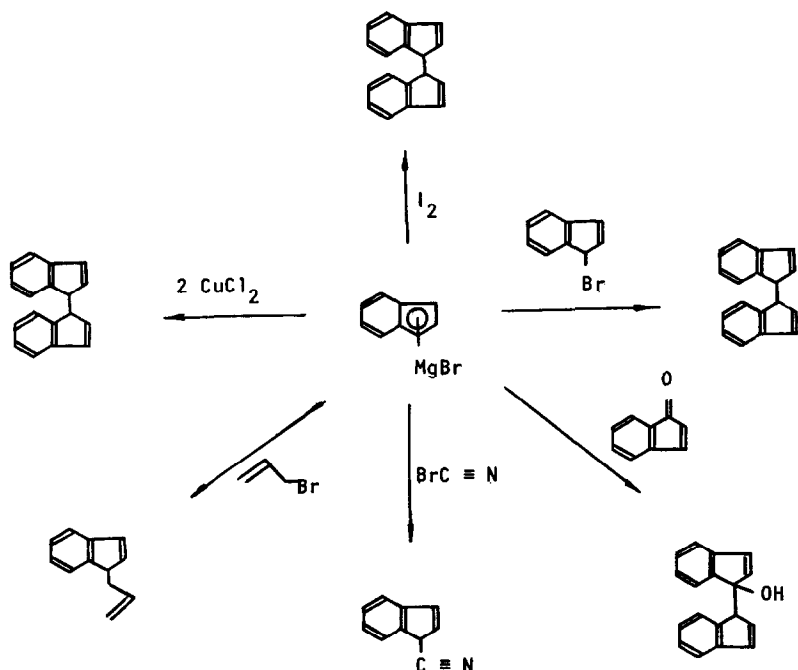


The reaction of n-butyl(sec-butyl)magnesium with indene and fluorene is an exclusively effective method for preparing bis(indenyl)- or bis(fluorenyl)-magnesium [134].

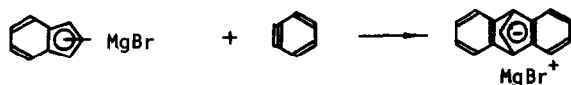


Studies of the crystal structure of bis(indenyl)magnesium show that $(\text{C}_9\text{H}_7)_2\text{Mg}$ in the solid state contains Mg atoms in two different surroundings each Mg atom being coordinated by three indenyl groups which suggests bis(indenyl)magnesium exists in the form of a vast polymer via bridged and terminal indenyl groups [176].

Owing to its high reactivity, bis(indenyl)magnesium finds application as an intermediate in the preparation of lanthanoid- and actinoid-indenyl complexes. For example, $(\text{C}_9\text{H}_7)_2\text{Sm}$, $\text{U}(\text{C}_9\text{H}_7)_3\text{Cl}$, and $\text{Th}(\text{C}_9\text{H}_7)_3$ have been synthesized from the reaction of $(\text{C}_9\text{H}_7)_2\text{Mg}$ in toluene and the appropriate metal chloride [177, 178]. Certain non-catalyzed transformations of indenylmagnesium bromide are reviewed in papers [179-181].

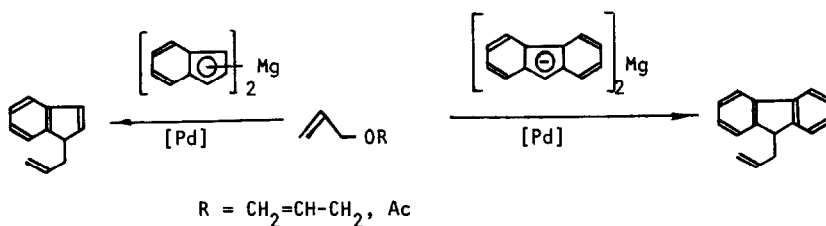


Like Cp_2Mg , indenylmagnesium bromide gives a cycloadduct with dehydrobenzene [182].



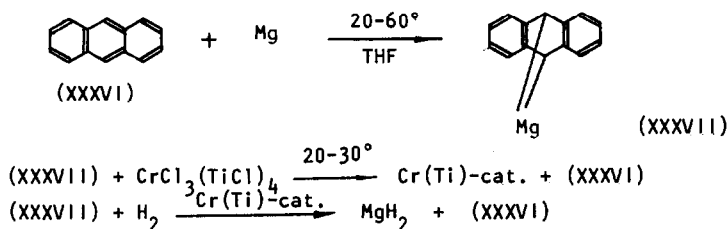
Authors [169] have found that bis(indenyl)- and bis(fluorenyl)-magnesium can be obtained in rather high yields by metallation of indene and fluorene with HAM. The reduction in the number of ^{13}C NMR signals in bis(indenyl)magnesium five and the doubling of their intensities reveals a high level of symmetry in the molecule. The symmetry plane passes through the C-2 carbon atom and the middle of C-5-C-6 bond. The high reactivity of aromatic OMCs has been demonstrated by an example of cross-coupling between fluorenylmagnesium bromide and allyl

bromide, affording 9-allylfluorene [183]. The reaction of bis-(indenyl) or bis(fluorenyl)magnesium and allyl esters, catalyzed by Pd phosphine complexes, gives 1-allylindene and 9-allylfluorene, respectively [169].



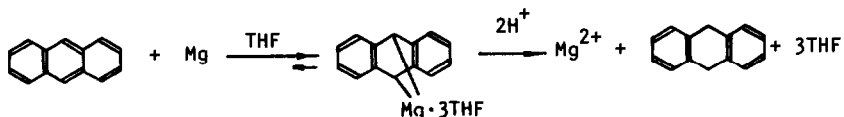
3. Synthesis and chemistry of anthracenemagnesium and cyclooctatetraenemagnesium

Anthracenemagnesium is a key intermediate in the catalytic magnesiation/hydrogenation cycle [95] and in HAM preparation [184, 185].

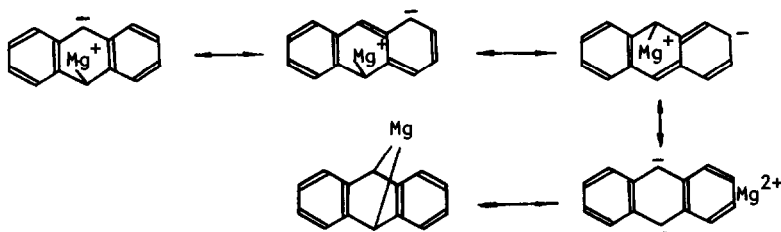


The reaction of metallic Mg and anthracene in THF leading to anthracenemagnesium was first reported in 1967 [10]. Later anthracene metallation with Mg was accomplished in HMPA and liquid ammonia [186, 187]. The complex C₁₄H₁₀Mg · 3THF has been obtained by transmetalation of anthracenesodium with MgBr₂, as well as by the interaction between anthracene and metallic Mg in the presence of a catalytic amount of MgBr₂ in THF [188]. Protolysis of anthracenemagnesium produces the Mg²⁺ ion, 9,10-dihydroanthracene and THF, in the molar ratio

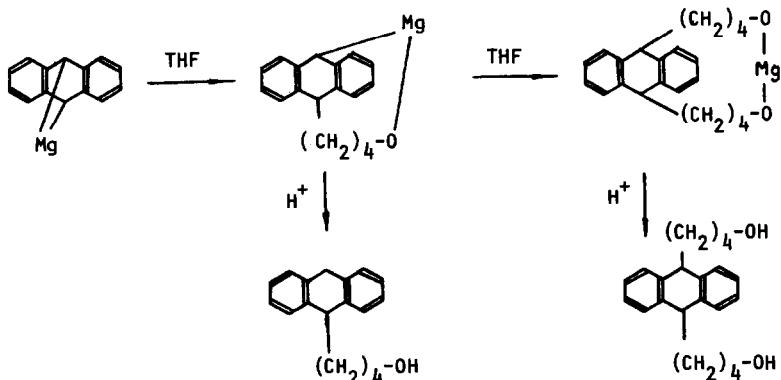
1:1:3 [189], which indicates coordination of 3THF molecules at a Mg atom.



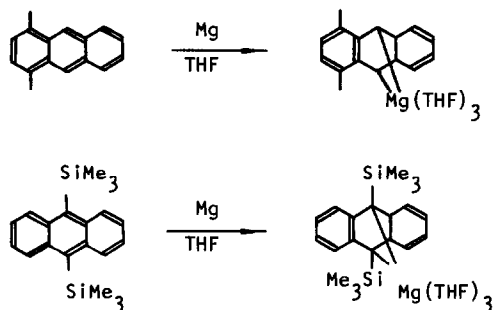
Based on the ¹H and ¹³C NMR spectra of those OMCs, a suggestion has been made [189] that anthracenemagnesium represents either an ionic couple with potent interaction between the Mg atom and the C-9 and C-10 carbon atoms in anthracene, or a covalent compound with large polar contribution of the structures shown below :



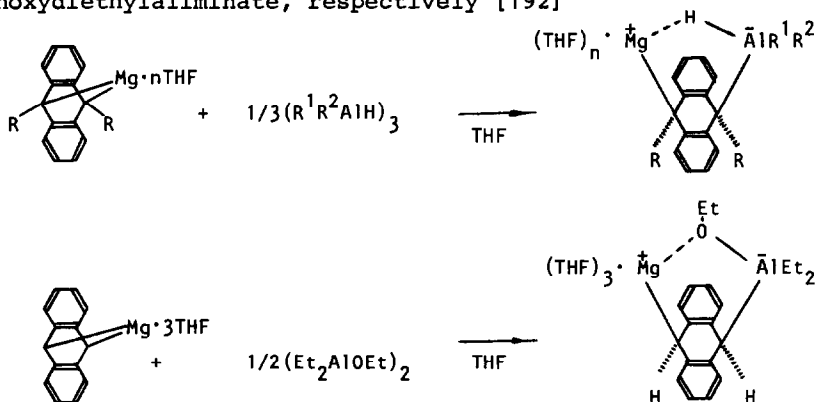
The interaction between anthracene and Mg in THF is reversible, the equilibrium depending on the reaction temperature. The formation of C₁₄H₁₀Mg · 3THF is favoured at 25°C, but at 60°C the equilibrium is shifted to the left. On increasing the metallation temperature or the reaction duration, the formation of byproducts is observed due to the insertion of THF molecules into the C-Mg bond.



Besides anthracenemagnesium, 1,4-dimethylantracenenemagnesium [190] and 9,10-bis(trimethylsilyl)anthracenenemagnesium [191] have been obtained and their crystal structures have been determined.

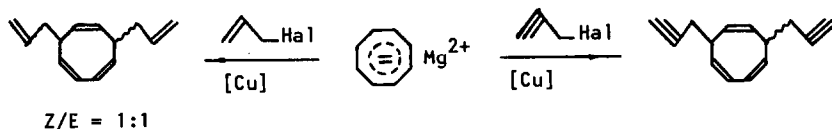


On interaction with dialkylaluminium hydrides, anthracenemagnesium reagents give magnesium (9,10-dihydro-9,10-anthracene)dialkylhydridoaluminates, while reaction with aluminium hydride or ethoxydiethylaluminium produces hydridoaluminate or ethoxydiethylaliminate, respectively [192]

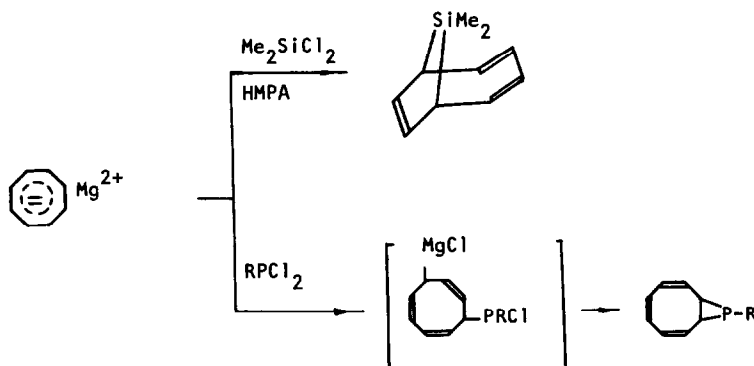


Similarly to anthracenemagnesium, cyclooctatetraenemagnesium has been obtained [193] by reaction between cyclooctatetraene and metallic Mg in the presence of catalytic amounts of MgBr_2 . Alternatively, cyclooctatetraenemagnesium is synthesized by transmetalation of potassium or sodium cyclooctatetraene derivatives with MgHal_2 [194, 195], or by direct metallation of cyclooctatetraene by HAM [169].

The deuteryolysis of cyclooctatetraenemagnesium by D_2O affords a mixture of 5,8-dideutero-1,3,6-cyclooctatriene and 7,8-dideutero-1,3,5-cyclooctatriene. However, high yields of stereoisomeric 5,8-diallyl- and 5,8-dipropargyl-1,3,6-cyclooctatrienes have been obtained with high regioselectivity on cross-coupling of cyclooctatetraenemagnesium with allyl or propargyl halides [168, 169].



A number of attractive syntheses of organosilicon and organophosphorus compounds has been accomplished using cyclooctatetraenemagnesium. For example, by reaction of cyclooctatetraenemagnesium and dimethyldichlorosilane in HMPA, 9,9-dimethyl-9-silabicyclo[4.2.1]-2,4,7-nonatriene has been prepared in a 20% yield [196]. The same reaction with dichlorophosphanes affords phosphabicyclononatrienes in reasonable yields [197].



CONCLUSION

More than 20 years have passed since the first publication on "non-Grignard" OMC preparation by direct metallation of conjugated dienes with metallic Mg. Since then, a large number of publications have appeared on the development of the method

with conjugated cyclic and linear dienes, on new types of OMC synthesis, and on the latter's reactivity in various organic and organometallic reactions.

The use of metal complex catalysts in the OMC chemistry make it possible to elaborate a number of novel approaches to catalytic hydro- and carbo-magnesiumation of olefins, dienes, and acetylenes using the simplest alkyl or hydride Mg derivatives. This considerably enhances the scope of preparative syntheses of "non-Grignard" OMCs, which can be of ever increasing interest from the side of organic and organometallic chemists.

Due to these investigations and essentially to the research work done by the authors of this paper, the methods of highly stereoselective acetylenes-to-Z-olefins hydromagnesiumation, of regioselective catalytic olefin carbomagnesiumation and cyclometallation as well as of regio- and stereoselective direct functionalization of unsaturated compounds via organomagnesium intermediates have come into routine synthetic practice. We have no doubt that "non-Grignard" OMCs obtained by non-traditional procedures will find broad application in the total synthesis of natural products and synthetic analogues thereof and of new catalysts and organometallic compounds of transition and non-transition metals as well as in modern chemical technology design.

In fact, a basis has been laid for a successful development of this novel branch in OMC chemistry which are "non-Grignard" OMCs in synthesis and catalysis.

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