Invited Lecture

Organomagnesium chemistry: nearly hundred years but still fascinating *

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Abstract

Victor Grignard discovered his famous reaction, the synthesis of organomagnesium halides or Grignard reagents from organic halides and magnesium, in 1900. Up to now, this reaction has proved tremendously useful in organic and organometallic synthesis, and many of the secrets of its formation, structure, and reactivity have been unravelled. Nevertheless, organomagnesium chemistry is still vital and full of surprises. This will be illustrated with a selection of recent developments, admittedly with a strong bias for results from the author's laboratory. The topics presented concern the intermediacy of carbanions during the conversion of organic halides to Grignard reagents, the induction of high coordination numbers of magnesium by (intramolecular) coordination of crown and polyethers which leads to special structures such as organometallic rotaxanes and catenanes as well as to increased reactivity, and finally small α,ω-di-Grignard reagents with one, two or three carbon atoms between the two magnesiums, which are of interest both for their unique structures and for their application in the synthesis of metallacycles and metal-carbene complexes.

Key words: Magnesium; Grignard reagents

1. Introduction

In 1900, Victor Grignard made the famous discovery [1] that organomagnesium halides, generally known as Grignard reagents, can be easily obtained by the reaction of readily available organic halides with metallic magnesium in a basic solvent, normally an ether (Scheme 1).

These Grignard reagents have proved to be extremely powerful synthetic tools because of their easy accessibility and high reactivity; they allow the nucleophilic introduction of organic groups as carbanion equivalents and for that reason, they belong to the standard repertoires of both organic and organometallic synthesis.

Not surprisingly, a considerable effort has gone into the investigation of the formation, the structure, the reactivity, and the applications of organomagnesium compounds [2], and as a consequence, Grignard reagents are so familiar to the preparative chemist that many would consider them a rather mature class of

Victor Grignard (*1900*)

R-X + Mg $\xrightarrow[\text{(ethers)}]{}$ R-Mg-X

Scheme 1.

compounds from which few new developments, let alone surprises, might be expected. In this overview, an attempt will be made to show that this is far from true. On the contrary, results presented from different areas of organomagnesium chemistry will be presented to illustrate that interesting and often unexpected developments do occur to this very day. For the sake of brevity, the examples are mainly chosen from work performed in the author's laboratory, and the numerous important contributions by others can only be mentioned incidentally. In a (chrono)logical sequence, the formation reaction of Grignard reagents, their structure and coordination, the influence of both on the reactivity, and finally some new developments in a particular area, the divalent Grignard reagents and their application for the synthesis of metallacycles, will be discussed.

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* Dedicated to Professor Dr. E.O. Fischer on the occasion of his 75th birthday.

2. The formation of the Grignard reagent

The reaction depicted in Scheme 1 is marvellous for many reasons. One is that, although a heterogeneous reaction at a metal surface, it proceeds surprisingly smoothly and in practically quantitative yield, if the proper conditions are fulfilled. For instance, the structure of the organic halide is of great importance; most synthetic chemists have the troublesome experience that with certain halides, the reaction may be quite reluctant to start, and many tricks such as activation, entrainment *etc.* have been devised. However, with simple, well behaved aliphatic or aromatic halides, in particular the bromides, and with adequate cautions and conditions, the reaction starts like a purple flash and gives practically quantitative yields. In our work, where we are often interested in the structure and physical properties of these air- and moisture-sensitive reagents, we mostly prepare them from highly purified reagents — including magnesium which has been freed from transition metal impurities by triple sublimation and is thus obtained as large, bright, shiny crystals which to our eyes are much more beautiful than silver or gold! Furthermore, we handle them in perfectly dried and evacuated, completely glass sealed apparatus without ground joints or stopcocks [3]. Under such conditions, the reactions start without the notorious induction period and go to completion to furnish a solution of the Grignard reagent which, especially in the case of an aliphatic compound, is clear as water.

Another marvellous aspect of the Grignard formation reaction is the simplicity of the reaction shown in Scheme 1: taken at face value, it would suggest the simple insertion of a metal atom, apparently jumping out of the metal surface into a carbon–halogen bond. Of course, everyone will immediately realize that such simplicity is deceptive because direct insertion is quite improbable, and indeed, the actual mechanism is highly complex — so much so that in retrospect, it may seem incredible that, in spite of it, the reaction proceeds with such a high rate and specificity.

Leaving aside possible side steps and side reactions, the essential steps of the mechanism of the formation reaction are shown in Scheme 2. There is good evidence and general agreement on the following aspects. By a single electron transfer (SET) from magnesium to the organic halide (step 1), the radical anion $RX^{\cdot-}$ is formed. It is either shortlived or even, in the aliphatic series, a transition state leading to the cleavage products organic radical $R^{\cdot}$ and halide anion X^- (step 2). The latter adds to the Mg^+, which at this stage still is part of the metal surface, to form MgX. Finally, $R^{\cdot}$ and MgX combine to form the Grignard reagent RMgX (step 3); it is especially at this stage of the reaction,
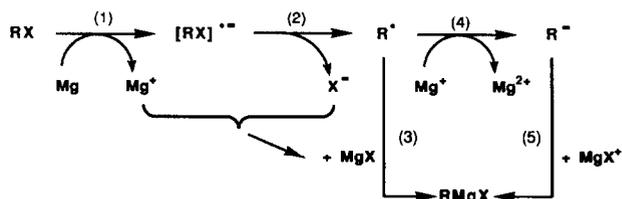
Scheme 2.

that the ether solvent plays an important role by dissolving MgX from the metal surface.

Two aspects of this scheme are still under discussion. In the first place, there is some controversy concerning the state of the radicals $R^{\cdot}$ formed in step 2, in particular whether they are absorbed to the metal surface [4] or freely diffusing [5]; this difficult matter will not be addressed in the present review. The second aspect concerns the conceivable intermediacy of carbanions R^-. As indicated in Scheme 2, this might occur by a second SET from Mg(X) to $R^{\cdot}$ under formation of R^- and MgX^+ (step 4), followed by their combination to give RMgX (step 5). A fundamental difficulty when trying to investigate these intermediates lies in the circumstance that step 2 is the slow, rate determining one, and all the processes afterwards are extremely rapid and difficult to analyse. Nevertheless, by good fortune, we have recently obtained two strong, independent pieces of evidence for the occurrence of such carbanion intermediates R^-.

The first piece of evidence was encountered when we tried to prepare the crown ether Grignard reagents **2** and **4** in the usual fashion in THF from the corresponding bromides **1** and **3**, respectively [6]. Although the starting materials were consumed quantitatively, the yield of the Grignard reagents was lower than the close to 100% we were used to, namely 80% (**1**) and a disappointing 16% (**4**) (Scheme 3).

A closer investigation, which will be elaborated here only for the somewhat simpler case of **1**, revealed the formation of the side products **7** and **8** (10% each) (Scheme 4). They are remarkable because **7** is a product of ether cleavage, but contains the (organomagnesium) functionality at the expected position 2 of the aromatic ring, in contrast to **8** which *does* retain the intact crown ether ring but lacks a functionality at this position. Labelling experiments showed the hydrogen at position 2 of **8** to be derived from the starting material and not from the solvent THF. As **1**, once formed, remained stable in solution for months, it was obvious that a very reactive, short-lived species formed during the reaction of **1** with magnesium must be responsible for the highly specific cleavage reaction,

and the 1:1 ratio of **7** and **8** suggested that their genesis was correlated.

A priori, both the radical **5** and the carbanion **6** (*cf.* R· and R⁻ in Scheme 2) might be candidates for this intermediate species. However, **5** could be excluded for several reasons. For instance, this radical should be active not only in the case of crown ether Grignard reagents such as **2**, but also in all the many other Grignard reactions; however, this is in general not the case. More in particular, it was shown that cleavage did not even occur in the case of the unsubstituted crown ether **8**: on addition of bromobenzene and magnesium (so that a new Grignard reagent is being formed), **8** was inert, whereas **2** was cleaved to give **7** under identical treatment; thus it appears that the Grignard functionality present in **2** is necessary for the cleavage reaction to occur. This would be difficult to reconcile with radical attack, and the same holds for the high regiospecificity of cleavage between O(2) and O(3); of a radical, one would expect attack at other hydrogens of the crown ether bridge of **2**, too, with a conceivable preference for the benzylic H‴.

In contrast, all these observations can be satisfactorily explained with the more or less "naked", highly reactive, carbanion **6** as the active principle. Being a strong base, it may perform an E2 elimination by attack on H′, with O(3) serving as the leaving group. Why are H′ and O(3) ideal candidates for this type of reaction? In general, E2 eliminations of ethers do not readily occur as the β-proton is not very acidic and the alkoxide oxygen is not a first class leaving group. However, through the activating influence of coordination to magnesium, H′ will be acidified via O(2) while O(3) will become a better leaving group. This rationalization derives support from the X-ray structure of **2** [6] which
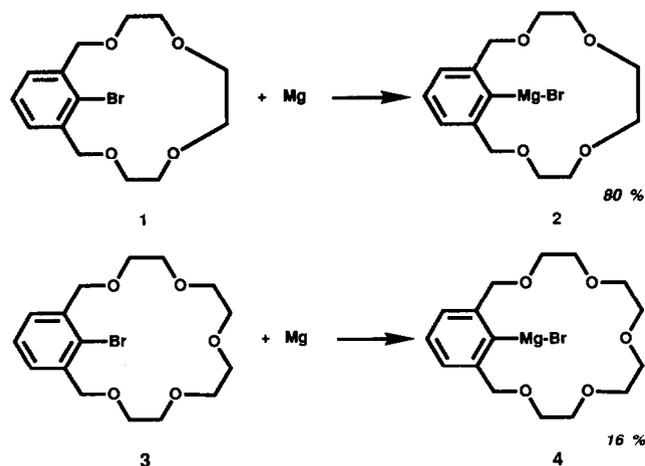
revealed that magnesium is more strongly coordinated to O(2) and O(3) than to O(1) and O(4); moreover, it showed the orientation of H′ and O(3) to be antiperiplanar as required for a smooth course of the E2 elimination process.

Completely independent, and not less surprising, evidence for a carbanionic intermediate came from an attempt to prepare the Grignard reagent **10** from the corresponding halide **9** [7a]. Analysis of the reaction mixture showed that the consumption of **9** was complete and the formation of Grignard reagent quantitative; but only 15% of the Grignard reagent obtained turned out to be **10**; a quench reaction with chlorotrimethylgermane gave, in addition to the expected product **14** (15%), **15** (derived from **11**, 29%), together with the 1:1 combination of **16** (28%) and **17** (derived from **12**, 28%).

Similarly, the reaction of **18** yielded, after quenching with chlorotrimethylgermane, only 21% of the expected product **19** (Scheme 6); in addition, two pairs of products were obtained in approximately equal amounts: the combination of **20** (9%) and tetramethylstannane (3%) on the one hand and that of **21** (70%, the main product) and methylmagnesium bromide (60–65%) on the other [7b]. It is important to point out that in both cases, like in the reactions of the crown ethers, the composition of the reaction mixtures remained unchanged for weeks after the starting bromide had been completely consumed, which means that, as expected, the Grignard reagent as such does not subsequently give rise to unusual secondary products.

We feel that once again reactive carbanionic intermediates are responsible for the fascinating migrations and transformations of the trimethyltin group. In the present context, we cannot discuss all the aspects, but will instead concentrate on two examples to illustrate the proposed reaction mechanism. According to Scheme 2, a double SET from magnesium to **9** will furnish the carbanion **22** (Scheme 7). It may either combine with MgBr⁺ to form **10**, or, favoured by entropy, immediately attack the trimethylstannyl group and close the ring to form the stannate species **23**. While the four-membered rings of stannacyclobutanes are rather strained and unstable [8], that of **23** is more comfortable spanning an apical and an equatorial position in a trigonal bipyramid. Attack by MgBr⁺ on **23** will furnish either **10**, or, more probably, cleave the benzylic bond to give **11** with rearranged functionalities. In a similar fashion, intermolecular exchange of tin can be envisaged to occur via attack of **22** on the tin atom of another molecule of **9** (not shown).

In an analogous manner, the formation of the major product **21** from **18** and magnesium is explained by the intramolecular reaction of the carbanion **24** to furnish
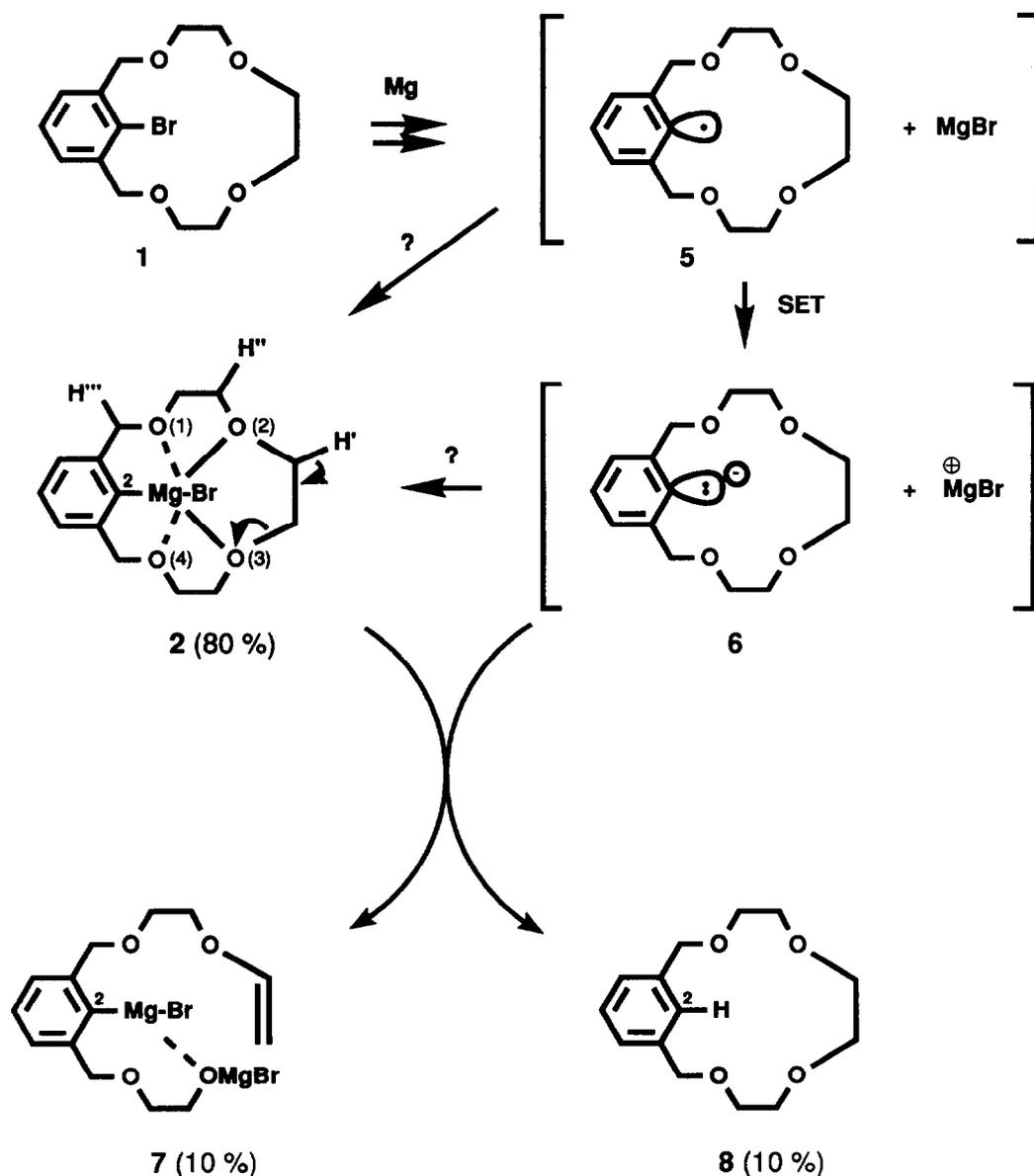

Scheme 3.

the stannate 25 (Scheme 8). In contrast to 23, the five-membered ring of 25 is probably diequatorial and stable enough to avoid ring opening; instead, methylmagnesium bromide is extruded and was identified as such in the reaction mixture by quantitative ¹H NMR spectroscopy. Again, intermolecular ate complex formation between 24 and 18 explains the formation of 20 and tetramethylstannane; the observed ratio (9 : 3) deviated from 1 : 1 (as required by stoichiometry) probably for technical reasons such as the volatility of tetramethylstannane.

It is thus evident that besides the long established

radicals, highly reactive carbanions must also be taken into account as intermediates in the formation reaction of the Grignard reagent. It remains to be established under which circumstances and to what extent they play a prominent role.

3. Structure, coordination and reactivity of organomagnesium reagents

In Grignard reagents RMgX or diorganylmagnesiums R_2Mg, magnesium is divalent and formally dicoordinate. Actually, only very few compounds with this

Scheme 4.

Scheme 5.

9 ?? Mg

10 ClGeMe₃ → 14 (15 %)

11 ClGeMe₃ → 15 (29 %)

16 (ClGeMe₃) → 16 (28 %)

12 ClGeMe₃ → 17 (28 %)
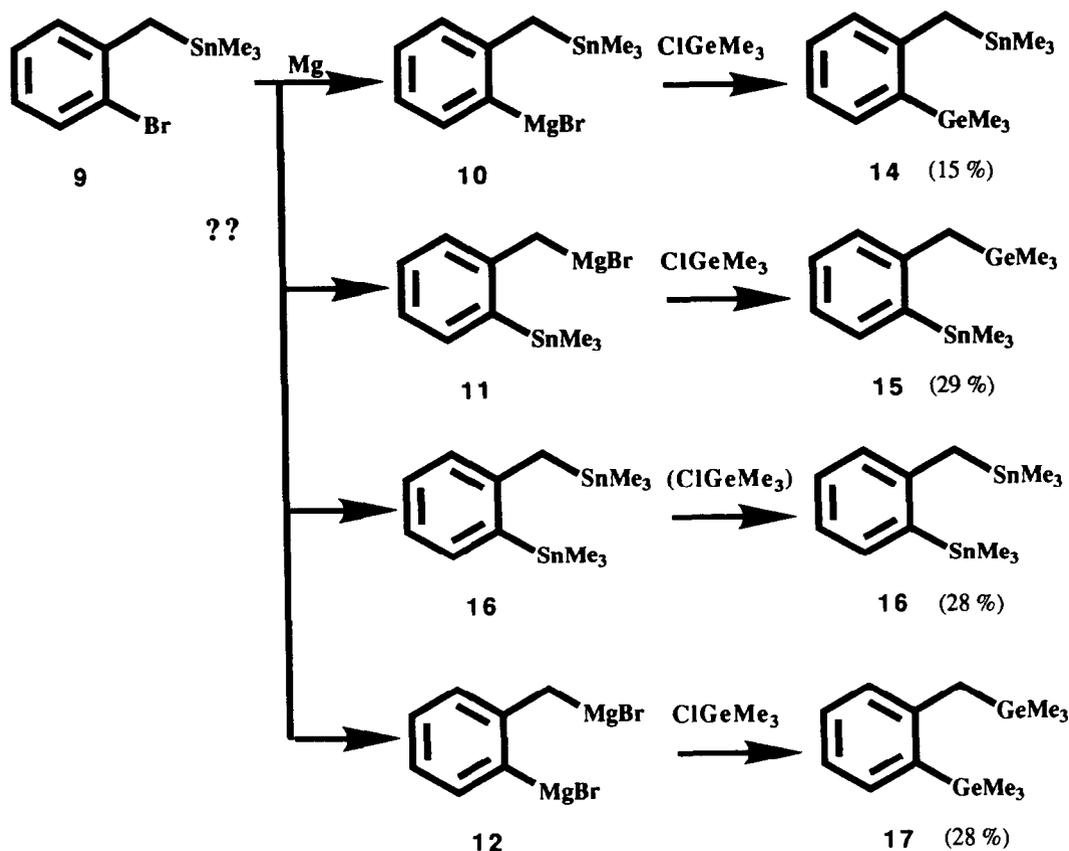
simple composition are known [9]. The inorganic di-halides $MgBr_2$ and MgI_2 and a few diorganylmagne-siums such as $(\eta^5\text{-}C_5H_5)_2Mg$ [10] and Np_2Mg (Np = neopentyl) [11] have monomeric, linear structures in the gas phase; the same holds for $[(Me_3Si)_3C]_2Mg$ in the crystalline state [12]. Such linear structures are in line with a theoretical description in terms of sp-hy-bridized magnesium, or VSEPR theory, or electrostatic repulsion between the two negatively charged ligands on magnesium, or by steric hindrance; note that the

18 + Mg → [??] ClGeMe₃ →

19 (21 %) ! + { 20 (9 %) + Me₄Sn (3 %) } + { 21 (70 % !) + MeMgBr (60 - 65 %) }
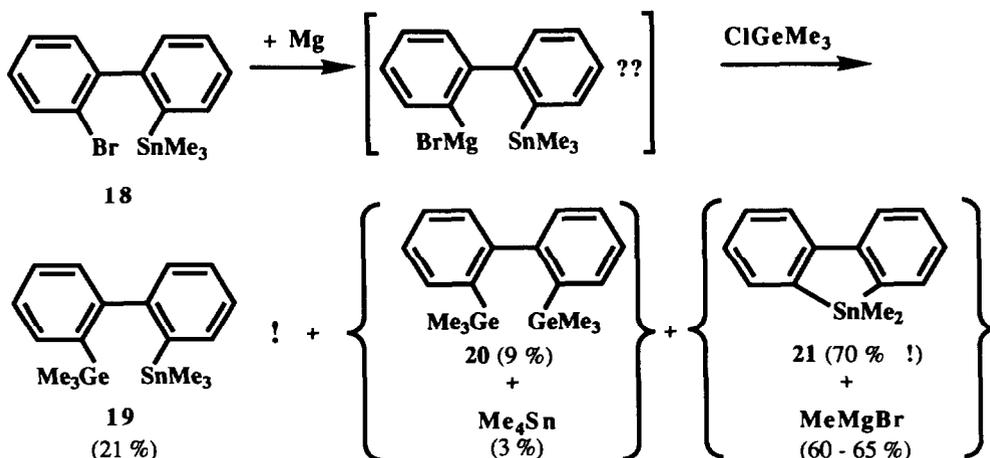
Scheme 6.

Scheme 7.

Scheme 8.
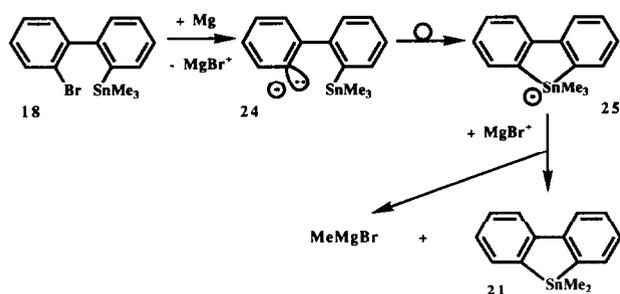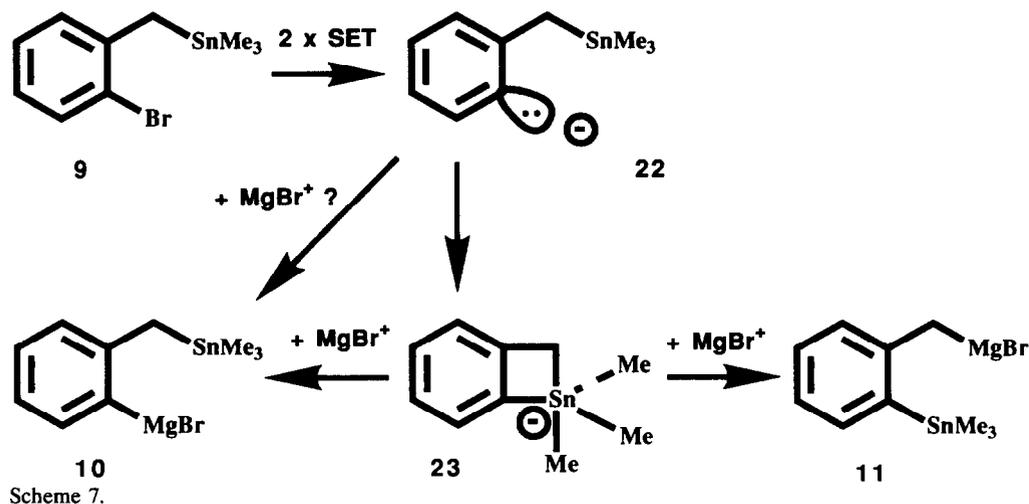
ligands in the three organometallic examples are rather bulky! Probably, several factors combine to make these structures linear.

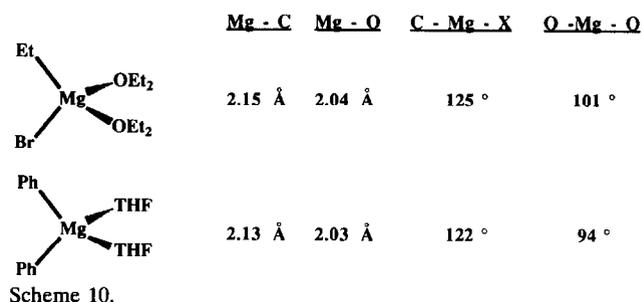In the vast majority of its organometallic compounds, however, magnesium is tetracoordinate. Unsolvated species attain this state by polymerization, forming chains constructed from four-membered rings which consist of two magnesium atoms μ-bridged by the organic rest through three-centre two-electron bonds [13] (Scheme 9).
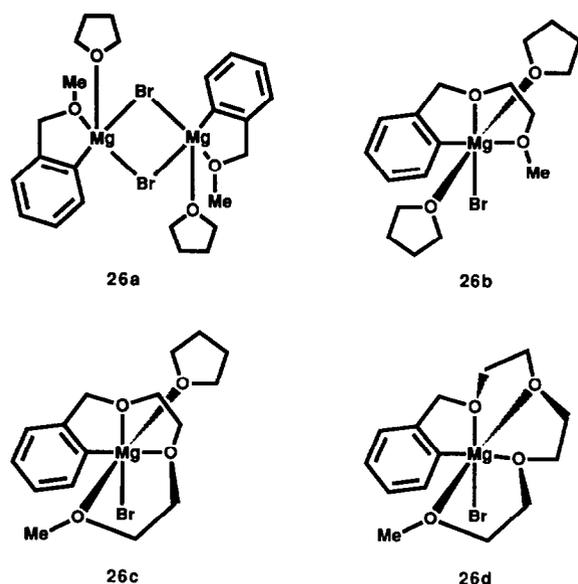
More often, especially in ethereal solvents in which they are traditionally prepared, tetracoordination is
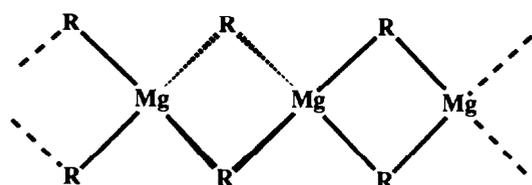
achieved by incorporation of two solvent molecules L into the molecule to yield complexes of the type RMgX · L_2; hereby the electron deficiency of the Lewis-acidic magnesium centre is saturated more efficiently. Typical examples are EtMgBr · $(Et_2O)_2$ [14] and $Ph_2Mg · THF_2$ [13c] (Scheme 10).

Higher coordination numbers are common in inorganic magnesium compounds (cf. the hexaquo cation $[Mg(H_2O)_6]^{2+}$), but rare in organomagnesium chemistry. This is probably mainly due to two factors: the lower charge on magnesium and steric hindrance by the ligand; note that organic groups and ethers are rather bulky ligands. Steric hindrance can be effectively reduced by replacing repulsive van der Waals interactions between the ligands by bonds; these may connect either the organic group and the solvating ether (intramolecular coordination) and/or the ether ligands as in crown or polyethers. An illustrative example is the series of substituted phenylmagnesium bromides 26 carrying oligoethylene glycol ether side chains (Scheme 11) [15], in which magnesium is able to achieve higher, electronically more favourable coordination numbers

Scheme 9.

	Mg - C	Mg - O	C - Mg - X	O -Mg - O
	2.15 Å	2.04 Å	125 °	101 °
	2.13 Å	2.03 Å	122 °	94 °

Scheme 10.

26a   26b

26c   26d

Scheme 11.

of 5 in **26a** (with one chelating ether function) and 6 in **26b–d** (two or more intramolecularly chelating ethers). While in **26b** and **c**, two or one external molecules of THF, respectively, are used to complete the coordination sphere — and can find sufficient space around magnesium to do so, **26d** is an interesting example of an organomagnesium species fully solvated intramolec-

27 [δ(1H*) = 7.87 ppm]   +   Ph₂M g

28 [δ(1H*) = 7.94 ppm]   29 [δ(1H*) = 8.79 ppm]
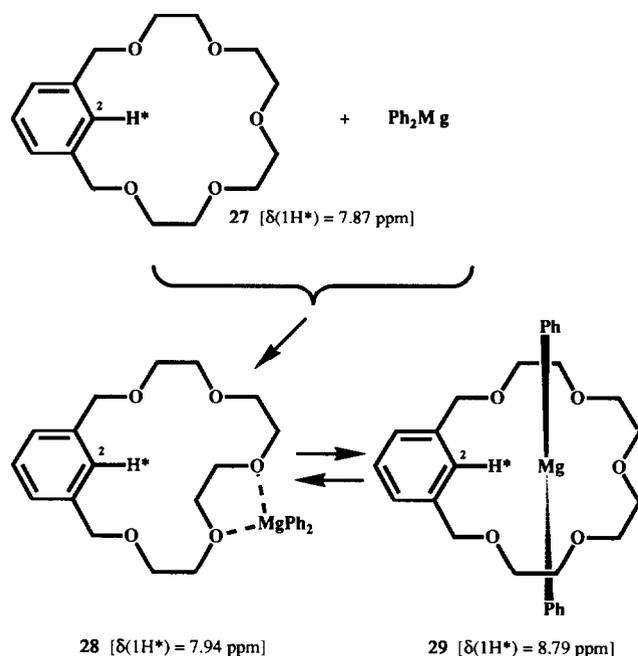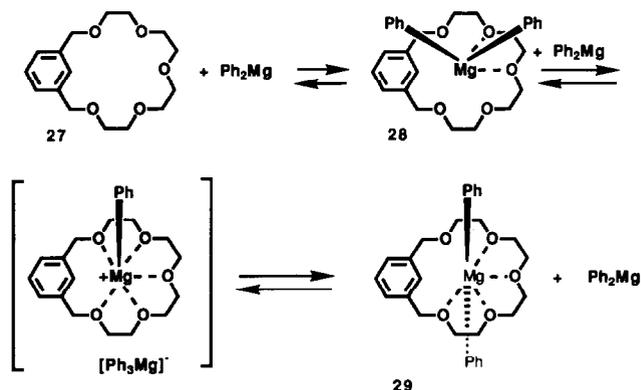
Scheme 12.

ularly without requiring external Lewis bases to reach the high coordination state of 6.

Efficient coordination by polyethers also has consequences for the structural and chemical behaviour of organomagnesium species. Thus, while investigating the interaction between 1,3-xylylene-18-crown-5 (**27**) with diphenylmagnesium, we discovered that in toluene as the solvent, an equilibrium between a side-on complex **28** and a rotaxane **29** was established (Scheme 12). The structure of **29** was confirmed by an X-ray crystal study, and the position of the equilibrium was established by ^{1}H NMR spectroscopy, in particular by the typical deshielding of the intraannular proton at position 2 of **29** which is probably caused by congestion inside the crown ether cavity [16].

The mechanism by which this equilibrium is established is of some interest. The crown ether cavity is large enough to accommodate the magnesium, but too small to allow the penetration of one of the benzene rings of diphenylmagnesium. If direct threading is impossible, one is forced to assume that the penetration proceeds by dissociation of one of the phenyl–magnesium bonds, probably assisted by ate complex formation as shown in Scheme 13.

In order unambiguously to prove the occurrence of bond cleavage in the threading process, we synthesized the cyclic diarylmagnesium compound **30** which with **27** established an equilibrium of side-on complex **31** and catenane **32** (Scheme 14) analogous to that of **28** and **29**, as indicated by the characteristic ^{1}H NMR spectra [17]. Interlocking of the two rings necessarily requires the intermediate opening of at least one of them, and clearly, the organometallic ring is the only one having this possibility available.

Numerous other examples could be cited to demonstrate the unusual and highly increased reactivity of organomagnesium compounds by high and intramolecular coordination, especially of crown ethers. Examples

27   28

[Ph₃Mg]⁻   29
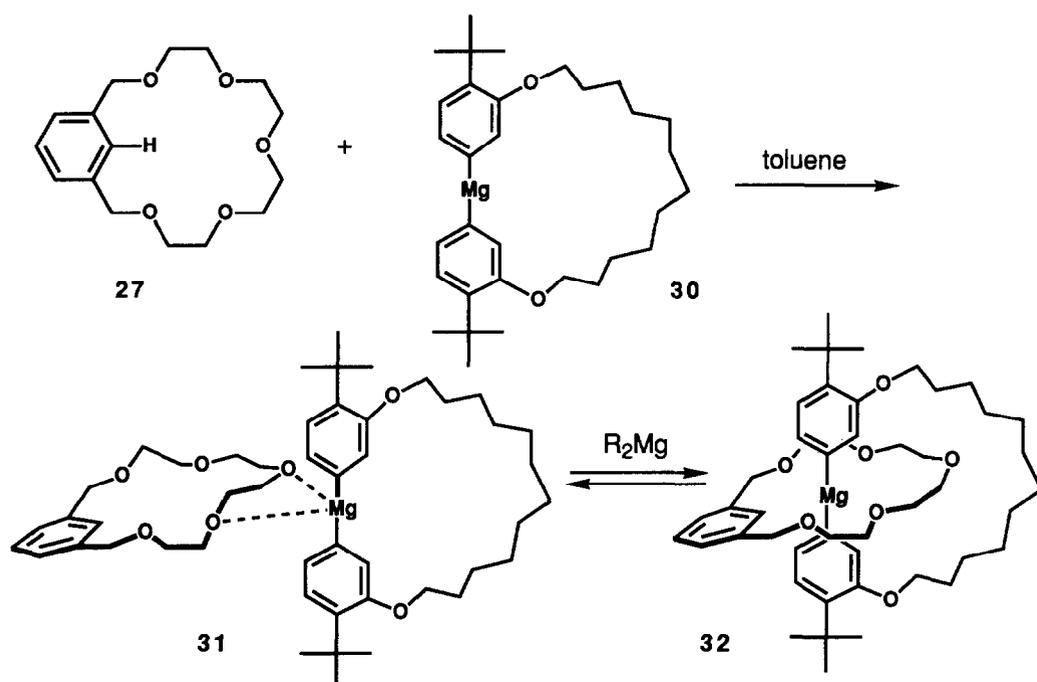
Scheme 13.

Scheme 14.

are the cleavage of aromatic methyl ethers [18] or the organolithium-like metallation [19] and halogen-metal exchange reactions [20] of diphenylmagnesium at the

well known or notorious position 2 between the crown ether bridgeheads. A recent illustration of the dramatic activation which may be achieved is the halogen-metal

Scheme 15.
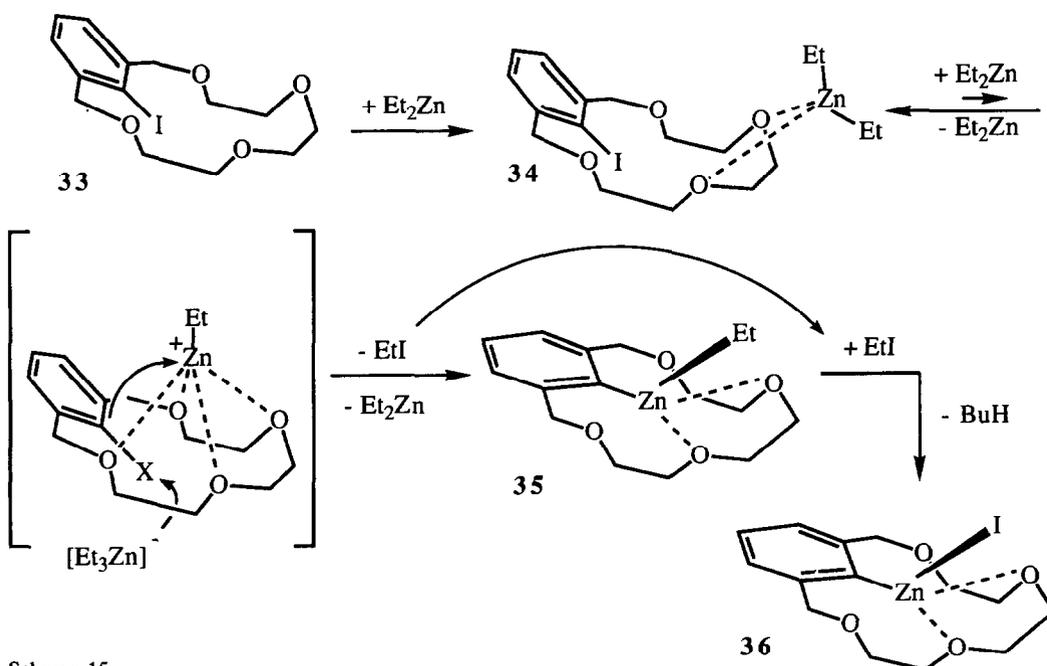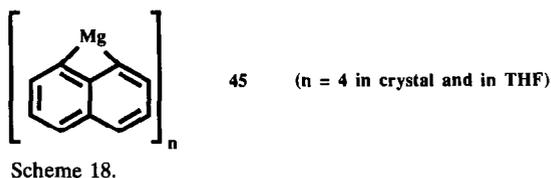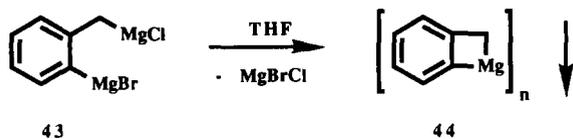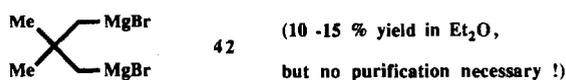
exchange between the aryl iodide **33** and organozinc derivatives [21]. In diethylzinc as the solvent, a side-on complex **34** (Scheme 15) was formed which slowly (one week at 60°C) reacted presumably to yield first the halogen-metal exchange product **35**. However, the reaction did not stop at this stage, and in a Wurtz-type reaction, exchange of the ethyl group of **35** by iodine furnished **36**, whose structure was established by X-ray analysis. Both halogen-metal exchange and the Wurtz reaction are quite unique in organozinc chemistry, especially under such mild conditions.

4. Bifunctional organomagnesium reagents and metal-lacycles

A third area of organomagnesium chemistry, in which interesting developments have taken place in the past decade, is that of divalent reagents. Once the principle of Scheme 1 had been established, it is straightforward to extrapolate the synthesis of Grignard reagents from organic halides to organic dihalides and indeed, the idea had occurred to Grignard in 1901 [22], only one year after his first discovery. However, this time, he had the misfortune that the organic dihalides easily available to him to test this idea turned out to be most unsuitable for this purpose (Scheme 16). The problem is not so much that the reaction of 1,2-dibromoethane or 1,3-dibromopropane with magnesium would not proceed; on the contrary, both are among the easiest reactions. It is for that very reason, that 1,2-dibromoethane is frequently used to promote Grignard reactions of organic halides which do not readily proceed by themselves ("entrainment"), and that the reaction of 1,3-dihalides with magnesium or zinc is one of the best methods to prepare three-membered rings, both in organic and inorganic chemistry; but the desired di-Grignard reagents **37** or **38** were not obtained in this fashion.

Only when shortly afterwards, von Braun had made the higher homologues of the aliphatic α,ω-dibromides accessible by convenient syntheses [23], both he and Grignard found that with four or more carbon atoms between the two bromine functions, the corresponding di-Grignard reagents **39** (Scheme 16) could be prepared in a more or less conventional way [24]. Subsequently, such reagents, and the corresponding dilithium compounds as well, proved to be valuable synthons for the preparation of a great variety of heterocycles containing main group or transition metals as hetero atoms [25].

Nevertheless, in the meantime, all representatives of the simple aliphatic di-Grignard reagents BrMg-$(CH_2)_n$MgBr ($n = 1$, 2, or 3) have been obtained, as well as some other di-Grignard reagents with three or

Scheme 16.

fewer carbon atoms between the organometallic functions. It is amusing that contrary to Grignard's negative experience, the highest member of this series, the 1,3-di-Grignard reagent of propane (**40**) did in fact turn out to be accessible from 1,3-dibromopropane by the "direct synthesis" (Scheme 17) [26]. The procedure is not too easy, and the key to success lies in obeying the very special reaction conditions mentioned above: an evacuated, sealed glass system, sublimed magnesium metal and, most important, extremely slow addition of the 1,3-dibromopropane to the metal in ether over several days. The yield is mediocre (about 30%), but **40** can be conveniently purified via its polymeric, poorly soluble diorganylmagnesium **41** as indicated in Scheme 17.

Other 1,3-di-Grignard reagents such as **42–45** (Scheme 18) can be synthesized by similar (**42**) [27] or by slightly more conventional procedures (**43, 45**). As in the case of **40** (Scheme 17), the Schlenk equilibrium offers an easy method for purification. In THF, this equilibrium is generally shifted towards the diorganyl-
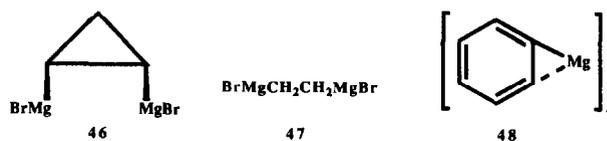

Scheme 17.

Scheme 18.

Scheme 20.

magnesium which, for divalent reagents, cannot form monomeric magnesacycles with small (*i.e.* six- to four-membered) rings because magnesium prefers large valence angles towards its two carbons [25]. Thus, they occur as poorly soluble oligomers (*e.g.* tetrameric 45 [29]) or nearly insoluble polymers (*e.g.* 44 [28]), which can be separated from side products by decantation.

By metathesis of 1,3-dimagnesium compounds with main group or transition metal derivatives of the type L_nMCl_2, a useful approach to metallacyclobutanes has been developed. Metallacyclobutanes have received
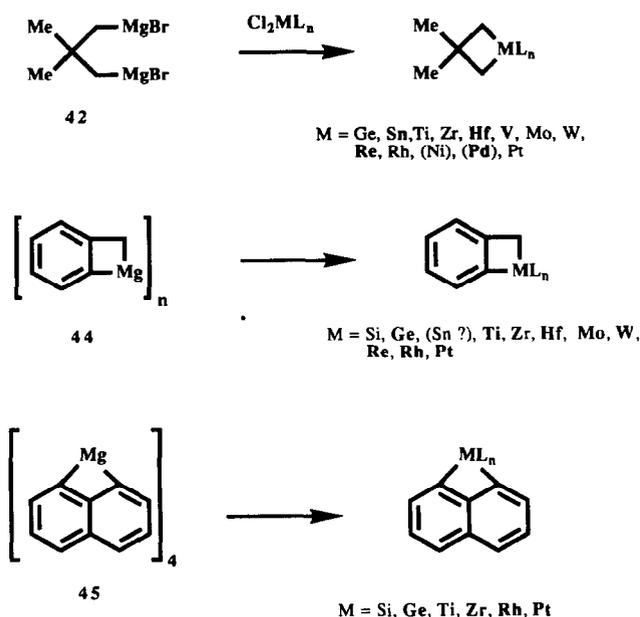
considerable interest both for their structures and for their role in catalytic processes such as olefin metathesis; for that reason, different syntheses are known which, however, are usually limited to a certain, limited number of metals. The approach via the 1,3-di-Grignard reagents is much more general as demonstrated by the representatives shown in Scheme 19; those not (yet) prepared by another method are indicated in bold type.

The next lower homologues, 1,2-di-Grignard reagents, are at present still the group most difficult of access, in particular in the aliphatic series where eliminations are usually the predominant escape reactions (*cf.* Scheme 16). The cyclopropane derivative 46 has been known for some time [30], and the parent compound 47 has recently been prepared [31], but the methods are tedious and the yields low (Scheme 20). In the aromatic series, where eliminations are more difficult, 1,2-dimagnesium compounds such as 48 can be conveniently prepared from the corresponding mercury derivative and magnesium [29].

Against this background, it may seem paradoxical that the smallest and most exotic looking member of the series, the 1,1-di-Grignard reagent of methane ($CH_2(MgBr)_2$, 49) has been known since as early as 1926, when it was first prepared by Emschwiller in the straightforward Grignard fashion from dibromomethane and magnesium in diethyl ether [32]. The yields were originally low and unreliable, but by several improvements such as the use of magnesium amalgam instead of magnesium metal [33] and of diisopropyl ether as the reaction medium [34], 49 is now available pure and in reproducible 80% yield (Scheme 21).

Scheme 19.

Scheme 21.

Scheme 22.

$(Me_3Si)_2C(MgBr)_2$ **51** + O=CHPh $\xrightarrow{\text{1 h}}$ $(Me_3Si)_2C=CHPh$ **52** (70 %)

+ O=CPh₂ $\xrightarrow{\text{23 d}}$ $(Me_3Si)_2C=CPh_2$ **53** (7 %)
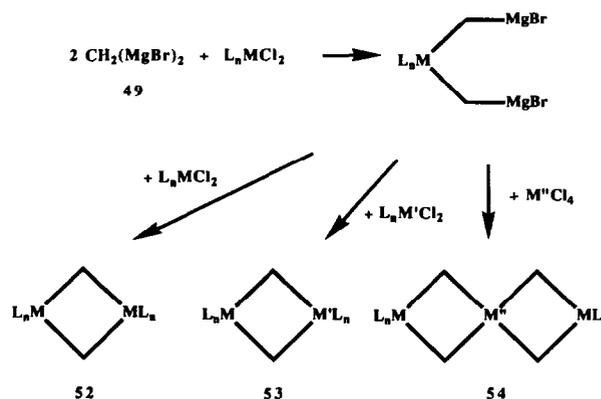
$\xrightarrow{D_2O}$ $(Me_3Si)_2CD_2$ **54**
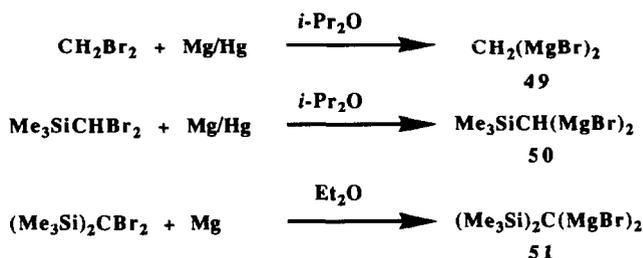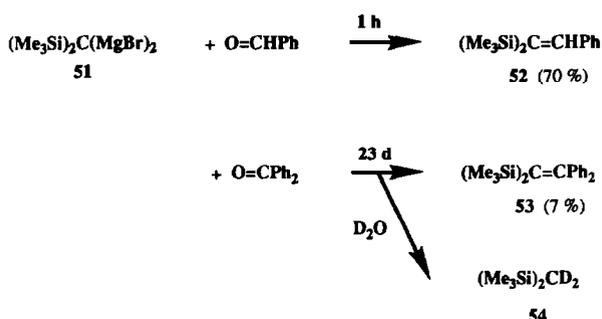
Unfortunately, this synthesis could not be extended to substituted 1,1-di-Grignard reagents except for the trimethylsilyl substituted compounds **50** [35] and **51** [36]. In the case of **51**, special conditions such as amalgam and diisopropyl ether are not required; the compound, formed in 60% yield, can be obtained pure in 35% yield by direct crystallization from diethyl ether. An unforeseen property of **51** was its low reactivity. Originally, we had anticipated that the close proximity of the two metal functions on the same carbon atom would lead to considerable accumulation of negative charge at this atom and, consequently, to high carbanionic reactivity. However, while **51** did still react with benzaldehyde within one hour to give the expected olefination product **52** in 70% yield, the corresponding reaction with benzophenone took 23 days to furnish no more than 7% of **53**; the remainder was unreacted **51**, as was shown by quenching of the reaction mixture with deuterium oxide to give **54** (Scheme 22) [36c].

Speculations on the reason for this lack of reactivity were placed on firm ground by the X-ray crystal structure of **51** which bore several surprises [36b]. Not unexpected was the extreme crowdedness of the molecule; in fact, the central anionic carbon atom is so deeply buried within the molecule that in space filling models, it is hardly visible from outside. Undoubtedly, steric hindrance towards approaching electrophiles makes an important contribution to the low reactivity. In spite of the crowded situation — and this was not anticipated — each of the two magnesiums is rather normally tetracoordinated by complexation to two molecules of THF each, so that the actual composition of a unit is $(Me_3Si)_2C(MgBr \cdot THF_2)_2$. Note that normally, crowded organomagnesium compounds relieve their uncomfortable situation by forming bridged oligomers involving electron deficient bonds, which reduces the total number of atoms in the coordination sphere [9]. The biggest surprise, however, came on inspection of the bond distances around the crowded central carbon atom. If anything, one would have pre-

dicted lengthening of these bonds as this would help to relieve the strain; in reality, all four bonds were found to be on the short side: C–Mg 2.10, 2.14 Å (*versus* normal average 2.15 Å [9]) and C–Si 1.81, 1.85 Å (*versus* normal 1.88 Å). We feel that this bond shortening results from a strengthening of the central bonds due to an electrostatic effect: each of the four positive metal(oid)s has a stronger Coulomb interaction with the anionic carbon, the negative charge of which is higher than that of ordinary carbons carrying one organomagnesium function only. This stabilization may also in part be responsible for the low reactivity of **51**.

While this result has a certain fundamental interest, it also had the unpleasant practical consequence that the reactivity of **51** towards transition metal salts was so low that we had to limit our exploration of the synthetic potential of "one carbon dianion" equivalents to **49** and **50**. One of the applications of **49** in organometallic synthesis is the construction of 1,3-dimetallacyclobutanes [37], the principle of which is illustrated in Scheme 23. By a judicious choice of the stoichiometry and the sequence of addition, one can achieve a considerable versatility in preparing homometallic (**52**) or heterometallic dimetallacyclobutanes (**53**) [37a], or even spiro derivatives **54** [37b].

Another application makes use of the methylene unit of **49** for the synthesis of metal-carbene complexes. Thus, from **49** and titanocene dichloride in benzene/diethyl ether, a solution of **55** was obtained (Scheme 24). The structure of **55** as drawn suggests a relationship to the well known Tebbe reagent **60** ($\delta(^1H) = 8.49$ ppm) [38] which is, however, not in line with the pronounced difference in the proton chemical shifts of the methylene groups between the two metals (**49**: $\delta(^1H) = 2.93$ ppm); for that reason, we assume that **55** has an open structure without the chlorine bridge between the two metals which is known to be

$2\ CH_2(MgBr)_2$ **49** $+\ L_nMCl_2 \longrightarrow L_nM\langle{}^{MgBr}_{MgBr}$

$+ L_nMCl_2$ $+ L_nM'Cl_2$ $+ M''Cl_4$

$L_nM\langle\rangle ML_n$ **52** $L_nM\langle\rangle M'L_n$ **53** $L_nM\langle\rangle M''\langle\rangle ML_n$ **54**
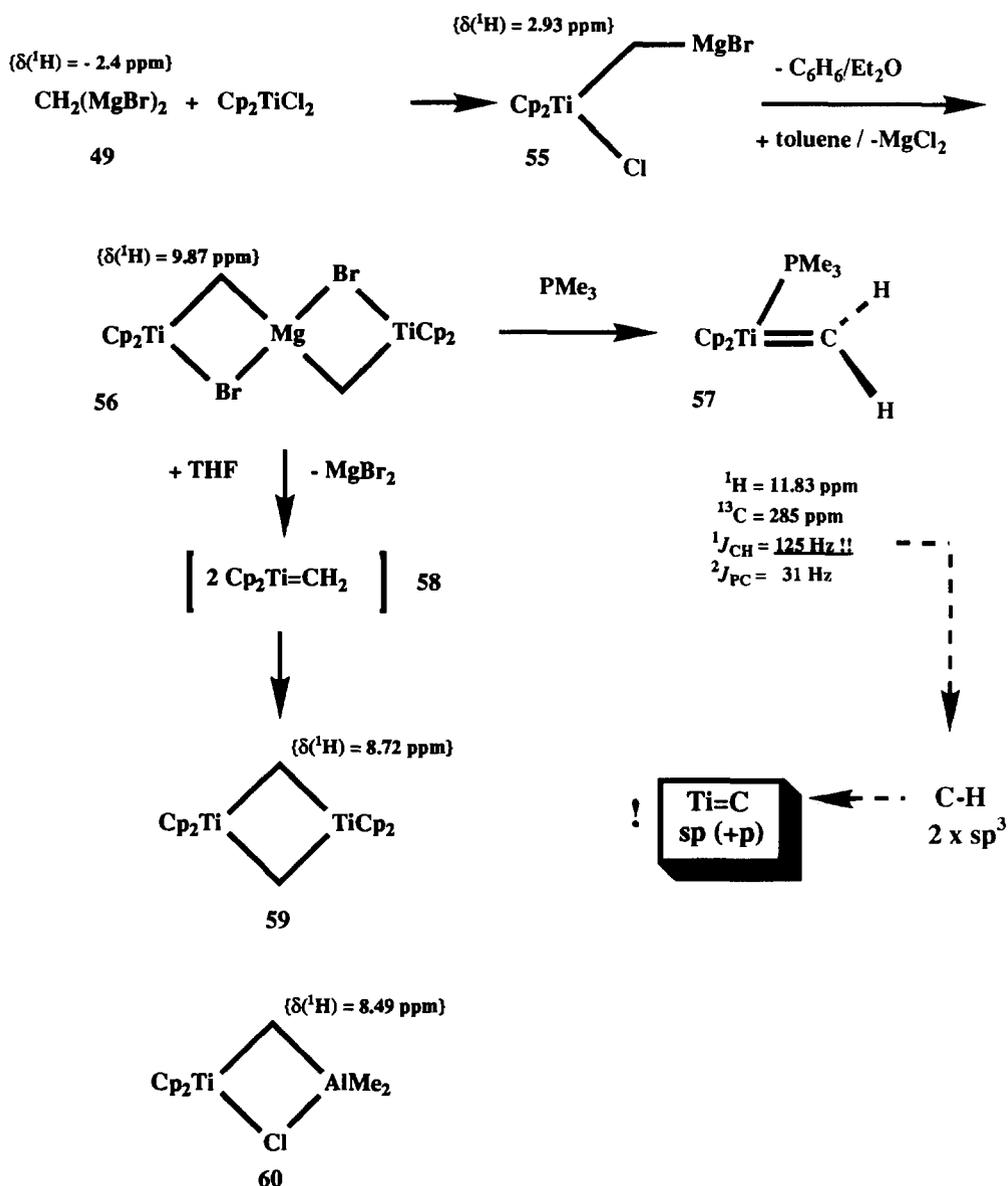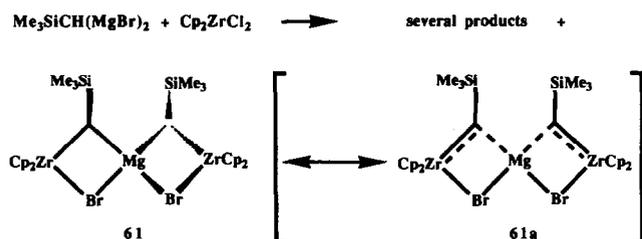
Scheme 23.

present in **60**. On the other hand, removal of the solvent and extraction with toluene gave a product with the elemental composition of **56** and a chemical behaviour typical of a carbene complex: under very mild conditions, it was transformed by THF to the known "carbene dimer" **59**, presumably via the unstable intermediate metal-carbene complex **58**, and by trimethylphosphine to the genuine carbene complex **57** [37c]. As indicated in Scheme 24, the NMR data of **57**, in particular the low coupling constant $^1J(CH) = 125$ Hz, lead to the conclusion that the σ part of the Ti=C double bond has a remarkably high s character (sp

hybridization). It is also worth mentioning that increasing deshielding of the methylene nuclei in combination with increasing reactivity indicate that the degree of "precarbene" character increases in the series **55** ≪ **60** < **59** < **56** < **57**.

The structure of a "spiro Tebbe" reagent suggested for **55** was rather speculative until recently, when we were able to obtain the related complex **61** (Scheme 25), whose structure was established by X-ray diffraction [36c]. Together with several other products, **61** was formed in low yield in the reaction between zirconocene dichloride and **50**, but it was so cooperative

Scheme 24.

Me₃SiCH(MgBr)₂ + Cp₂ZrCl₂ ——▶ several products +

Scheme 25.

as to crystallize from the reaction mixture. Besides confirming the proposed "spiro Tebbe" structure, the relatively short zirconium–carbon bonds (d(Zr–C) = 2.15 Å) and the slightly elongated magnesium–carbon bonds (d(Mg–C) = 2.19 Å) allow the description of the structure as that of a (rather tight) complex between a zircona-alkene and magnesium dibromide, as indicated in the structure **61a**.

5. Conclusion

It is not unintentional that this brief review of some novel organomagnesium chemistry closes with an example from metal-carbene chemistry. Rather, it was chosen because it seems satisfactory and appropriate to underline the importance of this important branch of organometallic chemistry which was initiated by E.O. Fischer in 1964 [39]. Furthermore, this example also nicely confirms the repeated and gratifying experience that new achievements in one area — in this case main group metal chemistry — may stimulate developments in others, like organometallic chemistry of transition metals.

Acknowledgments

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