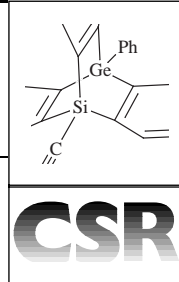# Travelling the organometallic road: a Wittig student's journey from lithium to magnesium and beyond

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Both organomagnesium compounds (Grignard reagents) and organolithium compounds are of utmost importance in synthesis. New developments in the area of *difunctional* organometallic compounds will be described against a historical background in which the author's interest gradually drifted from organolithium chemistry, in particular the deep red *ortho*-dilithiobenzene, to its magnesium analogue, the tetrameric *ortho*-phenylenemagnesium. The latter was applied in the synthesis of novel 1,2-disubstituted benzene derivatives such as 9,10-dimetallatriptycenes.

1 Introduction

The hundredth anniversary of Georg Wittig (1897–1987) was commemorated last year by a range of academic ceremonies. On 16 June 1997, precisely the centenary of Wittig's birthday, a special colloquium was held at the University of Marburg, his *alma mater*, in order to commemorate some aspects of his seminal contributions to organic chemistry in general and to organometallic and organoelement chemistry in particular, culminating in his discovery of the phosphorus ylides; generally known as Wittig reagents and indispensable in preparative organic chemistry, they earned him the Nobel Prize in 1979.

At such an occasion, recollections have to be, by necessity, selective. It happened to be the author's duty and pleasure to make a choice, and he did so by concentrating on certain developments in organometallic chemistry in which he himself had the good fortune to participate, first as a student in Wittig's

Friedrich Bickelhaupt obtained his PhD in organic chemistry at the University of Tübingen with G. Wittig in 1957. After a postdoctoral period with K. Wiesner (University of New Brunswick at Fredericton, Canada, alkaloid chemistry) and R. B. Woodward (Harvard University, chlorophyll synthesis), he joined in 1960 the research laboratories of Boehringer Mannheim (Germany, psychopharmaca). In 1964, he was appointed Professor of Organic Chemistry at the Vrije Universiteit in Amsterdam; since 1997, he has been Professor Emeritus. His research interests are in the fields of organometallic chemistry, low coordination chemistry in groups 14 and 15, and valence isomers of benzene and small cyclophanes. Awards: JSPS fellowship (1985); Max Planck Research Prize (with Professor Dr G. Erker, 1993).

laboratory in Tübingen and Heidelberg, and later in the course of his own academic career; this talk formed the basis for the present review. It will become apparent that Wittig's spirit is permeating through much of the chemistry to be addressed; this was not always conscious to those involved, but is, in retroperspective, clearly discernible.

2 Phenyllithium: Wittig's divining rod

Organolithium compounds had been known for some time, but they were curiosities of interest to the specialist mainly.[1] This changed in 1930 when Karl Ziegler, Wittig's colleague from the early Marburg days and his good friend (and sometimes rival), developed an easy preparative access to these highly reactive carbanionoid reagents through 'direct synthesis' from organic halides and lithium metal [eqn. (1)].[2]

$$2 \, Li + RHal \longrightarrow \mathbf{RLi} + LiHal \qquad (1)$$
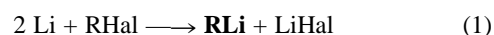
In the same period, Wittig was interested in the chemistry of triphenylmethyl type diradicals such as **1** which he hoped to obtain from the diol **2** *via* known pathways.[3] The problem, however, was the synthesis of **2**. An obvious approach by the Grignard route, starting from dimethyl phthalate (**3**) and phenylmagnesium bromide, failed because the organomagnesium reagent turned out to be insufficiently reactive (Scheme 1). Only one year after Ziegler's discovery, and possibly inspired by his close relationship with Ziegler, Wittig made use of the superior reactivity of phenyllithium to enforce the transformation **3** → **2**,[3] and he also investigated the difference in reactivity between the organolithium and the organomagnesium reagent in other applications.[4]
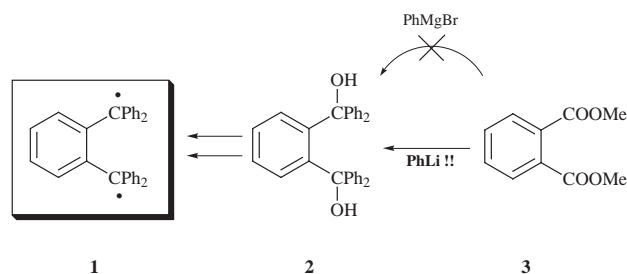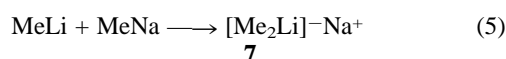

Scheme 1

Ever since, phenyllithium has been Wittig's divining rod ('Wünschelrute', as he called it), and it was to be a superb choice indeed. It led him to important discoveries in radical and carbanion chemistry, amongst which are the ylides including the Nobel Prize winning Wittig reagents, the Wittig rearrangement of ethers, dehydrobenzene (or benzyne, C_6H_4), ate complexes, pentaphenylphosphorus, the controlled aldol condensation — too many to name them all in the present context;
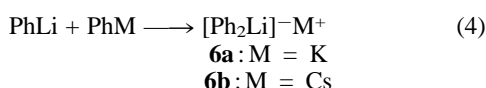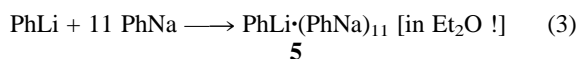
however, they have been adequately reviewed recently by his student Tochtermann.[5]

A particular category of ate complexes is that of the alkali metals such as 'phenyllina' ([Ph$_2$Li]$^-$Na$^+$, **4**), obtained by the interaction of phenyllithium with phenylsodium [eqn. (2)].[6] Wittig was fascinated not only by the analogy with 'his' borate complexes such as kalignost (sodium tetraphenylborate, NaBPh$_4$), but also because the extremely reactive phenylsodium, which normally destroys diethyl ether instantaneously, was stabilised by one equivalent of phenyllithium in ether without losing much of its high reactivity.

$$PhLi + PhNa \longrightarrow [Ph_2Li]^-Na^+ \qquad (2)$$
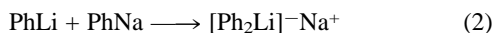
So in 1955, he coaxed the present author (who at that time would have slightly preferred to jump on the bandwagon of the newly discovered Wittig reagent) into investigating this phenomenon more closely. It turned out to be a worthwhile effort: phenyllithium proved to stabilise not only *one* equivalent of phenylsodium, but even a *tenfold excess* as in **5** [eqn. (3)], making this strongly carbanionic reagent available for synthetic applications in diethyl ether, an attractive polar medium. The stabilisation was further extended to combinations with the still more reactive phenylpotassium (**6a**) and phenylcaesium (**6b**) or, less effectively, to the corresponding methyl ate complex **7** [eqns. (4) and (5)].[7]

$$PhLi + 11\ PhNa \longrightarrow PhLi\cdot(PhNa)_{11}\ [in\ Et_2O\ !] \qquad (3)$$
$$\mathbf{5}$$

$$PhLi + PhM \longrightarrow [Ph_2Li]^-M^+ \qquad (4)$$
$$\mathbf{6a}: M = K$$
$$\mathbf{6b}: M = Cs$$

$$MeLi + MeNa \longrightarrow [Me_2Li]^-Na^+ \qquad (5)$$
$$\mathbf{7}$$

A problem which at that time remained unresolved was the structural identity of the stabilised ate complexes. In analogy to NaBPh$_4$, Wittig considered **8** to be a reasonable structure for **4** [eqn. (6)],[7] although the occurrence of, for example, **5** indicated

$$RLi + RNa \longrightarrow [R\cdot\bar{Li}\leftarrow R]\ Na^+\ ?? \qquad (6)$$
$$\mathbf{8}$$

$$[Ph_4Li]^{3-}\ [Na^+(TMEDA)]_3$$
$$\mathbf{9}$$
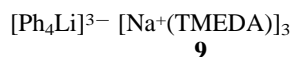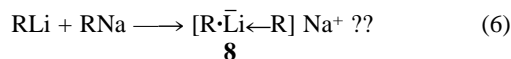
a more complex mode of aggregation. Thirty years later, Weiss proved by X-ray crystallography that another compound with a high PhNa/PhLi ratio having the composition PhLi·3PhNa·3T-MEDA has the structure **9**,[8] which is reasonably close to **8**, certainly in showing the capability of lithium to function as the central atom of an ate complex.

3 Difunctional organometallic compounds

Though pleased with these results, Wittig did not want to pursue the chemistry of lithium ate complexes any further. Instead, his insatiable curiosity was turning to a new topic for the second part of the author's PhD thesis: the preparation and investigation of *o*-dilithiobenzene (**10**). Undoubtedly, one of the reasons why he considered the synthesis of **10** a challenge was that it is *not* accessible by the normal approach towards organolithium compounds: (seemingly) obvious reactions of *o*-dibromobenzene (**11**) with either lithium metal according to Ziegler, or bromine–metal exchange with *n*-butyllithium proceed stepwise and thus necessarily pass through the stage of **12** which, instead of being converted to **10** in a second metallation step, immediately eliminates lithium bromide to form dehydrobenzene (**13**), incidentally another favourite of Wittig's (Scheme 2).[5]

Fortunately, Vecchiotti had synthesised the mercury analogue *o*-phenylenemercury (**14**)[9] from **11** and sodium amalgam;
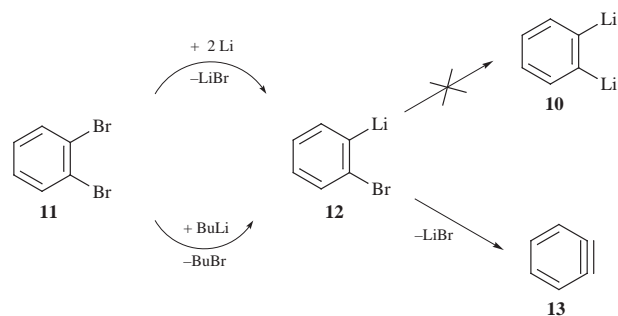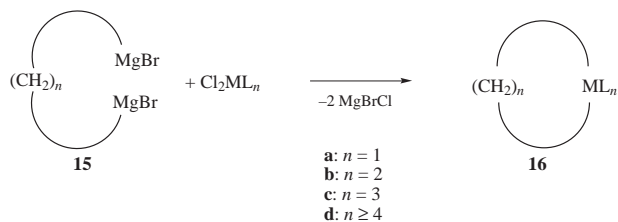

Scheme 2

he believed it to be a dimer (with a dihydroanthracene type structure), but eventually, it was shown to be a trimer with the usual linear C–Hg–C angles (Scheme 3; see also Scheme 7).[10] By the classical Schlenk procedure, *i.e.* shaking the mercury compound with metallic lithium, **14** could be converted to **10** in about 80% yield.[11] Compound **10** opened up a new route to (conventional) chemistry by reaction with organic electrophiles and (less conventional) transformations with main group and transition metals. However, the most profound impression on the young chemist's mind came from the intensely red colour of the compound. As very pure phenyllithium is practically colourless, a deep red colour is not what one would expect from inspection of the structural formula. Undoubtedly **10** has a higher aggregation state, but unfortunately, a satisfactory explanation of this phenomenon is presently not available.
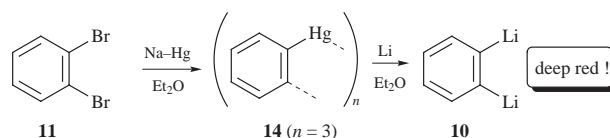
Scheme 3

After obtaining his PhD in Tübingen and after several years of travel and apprenticeship, the author finally continued his research in Amsterdam, where he was pleased, amongst other things, to realize that his own inclination towards organometallic compounds could smoothly be combined with certain investigations in the field of organomagnesium chemistry initiated by his predecessor Jan Coops, including highly sophisticated high vacuum techniques.[12] In the years to follow, many aspects of organomagnesium chemistry have been studied in our group such as the (unexpectedly complex) formation reaction of Grignard reagents RMgX, their structure and interaction with Lewis bases, and finally their application, in particular in organometallic synthesis.[13,14]

In the course of these investigations, and for various reasons, specific attention was paid to divalent organomagnesium compounds **15**. Apart from having structural interest of their own,[13] they are valuable synthons for applications in organic and especially in organometallic synthesis. Thus, they open a convenient and quite general route to organometallic heterocycles **16** (Scheme 4).

Scheme 4

This strategy had already been successfully applied since the early days of Grignard chemistry to the synthesis of **16d** starting from di-Grignard reagents **15d** with 4 or more carbon atoms

between the two organometallic functions. In contrast, it failed completely for the smaller members **15a–c** with 1, 2 or 3 carbon atoms between the metal functions, respectively, for the simple reason that they could not, or not in a satisfactory fashion, be obtained by direct synthesis from the corresponding dihalides.[13] This synthetic challenge together with the prospect that the reagents, if available, would offer an easy and general access to highly interesting small metallacycles such as metallacyclobutanes and analogues led us to develop several routes to small representatives of **15**; this permitted us to prepare a range of four-membered metallacycles as shown in Scheme 5.[13, 14] In

M, M', M'' = main group and/or transition metals
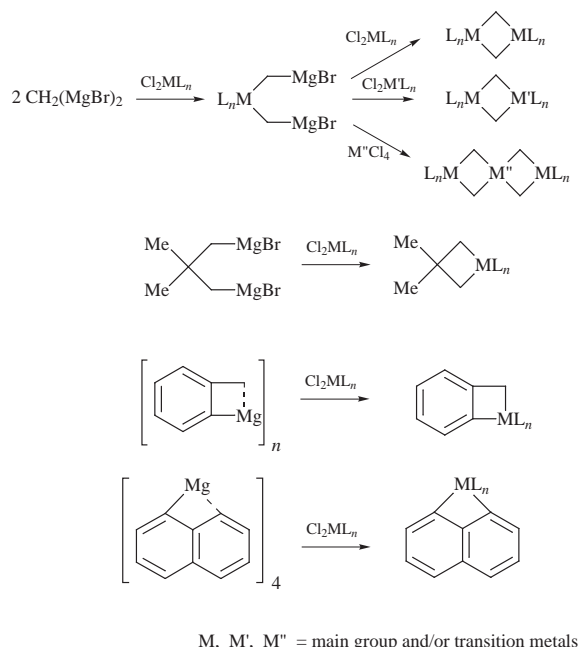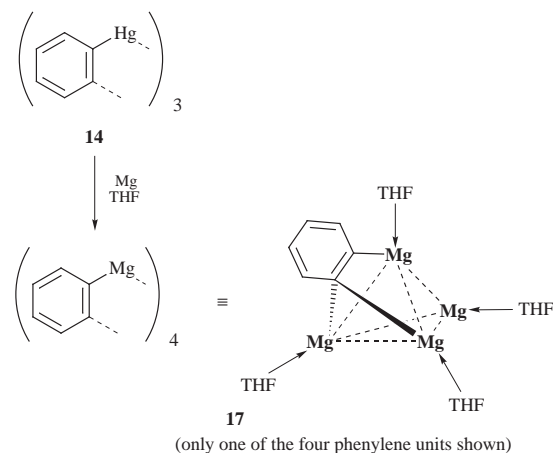
Scheme 5

contrast to **15a** and **15c** and several of their derivatives, which could be prepared and applied in a satisfactory way, great problems were encountered in the preparation of 1,2-bisbromomagnesioethane (BrMgCH$_2$CH$_2$MgBr, **15b**). Although it could be finally synthesised[15] in collaboration with G. W. Klumpp, another Wittig student, the low yield (10%) and the instability of the compound made preparative applications unattractive.

4 1,2-Dimetallated benzenes

4.1 Derivatives of Groups 2 and 12

Being nevertheless strongly interested in the missing link of 1,2-difunctional organometallics, we were looking for alternatives, and it was at this stage that we returned to 'Wittig chemistry' to try the synthesis of *o*-phenylenemagnesium (**17**), the magnesium analogue of **10**. Performing the synthesis was easier than its conception: shaking **14** with an excess of magnesium gave **17** in 65% isolated yield after crystallisation from THF (Scheme 6).[16] The formation of **17** was slower (2 weeks at room temperature and 10 hours at 70 °C) than that of **10** (4 days at room temperature), but **17** had two advantages over **10**: it was stable (in the absence of light) and, like organomagnesium compounds in general, it promised to give rise to less unwanted side reactions such as reduction when used for metathesis with transition metal salts.

A big surprise was the structure of **17**: while nobody had expected it to have the monomeric structure of a magnesacyclopropabenzene, it turned out to be a tetramer both in solution (molecular weight determination in THF) and in the crystalline

(only one of the four phenylene units shown)

Scheme 6

state (X-ray structure determination). The crystal structure showed a slightly distorted tetrahedron of 4 magnesium atoms with each triangle of the tetrahedron capped by a phenylene unit in such a fashion that one carbon is σ-bonded to one magnesium and the second carbon is μ-bridging between two other magnesiums (Scheme 6; only one phenylene unit shown). Similar tetrameric structures were found for 1,2-diphenylvinylenemagnesium (**18**) and the 1,3-dimagnesium derivative 1,8-naphthalenediylmagnesium (**19**). These tetrameric structures are reminiscent of those of many organolithium compounds. We have explained the analogy by the correspondence between complexes of two monovalent ions of (R−Li$^+$)$_4$ and those of two divalent ions (R^{2-}Mg^{2+})$_4$; apparently, in both series, electrostatic interactions are largely responsible for a tetrahedral arrangement.[16]

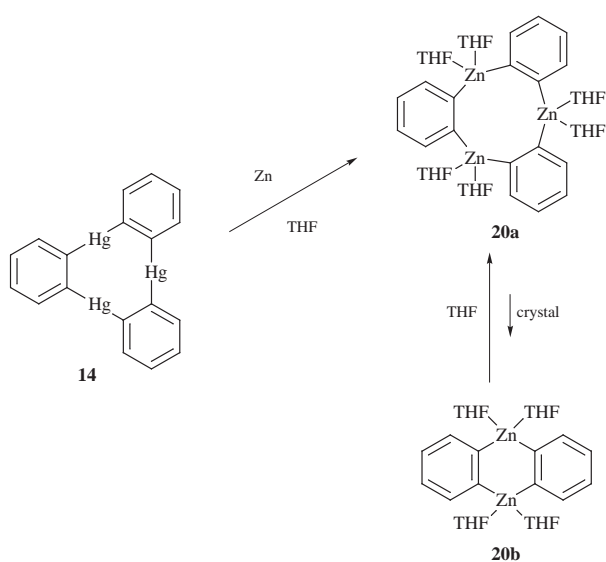As the reductive potential towards transition metal salts decreases steadily in the series RLi → R$_2$Mg → R$_2$Zn, we were also interested in the zinc analogue **20**. It could be smoothly obtained from **14** and zinc, and again, had two surprises. Firstly, while zinc is less electropositive than magnesium and therefore usually less reactive, the transformation **14 → 20** went much faster than the formation of the magnesium or even the lithium analogue; it took only 6 hours at room temperature for completion (Scheme 7).[17] The second surprise came again from the structure: in THF solution, **20** is strictly and concentration independently trimeric (**20a**), presumably as a slight variation of the structure of **14** with somewhat smaller bond angles at zinc; however, in the crystalline state, the compound occurs in the dimeric form of a 9,10-dihydro-9,10-dizincaanthracene (**20b**).
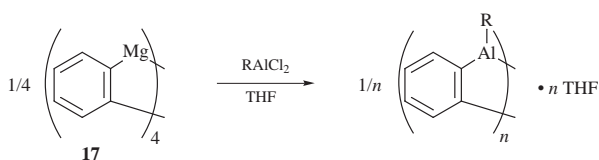
4.2 Derivatives of Group 13

So far, we have applied **17** and **20** mainly in the synthesis of main group metal derivatives. With organoaluminium dichlorides RAlCl$_2$, the results were not clear-cut. According to NMR spectroscopy in [D$_8$]THF, single species were obtained for R = Me or Et and mixtures of species for R = *t*-Bu, Ph and of organyl groups capable of intramolecular coordination (Scheme 8); though crystals formed, they easily crumbled so that X-ray structures could not be obtained.[18] Very probably, some of these species are of the dihydroanthracene type observed for **20b** (*vide supra*) and for the heavier metals of Group 13 in the case of gallium (**21**) and indium (**22**); in the crystal, both **21**[18] and **22**[19] have an essentially planar central ring (Scheme 9).

4.3 Derivatives of Group 14

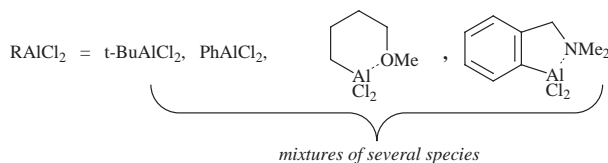While 9,10-dihydro-9,10-disilanthracenes such as **23a** were known for some time, the germanium and tin analogues **23b** and
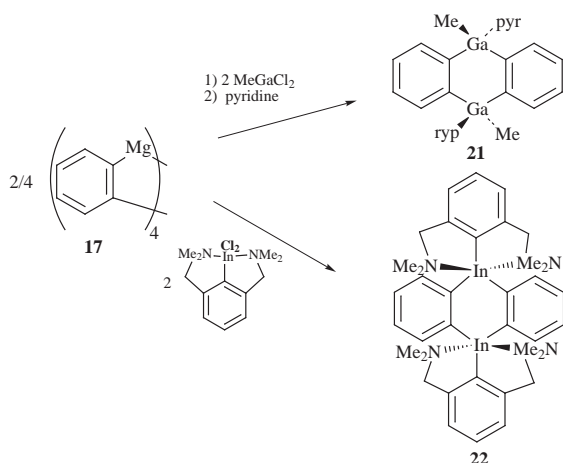
Scheme 7

Scheme 8

RAlCl$_2$ = MeAlCl$_2$, EtAlCl$_2$: single species (n = 2 ?)

RAlCl$_2$ = t-BuAlCl$_2$, PhAlCl$_2$,

mixtures of several species

Scheme 9

Scheme 10

23a M = Si : 30%
23b M = Ge : 32%
23c M = Sn : 27%

combine to form 6 new bonds; an overall yield of 68% for **24b** then means an average yield of 94% in each step. Furthermore, it is nontrivial that the reaction partners apparently make little use of ample opportunities to crosslink and polymerise!

Scheme 11

24a M = Si : 2%
24b M = Ge : 68%
24c M = Sn : 42%

The first hint as to what was going on came from the attempt to prepare **25**, the phenyl analogues of the dimethyltriptycenes **24**, because the yield of **25** was zero! A closer investigation revealed that the situation was not quite as hopeless as it seemed because after deuterolysis, and regardless of whether the stoichiometrically required 2 equivalents of PhMCl$_3$ were applied or only one equivalent, we did obtain the trideuterated tetraphenylmetal compounds **26** in practically quantitative yield (Scheme 12).

25

26b : M = Ge
26c : M = Sn

Scheme 12

This result suggested that with remarkable specificity, one equivalent of PhGeCl$_3$ and three (monomer) units of **17** had combined to form the tri-Grignard reagent **27b** in quantitative yield (Scheme 13). This assumption was supported not only by deuterolysis yielding **26b**, but also by the addition of 1 molar equivalent of MeGeCl$_3$ to the intermediate reaction mixture: the digermatriptycene **28** bearing two different substituents at the bridgehead position was obtained in rather high yield (83%, Scheme 13). Two aspects of these results deserve further comment.

In the first place, the high specificity of the formation of **27b** is particularly unexpected against the background that Group 14

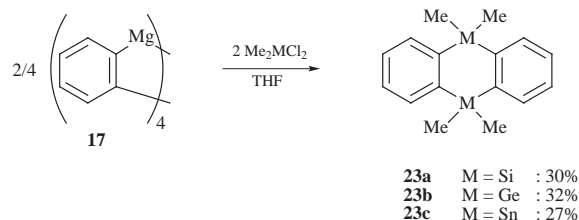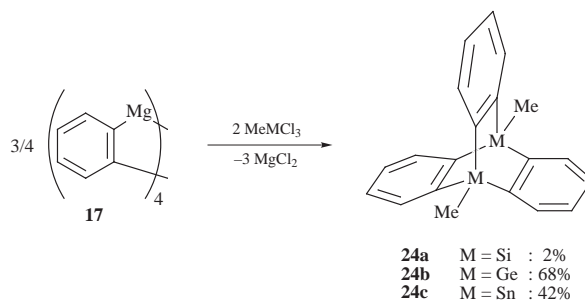**23c**, respectively, were not. All three heterocycles were conveniently prepared from **17** and the dihalides R$_2$MCl$_2$, though the yields were mediocre (Scheme 10).

It was therefore a little bit of a surprise that in the more ambitious attempt to obtain the 9,10-dimetallatriptycenes **24** from **17** and the trihalides MeMCl$_3$ (Scheme 11), the yields of **24b** and **24c** were rather good, especially if one considers that in this one-pot reaction, 5 formal monomeric units have to
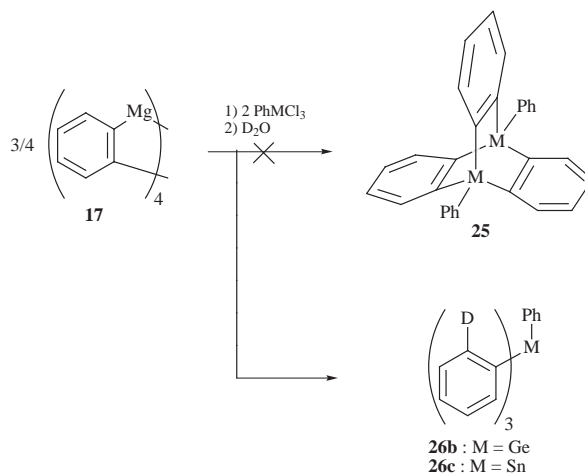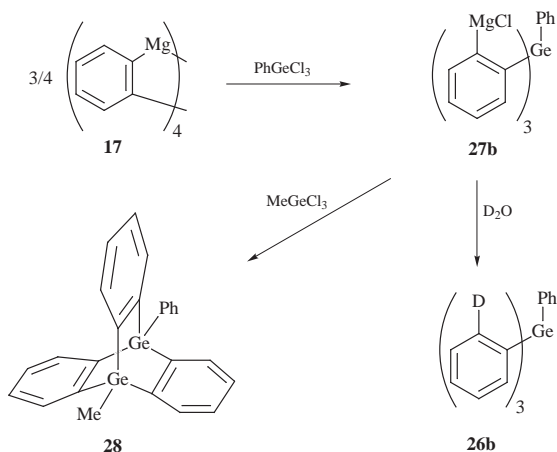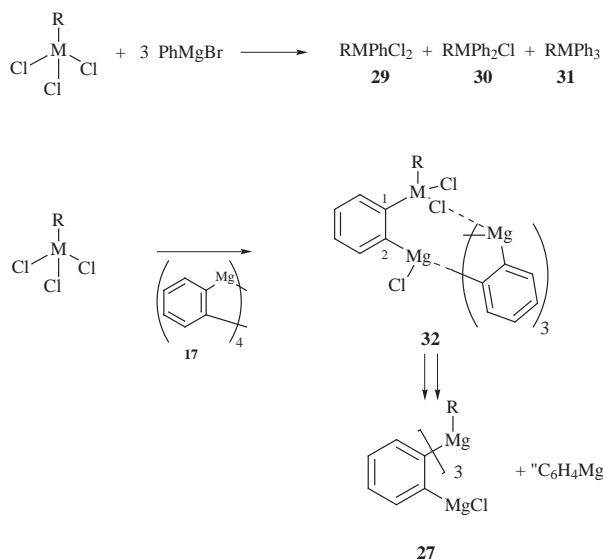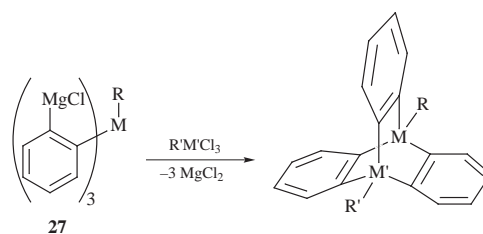
Scheme 13

17   27b   28   26b

trihalides are well known to react in a nonselective manner with Grignard reagents; thus, 3 molar equivalents of PhMgBr and $RMCl_3$ will give a mixture of **29**, **30** and **31** (Scheme 14). The

$$R-MCl_3 + 3\ PhMgBr \longrightarrow RMPhCl_2 + RMPh_2Cl + RMPh_3$$
$$\textbf{29} \qquad\qquad \textbf{30} \qquad\qquad \textbf{31}$$

Scheme 14

17   32   27   + "C_6H_4Mg"

question arises: why is **17** so specific in substituting all three chlorines of one molecule of $RMCl_3$ before attacking the next one, especially in view of the general rule that the reactivity of an organometallic polyhalide decreases with decreasing number of halogens? We feel that the answer must come from the unusual tetrameric structure of **17**. As shown in Scheme 14, the first encounter between **17** and $RMCl_3$ presumably leads to a complex **32** in which one Mg–Cl bond has been replaced by Mg–C(1); the replaced Cl may reside on a magnesium at position 2 of the phenylene ring (or an equivalent position). Whereas normally, the following step is the attack by a second, *external* organometallic reagent, in **32** all the ingredients for further reactions are closely assembled in one agglomeration due to the tetrameric structure of the starting material **17**, which gives the entropic advantage of an intramolecular process. Thus, rather than attacking a second molecule of $RMCl_3$, the two remaining chlorines of the MCl_2 group in **32** are arylated first with formation of **27**; one equivalent of C_6H_4Mg is left over and may engage anew in aggregation and arylation.

The formation of the dimetallatriptycenes thus proceeds in two stages: first formation of a tri-Grignard reagent such as **27**, followed by a triple ring closure to yield the triptycene. This hypothesis also explains the second surprising observation concerning this reaction, *i.e.* the fact that the second stage is of the 'Go/NO GO' type: as illustrated in Scheme 15, the
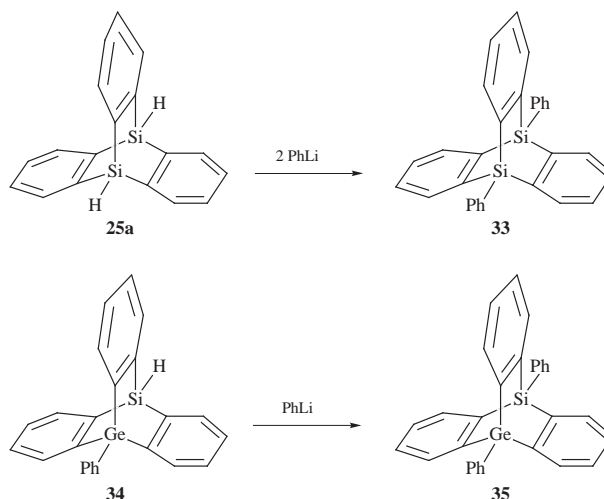
Scheme 15

M	R	M'	R'	Yield
Si	H	Si	H	20–30%
Si	Me	Si	H	73%
Si	Me	Si	Me	2%
Ge	Me	Ge	Me	68%
Ge	Ph	Ge	Me	83%
Ge	Ph	Ge	Ph	0%
Ge	Ph	Si	H	76%
Ge	Ph	Si	Me	0%
Sn	Me	Sn	Me	42%
Sn	Ph	Sn	Ph	0%

triptycene is formed either in good to reasonable yield or not at all. While the size of the Group 14 metal and its substituent have no influence in the first stage, *i.e.* the formation of the tri-Grignard reagent **27** (as monitored by quantitative yield of the trideuterated product on deuterolysis), steric factors are apparently decisive in the second stage to an extent far beyond our intuition. Thus, the small silicon tolerates only one methyl group, whereas the larger germanium allows ring closure with up to one methyl and one phenyl group, but not with two phenyl groups; tin behaves similarly. This leads to the seemingly absurd situation that in the reaction of 3 equivalents of **17** with 2 molar equivalents of $PhMCl_3$ (Scheme 12), **27** is formed selectively and sits next to the second equivalent of $PhMCl_3$ in solution without reacting![18]

That the second phenyl group in **25** cannot be introduced by this approach is not a consequence of these compounds being incapable of existence. This was proven by the synthesis of **33** from **25a** and of **35** from **34** (Scheme 16).[20]

Scheme 16

25a   33   34   35

4.4 Other bridging atoms

The reaction of **17** with Group 15 trihalides proceeds easily. In particular, we investigated the reaction with arsenic trichloride which gives **36** (Scheme 17),[20] the oldest known triptycene and
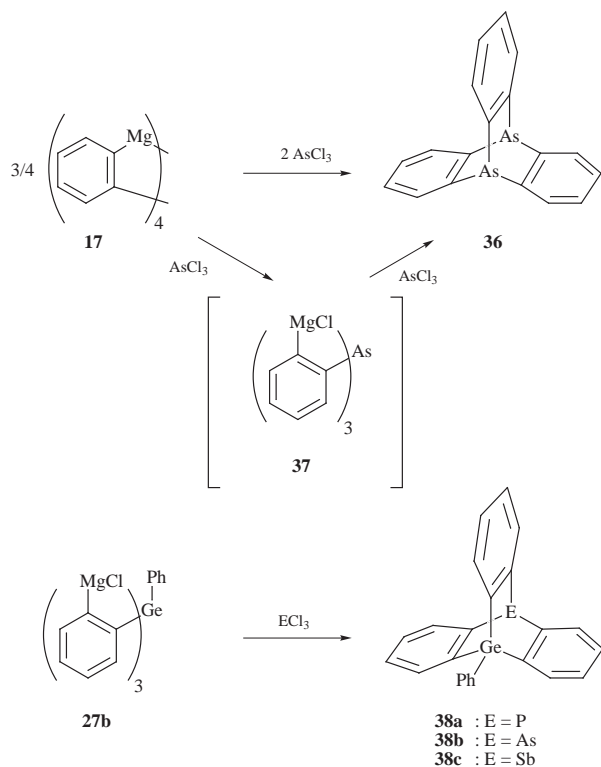
Scheme 17

prepared as early as 1927.[21] Its tendency of formation is so high that in this case, it is difficult to stop the reaction at the intermediate tri-Grignard stage of **37** (which is analogous to the readily formed and stable **27**, see Scheme 13). Probably **36** is so readily formed because it is practically strain-free; the strain imposed on the triptycene skeleton by geometric boundary conditions[22] is minimised by the inherently small valence angle of Group 15 elements. Similarly, the mixed triptycenes **38a–c** were obtained from **27** and the corresponding trichloride.[18,20]

So far, we have been less successful in preparing triptycenes with transition metals in the bridgehead positions. Reactions of **17** or **20** with CpTiCl$_3$ gave decomposition products only; with CpZrCl$_3$, ^{1}H-NMR spectroscopy indicated the formation of up to 50% of **39** (Scheme 18), but the compound decomposed above −5 °C and was not isolated in pure form.[23]
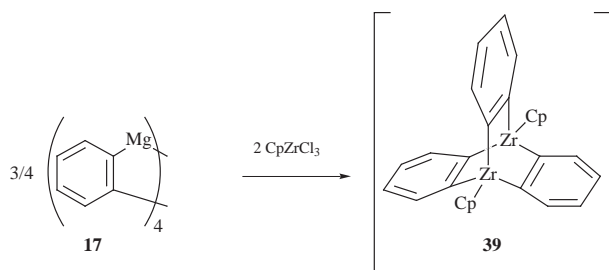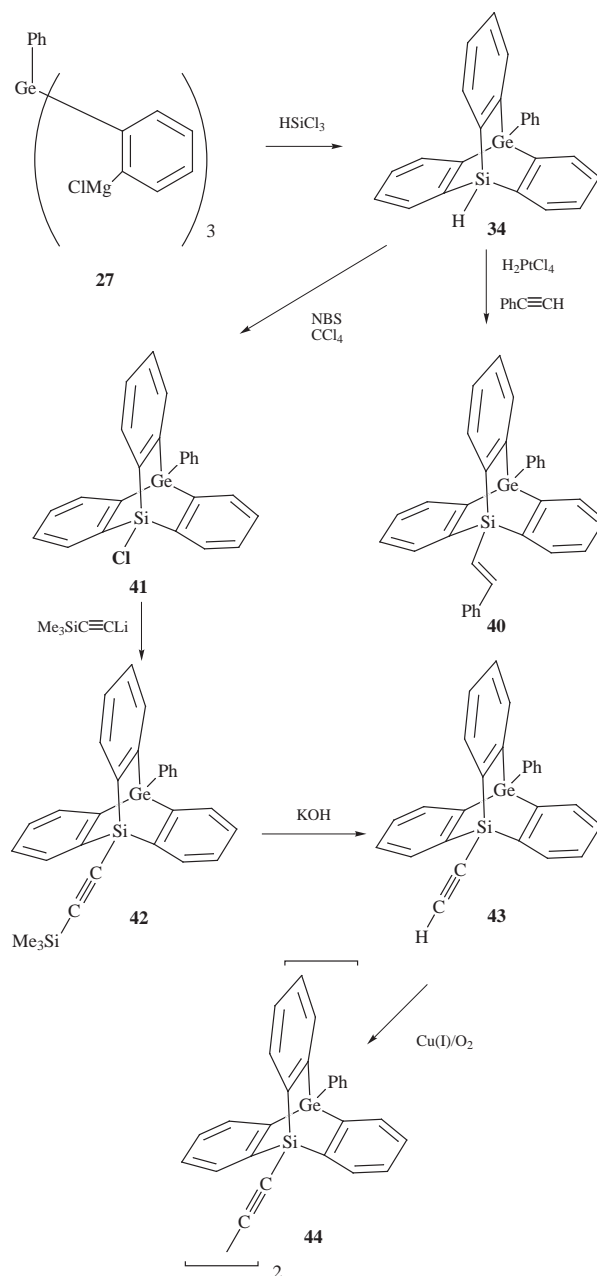
Scheme 18

4.5 Possible applications

We have also started to prepare dimetallatriptycenes with unsaturated organic substituents as they may be expected to transfer optical or electrical information along chains containing these triptycenes. Such triptycene containing polymers may have a rod-like, rigid structure, and conjugative interaction will not be blocked by the saturated Group 14 bridgehead atoms because their distance in the triptycene skeleton is shorter than

the sum of their van der Waals radii, and especially the heavier metal atoms are known to transfer interactions of this kind.

The SiH functionality of **34** (Schemes 16 and 19) offered a number of routes to functionalisation at the bridgehead. Thus, platinum catalysed hydrosilylation of phenylacetylene with **34** gave **40**; it may be considered as a model for conjugation through a double bond if the reaction is extended to alkynyl substituted triptycenes (such as **43**, *vide infra*) which offer the construction of unsaturated poly-triptycene chains.
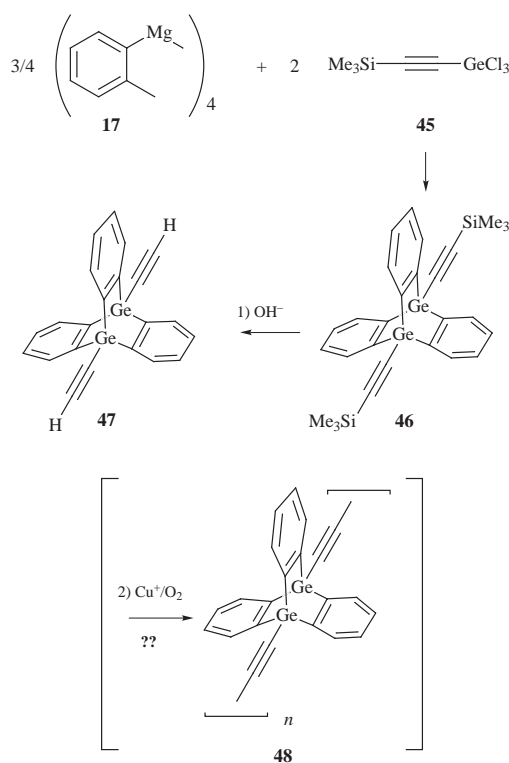
Scheme 19

On the other hand, transformation of **34** with *N*-bromosuccinimide (NBS) in carbon tetrachloride gave interestingly not the expected silyl bromide, but the chloride **41** instead. Compound **41** was substituted with lithium trimethylsilylacetylide to give **42** which was deprotected to furnish the triptycylacetylene **43**. Copper(I) catalysed oxidation of the latter gave **44** which in its turn may stand as a model for rod-like oligomers if one starts from 9,10-dialkynyltriptycenes.

The synthesis of a repeating unit for this strategy is illustrated in Scheme 20. First, the disubstituted acetylene **45** was synthesised to furnish a spacer between two triptycene units.

Reaction of **17** with **45** gave **46** (19% yield) which was deprotected in 80% yield to furnish **47**;[18] it remains to be seen if this strategy will furnish oligomeric or polymeric diacetylenes **48** on oxidative coupling.

Scheme 20

5 Conclusions

Starting from (relatively) simple organolithium chemistry, coincidental circumstances and a strong interest in difunctional organometallic species have led the author into the interesting field of 1,2-metallated benzene derivatives which show a great variety of structures and reactions. Thus, the 1,2-dimetallated benzenes may be dimers (M = Zn, Al?, Ga, In), trimers (Zn, Hg) or tetramers (Mg). The latter, *o*-phenylenemagnesium, has been applied for the synthesis of a number of novel 9,10-dimetallaanthracenes and 9,10-dimetallatriptycenes. Especially the triptycenes exhibit fascinating structural aspects,[22] and they may have promise for the preparation of compounds with interesting material properties.

It is obvious that the work described here — though mostly performed in high vacuum glass apparatus — did not develop in a scientific vacuum; many others have made important contributions to the area of polyfunctional organometallics. As a thorough overview of the entire field is beyond the scope of the present report, the interested reader is referred to more comprehensive literature.[24–27]

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