ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 600 (2000) 174–185

Journal of Organometallic Chemistry

Future prospects in organometallic chemistry of the Main Group metals: small molecules — supramolecular chemistry

Philip C. Andrews, Colin L. Raston *

Department of Chemistry, Monash University, Clayton, Melbourne, Victoria 3800, Australia

Received 13 December 1999; accepted 23 January 2000

Abstract

Bulky alkyl ligands functionalised with N-donor groups of the type 2-C$(SiMe_3)_2$(6-R-2-pyridyl), R = H or Me, stabilise unusual bonding configurations, and lead into *geminal* bimetallic complexes, including the formation of a tetrametallic zinc cluster. This chemistry is poised for major advances in mixed metal complexes of the Main Group metals and beyond. Magnesium(anthracene)$(THF)_3$ and related complexes solve the ‘missing link’ in Grignard-reagent formation with the ability to routinely prepare Grignard reagents of benzylic halides. Future directions on the use of reactive metals in synthesis will adopt the principles of green chemistry, for example in the indium(0)-promoted reactions of organic halides with various functional groups in water. Supramolecular chemistry of *o*-carboranes in association with ‘rigid’ container and saddle-shape molecules has led to new classes of inclusion complexes of varying stoichiometry, and extension of this work into materials of higher complexity, with other carboranes and larger globular molecules, and with functionalised container molecules is a realisation.

Keywords: Bulky ligands; Carboranes; Anthracenyl; Grignard; Supramolecular

1. Introduction

Organometallic chemistry is a well-established area of research endeavour in the chemical sciences, having reached a level of maturity that takes it into other areas of chemistry, and indeed into other areas of science, and beyond. We have been interested in small-molecule organometallic chemistry of the s-block and p-block metals and metalloids, mainly in the areas of (i) stabilising unusual bonding configurations [1–6], and (ii) applications in organic synthesis [7]. More recently we have extended our organometallic chemistry interests into supramolecular chemistry of carboranes [8,9]. Area (i) is concerned mainly with the use of bulky alkyl ligands functionalised with N-donor groups, of the type 2-C$(SiMe_3)_2$(6-R-2-pyridyl), R = H or Me [1–6], leading to *geminal* bimetallic complexes, including the formation of a tetrametallic zinc cluster [6]. This alone has implications in the construction of nano-structures based on aggregates of metal ions, and is relevant to the newer areas of supramolecular chemistry [10], and related areas of materials and nano-chemistry, and crystal engineering. Supramolecular chemistry deals with self-assembly processes and is particularly challenging in gaining control over inherently weak interactions, amongst other things. It has seen dramatic advances in recent years and the contribution to the field using organometallic synthons or tectons (the building blocks) is poised for it to be taken to new heights.

Our interests in the application of organometallic reagents in organic synthesis, area (ii) above, has been mainly concerned with Grignard-reagent formation using activated forms of magnesium metal, and the formation of benzylic Grignard reagents involving the addition of an organic halide to magnesium(anthracene)$(THF)_3$ in tetrahydrofuran (THF). This aspect of the work has taken us into polymer- and silica-supported materials, exemplified by the synthesis of recyclable polystyrene- and silica-supported ‘magnesium(anthracene)’ [7]. The impetus for developing these materials was to overcome the objection of generating solutions of Grignard reagents loaded with

---

* Corresponding author. Tel.: +61-3-99054593; fax: +61-3-99054597.

E-mail address: c.raston@sci.monash.edu.au (C.L. Raston)

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00081-4

anthracene, when using magnesium(anthracene)(THF)$_3$ as the source of magnesium.

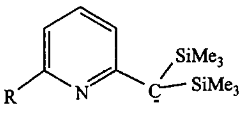
However, a growing concern in organic synthesis, which is applicable to organometallic chemistry, is the need to consider more and more the use of benign reagents, in accordance with the principles of green chemistry, which is the development of chemical processes and materials that are environmentally more acceptable than those of current state-of-the-art [11,12]. There are also moral, legal and ethical grounds to be moving in this direction. Developing green chemistry should not be an impediment to research, rather it should be an opportunity for innovation. Green chemistry also encompasses the recent area of combinatorial chemistry, viz. rapid reaction optimisation or high throughput synthesis [13]. This approach to chemical synthesis reduces the amount of solvent for each reaction, but moreover it has the potential for rapidly making new compounds, the original focus of combinatorial chemistry, and new materials. Supramolecular chemistry has the potential to play an important role in preparing new materials using combinatorial chemistry. Here the virtual libraries of the supramolecular synthons can unlock new assembly processes leading to material with novel function [14].

Herein we give an overview of our endeavours in areas (i) and (ii), and supramolecular/materials chemistry, together with some insight into possible future trends in organometallic chemistry of metal/metalloid Main Group elements in general, including aspects of green chemistry. New advances are likely to become more multidisciplinary in integrating synthesis, applications, fabrication and characterisation techniques. The latter are likely to require techniques beyond those typically used in organometallic chemistry, taking the research into the realms of solid state NMR, calorimetry, surface characterisation techniques, and more.

2. Stabilisation of unusual Main Group species

The use of bulky aryl or trimethylsilyl ligands in Main Group chemistry has been extremely important in the synthesis, isolation and characterisation of complexes in which the metal(loid) is found in an unusual valence or bonding arrangement. One prominent target in recent years has been kinetically controlled complexes, which involve the Main Group metal(loid)s in double bonding. By far the most common ligands employed are those of the 1,3,5-tri-substituted phenyls, [$R_3H_2C_6$] (e.g. R-^{t}Bu, Me_3Si, CF_3 ^{i}Pr), and $(Me_3Si)_2CH_2$. The first stabilised arsaphosphaallene, RP=C=AsR [15], incorporated the 1,3,5-(^{t}Bu)$_3$C$_6$H$_2$ ligand while the first crystallographically characterised plumanediyl dimer (RR′Pb=PbRR′) contains both Me_3Si and 1,3,5-(CF)$_3$C$_6$H$_2$ from ligand mixing [16]. The fascinating and hotly debated Ga–Ga triple bond (gallyne) was stabilised by the extremely bulky (mes$^*_2$C$_6$H$_3$) ligand (mes = 2,4,6-^{i}PrC$_6$H$_2$) [17]. A recent excellent review by Driess and Grützmacher combines both solid-state characterisation and theoretical aspects in exploring the structures and energy changes of such unusual complexes [18].

The bulky ligands that we have been interested in for some years now are the mono and bis-Me_3Si substituted pyridines. The majority of complexes that have been structurally authenticated by single-crystal X-ray diffraction have utilised the more bulky bis-substituted ligands 2-C(SiMe$_3$)$_2$(6-R-2-pyridyl) **1** (R = H) and **2** (R = Me).

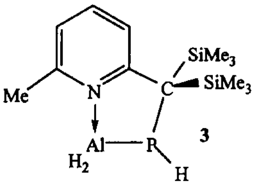


1, R = H
2, R = Me

The two trimethylsilyl groups offer kinetic protection, while the N on the pyridyl ring is an important internal coordination site that can aid stabilisation without employing additional Lewis donors or solvents. Another important aspect is that the ligand(s) are devoid of an accessible H that could possibly be utilised in low energy β-H elimination decomposition pathways. Most of the complexes synthesised and characterised are the substituted metal(loid) chlorides from the straightforward metathesis reactions of Main Group metal chlorides with the lithiated ligand [1]. These complexes are open to further reduction and Cl^- abstraction, and, as such, are useful precursors to more interesting complexes. Perhaps the most structurally interesting complexes from a previous review of this chemistry were the unusual two coordinate dimeric M(I) complexes of Li, Cu, Ag and Au [1]. More recently, in assessing the ability of **2** (=R′) to involve the Main Group elements in double bonding, the general precursor complexes, R′PCl$_2$ and R′AsCl$_2$, were synthesised and characterised [19]. Remarkably, in the solid state the phosphorus dichloride species showed internal N–P bonding with this bond being the shortest yet reported in a neutral P(III) complex. In the analogous As complex the short N–As is also present, and is comparable with the shortest bond yet described for As(III) in Me_3N–$AsMe_3$.

One route into double-bond formation is the elimination of two equivalents of HCl on reaction of R′PCl$_2$ with R′PH$_2$ [20]. Phosphorus dihydride species are normally formed from the $LiAlH_4$ reduction of phosphine, phosphinous and phosphonic sources [21]. However, the reduction of R′PCl$_2$ with $LiAlH_4$ resulted not in R′PH$_2$ but on every occasion the N-functionalised di-secondary diphosphane, (R′PH)$_2$. This was the first structurally characterised uncomplexed diphosphane, and it has the potential, due to its four possible coordination sites, to be a highly flexible ligand [22]. If a similar result can be accomplished with chiral substituents on P then there is the potential for such flexible ligands to be of great use in asymmetric synthesis and catalysis.

The diphosphane is formed in Et_2O at low temperature. If the reaction of $R'PCl_2$ with $LiAlH_4$ is carried out in the alternative ether solvent THF, then the potential single source CVD precursor for AlP, $[R'P(H)–AlH_2]_2$ (3), is formed [19]. The structure of this complex, which is dimeric via weak hydride bridging, has been established. The difference in using Et_2O and THF as the solvent medium is surprising. The AlH_3 formed in the reaction, after LiCl elimination, is stabilised by coordination of THF; probably forming a five-coordinate monomer as evidenced by previous solid-state studies [23]. The stabilised alane can then react with any $R'PH_2$ formed to give the mixed Al/P complex. However, the Et_2O complex of AlH_3 is not stable and readily breaks down to give polymeric alane, which it appears does not then react with the newly formed phosphorus dihydride species. The analogous reaction with $R'AsCl_2$ gives the same result, $[R'As(H)–AlH_2]_2$, and again from X-ray studies it is shown to exist as a dimer. The incorporation of E bound AlH_2 or GaH_2 in these complexes is potentially a great step forward in the rational design of potential single source CVD precursors which meet the necessary requirements of purity (crystalline), stability, low carbon content, volatility and low toxicity. The use of inexpensive reactants, such as $LiAlH_4$, also has clear cost benefits.



3

It was finally the reproducible preparation and characterisation of the only stable double-bonded complex incorporating one of these ligands that led us into the area of *geminal* organodimetallic complexes; a class of compounds which are yet to be fully exploited and which have the potential to alter, and improve, standard synthetic processes while at the same time producing novel outcomes [24].

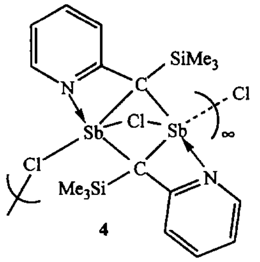
Monofunctional organometallic complexes, such as organolithium compounds (RLi), Grignards (RMgX) and alkylaluminium species (R_3Al), are invaluable and ubiquitous reagents in organic and inorganic synthesis. Due to the recognised importance of understanding structure as a guide and rational method of understanding selectivity, and as a result of better handling and analytical techniques, the last two decades has seen a proliferation in the solid-state analyses of these type of complexes. *Geminal* organometallics have the obvious advantage of having two metals of similar or differing reactivity on a single nucleophilic carbon, and hence the potential exists for reducing the number of stages in a synthetic procedure. As with the monofunctional organometallic species, an understanding of their structures is fundamental to understanding their reactivity. However, despite the increasing visibility and importance of *geminal* organodimetallic complexes as reactive intermediates in organic synthesis [25], these intriguing complexes have yet to be characterised in the solid state, or even in solution, to any degree [26].

Various *geminal* organodimetallic complexes have been described in the literature as reactive intermediates, though most are dimetallic methanes, $[CH_2M_2]$, and/or contain only one type of metal. Thus, selectivity and application is seriously reduced. Most notably Knochel (Mg/Zn) [27], Kauffmann (Li/Sb, Bi, Sn, Pb) [28] and Sato (Li/Sn) [29] have investigated the synthetic utility of mixed metal systems.

In solution, control over reactivity and selectivity will only be obtained by the development of *geminal* compounds that contain different metals: complexes comprising only of p-block elements can be highly selective ‘soft’ nucleophiles while the presence of an s-block element (Groups 1 and 2) provides for not only increased, and significantly differing, reactivity but is also a potential route into other Main Group or transition-metal *geminal* complexes. Unexplored and potential uses for these type of complexes outside of synthesis include single-source precursors for CVD and mixed metal oxides, the technological applications of which are realised in their use in thin films, catalysis and as chemical detectors [30].

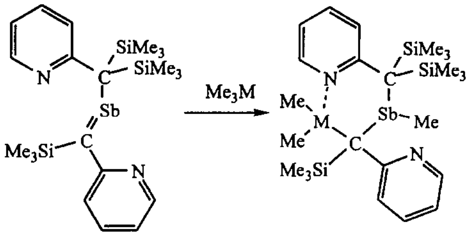
Marek and Normant recently reviewed the, as yet, limited but potentially exciting synthetic usefulness of organodimetallic complexes [25], as had Kauffmann [28] with regards to his own work on p-block methylithium derivatives much earlier in 1982. In an age rightfully concerned with the ‘greening’ of chemistry, any move to reduce the number of steps in a chemical reaction, and hence solvents and accompanying chemical wastes, is highly desirable. Therefore an important outcome would be not only to produce novel pathways to important new molecules but to develop new reagents capable of making already important molecules more efficiently and cleanly.

We have synthesised and structurally characterised a series of Group 13/15 *geminal* organodimetallic complexes, by carbometallation of a stiba-alkene, and the first 1,1-dizinc complex as well as a 1,1-distibine polymer. The 1:1 metathesis reaction of RLi with $SbCl_3$ produces the expected antimony dichloride species as yellow crystals [3]. On warming in toluene for 4 h at 60°C, a yellow precipitate forms, which can be isolated and redissolved in CH_2Cl_2. Crystallographic analysis revealed that Me_3SiCl elimination had occurred producing a transitory stiba-alkene species, [Py(Me_3Si)-C=SbCl], which undergoes [2 + 2]-cycloaddition and polymerisation via intermolecular Sb···Cl interactions, **4** [4]. What is not apparent from the structure is that cycloaddition resulted in an unusual *cis* arrangement for the pyridyl rings relative to the slightly buckled four-membered $(CSb)_2$ ring, which is capped by a bridging Cl^-.



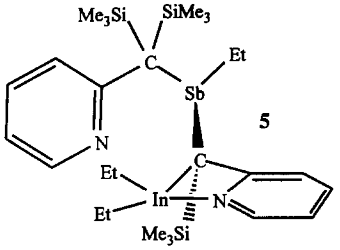
4

While Me_3SiCl elimination has to be thermally promoted in the $RSbCl_2$ complex, elimination occurs in the R_2SbCl complex from about −40°C. The addition of two molar equivalents of RLi·tmeda to $SbCl_3$ in THF at −78°C produces a yellow solution. On warming slowly to room temperature over 12 h, a deep-red solution is produced. Removal of THF and addition of hexane allows LiCl to be removed by filtration and the subsequent in vacuo removal of hexane leaves a stable thick red oil. This red oil has been shown by both EIMS and ESMS to be the stiba-alkene species, [Py$(Me_3Si)_2$C=Sb(Me_3Si)Py] [5]. To date, only one complex with a stable C=Sb bond has been described in the solid state [31]. We then subjected the red oil to a series of carbometallation reactions in the hope of producing *geminal* organodimetallic complexes by an entirely new route. The addition of Me_3M (M = Al, Ga, In), at low temperature, results in the carbometallated products, Eq. (1). Crystal structures obtained on the Al and Ga complexes, Eq. (1), show the complexes adopt six-membered chiral dimetallic heterocycles. In these complexes, ring closure is accomplished by N_{py}–M dative bonding.



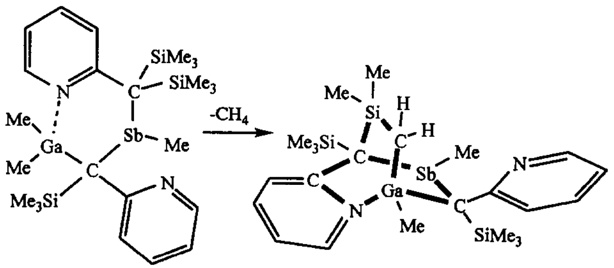
(1)

Crystals of X-ray quality have not yet been obtained for the analogous In complex. However, the addition of Et_3In produced pale-pink crystals, which on analysis were found to adopt a different structure from that found for the above Al and Ga compounds. Instead of forming the six-membered ring, the In preferentially forms a four-membered ring with N on the alternative pyridyl ring, **5**. There is evidence, though, that the In does bond with the other pyridyl ring; not directly with the pyridyl N but with the π-electron density found above the closest C–N bond.



5

On warming the Ga product to 60°C for several hours, or on addition of the THF solution of Me_3Ga to the red oil in hexane at ambient temperature, MeH is eliminated to produce a new Sb/Ga *geminal* complex with a bicyclo[2.2.2]-type core, Eq. (2). The transformation does not occur quantitatively but only in ca. 40% yield [32]. The reaction with Et_2Zn did not produce the carbometallated product but resulted in transmetallation to produce the first 1,1-dizinc complex, $[Py(Me_3Si)CZn]_4$, which exists as a tetramer with S_4 symmetry [6]. This complex is of great interest in its relationship to Simmonds–Smith cyclisation reactions, which involve a zinc carbenoid species. The analogous reaction with more electropositive metals (e.g. Mg) should produce similar 1,1-complexes.



(2)

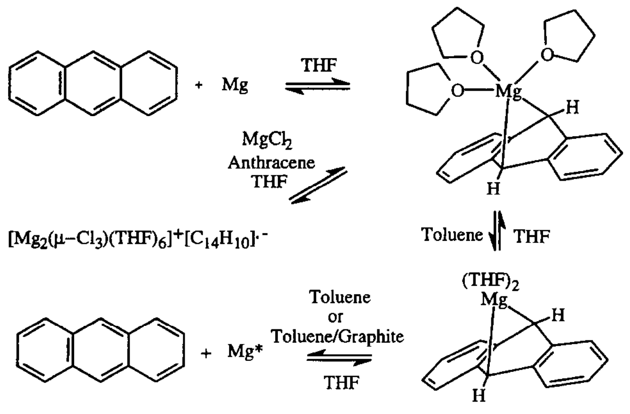
2.1. Other future prospects

There is great potential in exploring this new family of reactive intermediates. The challenge for the future is to synthesise complexes that contain mixed metals and to move away from simple methylene systems into groups that have a broader synthetic appeal, including the incorporation of chiral substituents. Many general synthetic methods already exist that can be utilised and expanded to turn such *geminal* organodimetallics from esoteric 'display' complexes to valuable, functioning synthetic tools. The other major application, particularly for small-molecule complexes, will clearly be as single-source precursors for CVD purposes, especially since any complex containing a Group 1 or 2 metal can be used as a basic building molecule for other Main Group and transition-metal complexes via simple transmetallation reactions. The double carbo- or hydrometallation of alkynes, or analogous metallation of vinylic organometallic compounds (e.g. $R_2C{=}C(R')$-$SnMe_3$) has yet to be fully exploited in the preparation of small-molecule organodimetallics.

3. Applications of Main Group metals and compounds in synthesis

Mg(anthracene)$(THF)_3$ is a versatile reagent that can react in a variety of ways [7,33–37]. We have focused mainly on its application, and the application of related magnesium–anthracene complexes in forming benzylic Grignard reagents. Magnesium–anthracene complexes are ambivalent in acting as diorganomagnesium species (electrophilic attack on the anthracene with heterolytic cleavage of the Mg–C bonds) or as sources of magnesium (homolytic cleavage of Mg–C bonds). For the latter there is a clear distinction between (i) the complexes acting as soluble sources of zero-valent magnesium or as single electron donors, and (ii) the complexes forming highly activated magnesium via equilibration with anthracene and metal which then reacts with the organic substrate. For (ii) the anthracene can be described as a phase-transfer catalyst for generating metallic magnesium, as long as it is not consumed in side reactions.

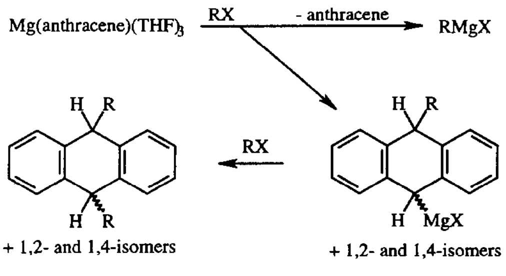
Mg(anthracene)$(THF)_3$ is an orange, pyrophoric compound, conveniently prepared in high yield directly from magnesium powder with anthracene in THF, Scheme 1. The same complex has also been prepared electrochemically using sacrificial magnesium [38] by the reaction of sodium anthracene and magnesium bromide in THF [39], and by treating Mg(butadiene)$(THF)_n$ with anthracene in THF [40]. It is sparingly soluble in THF [41,42], decomposing in non-donor solvents such as toluene, benzene and hexane to anthracene and elemental magnesium, as mirrors or highly activated, finely divided metal. In toluene and benzene this decomposition occurs via a yellow intermediate that analyses as the bis-THF adduct, Scheme 1 [43–45]. The presence of graphite in toluene or diethyl ether accelerates the decomposition of Mg(anthracene)$(THF)_3$ to its constituents, affording finely divided magnesium (particle size ca. 6 μm), which is dispersed on the graphite flakes. This form of magnesium is non-pyrophoric yet highly activated. Magnesium also reacts with a variety of substituted anthracenes in THF [43–49]. In addition, Mg(anthracene)$(THF)_3$ and magnesium-substituted anthracene–THF donor complexes undergo rapid donor ligand displacement reactions with a variety of N- and O-donor solvents, including TMEDA, (−)-sparteine, and dimethoxyethane [43,44].



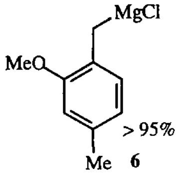
Scheme 1.

The products from the reactions of magnesium anthracene complexes with organic halides depend on the nature of the organic halide, the choice of solvent and temperature. Benzylic halides afford Grignard reagents in high yield, and allylic halides afford Grignard reagents in modest yields. With a few exceptions, other halides result in products from the reduced anthracene in the complexes acting as single electron donors, or as nucleophiles, Scheme 2 [34,50–52]. Benzylic and allylic type Grignard reagents can be difficult to prepare or are inaccessible using magnesium powder and turnings as in the classical method of Grignard-reagent formation. Magnesium–anthracene complexes are soluble sources of magnesium and further restrict Wurtz coupling.

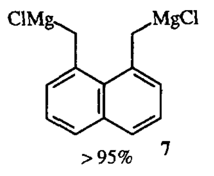
A typical experiment in preparing a Grignard reagent using magnesium–anthracene complexes involves the slow addition of a THF solution of the organic halide to a stoichiometric amount of the complex as a slurry in THF usually at 0°C or ca. 20°C and with a target concentration of the Grignard (or poly-Grignard) reagent close to 0.1 M. Immediately after addition of the first few drops of the halide solution, the mixtures turn from orange–yellow to deep-green (radical anion of anthracene), which persists until all the magnesium complex is consumed and addition of organic halide complete. Unusual benzylic Grignard reagents readily prepared using magnesium–anthracene complexes include **6**–**9**.



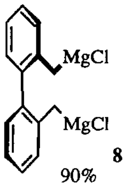
Scheme 2.



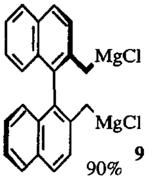
6



7



8



9

Magnesium–anthracene complexes undergo electron-transfer reactions in forming Grignard reagents of benzylic halides [34,48,51,52]. Where addition to anthracene prevails, Scheme 2, two reaction pathways are plausible, namely concerted nucleophilic substitution and formation of the diradical cage [Mg^{2+}, (anthracene)$^{\bullet -}$, $RX^{\bullet -}$]. In the absence of any detectable radical intermediates, this cage must collapse instead of releasing $RX^{\bullet -}$ and/or $R^{\bullet}$.

Benzylic and allylic Grignard reagents are formed using organic chlorides and bromides, although the organic chlorides are more reliable. Reactions involving other types of organic halides either (i) give exclusively the Wurtz-coupled product, e.g. benzyl iodide, (ii) fail to react, e.g. chlorobenzene and 1,2-diflurobenzene, or (iii) give predominantly addition product(s), Scheme 2. The last occurs for bromobenzene (along with proton abstraction from THF), vinyl bromide, and various alkyl halides [50,51,53,54]. With primary and secondary alkyl halides in THF the major products are the dialkyl substituted di-hydroanthracenes (9,10- and 1,4-isomers) and with *tert*-butyl halides the major products are the mono-alkyl substituted dihydroanthracenes (9- and 2-isomers of the substituted anthracenes), Scheme 2 [34,48,50,53].

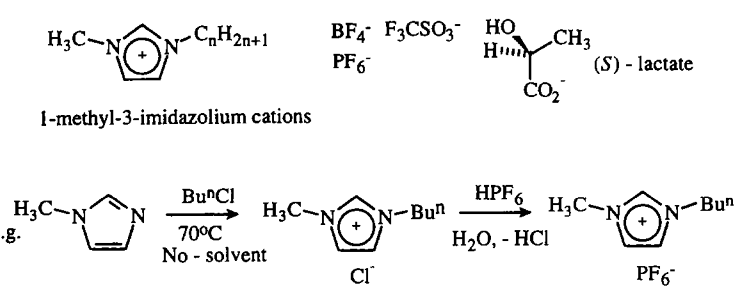
Both silica- and polymer-supported magnesium anthracene complexes [49,55,56] have been developed and shown to deliver magnesium to benzylic halides affording the corresponding Grignard reagents. This overcomes the practical inconvenience of having Grignard-reagent solutions loaded with anthracene when using Mg(anthracene)$(THF)_3$ and related compounds as the source of magnesium.

3.1. Future prospects

Grignard reagents of benzylic halides are often inaccessible using classical techniques involving bulk metal, or even using highly activated metal. The use of magnesium–anthracene reagents can be regarded as a missing link in preparing Grignard reagents, and procedures for preparing all classes of Grignard reagents are now available, using these complexes or supported analogues, magnesium powder, turnings or the various forms of activated magnesium, including that derived from using Mg(anthracene)$(THF)_3$ as a promoter/catalyst depending on the nature of the organic halide [7]. The supported magnesium–anthracene can be readily recycled and can be used in a column. This offers new directions in the application of Grignard reagents, and also the application of the material as potent reducing reagents without the resulting solutions being loaded with anthracene.

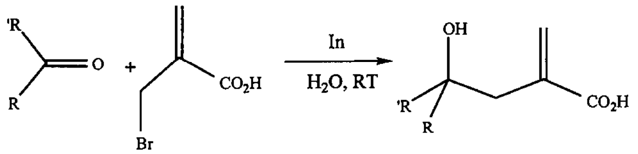
A century has passed since the discovery of the utility of organomagnesium chemistry in synthesis, initially in situ (Barbier) then the reaction of preformed Grignard reagents, and the technology has served industry well. However, there is a need to readdress the applications taking into account the impact the technology has on the environment, and how it can be improved. Several approaches are possible including the use of ionic liquids as the reaction medium and surprisingly using water as a solvent. Indeed, Li and Zhang [57] have established that many in situ Grignard trapping reactions can be carried out in water, despite the prospect of any Grignard reagent formed from contact of the metal with an organic halide being spontaneously quenched, namely conversion of the carbanion to the simple hydrocarbon. Seemingly the hydrophobic effect in water whereby the organic halide and the reactive organic substrate shroud the magnesium particles and any Grignard reagent formed is then trapped by the substrate [58]. The hydrophobic effect itself leads to increased rates of reaction of organic compounds in water [58]. The significance of this work is that water is a benign solvent; it is non-toxic, non-flammable and non-explosive, and leads to minimal waste. It can be regarded as moving towards the 'ideal synthesis' [59], which is a measure of the environmental acceptability of a reaction pertaining to high yield and atom efficiency, safety, available materials, few steps, no wasted reagents, and is simple. Another measure of acceptability is the so-called *E* factor, which is the ratio of waste in kg divided by 1 kg of product [60].

Li and Chan have recently described in some detail [56] the variety of reactions that can be undertaken in aqueous media, and the range of metals that can be used: Sn [61], In [62], Bi [63], Zn [64]. Mostly these metals are to be found in the p-block of the Periodic Table and are considered 'soft' in comparison to the more traditional metals used as reactive intermediates, Li, Na, Mg, which demand anaerobic and water-free conditions. By far the most common reaction is the Barbier–Grignard reaction of an allyl halide with a carbonyl substrate in the presence of the metal. While most industrial interest and application will centre on the use of tin, as a result of its abundance and low cost, there are associated problems of known environmental toxicity. It is noteworthy then, that indium(0) is the



Scheme 3.

most effective metal in promoting Barbier–Grignard type reactions in water [57]. A typical reaction is shown in Eq. (3) [57].



(3)

The advantages of the in situ trapping of the organometallic reagents for indium(0)-promoted reactions, include: indium(0) is unaffected by boiling water and alkali; no oxides form on the metal surface on exposure to air; the first ionisation potential is low (5.785 eV) and encourages electron-transfer chemistry; indium(0) is easily recovered by simple electrochemical deposition on an aluminium cathode; and there is a tolerance of a variety of functional groups, e.g. no need to mask free hydroxyl substituents, which is especially useful in carbohydrate and protein chemistry [65]. The problem with protection and deprotection is that it results in low percentage atom economy (large *E* factor) and considerable waste.

While many metals (Sn, Zn, Bi, In) have been found to promote alcohol formation via the addition of allylic halides to carbonyls in water, the challenge will be to expand the scope and potential of using metal and/or mixed metal reagents in water for other important synthetic transformations, e.g. reactions at C=C, C=N, deprotonations, enantioselective synthesis. One exciting possibility that may promote such an advance is the use of controllable microwave technology recently developed for high-temperature aqueous-based syntheses [66]. It should be possible to prevent arcing of metal turnings in the batch reactor, thereby allowing access to a whole new range of experiments and reaction conditions. Also, using the metal catalytically will be far more atom-efficient and is where electrochemical processes could become very important. The elucidation and application of solution and solid-state structural chemistry is only now being fully explored and exploited on traditional organometallic, amide, and phosphide reagents. The associated knowledge and techniques, which have been built up in this area, will need to be applied to studying the reaction mechanisms, intermediates and selectivity, of water-based metal reactions if a rational approach to their use is to develop in the future. Perhaps with this knowledge, a great majority of the known organic synthetic procedures could themselves become transformed.

The use of ionic liquids as the reaction medium in organometallic synthesis, and where the use of water in the in situ approach is excluded, has exciting possibilities because of the special properties they have and associated advantages over conventional organic solvents [67]. Examples of ionic liquids are shown in Scheme 3 [67,68].

The use of ionic liquids in synthesis follows from adopting the principles of green chemistry, and the important characteristics include:

- They have negligible vapour pressure, allowing distillation/sublimation of the product(s).
- They have reduced risk of combustion and reduced organic vapour emissions.
- The use of expensive high-pressure apparatus is not necessary.
- They are thermally robust and chemically inert.
- They minimise side reactions due to the tendency of ionic liquids to suppress conventional solvation and solvolysis phenomena.
- They have tunable parameters (e.g. length of alkyl chain changes their properties).
- They can solubilise ionic complexes, organics, and inorganics.
- They have a wide temperature range in the liquid phase, ca. − 80 to 200°C, and this facilitates excellent kinetic control.
- The ease of product separation and recycling potential.
- There is scope for imparting chirality in the product by using chiral ionic liquids (cation and/or anions).
- They have large electrochemical windows allowing electrochemical synthesis, as well as the use of reactive metals in synthesis.
- The ease of their preparation with potential for use of the ionic liquids on an industrial scale [68].

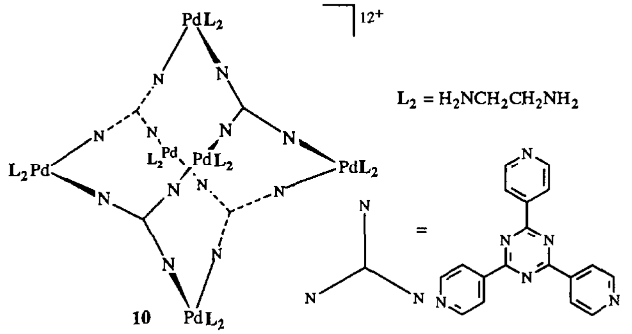
All of these have implications in using reactive metals in the organic synthesis of new organometallic reagents including Grignard reagents, lithium reagents, organoaluminium, -gallium, -tin, -bismuth and more. In the bigger picture of synthesis, the development of a benign synthetic protocol is essential in developing benign synthesis of important pharmaceuticals. In addition, green chemistry considerations aside, the net benefits of using ionic liquids as reaction medium are overwhelming. Why would you not want to use ionic liquids as a matter of routine?

4. Supramolecular chemistry: the search for new materials

4.1. Confinement of carboranes

Studies on the confinement of icosahedral carboranes ($C_2B_{10}H_{12}$ = dicarbadodecaborane(12)) in a variety of host molecules afforded novel self-assembled materials, and have implications in the confinement of related globular molecules, and in the separation of the *o*-, *m*-, *p*-carboranes [8,9]. A common type of interaction in this supramolecular chemistry is hydrogen bonding involving the C–H groups, including the formation of bifurcated hydrogen bonds ($C–H\cdots(N,O)_2$), involving for example cyclotriveratrylene (CTV), which is calculated to be energetically favoured by 5.48 kcal mol^{-1} for O-donors of the model compound dimethoxybenzene Fig. 1 [69–74]. Other types of interaction include $C–H\cdots\pi$ Coulombic interactions between the polarised C–H bonds and the base π-electrons of aromatic rings, Fig. 1(a). This is calculated to be energetically favoured by 2.74 kcal mol^{-1} [69]. Shape complementarity of the carborane with CTV and related molecules is important, noting the spherical nature of carboranes with a diameter of ~ 8.0 Å. A less common type of interaction involves $B–H\cdots H–N$ interplay with amines, Fig. 1(d) [75]. Carboranes also have a rich organometallic chemistry associated with direct metal–carbon bonds [76,77].

Water-soluble host–guest complexes of carboranes involve α-, β- and γ-cyclodextrins [78], and a self-assembled ionic capsule, **10**, arising from interplay between ethylenediamine palladium^{2+} ions and four triply bridging pyridyl ligands, which has a large internal volume capable of incorporating four *o*-carborane molecules, presumable as a tetrahedral aggregate [74].



10

Our interests have been in hydrophobic host container molecules such as calix[5]arene [72] and CTV [69,72,73]. These give a diverse range of complexes that can have excess host or excess carborane, giving com-

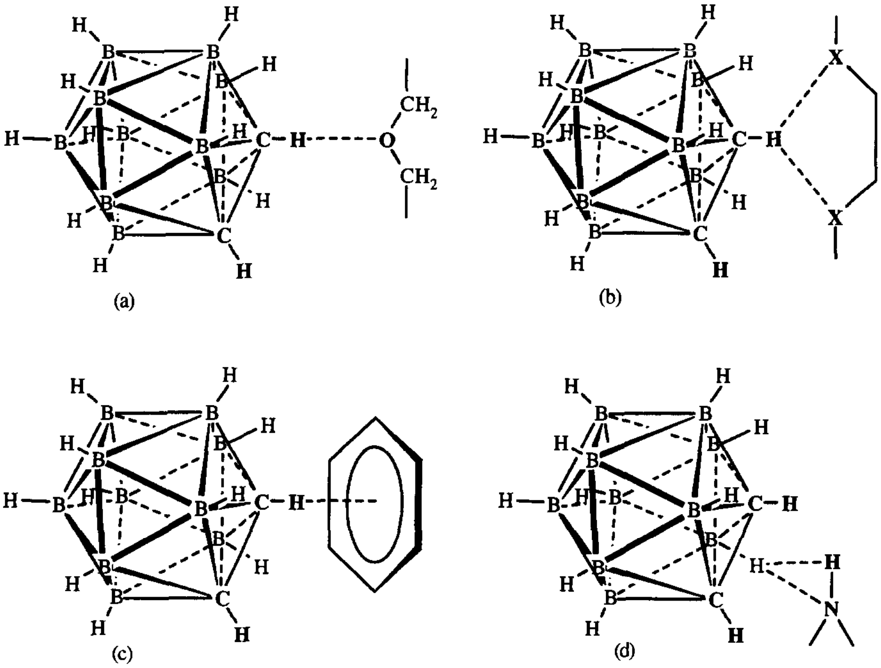


Fig. 1. Established types of interactions of carboranes (shown for the *o*-isomer): (a) classical $C–H\cdots O$ hydrogen bond, (b) bifurcated hydrogen bond, X = O (1,2-dimethoxylbenzene systems), N (in *o*-phenanthroline), (c) non-classical $C–H\cdots\pi$ hydrogen bond, and (d) $B–H\cdots H–N$ interplay.

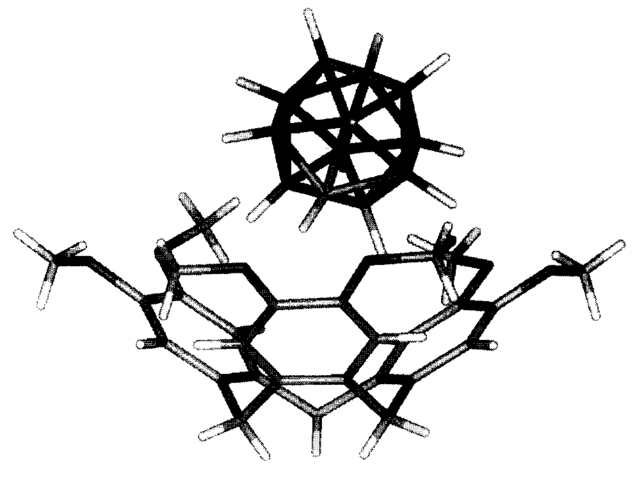


Fig. 2. Structure of the supermolecule (o-carborane)$\cap$(CTV) in the 1:2 complex [73].

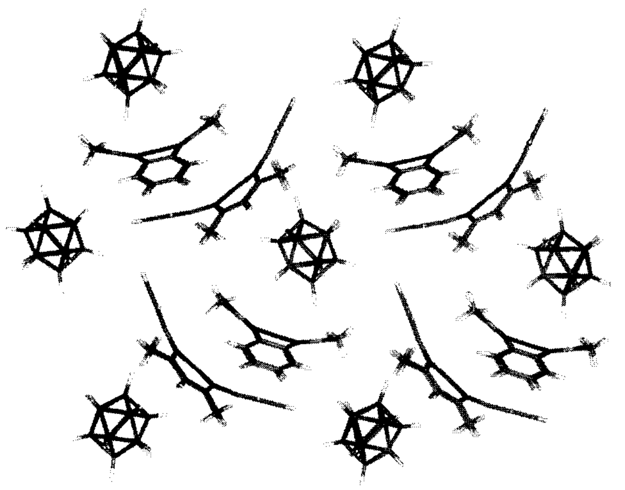


Fig. 3. Continuous structure of the Ni(II) macrocycle, 5,7,12,14-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinenickel(II) with o-carborane [76].

plicated strucutures, yet with a common structural motif of a 1:1 ball and socket nano-structure for the two supramolecular synthons. Calixarene complexes available include (o-carborane)(calix[5]arene)(CH_2Cl_2), (o-carborane)(calix[5]arene)(C_7H_8), carborane)(calix[5]-arene)$_2$(CH_2Cl_2)$_{0.5}$ [72] and (o-carborane)$_2$(calix-[5]arene) [73] where the second o-carborane forms a weak association with the hydroxy groups of the calixarene through one triangular face of the icosahedron. CTV forms two complexes with o-carborane with a 1:2 and 2:1 ratio of two synthons [69]. The one rich in CTV has the additional host CTV forming a zig–zag π-stacked column. Non-bonded contact distances of the supermolecule (o-carborane)$\cap$(CTV) in the 1:2 complex show that three hydrogens of a triangular face of the icosahedron are directed towards the aromatic rings of the CTV, albeit unsymmetrically, Fig. 2. This most likely arises from the energetically favoured $C–H_{carborane}\cdots\pi$ hydrogen bonds to two aromatic rings of the CTV versus repulsion between the B–H and the third aromatic ring of the CTV. In (o-carborane)$_2$(CTV) [73] one of the carborane molecules forms three symmetry-equivalent bifurcated hydrogen bonds to the methoxy groups of three equivalent CTV molecules in a hexagonal 2D hydrogen-bonded network.

A rigid saddle-shaped Ni(II) macrocycle, 5,7,12,14-tetramethyldibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinenickel(II), also binds o-carborane in the methyl group lined 'cavities' of the self-associate dimeric species, which thus acts as a divergent homotopic receptor, Fig. 3. Similar structures are found with the globular phosphorus chalcogenides P_4(S or Se)$_3$ in place of the carborane [79,80].

Diaza-18-crown-6 forms a 1:1 host–guest complex with o-carborane [71], involving $C–H_{carborane}\cdots O$ hydrogen and B–H···H–N interactions, and while mono-aza-18-crown-6 also forms in a 1:1 complex, it is an intercalation compound with alternating layers of o-carboranes and crown ethers. The striking difference in structure between the two complexes reflects the delicate balance between weak intermolecular interactions, host–host, host–guest and guest–guest, which are within the realms of crystal packing forces. ^{1}H-NMR in studies in benzene at 25°C for a range of concentration of diaza-18-crown-6 for a fixed o-carborane concentration (0.07 M) indicate a low equilibrium constant (< 5 M^{-1}), Eq. (4). Interestingly for m-carborane there is little or no complexation and there is no complex formation in the solid state.

$$o\text{-carborane} + \text{diaza-18-crown-6} \overset{\text{benzene}}{\rightleftharpoons} [(o\text{-carborane})\cap(\text{diaza-18-crown-6})] \quad (4)$$

The 1:1 complexes of hexamethylphosphoramide (HMPA) with o-, m- and p-carboranes [70], have extensive C–H···O hydrogen bonding and afford different supramolecular structures, in accordance with their different arrangement of C–H sites, dimers for the o-isomer, and extended arrays for the other isomers. Extended arrays are also found in the remarkable ternary system (C_{70})(o-carborane)(CTV)(1,2-dichlorobenzene) [73], where each o-carborane interacts with two CTV molecules and in turn, each CTV is hydrogen bonded to two carboranes forming an infinite helical chain, Fig. 4. Even more remarkable is that in the absence of the carborane C_{70} fails to form a complex with CTV, whereas C_{60} affords (C_{60})$_{1.5}$(CTV), which is one of two complexes formed in the absence of the carborane, the other being (C_{60})(CTV).

4.2. Future prospects

The structure of the ternary system (C_{70})(o-carborane)(CTV)(1,2-dichlorobenzene) [73] is the first lead

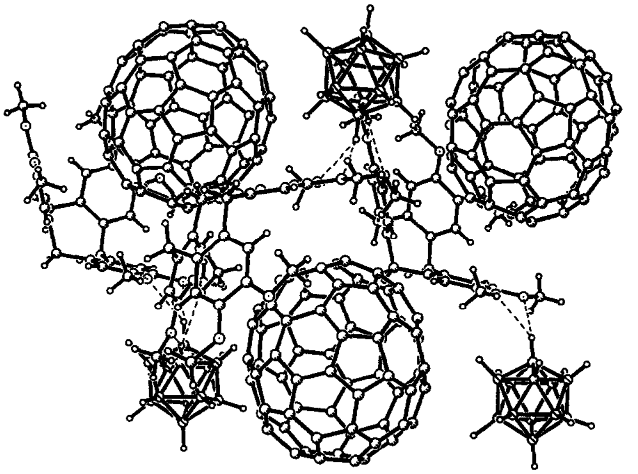


Fig. 4. Side view of a helix in [(C_{70})(*o*-carborane)(CTV)(1,2-dichlorobenzene)] showing the binding of C_{70} molecules within the CTV bowls [70].

into structures of higher complexity, and is a clue to the types of self-assembled materials that are likely to be accessible based on combinations of carboranes with other globular molecules, notably fullerenes including C_{76}, C_{78} and larger fullerenes as well as the endohedral fullerenes, e.g. $Ca@C_{60}$, and container molecules, with the choice of solvent another key consideration. Adding to the complexity is the use of functionalised carboranes as supramolecular synthons and this area is starting to be developed by others [81]. There is also the extensive array of carboranes beyond the $C_2B_{10}H_{12}$ icosohedral compounds, including for example $CB_{10}H_{12}^-$. Then there are the supramolecular possibilities of the recently reported icosahedral species *closo*-$B_{12}(CH_3)_{12}^{2-}$, which has a more hydrophobic surface, and is much larger than the simple carboranes [82]. Higher complexity is also possible through incorporating functional groups on the host molecules capable of binding metal ions while maintaining the binding of the carborane and/or other globular molecules.

The ground rules for complexation/confinement/molecular recognition of globular species are beginning to emerge. Foremost is the use of rigid concave host molecules with complementarity of curvature with the cage molecule, since any pre-organisational energy requirements of flexible host molecules may be at the expense of host–guest complexation. Moreover, combining carboranes with container molecules capable of bifurcated hydrogen bonding with the carborane (such as CTV) offers scope for swaying the competing energies of interaction in favour of host–guest complexes (for cage molecules other than for carborane, which has been demonstrated for C_{70}) where the host–guest components otherwise fail to assemble.

Advances in the area could make use of combinatorial chemistry, as applied to materials chemistry [83], whereby the possibilities of several components coming together in an ordered structure is mapped out, with additional synthetic parameters including the choice of solvent, temperature and the ratio of the components. Domains of reaction wells showing crystallisation of the self-assembled materials are a simple marker for further exploration within the boundary conditions. However, this approach does not address the possibility of self-assembly cascading processes forming discrete supermolecules in solution. To study this will require rapid screening of the kind of 'library' or large arrays of solutions, using mass spectrometry, NMR and other spectroscopic techniques. The choice of solvent can play a vital role in determining the crystal packing and overall topology of the systems. Interactions involving carboranes with themselves, including the formation of micelle like species, and with solvent and other molecules has potential in assembling complex structures.

A major advance in supramolecular chemistry is the ability to construct large encapsulating supermolecules assembled by hydrogen-bonding [84] or metal coordination chemistry [74,85,86]. For the latter, the very large internal void accommodates, and incarcerates, four carboranes [85]. Incarceration of even larger Main Group cage species is possible. In this context the recent work of Harthorne et al. in preparing liposomes with amphophilic carboranes incorporated into the phospholipid bilayer, which can carry massive amounts of water-soluble boranes, is noteworthy [86].

Supramolecular chemistry has exciting possibilities in stabilising new species, in their separation from complex mixtures, and in generating novel structures and materials. Further insight into the level of complexity possible also comes from tetrameric macrocycles, mercuracarborand-4 and octaethylmercuracarborand-4, which act as hosts for *closo*-$B_{12}H_{12}^{2-}$, as well as related globular borane anions *closo*-$B_{10}H_{10}^{2-}$ and *closo*-$B_{10}I_{10}^{2-}$ [76,77]. Furthermore the controlled formation of supramolecular arrays of carboranes on surfaces is a synthetic challenge in gaining access to surfaces with novel function.

References

[1] T.R. van den Anker, C.L. Raston, J. Organomet. Chem. 500 (1995) 289.

[2] (a) P.C. Andrews, S.J. King, C.L. Raston, B.A. Roberts, Chem. Commun. (Cambridge) (1998) 547. (b) P.C. Andrews, T.R. van den Ancker, S.J. King, C.L. Raston, B.A. Roberts, unpublished results.

[3] C. Jones, L.M. Engelhardt, P.C. Junk, D.S. Hutchings, W.C. Patalinghug, C.L. Raston, A.H. White, Chem. Commun. (Cambridge) (1991) 1560.

[4] P.C. Andrews, C.L. Raston, B.W. Skelton, V.-A. Tolhurst, A.H. White, Chem. Commun. (Cambridge) (1998) 575.

[5] P.C. Andrews, P.J. Nichols, C.L. Raston, B.A. Roberts, Organometallics 18 (1999) 4247.

[6] P.C. Andrews, C.L. Raston, B.W. Skelton, A.H. White, Organometallics 17 (1998) 779.

[7] C.L. Raston, Applications of magnesium anthracene in forming Grignard reagents, in: H.G. Richley (Ed.), Grignard Reagents — New Developments, Wiley, New York, 1999, pp. 277–298.

[8] P.C. Andrews, M.J. Hardie, C.L. Raston, Coord. Chem. Rev. 189 (1999) 169.

[9] M.J. Hardie, C.L. Raston. Chem. Commun. (Cambridge) (1999) 1153.

[10] J.-M. Lehn, Supramolecular Chemistry, Concepts and Perspectives, VCH, Weinheim, 1995.

[11] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford Science, London, 1998.

[12] P.T. Anastas, T.C. Williamson, Green Chemistry: Environmentally Benign Chemical Synthesis and Processes, Oxford Science, London, 1998.

[13] S.R. Wilson, W. Czarnik (Eds.), Combinatorial Chemistry — Synthesis and Applications, Wiley, New York, 1997.

[14] M.C. Calama, R. Hulst, R. Fokkens, N.M.M. Nibbering, P. Timmerman, D.N. Reinhoudt, Chem. Commun. (Cambridge) (1998) 1021.

[15] H. Ranaivonjatavo, H. Ramdane, H. Gornitzka, J. Escudié, J. Satgé, Organometallics 17 (1998) 1631.

[16] K.W. Klinkhammer, T.F. Fässler, H. Grützmacher, Angew. Chem. Int. Ed. Engl. 37 (1998) 124.

[17] (a) J. Su, X.-W. Li, R.C. Crittendon, G.H. Robinson, J. Am. Chem. Soc. 119 (1997) 5471. (b) Y. Xie, R.S. Grev, J. Gu, H.F. Schaefer III, P.v.R. Schleyer, J. Su, X.-W. Li, G.H. Robinson, J. Am. Chem. Soc. 120 (1998) 3773.

[18] M. Driess, H. Grützmacher, Angew. Chem. Int. Ed. Engl. 35 (1996) 828.

[19] P.C. Andrews, T.R. van den Anker, S.J. King, C.L. Raston, B.A. Roberts, unpublished results.

[20] A.H. Cowley, Polyhedron 3 (1984) 389.

[21] D.E.C. Corbridge, Phosphorus, An Outline of Its Chemistry, Biochemistry and Technology, fourth ed., Elsevier, Amsterdam, 1990, Section 4.2.

[22] P.C. Andrews, S.J. King, P.J. Nichols, C.L. Raston, B.A. Roberts, unpublished results.

[23] (a) I.B. Gorrell, P.B. Hitchcock, J.D. Smith, J. Chem. Soc. Chem. Commun. (1993) 189. (b) M.G. Gardiner, C.L. Raston, Coord. Chem. Rev. 166 (1997) 1.

[24] A. Hirai, M. Nakamura, E. Nakamura, J. Am. Chem. Soc. 121 (1999) 8665.

[25] I. Marek, J.-F. Normant, Chem. Rev. 96 (1996) 3241.

[26] (a) H.-J. Gais, J. Vollhart, H. Guenther, D. Maskau, H.J. Lindler, S. Braun, J. Am. Chem. Soc. 110 (1988) 978. (b) M. Hogenbirk, G. Schat, O.S. Akkerman, F. Bickelhaupt, J. Am. Chem. Soc. 114 (1992) 7303. (c) F. Bickelhaupt, J. Organomet. Chem. 475 (1994). (d) A.F. Chiffley, J. Evans, W. Levason, M. Webster, Organometallics 14 (1995) 1522. (e) M. Layh, W. Uhl, Polyhedron 9 (1990) 277.

[27] P. Knochel, in: G.S. Silverman, P.E. Rakita (Eds.), Handbook of Grignard Reagents, Marcel Dekker, New York, 1996 (Chapter 30).

[28] T. Kauffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 410.

[29] T. Sato, S. Ariura, Angew. Chem. Int. Ed. Engl. 32 (1993) 105.

[30] (a) A.C. Jones, Chem. Soc. Rev. (1997) 101. (b) C.D. Chandler, C. Roger, M.J. Hampden-Smith, Chem. Rev. 93 (1993) 1205.

[31] P.B. Hitchcock, C. Jones, J.F. Nixon, Angew. Chem. Int. Ed. Engl. 34 (1995) 492.

[32] P.C. Andrews, P.J. Nichols, unpublished results.

[33] (a) C.L. Raston, G. Salem, Preparation and use of Grignard and Group II organometallics in organic synthesis, in: F.R. Hartley (Ed.), The Chemistry of the Metal–Carbon Bond, vol. 4, Wiley, New York, 1987 (Chapter 2). (b) G.S. Silverman, P.E. Rakita, Handbook of Grignard Reagents, Marcel Dekker, New York, 1996.

[34] B. Bogdanovic, Acc. Chem. Res. 21 (1988) 261.

[35] C.L. Raston, G. Salem, J. Chem. Soc. Chem. Commun. (1984) 1702.

[36] B. Bognanovic, S. Liao, M. Schwickardi, P. Sikorsky, B. Spliethoff, Angew. Chem. Int. Ed. Engl. 19 (1980) 818; B. Bognanovic, Eur. Patent 3564, 1982; Chem. Abstr. 91 (1979) 15 9787; US Patent 45541533, 1985.

[37] X. Yaping, B. Meizhi, Hauxue Shiji 16 (1994) 49.

[38] P.K. Freeman, L.L. Hutchinson, J. Org. Chem. 48 (1983) 879.

[39] K. Mashima, Y. Matsuo, H. Fukumoto, K. Tani, H. Yasuda, A. Nakamura, J. Organomet. Chem. 545 (1997) 549.

[40] B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte, U. Westeppe, Chem. Ber. 117 (1984) 1378.

[41] B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte, U. Westeppe, Magensium–anthracene·3THF, in: R.B. King, J.J. Eisch (Eds.), Organometallic Syntheses, vol. 4, Elsevier, Amsterdam, 1988, p. 410.

[42] T. Alonso, S. Harvey, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, Organometallics 6 (1987) 2110.

[43] B. Bogdanovic, N. Janke, H.-G. Kinzelmann, U. Westeppe, Chem. Ber. 121 (1988) 33.

[44] W. Brooks, C.L. Raston, R.E. Sue, F.J. Lincoln, J.J. McGinnity, Organometallics 7 (1991) 2098.

[45] B. Bogdanovic, N. Janke, C. Kruger, R. Maynott, K. Schlichte, U. Westeppe, Angew. Chem. Int. Ed. Engl. 24 (1985) 960.

[46] H. Lehmkuhl, A. Shakoor, K. Mehler, C. Kruger, K. Angermund, Y.-H. Tsay, Chem. Ber. 118 (1985) 4239.

[47] B. Bagdanovic, N. Janke, H.-G. Kingelmann, K. Seevogel, J. Treber, Chem. Ber. 123 (1990) 1529.

[48] S. Harvey, C.L. Raston, J. Chem. Soc. Chem. Commun. (1988) 652.

[49] B. Bagdanovic, N. Janke, H.-G. Kinzelmann, Chem. Ber. 123 (1990) 1507.

[50] S. Harvey, P.C. Junk, C.L. Raston, G. Salem, J. Org. Chem. 53 (1987) 3134.

[51] B. Bogdanoviv, K. Schlichte, U. Westeppe, Chem. Ber. 121 (1988) 27.

[52] N. Janke, Dissertation, University of Bochum, 1986.

[53] W. Kong, S. Liao, Youji Hauxue 3 (1986) 207; Chem. Abstr. 106 (1987) 10 2346.

[54] T.R. van den Ancker, S. Harvey, C.L. Raston, J. Organomet. Chem. 502 (1995) 35.

[55] T.R. van den Ancker, C.L. Raston, Organometallics 14 (1995) 584.

[56] C. Li, T.H. Chan, Organic Reactions in Aqueous Media, Wiley, New York, 1997.

[57] C.-J. Li, W.-C. Zhang, J. Am. Chem. Soc. 120 (1998) 9103.

[58] J.H. Clarke, Green Chem. 1 (1999) 1.

[59] R.A. Sheldon, Chem. Ind. (1992) 903.

[60] H. Chan, Y. Yang, C.J. Li, J. Org. Chem. 64 (1999) 4452.

[61] L.A. Paquett, G.D. Bennett, M.B. Isaac, A. Chatriwalla, J. Org. Chem. 63 (1998) 1836 and references therein.

[62] M. Wada, M. Honna, Y. Kuramoto, N. Miyoshi, Bull. Chem. Soc. Jpn. 70 (1997) 2265.

[63] (a) D. Houllemare, F. Outurquin, C. Paulmier, J. Chem. Soc. Perkin Trans. 1 (1997) 1629. (b) H. Tanaka, S. Sumido, K. Sorajo, Y. Kameyama, S. Torii, J. Chem. Soc. Perkin Trans. 1 (1997) 637.

[64] (a) T.H. Chan, Y.-C. Xin, M. von Itzstein, J. Org. Chem. 62 (1997) 3500. (b) S.K. Choi, S. Lee, G.M. Whiteside, J. Org. Chem. 61 (1996) 8739. (c) T.H. Chan, M.C. Lee, J. Org. Chem. 60 (1995) 4228.

[65] C.R. Strauss, R.W. Trainor, Aust. J. Chem. 48 (1995) 1665.

[66] T. Welton, Chem. Rev. 99 (1999) 2071.

[67] J.D. Holbrey, K.R. Sneddon, J. Chem. Soc. Dalton Trans. (1999) 2133.
[68] R.J. Blanch, M. Williams, G.D. Fallon, M.G. Gardiner, R. Kaddour, C.L. Raston, Angew. Chem. Int. Ed. Engl. 36 (1997) 504.
[69] M.G. Davidson, T.G. Hibbert, J.A.K. Howard, A. Mackinnon, K. Wade, Chem. Commun. (Cambridge) (1996) 2285.
[70] P.D. Godfrey, W.J. Grigsby, P.J. Nichols, C.L. Raston, J. Am. Chem. Soc. 119 (1997) 9283.
[71] M.J. Hardie, C.L. Raston, Eur. J. Inorg. Chem. (1999) 195.
[72] M.J. Hardie, P.D. Godfrey, C.L. Raston, Chem. Eur. J. (1999) 5 (1999) 1828, and unpublished results.
[73] T. Kusukawa, M. Fujita, Angew. Chem. Int. Ed. Engl. 37 (1998) 3142.
[74] T.B. Richardson, S. deGala, R.H. Crabtree, P.E.M. Seigbahan, J. Am. Chem. Soc. 117 (1995) 12 875.
[75] See for example: M.F. Hawthorne, Z. Zheng, Acc. Chem. Res. 30 (1997) 267 and references therein.
[76] X. Yang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 115 (1993) 4904.
[77] A. Harada, S. Takahashi, J. Chem. Soc. Chem. Commun. (1988) 1352.
[78] P.C. Andrews, J.L. Atwood, L.J. Barbour, P.J. Nichols, C.L. Raston, Chem. Eur. J. 4 (1998) 1384.
[79] O. Ermer, Helv. Chim. Acta 74 (1991) 1339.
[80] G. Harakas, T. Vu, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 120 (1998) 6405.
[81] T. Peymann, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 121 (1999) 5601.
[82] W.F. Maier, Angew. Chem. Int. Ed. Engl. 38 (1999) 1216.
[83] (a) L.R. MacGillivray, J.L. Atwood, Nature 389 (1997) 469. (b) T. Heinz, D.M. Rudkevich, J. Rebek, Nature 394 (1998) 764 and references therein.
[84] T.N. Parac, D.L. Clauder, K.N. Raymond, J. Am. Chem. Soc. 120 (1998) 8003.
[85] (a) K. Umemoto, K. Yamaguchi, M. Fujita, Nature 398 (1999) 794. (b) B. Olenyuk, J.A. Whiteford, A. Fechtenkötter, P.J. Stang, Nature 398 (1999) 796 and references therein.
[86] R.L. Rawls, Chem Eng. News, March 22 (1999) 27.