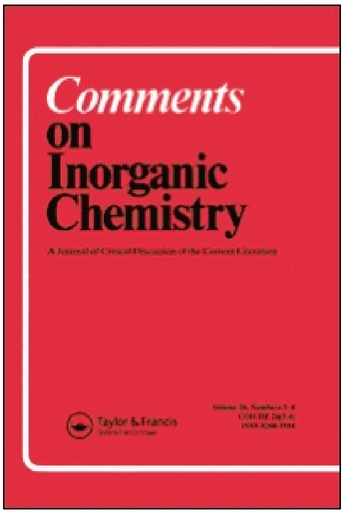

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THE FUTURE OF MAIN GROUP CHEMISTRY

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THE FUTURE OF MAIN GROUP CHEMISTRY

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After a brief reflection on the important discoveries in main group chemistry during the past century, this article provides some suggestions concerning areas in which studies of s- and p-block element compounds are likely to have a major impact on the discipline of chemistry and upon society in general in the context of significant advances that have been made in the last decade. These areas range from fundamental to applied aspects of the subject. In the former category, novel aspects of chemical bonding and new reagents for synthetic applications are considered. From a more practical perspective alternative energy sources (especially hydrogen storage), new materials (notably nanomaterials and chemical sensors), catalysis (in the context of green chemistry), and medicinal chemistry (both diagnostic and therapeutic applications) are discussed.

1. INTRODUCTION

This article was written in response to an invitation to provide some thoughts on the importance of main group chemistry for the 21st century. In a short article of this nature the choice of areas to focus on is necessarily selective and, to some extent, subjective. However, it is hoped that the ideas expressed herein will stimulate some reflection on future possibilities in this exciting area of inorganic chemistry. At the same time, it is recognized that attempting to forecast the most

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influential discoveries or important new ideas in any area of chemistry (or science, for that matter) is akin to "predicting the unpredictable."

Our first thought in addressing this challenge was to consider the important developments in main group chemistry that occurred during the 20th century and how they have influenced other areas of chemistry. In a thoughtful article entitled "Highlights in inorganic chemistry over the last 100 years," which was published in 2004, McCleverty summarized the impressive developments in inorganic chemistry during the 20th century and early part of the 21st century.[1] Before reading McCleverty's synopsis we had decided that a consideration of the areas of main group chemistry for which Nobel Prizes have been awarded would be a good place to start. Those that recognized achievements in the general area of inorganic chemistry are summarized below together with the citation in order to put the highlights from main group chemistry in a broader perspective.[2]

1906: H. Moissan – "*in recognition of the great services rendered by him in his investigation and isolation of the element fluorine*. . . ."

1912: V. Grignard – "*for the discovery of the so-called Grignard reagent, which in recent years has greatly advanced the progress of organic chemistry*."

1913: A. Werner – "*in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry*."

1918: F. Haber – "*for the synthesis of ammonia from its elements*."

1930: H. Fischer – "*for his researches into the constitution of haemin and chlorophyll*."

1934: H. C. Urey – "*for his discovery of heavy hydrogen*."

1935: F. Joliot and I. Joliot-Curie – "*in recognition of their synthesis of new radioactive elements*."

1944: O. Hahn – "*for his discovery of the fission of heavy nuclei*."

1951: E. M. McMillan and G. T. Seaborg – "*for their discoveries in the chemistry of the transuranium elements*."

1954: L. C. Pauling – "*for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances*."

1963: K. Ziegler and G. Natta – "*for their discoveries in the field of the chemistry and technology of high polymers*."

1973: E. O. Fischer and G. Wilkinson – "*for their pioneering work, performed independently, on the chemistry of the organometallic, so-called sandwich compounds.*"
1976: W. N. Lipscomb – "*for his studies on the structures of boranes illuminating problems of chemical bonding.*"
1979: H. C. Brown and G. Wittig – "*for their development of the use of boron- and phosphorus-containing compounds, respectively, into important reagents in organic synthesis.*"
1983: H. Taube – "*for his work on the mechanisms of electron transfer reactions, especially in metal complexes.*"
2005: Y. Chauvin, R. H. Grubbs and R. R. Schrock – "*for the development of the metathesis method in organic synthesis.*"

A perusal of this list reveals that, based on the recognition of a Nobel Prize, the most influential discoveries in main group chemistry have involved reagents that have wide applications in organic synthesis, e.g., Grignard reagents, Wittig reagents, and the use of boron hydrides in hydroboration reactions. Developments in main group chemistry have also been pivotal in providing a broader understanding of chemical bonding, e.g., in electron-deficient compounds through the study of boron hydrides. The contributions of Pauling to our understanding of the nature of the chemical bond are indelibly recorded in his seemingly timeless book, which deals primarily with compounds of the s- and p-block elements.[3] The discovery of the highly reactive element fluorine led to the synthesis of a wide range of element fluorides including PtF_6, which was used to prepare the first compound of xenon[4] and, subsequently, a variety of binary fluorides of the so-called "inert" gases were isolated. Experimental and theoretical investigations of binary fluorides of the main group elements and related molecules led to the development of Valence Shell Electron Pair Repulsion (VSEPR) for predicting and rationalizing their molecular structures, as well as to an understanding of bonding in hypervalent molecules.[5]

Main group chemistry also played a role in the evolution of ideas that led to the award of several other Nobel prizes. For example, studies of the coordination chemistry of s-block metal ions of crown ethers preceded the acknowledgement of D. J. Cram, J.-M. Lehn and C. J. Pedersen in 1987 for "their development and use of molecules with structure-specific interaction of high selectivity", i.e., host-guest chemistry.[6] The 2000 prize awarded to A. J. Heeger, A. G. MacDiarmid and H. Shirakawa for their "discovery and development of conductive polymers" was prefaced by MacDiarmid's pioneering investigations of the conducting polymer $(SN)_x$.[7]

Conversely, the development of seminal ideas in other areas of chemistry has been instrumental in promoting major advances in main group chemistry. As an example, investigations of superacid solvents for handling highly electrophilic species were essential in studies of "carbocation chemistry" for which G. A. Olah received the 1994 prize.[8] The use of such solvents also proved to be vital for the isolation of a wide variety of polycations of electronegative p-block elements, i.e., the chalcogens and halogens, by Gillespie and co-workers.[9] Discoveries of various physical techniques, notably the ability to garner structural information in the solid state by X-ray crystallography and in solution by NMR spectroscopy, have had an enormous impact on main group chemistry (and inorganic chemistry, in general) and these breakthroughs have been accorded appropriate recognition through the award of a variety of Nobel Prizes.[2] Finally, density-functional theory (DFT) calculations (Kohn–Nobel Prize in 1998) have become the *sine qua non* to explain new bonding concepts in main group compounds with unusual structures.

Although p-block element compounds represent a very large percentage of the commercial production of inorganic chemicals,[10] the industrial synthesis of main group compounds has been recognized only once (1918: F. Haber- ammonia synthesis). In this connection the development of methods for the manufacture of silicone (siloxane) polymers $(R_2SiO)_n$ in the 1930s and 1940s was a major achievement.[11] These materials are now regarded as commodity polymers rather than specialty products because they are used widely in modern society, e.g., as oils, greases, rubbers, polishes, coatings and insulating materials, and comprise a billion-dollar global industry. In a similar vein the preparation of zeolites has had an enormous impact on areas such as separation science and heterogeneous catalysis.[12] Zeolites are based on cage-like arrangements of p-block elements (aluminosilicates) whose pore sizes can be tailored for a specific application. The first laboratory syntheses were described by Barrer in the 1930s and 1940s[13] and these materials were subsequently developed as cheap, molecular sieve absorbents and shape-selective catalysts by Union Carbide and Mobil Corporation in the USA in the 1960s. Studies of the ion exchange of sodium and calcium in zeolite A[14] led to its use as an environmentally benign replacement for phosphates in detergents in the 1970s. Barrer's pioneering studies on zeolites were not recognized by a Nobel Prize.

In the context of this introductory background it seems likely that the areas of main group chemistry that will have the highest impact in the future are those in which the unique properties and/or reactivity of compounds of the s- or p-block elements are employed in the advancement of other branches of chemistry. With this in mind the subsequent discussion is organized under the following topics: (a) new aspects of chemical bonding; (b) new reagents in synthesis; (c) new energy sources (in the hydrogen economy and electronics industries); (d) new materials (polymers and nanomaterials); (e) catalysis; and (f) medicinal applications. While it is convenient to systematize the discussion in this way, it is emphasized that there is an overlap between these various sub-topics. For example, compounds with unusual structures will frequently exhibit unique reactivity that leads to the development of new reagents; catalysis by s- or p-block element compounds may lead to new polymers or related materials with unique properties. Although the potential applications of main group compounds in the advancement of sustainable chemistry in industrial processes are not accorded a separate section, the chemistry described in several sections (e.g., 3.4, 4.1, 6.1, and 6.2) has a direct connection to sustainability and the development of green chemistry.

In June 2008 the Royal Society of Chemistry (U.K.) organized a Dalton Discussion meeting on the topic “The Renaissance of Main Group Chemistry” in Berkeley, California. Subsequently, a special theme issue of Dalton Transactions containing the contributions that were presented orally at that meeting was published.[15] Although there is inevitably some overlap between the themes identified for that meeting and those discussed in this article, we attempt in this comment to project what the current trends in main group chemistry presage for the future of other areas of chemistry and materials science in the context of significant developments that have occurred during the first decade of the 21st century.

2. NEW ASPECTS OF BONDING

2.1. Multiply Bonded Compounds

Just as the discovery of xenon fluorides in the 1960s[16] caused a paradigm shift in the way chemists think about bonding,[17] so too did the synthesis and structural characterization of multiply bonded species involving the heavier p-block elements, e.g., $R_2Si{=}SiR_2$ ($R = $ mesityl)[18] and $RP{=}PR$ ($R = 2,4,6\text{-}^tBu_3C_6H_2$),[19] in the early 1980s. Up to that point it was generally thought that such compounds could not exist as stable isolable compounds. Indeed a well-known textbook on inorganic chemistry stated unequivocally “Si, Ge, Sn, and Pb do not form multiple bonds using p_π orbitals. Consequently, numerous types of carbon compounds such as alkenes, alkynes, ketones, and nitriles, have no analogues.”[20] In the last two decades of the 20th century this dogma has been refuted with the isolation of examples of the entire series of homo- and hetero-dinuclear doubly bonded molecules involving group 14 and group 15 elements, including a deep purple dibismuthene RBi=BiR [R = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl)][21a] and the red diplumbene $R_2Pb{=}PbR_2$ (**1**, R = 2,4,6-$^iPr_3C_6H_2$),[22] by using the concept of steric protection of the reactive functionalities stabilization by bulky organic substituents (kinetic stabilization). In a more recent example of a dibismuthene the Bi=Bi double bond is stabilized by a gallium analogue of an N-heterocyclic ligand.[21b] In contrast to C=C double bonds, the multiple bonds between the heavier group elements – especially in the case of lead—arise through a double donor-acceptor interaction between the respective doubly occupied 6s orbitals and the empty 6p orbitals of two singlet plumbylene (R_2Pb) molecules (Figure 1). In addition, all members of a class of compounds of the type $R_2M{=}E$ (M = Ge, Sn; E = S, Se, Te), which have become known as “heavy ketones,” have now been isolated by using the concept of stabilization by steric protection.[23]

After the successful synthesis and characterization of the aforementioned heavy p-block element analogues of doubly bonded organic molecules such as alkenes, including heavy group 14 analogues of cycloalkenes, such as cyclopropene,[24a] cyclobutene and cyclobutadiene,[24b] main group chemists took up the challenge of preparing stable congeners of alkynes with a focus on the bonding in these formally triply bonded molecules. Interestingly, examples of the heavier members of this series ArM≡MAr (M = Pb,[25a] Sn,[25b] Ge[25c]) were achieved before the silicon analogue. Since each group 14 element has only one substituent it

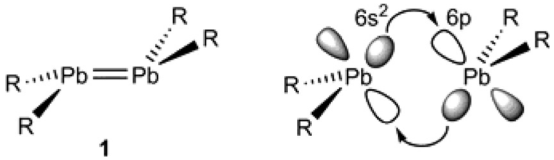

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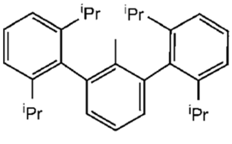
Figure 1. Orbital interactions in a diplumbene.

was necessary to develop even larger substituents to provide steric protection for the reactive M≡M functionality. Typically, Ar is a terphenyl ligand of the general form C_6H_3-2,6-(Aryl)$_2$ in which the flanking aryl groups carry alkyl substituents at their *ortho* and, sometimes, *para* positions, e.g., **2**.[26] The first disilyne RSi≡SiR was reported in 2004;[27] the Si≡Si triple bond is stabilized by bulky silyl substituents [**3**, R = Si^{i}Pr{$(Me_3Si)_2CH$}$_2$].



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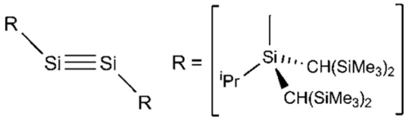

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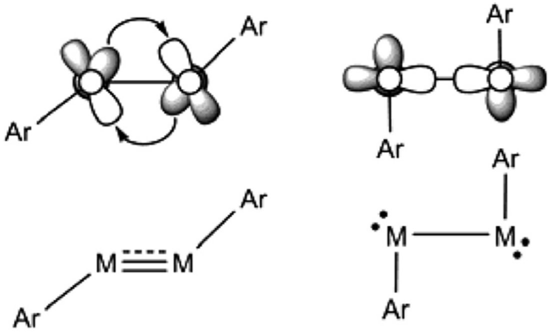
In contrast to alkynes, the group 14 dimetallynes ArM≡MAr or RSi≡SiR (**3**) adopt a *trans*-bent (C_{2h}) structure in the solid state. The Si–Si distance in RSi≡SiR is considerably shorter than that of a Si–Si double bond,[27] while metal-metal bond lengths in the heavier analogues ArM≡MAr (M = Sn, Ge) are close to Ge–Ge and Sn–Sn double bonds.[25b,c] In distinct contrast, the *trans*-bending is greatly increased in the lead analogue and the Pb–Pb distance is much longer than the Pb–Pb single-bond length exemplified by Ph_3Pb–$PbPh_3$.[25a] These fascinating structural observations have been addressed by high-level theoretical calculations that consider both multiply and singly bonded structures (Figure 2).[28] The important conclusions are that (a) in the



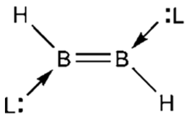
(a) (b)

Figure 2. (a) Multiple and (b) single-bonded modes in ArM≡MAr (M = Sn, Pb).

solid state the singly bonded *trans*-bent structure for the metallynes ArM≡MAr is increasingly favored for the heavier metals, and (b) the multiply bonded structure prevails in solution for Sn and Pb. The solid-state structures are ascribed to packing forces dictated by the bulky Ar substituents. A significant biradical character has been attributed to the germanium analogue ArGe≡GeAr to account for its remarkable reactivity, e.g., in the activation of molecular hydrogen (Section 6.1).[29] As yet there is no consensus regarding the bonding description in disilynes such as **3**.[30]

Silicon analogues of allenes and acyclic butadienes, i.e., $R_2Si{=}Si{=}SiR_2$ and $R_2SiR{=}SiR{-}SiR{=}SiR_2$, respectively, have been characterized recently[31a,b] and tetrasilacyclobutadiene ligands, *cyclo*-$(SiR)_4$, have been trapped as metal complexes.[31c,d] However, the preparation of heavier group 14 analogues of the cyclopentadienide anion $[C_5H_5]^-$ or benzene C_6H_6 remains as a formidable challenge to synthetic chemists. Progress towards these target molecules has so far been limited to five-membered rings that incorporate only three Si or Ge atoms.[32]

Some spectacular results on the stabilization of "naked" multiply bonded diatomics of p-block elements have been reported recently.[33a] The strategy employed for the successful isolation of these highly reactive species uses a N-heterocyclic carbene (NHC) with very bulky substituents on the two nitrogen atoms as a two-electron donor ligand. The breakthrough discovery involved the stabilization of the diborene HB=BH in this manner (**4**).[33b] This was followed by the isolation and structural characterization of the disilene complex L:Si=Si:L (**5**)[34] and a similar carbene-stabilized P_2 complex (**6**).[35] Intriguingly the Si-Si bond length in **5** is close to a typical disilene value while the P−P distance in **6** is consistent with a single bond rather than a triple bond as in the free P_2 molecule.



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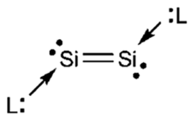

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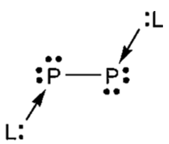

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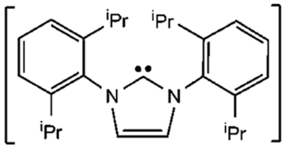


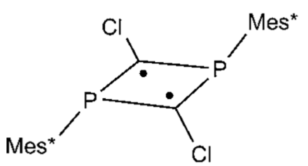
The discovery of **5** and **6** has major implications for (a) the stabilization of other highly reactive main group diatomics, and (b) reaction chemistry, since **5** and **6** represent much more soluble forms of the respective elements (see Section 3.4 for discussion of stable NHC adducts of silicon dihalides).

2.2. Biradicals

Biradicals are molecules that contain two unpaired electrons in two (approximately) degenerate non-bonding molecular orbitals. If the two electrons behave independently, their ground state can either be a low-spin singlet ($S = 1$, antiparallel spins, antiferromagnetic coupling of the spins) or high-spin triplet ($S = 3$, parallel spins, ferromagnetic coupling). In organic systems biradicals are usually very short-lived species that play a central role in bond-breaking and bond-formation processes. In selected cases the replacement of some or all carbon atoms in organic biradicals by other p-block elements produces species that can be isolated and structurally characterized in the solid state.[36] The penalty for the increased stability of these inorganic ring systems is a reduction of the biradical character. Hence, such species are referred to as *biradicaloids*. Recent work indicates that future investigations of such species have the potential to lead to interesting advancements in (a) the creation of new materials with novel properties, and (b) unusual reactivity involving main group compounds.

For example, the replacement of two antipodal CH_2 groups in cyclobutanediyls by PR groups generates $(RPCR')_2$, which is thermally stable for $R = Mes^*$, $R' = Cl$ (**7**).[37a] The four-membered P_2C_2 ring is planar, but both the carbon and the phosphorus(III) centers are pyramidal. The comparatively high inversion barriers at phosphorus impedes the formation of a planar six π-electron system and, hence, **7** exhibits biradicaloid character, which can be controlled by varying the substituents on the carbon and phosphorus centers.[37b] For example, C-bonded silyl groups (a σ-donor and a π-acceptor) stabilize the singlet state, whereas the combination of an NR_2 group at phosphorus and an alkyl group at carbon lowers the energy of the triplet state.[37] The thermally stable, boron-centered radical $(^iPr_2PB^tBu)_2$ (**8**)[38] is an isoelectronic analogue of **7**; both four-membered rings contain 22 valence electrons. However, the structures of the four-membered B_2P_2 rings are markedly dependent on the nature of the substituents on boron and on phosphorus.

For example, the yellow derivative **8** has a square-planar structure with a B–B distance that is ca. 0.7 Å longer than the longest B–B single bond, whereas the all-phenyl analogue $(Ph_2PBPh)_2$ forms a bicyclic arrangement with a transannular B–B single bond.[39]



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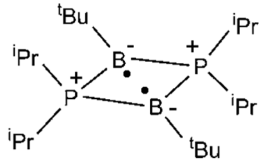

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The preparation of these stable main group biradicaloids stimulated an investigation of the prediction that linking singlet diradicals through appropriate spacer groups will produce antiferromagnetic low-spin polymers, in which the half-filled electron bands will confer the ability of metallic conduction without doping. In this context stable radicals in which two B_2P_2 rings are separated by *meta*- or *para*-C_6H_4 spacer groups have been prepared.[40a] Significantly, the *para* isomer **10** with almost planar B_2P_2 rings is violet, whereas the *meta* isomer **9** with folded four-membered rings and a transannular B–B interaction is colorless (Figure 3). Further studies of the effects of substituents attached to the

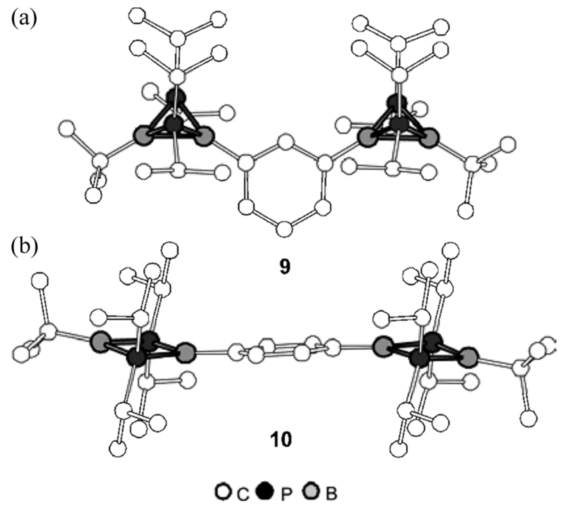
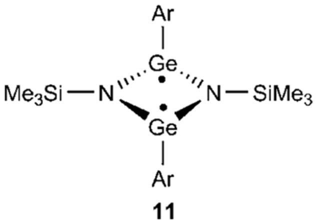


Figure 3. Molecular structures of (a) *meta*- and (b) *para*-$[{}^tBuB(\mu\text{-}P{}^iPr_2)B]_2C_6H_4$.

C_6H_4 spacer have established that the two B_2P_2 biradicals communicate through the phenyl ring provided that all three ring systems are coplanar.[40b] This finding augurs well for the generation of antiferromagnetic low-spin polymers based on main group element biradicaloids.

Another intriguing example of a biradicaloid is the germanium-nitrogen ring system ArGe(μ-$NSiMe_3$)$_2$GeAr (**11**), which is obtained as dark violet crystals by the reaction of the "digermyne" ArGeGeAr (Ar = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$) with trimethylsilyl azide.[41a,b] The related four-membered tin-nitrogen ring ClSn(μ-$NSiMe_3$)$_2$SnCl (**12**) has also been characterized.[41c] The unsymmetrical oxo/imido bridged analogue of **11** ArGe(μ-O)(μ-NC_6H_4-2-CH_3)GeAr is also a singlet diradicaloid.[41d]



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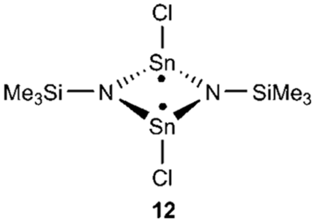

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The transannular distance between the two metal atoms in these four-membered M_2N_2 rings is substantially longer than the corresponding M–M single bond. DFT calculations support the lack of a bonding interaction between the two metal atoms and indicate a singlet ground state for both of these biradical species; the singlet-triplet energy gap is estimated to be *ca.* 17 kcal mol^{-1}.[41] The remarkably facile addition of molecular hydrogen to the Ge_2N_2 system **11**[41b] portends interesting new chemistry for main group biradicals. Addition of H_2 (at high pressures) to a cyclic P_2C_2 radical has also been reported recently.[42]

2.3. Homoconjugation/Homoaromaticity in Main Group Systems

Homoconjugation (through-space interaction) and the consequent Hückel-type homoaromaticity are well established in organic compounds and ions, e.g., the cyclohexyl cation. This phenomenon is also found in the transition state of some organic pericyclic reactions, e.g., the Diels-Alder reaction. By contrast, the role of homoconjugation in inorganic systems has only been established recently.[43] Quantum chemical calculations show that aromatic through-space interactions exist in a variety of main group compounds and ions according to the following three classifications: (a) pericyclic transition state-like homoaromaticity in the dications I_4^{2+}, $S_6N_4^{2+}$ and $E_2I_4^{2+}$ (E = S, Se), all of which form weakly associated dimers in the solid state through π^*-π^* involving the corresponding radical monocations; (b) bishomoaromaticity in the non-classical dication Te_6^{2+} and the bicyclic eight-membered rings 1,5-$R_2P(NSN)_2PR_2$ (R = Me, Ph); and (c) spherical homoaromaticity in the prismatic tetracation Te_6^{4+}.[43] Subsequently, it has been suggested that the description of 1,5-$R_2P(NSN)_2PR_2$ as bishomoaromatic (Figure 4)[43a] should be refined to trishomoaromatic.[44a] The current debate concerning the most appropriate bonding description for heterocycle 1,5-$R_2P(NSN)_2PR_2$, which has been known since 1982,[44b] serves to illustrate the important role that p-block compounds (and ions) continue to play in the development of an understanding of the chemical bond.

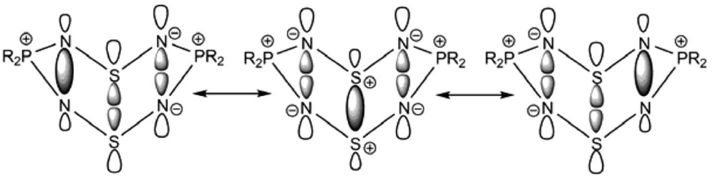
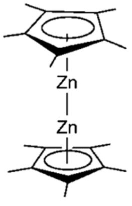


Figure 4. Three valence-bond structures representing the through-space homoconjugation in 1,5-$R_2P(NSN)_2PR_2$.

2.4. Metal-Metal Bonding with s-block Metals

The landmark discovery of a stable compound of Zn(I) with a Zn–Zn bond, decamethylzincocene [Cp*Zn–ZnCp*] (Cp* = C_5Me_5) (**13**), in 2004 attracted much publicity.[45] In addition to promoting activity in the area of group 12 metal-metal bonds, the chemical similarity between zinc and the lighter group 2 metals diverted the attention of both theoretical and synthetic chemists to the possible preparation of subvalent compounds of the type RMMR (M = Be, Mg, Ca). This challenge was met in 2007 with the synthesis of the first stable magnesium(I) compounds LMg–MgL in which the $[Mg_2]^{2+}$ unit is stabilized by bulky guanidinate or β-ketiminate ligands (L) (e.g., **14**).[46a] The Mg–Mg distances are significantly longer than twice the covalent radius of magnesium and DFT calculations indicate predominantly s character for these metal-metal bonds.



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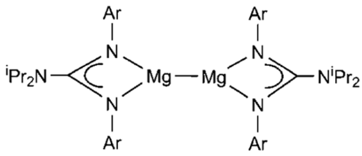

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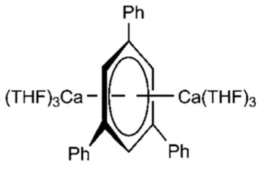

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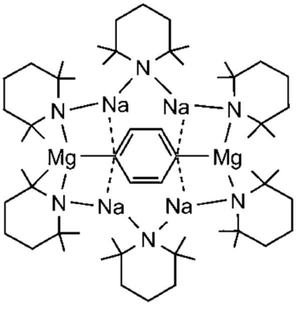
The synthesis of Be or Ca analogues has yet to be achieved[46b] and investigations of the reactivity of these s-block metal-metal bonded systems will be of great interest. In this connection the contrasting behavior of activated Mg or Ca towards bromo-2,4,6-triphenylbenzene is pertinent. Whereas the lighter alkaline earth forms a typical Grignard reagent $ArMg(THF)_2Br$, the reaction with calcium produces an "inverse" sandwich complex $\{(THF)_3\{\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3\}Ca(THF)_3]$ **(15)** with most unusual properties.[46c] This black paramagnetic calcium(I) complex ($S = 1$, triplet), which exhibits thermochromic behavior, is comprised of two Ca^+ cations bridged by a doubly negatively charged arene ligand.

3. NEW REAGENTS IN SYNTHESIS

3.1. Bimetallic Reagents

Among the extensive variety of main group compounds that are used in organic synthesis, commercially available organolithium and organomagnesium (Grignard) reagents are probably the most widely used. It has been recognized for some time that the combination of two s-block metal reagents, e.g., an organolithium reagent and potassium *tert*-butoxide, provides a more powerful base for deprotonation (hydrodemetallation) reactions than single-metal organometallic species.[47]

More recent studies of the synergic effect of heterobimetallic regents have revealed extraordinary reactivity in deprotonation processes. Two examples will serve to illustrate such transformations. The combination of NaTMP and $Mg(TMP)_2$ (TMP = tetramethylpiperidyl) effects double deprotonation of benzene to give $[Na_4Mg_2(TMP)_6(C_6H_4)]$ **(16)**,[48] although neither of these reagents deprotonates benzene on its own. An equally impressive demonstration of the synergic reactivity of s-block metal amides is observed in the reaction of ferrocene with a mixture of ^{n}BuNa, Bu_2Mg and diisopropylamine. In this example, tetradeprotonation occurs regioselectively to give the 1,1,3,3-tetranion of ferrocene (**17**), which is trapped by coordination to the eight metal centers (Na_4Mg_4) of a 16-membered heterometallic amide ring. Similar transformations occur for ruthenocene and osmocene.[49] Interestingly, the regioselective dimetallation of toluene is dependent on the nature of the bimetallic reagent. Thus sodium-magnesium cooperativity in the reagent [Na(^{n}Bu)(TMP)Mg(TMP)] results in 2,5-dimagnesiation, whereas the closely related TMEDA-coordinated complex [(TMEDA)-Na(^{n}Bu)(TMP)Mg(TMP)] effects only monomagnesiation at the 3-position.[50] The regioselectivity of the dimetallation process is changed to the 3,5-positions by the use of a trimethylsilylmethyl group (instead of butyl) in the reagent $[Na_4Mg_2(TMP)_6(CH_2SiMe_3)_2]$.[51]



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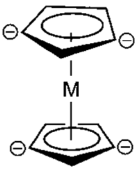

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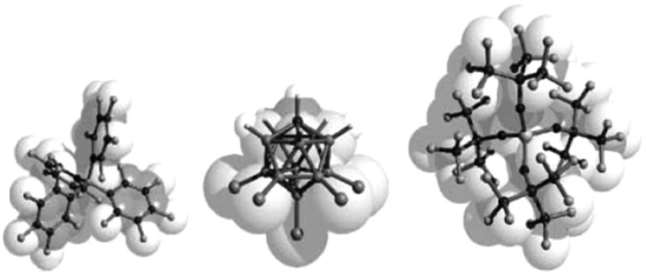
Numerous variations of these bimetallic reagents can be envisaged, since (a) the alkali metal, (b) the cooperating metal (Mg, Zn, Al etc.), (c) the anionic ligand (amide or alkyl), and (d) the donor ligand (TMEDA, THF, etc.) can be combined in almost limitless ways.[52a] For example, *in situ* mixtures of LiTMP and group 12 dihalides $MCl_2 \cdot TMEDA$ ($M = Zn$, Cd) are highly effective metalators of a large range of arenes with reactive functional groups as well as a variety of heterocycles.[52b] While future investigations of these bimetallic systems will undoubtedly lead to further examples of unprecedented chemical transformations, the biggest challenge in this area is the development of catalytic processes based on a fundamental understanding of stoichiometric metalations.[52c]

3.2. Weakly Coordinating Anions

Polyanions of the p-block elements, e.g., M_9^{4-} (M = Sn, Pb) and Sb_7^{3-}, were identified by Zintl in the 1930s, but these strongly reducing species were not obtained as stable crystalline salts until 1975. This was achieved by encapsulation of the alkali metal counter-cation in a 2,2,2-cryptand ligand in order to inhibit internal electron transfer.[53] In a complementary approach the isolation of highly electrophilic polycations of electronegative p-block elements, e.g., E_4^{2+}, E_8^{2+} (E = S, Se, Te), required the use of anions of very strong acids such as SO_3F^-, MF_6^{2-} (M = As, Sb), $AlCl_4^-$.[54] However, the nucleophilic halide ligands of these anions engage in weak interactions with the counter-ion and, consequently, they are not suitable partners for extremely electrophilic species such as silylium cations R_3Si^+.

The recent development of chemically robust, weakly coordinating anions (WCAs) based on p-block elements has had a major influence in areas such as olefin polymerization, lithium battery technology, and ionic liquids. The combination of low nucleophilicity, chemical inertness, and solubility of the perfluorotetraphenylborate anion $[B(C_6F_5)_4]^-$ (**18**, Figure 5) first reported in 1964,[55] and related highly fluorinated borate anions, has led to their widespread use as counterions for cationic Lewis acid catalysts.[56] Halogenated derivatives of carborane-based anions, e.g., $[CHB_{11}H_5X_6]^-$ (X = Cl, Br) (**19**, Figure 5), are particularly well suited for the stabilization of highly electrophilic cations because of their chemical robustness.[57] For example, this counter-ion has facilitated



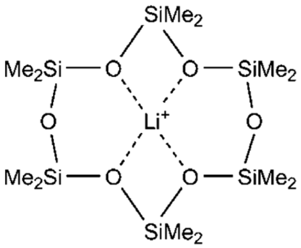
(**18**) (**19**) (**20**)

Figure 5. Examples of weakly coordination anions (WCAs): $[B(C_6F_5)_4]^-$ (**18**), $[CHB_{11}H_5X_6]^-$ (X = Cl, Br) (**19**) and $[Al\{OC(CF_3)_3\}_4]^-$ (**20**). Reproduced with permission from reference 56(a). © Wiley-VCH Verlag GmbH & Co.

the preparation of a R_3Si^+ cation,[58] stable fullerene ions C_{60}^+ and $[HC_{60}]^+$,[59a] and thermally stable (to >150°C) protonated benzene and toluene salts.[59b] The commercial availability of $Li[B(C_6F_5)_4]$ and salts of the halogenated carborane anions **19** will undoubtedly accelerate their use in both fundamental and applied inorganic and organic chemistry.

More recently, monoprotic carborane acids of the type $H(CHB_{11}X_{11})$ ($X = Cl$, Br) have been shown to be the strongest pure acids isolated to date[60a] and the related diprotic acids $H_2(B_{12}X_{12})$ have comparable acidities, i.e., at least 10^5 greater than that of 100% H_2SO_4.[60b] Significantly, both protons in these diprotonic superacids are able to protonate benzene. The all-boron acids are cheaper to synthesize than their carborane analogues and this advantage may lead to their preferred use in certain applications.

Another class of WCAs that is attracting increasing attention is perfluoroalkoxymetallates, notably the aluminate $[Al\{OC(CF_3)_3\}_4]^-$ (**20**, Figure 5).[56] Although chemically less rugged than the perfluorinated borates, e.g., **18**, or halogenated carborane anions **19**, the aluminate **20** is a more weakly coordinating partner for electrophilic cations as a result of the steric bulk of the four perfluoro-*tert*-butoxy groups. The Li^+ salt is readily prepared in high yield[61] and is also commercially available from Strem Chemicals. A striking example of the ability of **20** to generate new chemistry is provided by the synthesis of the first examples of alkali-metal complexes of cyclosiloxanes, e.g., $[Li(Me_2SiO)_6]^+$ (**21**) as the $[Al\{OC(CF_3)_3\}_4]^-$ salt.[62a] Thermochemical considerations showed that the use of WCAs rather than, for example, iodide as a counter-ion is essential because they minimize changes in lattice energy and reduce the possibility of unfavorable cation-anion interactions. In a related study, the silver salt $Ag[SbF_6]$ was shown to bring about ring expansion of cyclosiloxanes,[62b] raising the possibility of metal-templated ring



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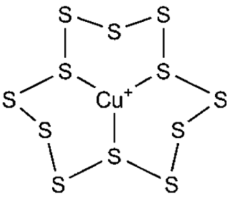

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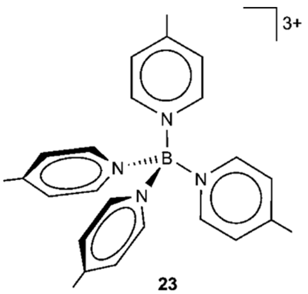
transformations or, perhaps, ring-opening polymerization for a wide range of inorganic hetero- and homo-cycles of the p-block elements.[63] A cogent example is the ring expansion observed in the formation of [Cu(*cyclo*-S_{12})]$^+$ **(22)** from the reaction of *cyclo*-S_8 with [Cu(1,2-$F_2C_6H_4$)$_2$]$^+$ [Al{OC(CF_3)$_3$}$_4$]$^-$.[64]

In addition to their use as partners for the stabilization of unusual, highly electrophilic main group species, the use of known WCAs and the development of new examples of WCAs are likely to play an influential role in fields such as catalysis, as counter-ions for electrophilic transition-metal centers, in ionic liquids to generate low viscosities,[65] and in lithium batteries.

3.3. Ligand-Stabilized Polycations of Isolated p-block Elements

The synthesis, structural characterization, and elucidation of bonding in polyatomic cations of the electronegative elements (chalcogens and



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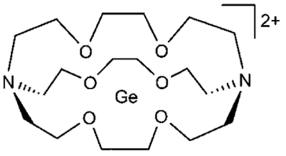

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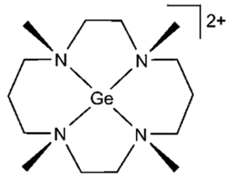

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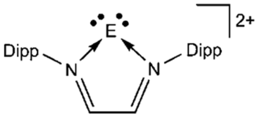
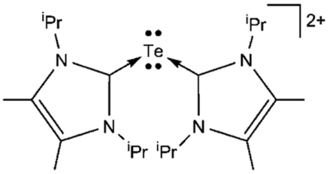
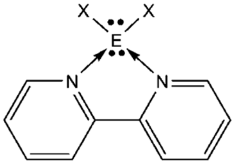


26a (E = S)
26b (E = Se)



26c



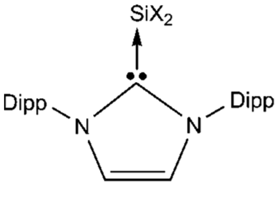
27 (E = Se, Te; X = Cl, Br)

halogens) (see Section 1) was a major achievement in main group chemistry during the 20th century. However, applications of these highly electrophilic species in synthesis have been very limited. In the last few years major advances in the stabilization of polycations of a single p-block element have been achieved by the judicious choice of chelating ligands or encapsulation in azamacrocycles, crown ethers, or cryptands. Examples from boron (**23**),[66] germanium (**24** and **25**),[67] sulfur (**26a**),[68a] selenium (**26b**),[68b] and tellurium (**26c**)[68c] chemistry are shown above as representatives of this interesting class of compounds. Novel chemistry may be anticipated from reactions of these electrophilic main group centers. As an illustration, the dicoordinate P-centered cation $[(Me_2N)_3P]_2P^+$ serves as a source of "P^+" in reaction with $Cp_2Zr(H)Cl$ to give the intriguing square-planar phosphonium cation $P[Zr(H)Cp_2]_4^+$.[69]

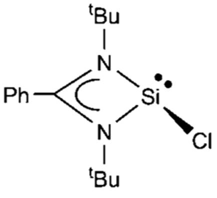
In related work the stabilization of labile (or unknown) binary chalcogen halides EX_2 (E = Se, Te; X = Cl, Br) has been achieved by coordination to 2,2′-bipyridine (**27**).[70] The study of synthetic applications of these potentially useful new reagents is in its infancy.

3.4. Low-Coordinate Main Group Element Centers

As a result of relativistic effects lower oxidation states become more stable for p-block elements as one descends a particular group. For example, Tl(I) and Pb(II) compounds are more stable than the corresponding Tl(III) and Pb(IV) derivatives, respectively. It follows that the stabilization of the lower oxidation states of the lighter p-block elements is a significant synthetic challenge with the incentive that it may provide easily handled new reagents for the development of novel chemistry. The use of donor ligands can, however, mitigate the tendency for disproportionation to occur. As an illustration, metastable donor-stabilized aluminum(I) halide complexes, e.g., $AlCl(OEt_2)_2$, have been used in the synthesis of a wide variety of unusual aluminum cluster compounds such as tetrahedral $(AlCp^*)_4$ ($Cp^* = C_5Me_5$). In group 14, whereas tin and lead dihalides are commercially available reagents, germanium dichloride is commonly used as the 1,4-dioxane adduct and silicon dihalides are gas-phase species. The recent reports of thermally stable NHC adducts of silicon dihalides, SiX_2 (**28a**, X = Cl; **28b**, X = Br) herald a new era in silicon chemistry.[71]



28a (X = Cl)
28b (X = Br)



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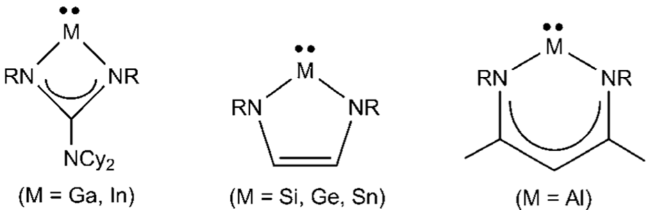
In addition to the examples of p-block element cations discussed in Section 3.3, many examples of the stabilization of low-coordinate main group metals by the use of anionic chelating *N,N'*-ligands with bulky *N*-aryl substituents have been reported in recent years. These include amidinates or guanidinates (four-membered rings, cf. **14** for the stabilization of a Mg(I) complex),[72a,b] analogues of five-membered NHCs that are isovalent with **26a,b**,[72c] and *β*-diketiminates (six-membered rings).[72d] Some typical examples are shown in Scheme 1. These carbene analogues exhibit a rich range of chemistry that promises to be more diverse than carbene chemistry. For example, there are no carbene analogues of the silicon(II) compound LSiCl (**29**, L = amidinate).[72e] With a wide range of stable, soluble reagents with low-coordinate main group element centers now available,[72f] further fascinating developments of this exciting field are likely in the future.



Scheme 1. Stabilization of low-valent metal centers by anionic *N,N'*-ligands.

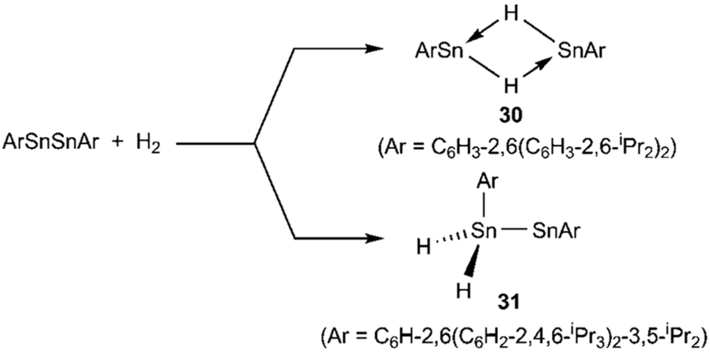
3.5. Activation of Small Molecules

The activation of small molecules such as hydrogen or alkenes has traditionally been the domain of transition metals which, through the availability of a combination of filled and vacant d orbitals, are able to engage in synergic activations of H–H or C=C bonds. Activation of the H–H bond by p-block element compounds was not known until

2005 when the reaction of a digermyne complex ArGeGeAr (Ar = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$) with H_2 under ambient conditions was reported to give the addition compounds Ar(H)GeGe(H)Ar and ArH_2GeGeH_2Ar.[73a] More recently, it has been shown that distannynes ArSnSnAr (Ar = terphenyl ligand) undergo a similar, but cleaner, reaction with H_2 to give either a symmetric hydrogen-bridged dimer $ArSn(\mu\text{-}H)_2SnAr$ (**30**) or the unsymmetrical stannane $ArSnSnH_2Ar$ (**31**) (Scheme 2).[73b] The activation of H_2 by ArGeGeAr is thought to be due in part to the singlet diradical character of the ground state,[29] but the mechanism of the corresponding process for distannynes ArSnSnAr is not well understood.[73b]

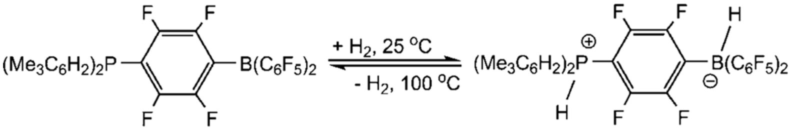
The seminal finding of H_2 activation at non-metal centers was followed by reports of H−H bond cleavage by certain singlet carbenes, e.g., $^iPr_2N(^tBu)C$:.[74] Such carbenes also activate the N−H bonds of liquid ammonia.[74] In contrast to the oxidative addition of H_2 to transition metals, activation by a carbene occurs heterolytically as a result of asymmetric donation of electrons from the carbon center into the σ^* orbital of H_2.

Perhaps the most intriguing and certainly the most versatile example of H_2 activation by p-block elements involves the use of a Lewis base-acid strategy. For example, equimolar amounts of P^tBu_3 [or $P(C_6H_2Me_3)_3$] and $B(C_6F_5)_3$ do not form adducts even at −50°C owing to steric inhibition by bulky groups on P; the term Frustrated Lewis Pairs (FLPs) has been coined to describe this behavior.[75a] However, exposure of this mixture to one atmosphere of H_2 at room temperature generates phosphonium hydridoborates, e.g., $[^tBu_3PH][HB(C_6F_5)_3]$.[75b]



Scheme 2. Activation of H_2 by distannynes.

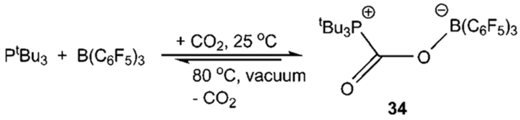
While this unusual reactivity at p-block elements is intriguing, the process of H_2 activation must be reversible for a material to be considered for H_2 storage applications. In this context the finding that a phosphinoborane in which the P and B centers are separated by a bridging C_6F_4 spacer (**32**) adds H_2 under ambient conditions and the resulting phosponium borate (**33**) undergoes loss of H_2 at 100°C is especially significant (Eq. 1).[75c] Although the low hydrogen content of **33** rules out its use for this purpose, further advances in an understanding of the mechanism of H_2 activation by FLPs may aid in the development of practical hydrogen-storage materials (see Section 4.1).[75d]



32 **33**

(1)

The ability of FLPs to activate small molecules is not limited to H_2. For example, the addition of alkenes to a combination of P^tBu_3 and $B(C_6F_5)_3$ produces the salts $[^tBu_3PCH(R)CH_2B(C_6F_5)_3]$ ($R = H$, CH_3, C_4H_9).[76] The activation of carbon dioxide is also of considerable current interest with a view to using this greenhouse gas as a C_1 chemical feedstock. Typical strategies focus on the use of transition-metal catalysts for this purpose. However, a number of main group reagents including metal amides, e.g., $Sr[N(PPh_2)_2]_2$,[77] and FLPs,[78] have shown promise in this regard. For example, a solution of P^tBu_3 and $B(C_6F_5)_3$ reacts with CO_2 at atmospheric pressure to give the addition compound **34**; this process is reversible upon warming under vacuum (Eq. 2).[78a] A similar reaction occurs with nitrous oxide, N_2O, another greenhouse gas.[78b] The development of the full potential of FLPs is clearly in its infancy and there are already indications of applications as catalysts for hydrogenation reactions (see Section 6.2).[75a]



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(2)

The conversion of alkanes to more valuable functionalized products, e.g., methane → methanol, is topical in the context of the growing concern for energy production. C–H bond activation, like hydrogen activation, has traditionally been restricted to transition-metal compounds. Recently, it has been shown by using gas-phase mass spectrometry data that the cation radicals of certain main group element oxides, e.g., SO_2 and P_4O_{10}, are able to abstract a hydrogen atom from methane (Eqs. 3 and 4).[79] The relatively low cost (high abundance) of phosphorus- or sulfur-containing compounds is a potential advantage for their future applications in C–H oxidations.

$$CH_4 + [SO_2]^{\bullet +} \rightarrow CH_3^{\bullet} + [SO_2H]^{+} \tag{3}$$

$$CH_4 + [P_4O_{10}]^{\bullet +} \rightarrow CH_3^{\bullet} + [P_4O_9(OH)]^{+} \tag{4}$$

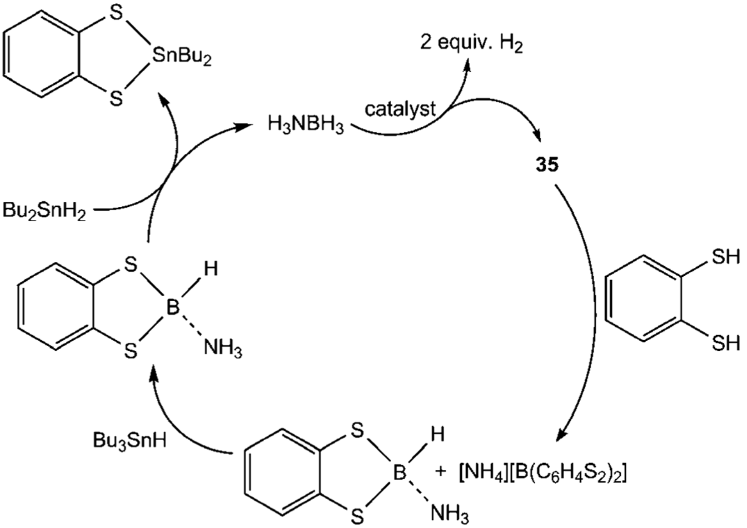
4. ALTERNATIVE ENERGY SOURCES

4.1. Hydrogen Storage

The search for alternative fuels is a major 21st century challenge in view of the decline in oil reserves combined with an increasing demand for oil. Hydrogen, in combination with a fuel cell, is deemed to be an attractive alternative if a safe and efficient method for storing and transporting H_2 can be developed. Hydrogen-powered cars and buses have been manufactured, but their use has been limited to short journeys owing to problems associated with the storage of large volumes of hydrogen. The US Department of Energy has established targets for hydrogen storage materials so that a vehicle can travel >500 km on a single hydrogen fill; the target gravimetric hydrogen content is 9 wt%.[80] Compounds that can be exploited to store hydrogen in the form of E–H bonds (where E is a light main group element) are possible candidates for this purpose. More specifically, promising contenders such as ammonia-borane $H_3N \cdot BH_3$,[81] ammonia-triborane $H_3N \cdot B_3H_7$,[82] hydrazine-borane adducts $N_2H_4 \cdot (BH_3)_n$ ($n = 1, 2$),[83] s-block metal salts of aminoborane $M[H_2NBH_3]$ (M = Li, Na, Ca),[84] $Mg(BH_4) \cdot 2NH_3$,[85] AlH_3,[86a] and alkali-metal aluminohydrides $M[AlH_4]$[86b] are being investigated vigorously in view of the combination of their low molecular weights and high gravimetric hydrogen capacity. Ammonia-borane has a gravimetric hydrogen storage capacity of 19.6 wt% compared to 15.37 and 16.88 wt% for $N_2H_4 \cdot (BH_3)_n$ ($n = 1, 2$, respectively) and 10.9 and 7.5 wt% for alkali-metal aminoboranes (M = Li, Na, respectively).

There are advantages and disadvantages to the use of all these hydrogen-storage materials. Adducts incorporating higher boranes are explosive. Although the s-block metal aminoboranes release H_2 at significantly lower temperatures than $H_3N \cdot BH_3$ without foaming and they do not produce borazine as a by-product (*vide infra*), H_2 uptake is not readily reversible for these promising materials.[83,84] The problem of reversibility has been addressed for $LiAlH_4$ by using Ti-doped material and dimethyl ether (Me_2O) as the solvent.[86b]

Ammonia-borane $H_3N \cdot BH_3$ has been studied most thoroughly in view of its high gravimetric capacity, low molecular weight, and the juxtaposition of protic and hydridic hydrogen atoms. It is a thermally stable white solid that is easily stored and transported. Hydrogen can be released from $H_3N \cdot BH_3$ via hydrolysis, dehydrocoupling or thermal decomposition. Although the rate of dehydrogenation in solution is relatively slow, it can be accelerated by the use of catalysts or by using ionic liquids as solvent.[87a] By-products of the reaction include the volatile cyclic molecule borazine, $B_3N_3H_6$, which may act as a poison in fuel cell applications. The regeneration of spent $H_3N \cdot BH_3$ is a major challenge, but the recent discovery of an efficient one-pot process



Scheme 3. Regeneration of spent $H_3N \cdot BH_3$ by stepwise addition of a digesting agent (1,2-benzenedithiol) and a reducing agent ($^nBu_2SnH_2$); **35** = polyborazylene.

for the regeneration of the predominant product, polyborazylene (**35**), represents a major breakthrough towards practical applications (Scheme 3).[87b,c]

The development of a practical hydrogen-storage material will continue to be a major challenge over the next decades and main group chemistry is poised to play an important role. A solution to this problem may involve the application of the knowledge gained from the fundamental studies described above[79–86] in the construction of a hybrid or doped material, which is safe, economical and takes up H_2 reversibly and efficiently.

4.2. Solar and Thermoelectric Energy

The use of solar energy is an environmentally benign method of producing energy. Silicon and GaAs are widely employed for this purpose. Cadmium telluride is viewed as a very promising material for use in solar cells because of high efficiency for electric power generation.[88a] The major manufacturer of CdTe solar cells is First Solar based in Phoenix, Arizona (USA). CdTe technology is expected to increase tenfold over the next 10 years.[88b] However, the extremely low natural abundance of tellurium (*ca.* 1 parts per billion in the earth's crust)[88a] places limitations on the use of this photovoltaic as an alternative energy source.

Semiconducting main group metal selenides and tellurides, e.g., Sb_2Te_3, Bi_2Te_3, PbTe, are also of current interest for possible applications in thermoelectric (heat-to-electrical-energy converters) generators. However, these binary tellurides operate at low efficiency and, consequently, their use is limited to solid-state refrigeration and cooling. If the efficiency can be improved applications of these thermoelectrics in, for example, the automotive industry and the conversion of waste heat from nuclear reactors and industrial equipment can be envisaged. The thermoelectric power factor of PbTe is enhanced by co-nanostructuring with two kinds of metallic nanoparticles (Pb and Sb).[89] The electrical conductivity also increases at high temperatures without loss of thermopower. Further development of the concept of synergic nanostructuring can be expected to result in improvements in the efficiency of thermoelectric materials.

Modern technology often requires the growth of thin layers of different materials on top of one another via metal-organic vapor phase epitaxy (MOVPE) involving the transport of two precursors (one for the metal and the other for the chalcogen) to the heated surface on which the semiconducting film is to be deposited. In the case of chalcogenides the precursors are highly toxic compounds such as H_2Se or dialkyl tellurides. Consequently, single-source precursors (SSPs) in which the metal and chalcogen are contained (preferably as nearest neighbors) in one compound are being developed. Although the MOVPE process requires the SSP to be reasonably volatile, the recently developed techniques of Aerosol-Assisted or Low Pressure Chemical Vapor Deposition (AACVD or LPCVD) can be used when the precursor has low volatility.[90] The design and synthesis development of suitable SSPs for the generation of highly pure chalcogenides and other semiconducting materials represents a significant challenge for main group chemists.

An alternative synthesis of main group metal chalcogenides in the form of thin films uses soft solvothermal methods. In this approach a metal chalcogenide is treated with an excess of a chalcogen in anhydrous hydrazine or hydrazine hydrate (to reduce the risk of explosion) at ambient temperature to give a more soluble form of the metal chalcogenide in the form of complex chalcogenometallates, e.g., $[Sn_2E_6]^{4-}$ (E = S, Se) (Eq. 5). Phase-pure metal chalcogenide thin films are subsequently generated by thermal decomposition of hydrazinium salts, e.g., M_2Se_3 (Ga, In), GeE_2 (E = S, Se), and Sb_2E_3 (E = Se, Te) have been generated in this manner.[91a,b] This method can be adapted for the synthesis of ternary chalcogenides containing two different metals and a single chalcogen, e.g., $CuInE_2$ (E = Se, Te), or one metal and two different chalcogens, e.g., $SnSe_{2-x}S_x$; this versatility bodes well for future applications. The anionic ligand $[Sn_2S_6]^{4-}$ has also been used as a capping agent for a variety of metal chalcogenide nanocrystals.[91c,d]

$$5N_2H_4 + 2E + 2SnX_2 \rightarrow N_2 + [N_2H_5]_4[Sn_2E_6] \quad (E = S, Se) \qquad (5)$$

5. NEW MATERIALS

5.1. The Electronics Industries

In addition to the metal chalcogenides discussed in Section 4.2, many main group elements and compounds are important materials in the electronics industries. For example, the unique properties of gallium nitride (GaN), including superior robustness and power efficiency compared with silicon or gallium arsenide, combine to make this wide-bandgap (3.5 eV) semiconductor a promising candidate for reducing the demand for electricity.[92a] It has been suggested that GaN is the most important semiconductor material since silicon.[92b] It emits brilliant light as well as being the key material for next generation high-frequency, high-power transistors capable of operating at high temperatures. Among the many applications of GaN light-emitting diodes (LEDs), their use in traffic lights is perhaps the most impressive. Increasing demand for blue-violet laser diodes, UV LEDs, and other devices is forecast to almost double the market for GaN-based materials, including AlN, InN and related ternary semiconductors.[93] Gallium nitride thin films are generated by the reaction of trimethyl gallium and ammonia at high temperature (*ca.* 1000°C) and high pressure (*ca.* 700 torr). The development of more economic routes to such devices will require the combined skills of materials scientists, solid-state physicists and electrical engineers, as well as main group chemists whose specific role is the refinement of the precursor chemistry necessary for the production of highly pure materials, possibly through the use of single-source precursors.[94]

5.2. Nanomaterials

The properties of nanomaterials, i.e., materials with at least one of the dimensions in the 1–100 nm range, depend on their size and shape. This versatility gives rise to the prospect of materials with properties designed to perform a specific function and a wide range of applications in fields as diverse as engineering and medicine are foreseen.[95] A variety of approaches involving either physical or chemical methods can be used for the generation of nanomaterials, but chemical synthesis has been shown to be more effective.[96] Since many nanomaterials based on main group element compounds are under active investigation, only selected examples will be considered in an article of this broad scope.

Carbon nanotubes (CNTs) are perhaps the best-known nanomaterials. Isoelectronic boron nitride nanotubes (BNNTs) were first synthesized in 1995.[97] BNNTs continue to be of considerable interest because they exhibit advantageous properties compared to those of CNTs.[98] For example, BNNTs are wide-band-gap semiconductors, independent of diameter and chirality, whereas the electrical properties of CNTs are difficult to control. In addition, BNNTs exhibit excellent mechanical properties, high thermal conductivity, and impressive resistance to oxidation. Consequently, applications in nanoscale conductors working in oxidative environments at high temperatures or in providing improved mechanical properties as additives in composites are envisaged for BNNTs. However, the development of BNNTs is hampered by their insolubility and the relatively high manufacturing cost. In order to circumvent the former handicap, recent efforts have focused on making soluble BNNTs through sidewall functionalization, e.g., with long alkyl chains[99a] or amino groups.[99b] The former modification produces BNNTs that are soluble in many organic solvents.

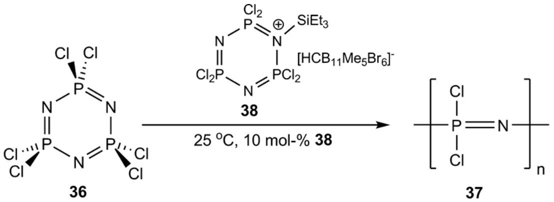
Another class of main group nanomaterials that are the focus of intense investigations are those related to the electronic materials discussed in Section 5.1, i.e., group 13 pnictides such as GaN, AlN, and InN (see Section 5.1), and their heavier congeners, GaP, AlP and InP.[96] A variety of synthetic approaches involving either two reagents, one involving the group 13 metal and the other providing the group 15 non-metal, or a single-source precursor in the presence of a capping agent have been used. For example, high quality InP nanocrystals are obtained by the reaction of Me_3In with $P(SiMe_3)_3$ in a coordinating ester solvent.[100] Alternatively, the single-source precursors $M(P^tBu)_3$ ($M = Ga$, In) have been used to generate MP ($M = Ga$, In) nanocrystals via thermolysis in 4-ethylpyridine.[101]

The future development of functional nanomaterials will require an interdisciplinary endeavor. There are almost unlimited opportunities for synthetic main group chemists to devise methods to generate known materials with specific shapes and dimensionalities, as well as for the discovery of routes to as-yet unknown nanomaterials based on p-block elements either in the form of single elements, e.g., silicon,[102] selenium,[103a] and tellurium,[103b] or as binary systems.

5.3. Inorganic Polymers

Silicone polymers of the type $(R_2SiO)_n$ and related materials based on an Si-O backbone are manufactured on a massive scale for a variety of uses (see Section 1). Further developments of an understanding of the intriguing properties of poly(dimethylsiloxane) $(Me_2SiO)_n$ such as their very high permeability to gases may be expected to lead to additional commercial applications of these inorganic polymers.[104,105]

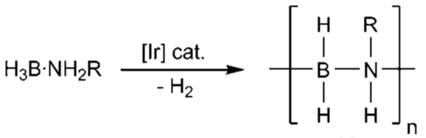
In some applications, polyphosphazenes $(R_2PN)_n$ ($R = $ halogen, alkyl, aryl, alkoxy, alkylamino), i.e., polymers based on a P-N backbone, rival or outperform the isoelectronic silicone analogues because the Cl substituents in the precursor (**37**) can be replaced by a variety of alkoxy or alkylamino groups via nucleophilic substitution. The potential applications of these materials include their use as high-performance elastomers, polymer electrolytes, and biomedical membranes.[106] The major barriers to the development of phosphazene polymers on an industrial scale have been the cost of producing very pure cyclic trimer $(Cl_2PN)_n$ (**36**) for the ring-opening polymerization (ROP) and the relatively high temperature (ca. 250°C) required for ROP. The recent discovery of the room-temperature ROP of $(Cl_2PN)_n$ (**36**) using trialkylsilylium carboranes (**38**) as catalysts (Eq. 6) may pave the way for industrial synthesis of phosphazene polymers.[107]



(6)

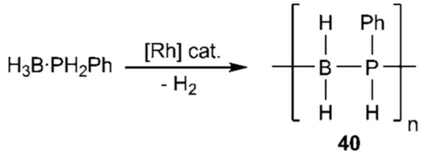
Transition-metal catalyzed dehydrocoupling reactions constitute a relatively new and potentially versatile method for the generation of novel polymers involving either homonuclear or heteronuclear bonds between main group elements.[108] For example, dehydropolymerization of secondary stannanes in the presence of a zirconocene catalyst yields high molecular weight polystannanes $(SnR_2)_n$, as well as cyclic oligomers.[109] These polymers possess highly delocalized σ-electrons, cf. polysilanes (Section 1). Highly branched polystannanes with high molecular weights have been produced by using a rhodium catalyst.[110] The more rigid structure confers greater stability towards light and oxidation on these branched polymers compared to their linear analogues.

Exciting new applications of the dehydrocoupling reaction involves the formation of soluble, high molecular weight analogues of polyolefins, e.g., $[R(H)N{-}BH_2]_n$(**39**), using an iridium catalyst[111] or the polyphosphinoborane $[Ph(H)P{-}BH_2]_n$(**40**) in hot toluene in the presence of a rhodium catalyst (Eqs. 7 and 8).[112] The latter is an analogue of polystyrene with B-P instead of C-C bonds. These materials are of interest as precursors to BN- or BP-based ceramics, respectively. The B-P backbone polymers also show promise as flame retardants. In addition, they have been used as lithographic resists when coated as thin films on silicon.[113]



$$H_3B{\cdot}NH_2R \xrightarrow[-\,H_2]{[Ir]\ cat.} [BH_2{-}NHR]_n \qquad (7)$$

39

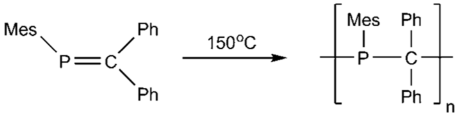


$$H_3B{\cdot}PH_2Ph \xrightarrow[-\,H_2]{[Rh]\ cat.} [BH_2{-}PHPh]_n \qquad (8)$$

40

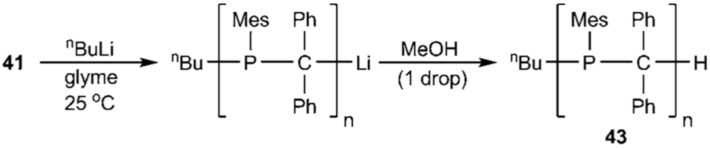
Although impressive advances have been made in recent years, the formation of main group polymers by metal-catalyzed dehydrocoupling reactions is still at an early stage of development. In view of the potential versatility of this method the opportunities for further advances in the generation of materials with properties that are not found in organic polymers are manifold.

The most common route to inorganic polymers is ring-opening polymerization initiated either thermally or by the action of nucleophiles or electrophiles. By contrast, addition polymerization is widely used for preparing organic polymers. The first well-characterized example of using this approach for the synthesis of polymers involving p-block elements was reported in 2003.[114] The phosphaalkene **41** undergoes polymerization slowly at 150°C to give poly(methylenephosphine) materials **42** with molecular weights in the 30,000 range (Eq. 9). More recently, addition polymerization has been employed for the synthesis of a polymer with a Ge-C backbone.[115] The wider application of this route to inorganic polymers will require the judicious selection of monomers with multiple bonds that have sufficient kinetic stability and for which polymerization is thermodynamically favorable.



$$Mes{-}P{=}CPh_2 \xrightarrow{150^{\circ}C} [P(Mes){-}CPh_2]_n \qquad (9)$$

41 **42**

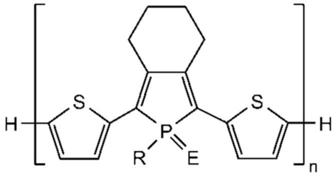


Scheme 4. Living anionic polymerization of a phosphaalkene.

Phosphaalkenes have also been shown to undergo living anionic polymerization at room temperature in the presence of ^{n}BuLi in a process that is analogous to that used to make polystyrene (**43**, Scheme 4).[116] This new methodology is also effective for the preparation of polystyrene-poly(methylenephosphine) block copolymers.

Block copolymers are macromolecules that link two (or more) homopolymer building blocks. The introduction of p-block elements into block copolymers provides additional functionalities that can complement those of the organic components. For example, isoprene-phosphaalkene block copolymers are excellent ligands for sequestering gold(I) and have been used to control the size and shape of gold nanostructures.[117] The design and synthesis of such materials is an interesting challenge for main group and macromolecular chemists.[118]

Another class of phosphorus-containing polymers that are attracting increasing attention for a variety of potential applications are phosphole-containing oligo- and poly-thiophenes, e.g., **44**.[119] These materials are being considered for possible uses in light-emitting diodes, photovoltaic cells, field-effect transistors, non-linear optical devices, and as polymeric sensors (see Section 5.4). While the development of functional materials based on these heteroatom systems is at an early stage the dramatic effects engendered by functionalizing the P(III) centers or changing substituents in other parts of the molecule provide a driving force for future studies. A different strategy for the future development of electron-transport materials based on oligothiophene frameworks involves the installation of bulky (kinetically inert) boryl substituents, e.g., **45**.[120]



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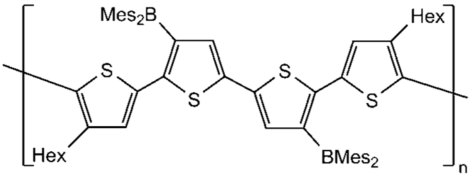
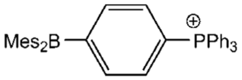


45

5.4. Chemical Sensors

The detection and capture of anions by using organic molecules (molecular sensors) have been investigated widely. The sensing of fluoride and cyanide ions is of prime interest because of their biological, environmental, and industrial importance, e.g., the presence of fluoride in drinking water, toothpaste, and certain drugs.[121,122] These small anions are commonly found in aqueous media in which they are strongly solvated. Since excessive intake of fluoride or cyanide poses potential health risks, e.g., fluorosis, it is important to develop sensors that partake in very strong host-guest interactions with these anions in water. For example, in the USA the maximum contaminant level for fluoride in drinking water set by the Environmental Protection Agency (EPA) is 4 ppm (210 μM).[123] In the European Union (EU) the corresponding limit for cyanide is 50 ppb (1.9 μM).[124]

A successful strategy for meeting these stringent requirements involves Lewis acidic boron-based hosts that incorporate both acceptor sites and cationic ammonium, phosphonium, or sulfonium groups to provide water solubility. For example, the phosphonium borane **46** binds fluoride ions below the EPA contaminant level and provides a basic design for molecules that could be used in drinking water analysis.[123] In a slightly different approach dicationic azaborines with two peripheral ammonium or phosphonium groups, e.g., **47**, form strong complexes with fluoride or cyanide in aqueous solution.[122] The chelating sulfonium borane **48** is an effective sensor for the detection of aqueous cyanide at close to the EU maximum allowable concentration.[124] The formation of the fluoro- or cyano-borate complexes formed from the interaction of **46–48** and the corresponding anions is monitored by UV-visible or fluorescence spectrometry. Further refinements of the design strategies embodied in these cationic boron-based sensors are



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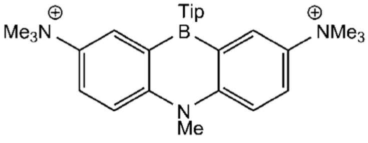

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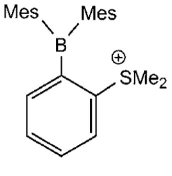


48

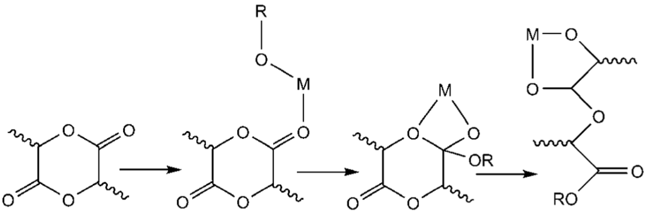
needed to produce economically attractive reagents for the detection of fluoride, cyanide, and other anions such as azide in aqueous media.

6. CATALYSIS

6.1. Lactide Polymerization

In the context of a decline in petrochemical feedstocks and an increase in concern for the environment, polylactide (PLA) has emerged as an attractive alternative to conventional organic polymers. PLA is used in bulk packing and fibers under the trade name Ingeo^{TM}. Among their desirable properties PLA-based plastics are biocompatible, readily biodegradable, and easily recycled. Lactide monomer (**49**) is produced in several steps from a starch or sugar feedstock, e.g., corn.[125] High molecular weight PLA (**50**) is then manufactured by ring opening polymerization using a homogeneous metal catalyst, typically a metal alkoxide (Scheme 5).

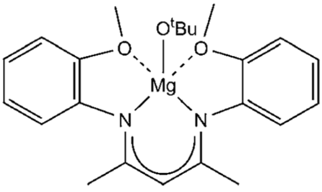
In addition to the relatively high production costs, the major impediments to the further development of PLA as a commodity polymer are poor activity and stereochemical control of the known catalyst systems. Following early work on zinc complexes,[126] group 2 (Mg, Ca) and group 13 (Al, In) metal catalysts are under active investigation. The Mg and Ca catalysts generally exhibit high activities, but afford poor control of the stereochemistry. An exception is the Mg alkoxide complex with hemilabile ether sites, **51**, which exhibits good stereoselectivity but relatively poor activity.[127] The catalytic properties of aluminum-salen complexes such as **52** can be adjusted by changes in the bridging unit between the two coordinated nitrogen atoms or the substituents on the phenoxy ring.[128] Although these Al-salen catalysts exhibit good site



49 **50**

Scheme 5. Formation of polylactide by using a metal alkoxide catalyst.

control, they have low reactivity and poor tolerance to functional groups. The unusual chiral indium catalyst **53** is highly active for living lactide polymerization.[129]



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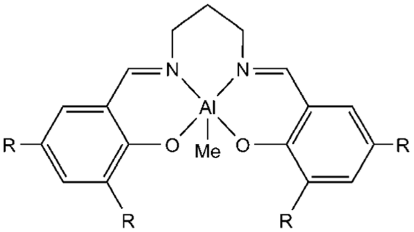

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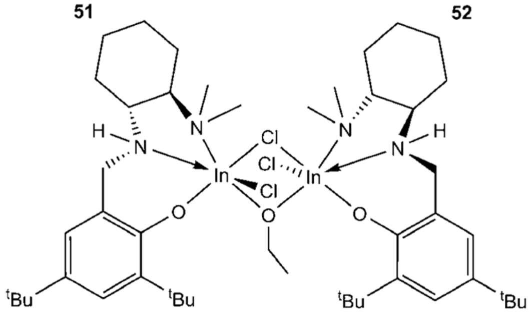

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On the basis of these early results, it appears that main group metal-based catalysts are poised to make a major contribution to the future development of PLA as a commodity polymer. As exemplified by the Mg and Al examples, **51** and **52**, the typical coordination complexes that have been investigated offer numerous possibilities to alter the electronic and steric environment at the metal center and, hence, the activity and stereochemical control. It has been suggested[125] that the availability of sterically and electronically unsaturated metal centers, e.g., in complexes of neutral rather than monoanionic coordinating ligands, may give rise to highly active catalysts while retaining stereocontrol.

6.2. Organic Synthesis

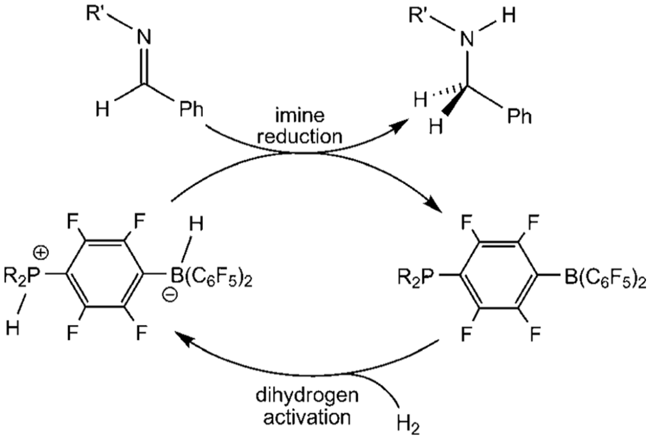
The use of main group element compounds as stoichiometric reagents in organic transformations are manifold. Perhaps the best known are boron hydrides, e.g., B_2H_6, in hydroborations and phosphorus ylids, e.g., $Ph_3P{=}CH_2$, in the Wittig reaction (see Section 1). Main group reagents (too numerous to mention here) are also used widely in selective oxidation, reduction, and halogenations reactions. In addition to the ubiquitous use of organolithium and Grignard reagents, many other main group organometallics perform important functions in the synthesis of organic compounds. For example, organotin compounds, notably dialkyltin oxides and bis(tributyltin) oxide, are widely used to achieve regioselectivity in carbohydrate synthesis.[130]

Although their uses as stoichiometric reagents in organic synthesis are diverse, the applications of main group compounds as catalysts for organic transformations are much less common than those of transition-metal catalysts. The current emphasis on "green chemistry" has led to a trend away from using organic solvents and toxic reagents as catalysts in organic synthesis. In the area of Lewis acid catalysis the replacement of moisture-sensitive catalysts that are consumed in the reaction, e.g., $AlCl_3$, by water-tolerant, recyclable catalysts is highly desirable. In this regard indium(III) salts, e.g., $InCl_3$, have been extensively investigated because of their low toxicities and stability in air and water.[131] A water-tolerant chiral In(III) catalyst has also been developed and shows promise in enantioselective reactions.[132]

The addition of hydrogen to unsaturated organic compounds (hydrogenation) is used extensively in industry in transformations as diverse as the processing of oils and the production of chemicals for use in the agricultural and pharmaceutical industries. These processes are usually mediated either by homogeneous or heterogeneous transition-metal-based catalysts. The recent discovery of the activation of H_2 by a variety of non-metallic systems, notably FLPs (see Section 3.4),[74] has shifted attention to main group element catalysis for hydrogenations. For example, it has been shown that phosphonium borate **33** is an effective catalyst for addition of H_2 to imines, nitriles, and aziridines.[133] The catalytic cycle for the reduction of imines is shown in Scheme 6. Subsequently, it was shown that hindered imines[134] or bulky amines[135] can act as the Lewis base partner with $B(C_6F_5)_3$ to achieve heterolytic H_2 activation.

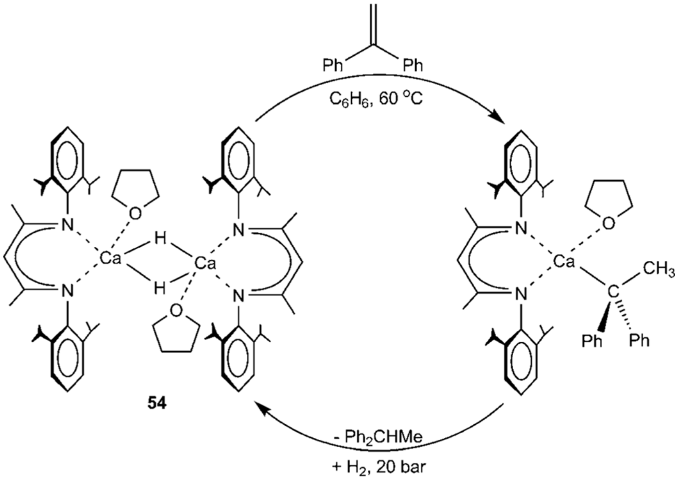
Coordination complexes of calcium represent another class of main group element catalyst that is being explored for hydrogenations because of the relatively low cost and high abundance of calcium compared to precious metal catalysts.[136] The calcium hydride complex **54**[137] has been shown to catalyze the hydrogenation of 1,1-diphenylethylene under relatively mild conditions (Scheme 7).[136]

In summary, the prospects of the replacement of precious metal catalysts by s- or p-block element catalyst in hydrogenation reactions



Scheme 6. Reduction of imines using a phosphonium borate catalyst.

are very promising. Intense activity in this area of main group element chemistry can be anticipated in the immediate future. The relatively high natural abundance and low cost of many main group elements compared to most transition metals provide a strong incentive for these investigations.



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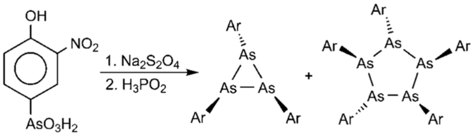
Scheme 7. Catalytic hydrogenation of 1,1-diphenylethylene by a calcium catalyst.

7. MEDICINAL CHEMISTRY

A main group compound played a historically important role in the development of chemotherapy. The drug 3-amino-4-hydroxyphenyl arsenic(I), known as Salvarsan, was revealed in 1910 by Ehrlich and used to cure syphilis. Ehrlich referred to Salvarsan as "the magic bullet." His discovery became the subject of a 1940 movie featuring Ehrlich as the founder of chemotherapy. Originally represented as an arsenic(I) analogue of azobenzene, $ArAs = AsAr$, it was not until 2005 that the correct composition of Salvarsan was established.[138] Electrospray ionization mass spectrometry showed that it is comprised of a mixture of cycloarsines $(ArAs)_n$ ($n = 3$–8), the major components of which are the trimer and pentamer (Eq. 10).



(10)

The best known inorganic pharmaceuticals involve transition-metal complexes, i.e., platinum anti-cancer drugs and gold anti-arthritis drugs. However, a variety of main group compounds have medicinal applications ranging from salts of Li^+, the lightest alkali-metal cation, to complexes of bismuth, the heaviest pnictogen. Lithium salts, most commonly in the form of Li_2CO_3, are used for the treatment of manic depression. The precise mechanism of action of Li^+ as a mood-stabilizing agent is not fully understood, although recent studies suggest that three different pathways may act synchronously.[139] The most interesting proposal, and perhaps the most provocative to main group chemists, is that lithium may interact with the nitric oxide (NO) signaling pathway in the central nervous system.[140]

The bioutility of bismuth compounds has a venerable history.[141] Today bismuth compounds that are marketed under the trade names Pepto-Bismol (bismuth subsalicylate) and De-Nol (colloidal bismuth sub-citrate) are used for the treatment of various gastrointestinal disorders. Despite these well-established applications, a clear understanding of the biological activity of bismuth at a molecular level has not been developed. In attempts to rectify this deficiency, main group chemists have investigated bismuth coordination complexes with ligands that contain biologically relevant functionalities, e.g., thiol, amino and carboxyl groups.[142] The very low solubility of bismuth complexes presents a major challenge for solution studies and for the production of single crystals for X-ray diffraction studies. However, electrospray ionization mass spectrometry has been used effectively to determine the molecular compositions of such complexes.[142]

Carboranes have been widely studied for their medicinal applications.[143] Early work focused on the use of carboranes in boron neutron capture therapy (BNCT); the isotope ^{10}B (abundance ca. 20%) has a high neutron capture cross-section and carboranes have a high percentage boron content. Their attractive properties include high oxidative and hydrolytic stability, low toxicity, and the ability to be functionalized to provide water solubility. In this connection, carborane-containing polyester dendrimers with a hydrophilic surface have been synthesized.[144] Research on the medical applications of this well-known class of main group compounds has broadened to include drug discovery, molecular resonance imaging (MRI), and targeted radionuclide therapy.[145] For example, carboranes containing both ^{19}F and ^{10}B nuclei have been developed for MRI studies.[146] The presence of the abundant ^{19}F (100%) nuclei greatly enhances the effectiveness of carboranes for imaging and may allow for the determination of the exact location of tumor cells. In another interesting study carborane-based nanoparticles with ester or ether linkages have been constructed with the intention that they would mimic liposomes in their ability to pass into the tumor cell vasculature.[147] Although carboranes show great promise as BNCT agents in other medicinal applications, the implementation of these main group drugs will depend on (a) approval for clinical trials by drug administration agencies, and (b) cost considerations. The high cost of synthesizing such specialty drugs is offset, however, by the very low concentrations that are needed for diagnostic applications.

There are numerous other areas in which main group compounds have potential biomedical applications. Only some selected examples are included here. The demonstration of the binding of 1,2-azaborines inside the cavity of a lysozyme suggests that certain boron-containing compounds have the ability to serve as hydrophobic arene mimics in biological systems.[148] The pharmacological effect of the replacement of carbon by silicon in certain drugs is also an area of intense investigation.[149] The use silicone polymers, viz. $(Me_2SiO)_n$, in the manufacture of contact lenses is well established. The established biocompatability of phosphazene polymers may presage their future applications as biomedical materials.[106] Finally, we draw attention to the medicinal interest in complexes of heavier group 13 elements, notably gallium and indium, as diagnostic and therapeutic agents. In this context ^{67}Ga emits gamma radiation, making it suitable for use in single photon emission computed tomography while the positron emitter ^{68}Ga is of interest for use in positron emission tomography. The challenge for the main group coordination chemist is to find complexes that have a sufficiently high stability to minimize toxicity in *in vivo* applications.[150]

8. CONCLUSIONS

The large number of exciting advances in main group chemistry that have occurred in very recent years suggests that this sub-discipline of inorganic chemistry will become increasingly important in the 21st century. An expanding emphasis on the relatively little explored chemistry of the heavier s-and p-block elements is likely to provide novel structural arrangements that challenge traditional concepts of chemical bonding as well as fascinating new reagents for chemical transformations. From a broader perspective, the relatively high abundance (low cost) of the natural sources of many s- and p-block elements provides an incentive to exploit their novel physical properties and reaction chemistry. In particular, main group chemistry is poised to respond to societal demands for, *inter alia*, alternative energy sources, green chemistry, smart materials, and new medicines for both diagnostic and therapeutic applications. Seminal advances in these areas are likely to come from interdisciplinary collaborative efforts between main group chemists and other scientists with the appropriate expertise. At the same time the recognition of the vast potential of compounds of more than thirty s- and p-block elements by investigators with a primary background in materials (including macromolecular) chemistry, organic chemistry, physical chemistry, and biochemistry could attract fresh ideas to the field. It is to be hoped that funding agencies will respond to this untapped opportunity with increased support for main group chemistry. Finally, we hope that this article will be a catalyst for new areas of study for younger scientists who are contemplating entering this field, as well as more experienced investigators. The most exciting advances will undoubtedly come from innovative approaches and serendipitous discoveries that are impossible to predict.

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