Review

Some past achievements and future perspectives in main group chemistry

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Abstract

A survey of some recent developments and past achievements in low-valent main group chemistry is presented. Some emerging implications of this area of chemistry in materials science, catalysis and new reagent development are also discussed.
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1. Introduction

Main group chemistry continues to thrive. In part, the surge of interest over the past few years has been driven by the demands of materials science as well as medical science, particularly in the field of non-invasive diagnostics in the case of the latter. There is also an on-going quest for improved catalysts and cocatalysts that can be used for effecting industrially important chemical transformations. However, there is, at the heart of the foregoing developments a healthy drive on the part of the main group and organometallic chemist to seek unprecedented structures, novel bonding arrangements, and unusual patterns of reactivity. In this context, there has been considerable recent activity in the area of the low oxidation state chemistry of the group 13, 14 and 15 elements. The present article has, as its purpose, the twin objectives of tracing a selection of the intriguing developments in this particular area of chemistry and highlighting some of its future challenges.

2. Low oxidation state/low coordination number main group chemistry

In contrast to the situation that existed four or five decades ago, much current emphasis in synthetic, structural and theoretical main group chemistry is placed on species with low oxidation states and/or low coordination numbers. One such area that has attracted attention for several years is the chemistry of stable compounds that are the formal analogues of alkenes and diimines. The first structurally authenticated example of this type of compound was the ditin derivative {(Me$_3$Si)$_2$CH}$_2$SnSn{CH(SiMe$_3$)$_2$} [1] (Fig. 1). As in the case of the germanium anlogue, which was structurally characterized later [2], the dimer undergoes facile monomerization in solution.
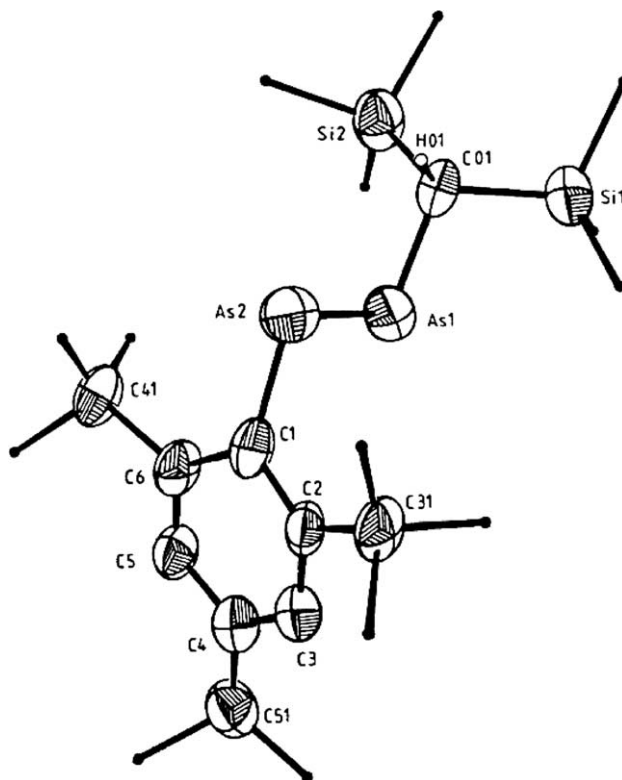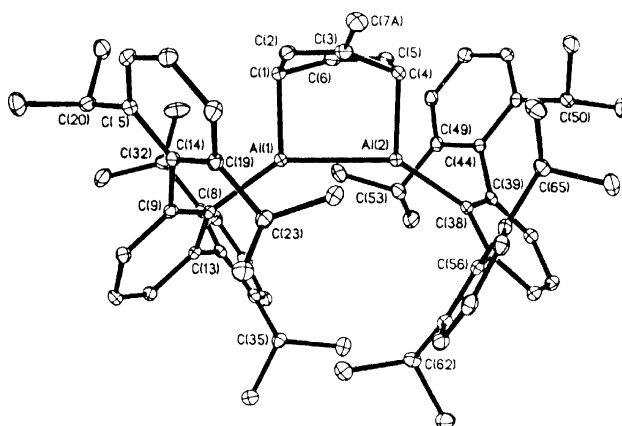
Considerable impetus was given to the field by the disclosure in 1981 of (mesityl)$_4$Si$_2$, the first example of a stable disilene [3] (Fig. 2). Within a short period of time, the first examples of compounds with stable phosphorus–phosphorus [4], arsenic–arsenic [5] (Fig. 3), and phosphorus–arsenic [6] double bonds were published. Since the mid-1980s, many of the remaining double bonding possibilities for the group 14 and 15 elements have been realized [7].

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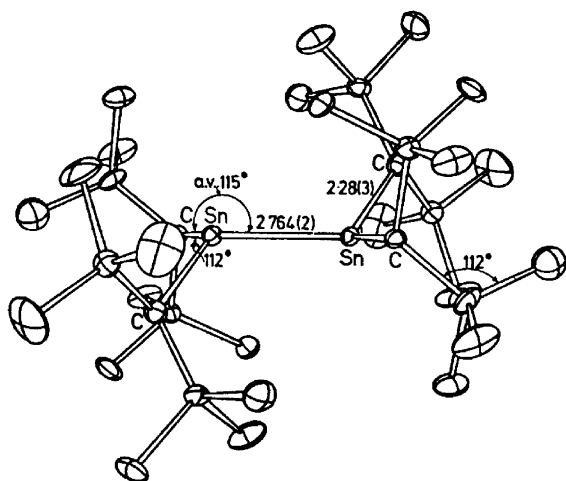
Fig. 1. View of [Sn{CH(SiMe$_3$)$_2$}$_2$]$_2$.
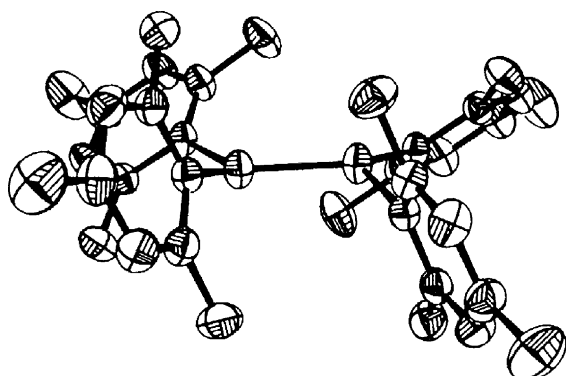
Fig. 2. View of Si$_2$(mesityl)$_4$ showing the pyramidalization at silicon.

Fig. 3. View of [2,4,6-(t-Bu)$_3$C$_6$H$_2$As=AsCH(SiMe$_3$)$_2$].

Although the diboron dianions [Mes$_2$BBMes$_2$]$^{2-}$ and [Me$_2$N(Ph)BB(Ph)NMe$_2$]$^{2-}$, which are isoelectronic with alkenes [8], possess boron–boron bond orders greater than unity, the chemistry of neutral group 13 compounds of formula RBBR (diborenes) has been slower to develop and therefore represents a challenging area for future research. Theoretical calculations on the parent diborene, HBBH [9], predict that this molecule is a ground state triplet, thus portending a high reactivity for this class of compound. Despite several attempts to synthesize such compounds, the present situation is that two amido-substituted diborenes have been claimed but not isolated as pure compounds [10]. Likewise, in the case of the dialuminene, Ar′AlAlAr′ (Ar′ = C$_6$H$_3$-Dipp$_2$; Dipp = C$_6$H$_3$-2,6-i-Pr$_2$) it was not possible to isolate this compound per se; however, its existence was inferred from the isolation of the 2 + 4 cycloaddition product with toluene [11] (Fig. 4). Interestingly, the heavier analogues Cp′In···InCp′ and Cp′Tl···TlCp′ (Cp′ = η^5-C$_5$(CH$_2$Ph)$_5$) have been known for several years [12] (Fig. 5). These and the subsequently reported diindium and dithallium species [7] possess distinctly trans-bent structures and long, weak metal–metal interactions as a consequence of increased lone pair character as group 13 is descended.

Fig. 4. View of the cycloaddition product of Ar′AlAlAr′ (Ar′ = C$_6$H$_3$-2,6-Dipp$_2$; Dipp = C$_6$H$_3$-2,6-i-Pr$_2$) with toluene.

The recently reported digallium derivative, Ar′GaGaAr′ (Ar′ = C$_6$H$_3$-Dipp$_2$; Dipp = C$_6$H$_3$-2,6-i-Pr$_2$) also possesses a trans-bent structure and, like the heavier congeners, undergoes monomerization in solution [13] (cf. the facile dissociation of e.g., distannenes and digermenes, particularly those with π-donor substituents [1]).

The group 13 dianions, [RMMR]$^{2-}$, are of particular interest because of their isoelectronic relationship with alkynes. At the present time, the only examples of dianions of this type are the intriguing salts Na$_2$-{GaC$_6$H$_3$-2,6-Trip}$_2$ (Trip = C$_6$H$_2$-2,4,6-i-Pr$_3$) [14]
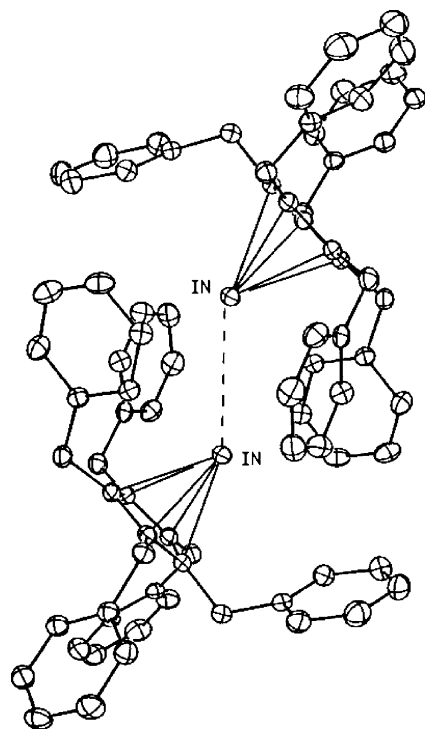
Fig. 5. View of the In{C$_5$(CH$_2$Ph)$_5$} dimer.
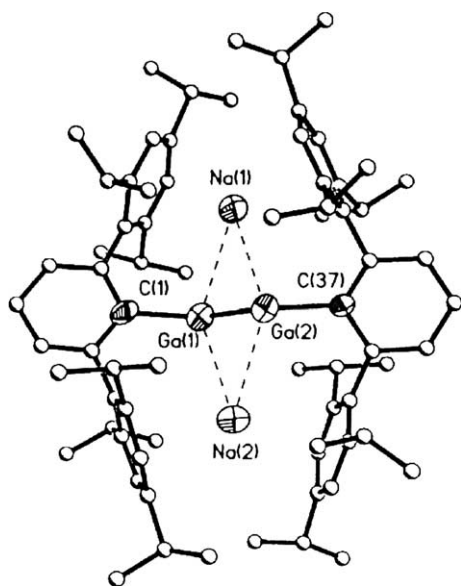
Fig. 6. View of Na$_2$[Ga$_2$(C$_6$H$_3$Mes*)$_2$] (Mes* = 2,4,6-i-Pr$_3$C$_6$H$_2$).

(Fig. 6) and Na$_2${GaC$_6$H$_3$-2,6-Dipp}$_2$ (Dipp = C$_6$H$_3$-2,6-i-Pr$_2$) [15]. Considerable discussion has arisen regarding the nature of the gallium–gallium bonding in such dianions with a particular emphasis on the Ga–Ga bond order. The skeletal structures of both dianions are similar and feature a planar, *trans*-bent C(ipso)GaGaC(ipso) moiety and the gallium–gallium separation is only slightly shorter than those of some gallium–gallium single bonds. A further complicating feature is the influence

on the Ga–Ga separation of n^6 interactions between the Na$^+$ cations and *ortho*-aryl substituents [16]. More recently, the related sterically protected group 14 dimers, RMMR (R = Ge, Sn, Pb), have been prepared and structurally characterized [17]. These compounds also exhibit distortions from the classical linearity of alkynes due to the accumulation of lone pair type electron density at the group 14 element centers. The nature of the M–M bonding in group 13 dianions, [RMMR]$^{2-}$, and group 14 neutral molecules, RMMR, has been probed theoretically. At the present time, the results are somewhat confusing because localized molecular orbital (LMO) and canonical molecular orbital (CMO) treatments lead to seemingly different conclusions when applied to the heavier group 13 and 14 elements. (For further discussion on this point, see reference [17].) Theoretical calculations notwithstanding, the heuristic trend is the transformation of the classical π-type bonds of the lighter elements into orbitals with varying degrees of nonbonding character as the atomic number increases. Conspicuous by their absence are well-characterized examples of a disilyne, RSiSiR, and heteronuclear analogues of the same stoichiometry in which silicon is bonded to a different group 14 element. The syntheses and structural assays of such compounds are therefore important challenges for the preparative chemist. The fact that disilynes have been proposed as intermediates [18] and the recent preparation of a molybdenum complex with considerable silylyne character [19] provides some encouragement for these quests.

Depending on the steric demands, electronic characteristics and crystal packing, group 13 RM fragments can assemble into clusters rather than the dimers that were discussed above. Such clusters are known for all the group 13 elements and are exemplified by tetrahedral (t-BuB)$_4$ [20], (η^5-C$_5$Me$_5$Al)$_4$ [21] (Fig. 7), [(Me$_3$Si)$_3$-CIn]$_4$ [22], [(Me$_3$Si)$_3$CTl]$_4$ [23], octahedral (η^5-C$_5$Me$_5$Ga)$_6$ [24], and tricapped trigonal prismatic (t-BuGa)$_9$ [25]. With the exception of (t-BuB)$_4$, which is quite unreactive, the heavier clusters can serve as useful sources of monomers when vaporized or placed in solution. If the very bulky 2,6-Trip$_2$C$_6$H$_3$ (Trip = 2,4,6-
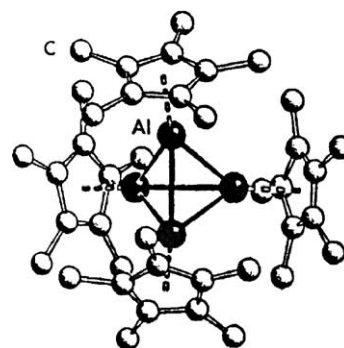

Fig. 7. View of [Al$_4$(η^5-C$_5$Me$_5$)$_4$].

i-Pr$_3$C$_6$H$_2$) ligand is employed, the (aryl)M monomers (M = In, Tl) are stable in the crystalline state [26]. More recently, the aluminum(I) and gallium(I) monomers, [HC(MeCNAr$_2$)$_2$M] (M = Al [27], Ga [28]; Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) supported by a β-diketiminate ligand have been prepared and structurally characterized (Fig. 8). DFT calculations on the singlet and lowest-lying triplet states of the univalent group 13 ligands MeM, (η^5-C$_5$H$_5$)M, (η^5-C$_5$Me$_5$)M, and (H$_3$Si)$_2$NM (M = B, Al, Ga, In) reveal that, regardless of the substituents R, the ground state is a singlet in each case and that the singlet–triplet energy gap increases with atomic number [29]. As a consequence of the singlet ground state, the HOMO's of RM fragments typically exhibit pronounced lone pair character. The anticipated Lewis basicity is evidenced by the observation that e.g., [(η^5-C$_5$Me$_5$)Al]$_4$ reacts with B(C$_6$F$_5$)$_3$ to form a 1:1 complex with an aluminum(I)–boron donor–acceptor bond [30] (Fig. 9). The list of comparable complexes has grown rapidly and now includes complexes with Al→Al [31], Al→Ga [32], Ga→B [33,34], Ga→Al [32], Ga→Ga [34], and In→B [35] donor–acceptor bonds. In all the above
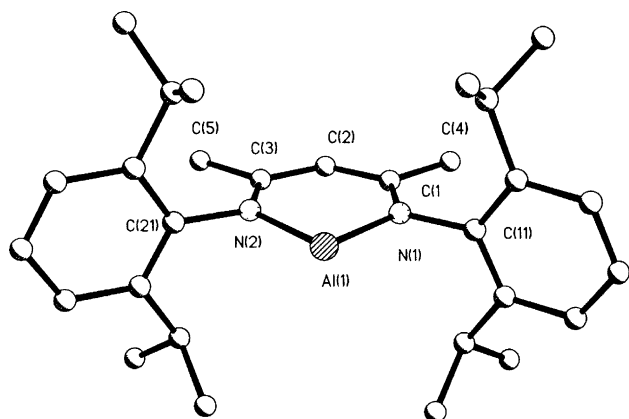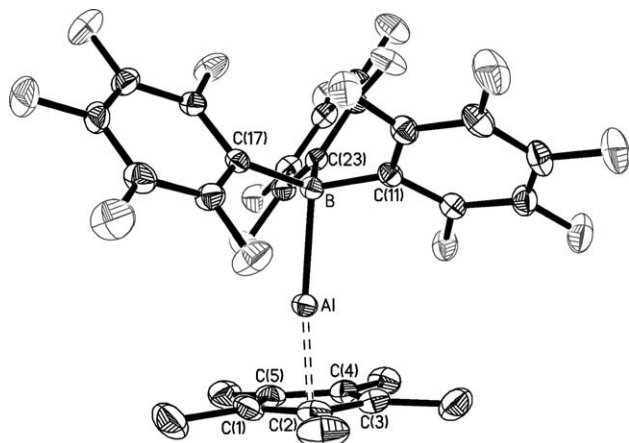
cases, the monomeric, univalent group 13 donor molecule was readily available by dissociation of the appropriate cluster or dimer. However, since [(C$_5$Me$_5$)B]$_x$ does not exist and (*t*-BuB)$_4$ is a robust cluster, it was necessary to make the first compounds with B→B donor–acceptor bonds by a less direct route [36]. One assessment of Lewis basicity relies on the extent of distortion of B(C$_6$F$_5$)$_3$ from trigonal planarity as complex formation takes place [37]. On this basis, since the sum of bond angles at boron in e.g., (η^5-C$_5$Me$_5$)Al→B(C$_6$F$_5$)$_3$ is 339.8(2)° [30] and virtually identical to that in Ph$_3$P→B(C$_6$F$_5$)$_3$ [37], it can be implied that (η^5-C$_5$Me$_5$)Al and Ph$_3$P are of comparable Lewis basicity with respect to B(C$_6$F$_5$)$_3$.

Given the above-mentioned similarity between monovalent RE fragments and phosphines in terms of donor behavior, it is not surprising that RE clusters and monomers will displace weaker bonded ligands such as CO and alkenes in transition metal complexes. This ligand substitution method represents a potent new addition to the established methods [38] for effecting group 13/transition element bond formation. Typically, RE clusters and monomers react with transition metal carbonyls to replace one CO per metal. Access to higher degrees of substitution is gained by using polyalkene metal complexes. For example, the reaction of [(Me$_3$Si)$_3$CIn]$_4$ with [Ni(cod)$_2$] affords the homoleptic complex [Ni{InC(SiMe$_3$)$_3$}$_4$] [39]. Another impressive example of the rich potential of the ligand exchange methodology is the formation of a novel cluster with three linearly arranged palladium atoms wrapped in a shell of eight (η^5-C$_5$Me$_5$)In ligands by treatment of [tmeda)Pd(CH$_3$)$_2$] with [η^5-C$_5$Me$_5$In]$_6$ [40] (Fig. 10). Due to lack of a suitable boron(I) precursor, it was necessary to use a less direct (metathetical) route for the preparation of the first examples of terminal borylene (boranediyl) complexes [41]. These developments completed the range of group 13 RE ligands that are terminally bonded to transition metal fragments. As in the case of the REER dimers,

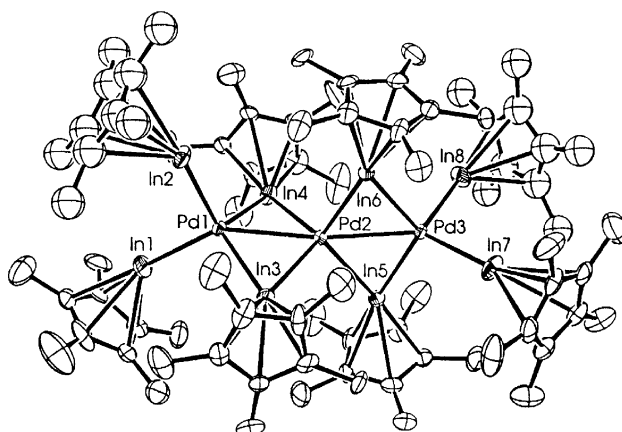Fig. 8. View of [{HC(CMeNAr)$_2$Al] (Ar = 2,4,6-*i*-Pr$_2$C$_6$H$_3$). The gallium analogue has a similar structure [28].

Fig. 9. View of (η^5-C$_5$Me$_5$)Al→B(C$_6$F$_5$)$_3$.

Fig. 10. View of [Pd$_3$(InCp*)$_4$(μ$_2$-InCp*)$_4$] (Cp* = η^5-C$_5$Me$_5$).
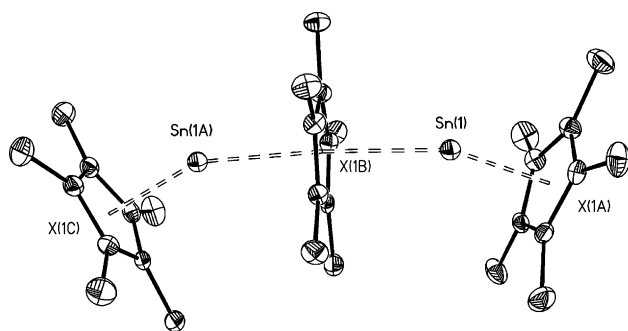
Fig. 11. View of the triple-decker cation, $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}C_5Me_5)\text{-}Sn(\eta^5\text{-}C_5Me_5)]^+$.

considerable discussion has arisen regarding the nature of the bonding between RE and transition metal moieties, primarily $Fe(CO)_4$. However, based on DFT calculations, the consensus view has emerged that the RE ligands behave predominantly as σ-donors toward transition metals [29,42,43].

In attempting to prepare Lewis acid–base complexes akin to the group 13 complexes of the type $RE \rightarrow ER'_3$, decamethylstannocene was treated $Ga(C_6F_5)_3$. However, instead of complex formation, this reaction resulted in the first example of a triple-decker main group cation [44]. Prior to this development, only two triple-decker main group anions had been reported [45,46]. In contrast to the *trans*-type geometry of the triple-decker anions, $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)]^+$ adopts a *cis*-type geometry (Fig. 11). The distance from the tin atoms to the centroids of the terminal C_5Me_5 rings (av. 2.246(18) Å) is shorter than that to the bridging C_5Me_5 moiety (av. 2.644(19) Å) which explains the fluxional behavior of this cation in solution. It was surmised that the initial step of the reaction is the abstraction of a $[C_5Me_5]^-$ anion by the strong Lewis acid $Ga(C_6F_5)_3$, to form $[Ga(C_6F_5)_3(C_5Me_5)]^-$ and $[C_5Me_5Sn]^+$, the latter of which electrophilically attacks $(\eta^5\text{-}C_5Me_5)_2Sn$ to form the triple decker cation. Clearly, at some point the $[Ga(C_6F_5)_3(C_5Me_5)]^-$ anion undergoes redistribution to form $[Ga(C_6F_5)_4]^-$. In subsequent work, a more rational approach to the synthesis of triple decker cations has been developed, viz. the addition of cationic fragments such as $[\eta^5\text{-}C_5Me_5M^+]$ (M = Sn, Pb) or In^+ [47] to the neutral metallocene, paying attention to the choice of the counteranion in order to maximize the lattice energy of the desired product.

3. Low valent main group chemistry – the materials science connection

The indium(I) derivative $[In(\eta^5\text{-}C_5H_5)]$ (which exists as a zig-zag chain in the solid state [48]) decomposes spontaneously at ambient temperature in dry anisole that contains polyvinylpyrolidone and a small quantity of

water to produce monodisperse nanoparticles of indium with a mean diameter of 6 ± 0.7 nm [49]. The reaction between $[In(\eta^5\text{-}C_5H_5)]$ and trioctylphosphine oxide (TOPO) containing $\sim$50 ppm of water produced well-separated, monodisperse indium particles of diameter 5.2 ± 0.5 nm. The use of long-chain amines as templates, together with photochemical decomposition of $[In(\eta^5\text{-}C_5H_5)]$, resulted in indium nanowire formation. This method was extended [50] to the controlled synthesis of nanowires of In_3Sn by UV irradiation of $[In(\eta^5\text{-}C_5H_5)]$ and $[Sn(NMe_2)_2]_2$ in the presence of hexadecylamine. More recently, it has been shown that good control of the nanoparticle and nanorod size can be achieved by depositing the indium inside the pore channels of mesoporous hybrid materials [51]. Oxidation of the indium nanoparticles to give indium oxide nanoparticles can be achieved without modification of their size and shape. Indium oxide, with a band gap of $\sim$3.6 eV, is known to exhibit luminescence and gas sensing properties.

Aluminum(I) and gallium(I) halides are producing a rich harvest of fascinating clusters [52]. These subhalides, which are generated in specially designed reactors, undergo disproportionation reactions at ambient temperature. Interception of the metal-forming process can be achieved by the use of ligands such as $(Me_3Si)_2N$ [53]. As a consequence, a protective shell is formed around an array of aluminum or gallium atoms that adopt the prototypical structures of these elements. The largest clusters of this type, $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ and $[Ga_{88}\{N(SiMe_3)_2\}_{20}]^{4-}$ [52], feature 57 aluminum and 68 gallium centers with purely metal–metal bonds and have diameters up to 2 nm. These and related clusters are beginning to provide valuable insights into the mechanisms of metal-forming processes by e.g., chemical vapor deposition. A particularly promising potential use of these large anions is for the synthesis of nanostructured alloys.

The availability of compounds with (p–p)π bonds involving the heavier group 15 elements renders them attractive targets for forming new classes of polymers. Although the spontaneous polymerization of $PhC\equiv P$ has been reported [54], only low-molecular weight oligomers were isolated. More recently, the phosphaalkene $MesP=CPh_2$ has been shown to undergo addition polymerization to form the corresponding polymer with a M_n of 11,500 g/mol and a polydispersity index of 1.25 [55]. Novel conjugated polymers analogous to the polyphenylenevinylenes that feature P=C or P=P linkages along the polymer backbone have also been reported recently [56,57].

4. Low-valent main group compounds as catalysts and reagents

Lower valent main group compounds have considerable potential as catalysts or reagents for chemical

synthesis. Diboron(4) compounds are noteworthy in this respect and have become commercially available. For example, the boron (+2) compound bis(pinacolato)diboron, in conjunction with palladium catalysts, is useful for a wide variety of transformations including the cross-coupling reactions of bis(pinacolato)diboron with haloarenes [58] or 1-alkenyl halides (triflates) [59], and the acylboration of allenes [60]. In the presence of a platinum catalyst, bis(pinacolato)diboron or bis(catecholato)diboron react with α,β-unsaturated ketones to afford the corresponding 1,4-addition products [61]. Another impressive use of diboron(4) compounds is the regiospecific, end-functionalization of alkanes using a rhenium catalyst under photolytic conditions [62]. It is likely that the selective functionalization results from a regiospecific reaction of a rhenium bis(boryl) complex with the alkane primary C–H bond.

More recently, interest has started to evolve in indium(I) mediated metal-catalyzed reactions. In particular, the use of allylic indium reagents is attracting attention because of the tolerance of such reagents to water, thereby permitting their use in environmentally benign aqueous synthetic procedures [63]. Another interesting development is the indium(I) chloride mediated coupling of epoxides with allyl bromide catalyzed by a reusable mesoporous silica-supported palladium catalyst to give homoallyl alcohols [64]. Also, the reductive homocoupling of aromatic aldehydes, ketones and imines to the corresponding 1,2-diols and 1,2-diamines has been reported by the use of a catalytic amount of $[In(\eta^5\text{-}C_5H_5)]$ in the presence of Me_3SiCl and metallic aluminum [65].

5. Conclusions

Despite the impressive progress that has been made in the lower valent chemistry of the group 13, 14, and 15 elements, it is clear that many more exciting discoveries remain to be made. It is also clear that significantly more uses will be found for the currently available and as-yet-unknown compounds in diverse fields such as materials science, catalysis, and synthesis.

Acknowledgement

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