SOME RECENT DEVELOPMENTS IN PRECURSOR ROUTES TO CERAMIC NANOCOMPOSITES

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Abstract—Reactive inorganic polymers and copolymers have recently been used to prepare homogeneously mixed crystalline ceramic solid solutions and composites. The polymers have considerable processing advantages over classical powders, and they may be used to obtain composite fibres, coatings, and dense or porous near net shape forms.

INTRODUCTION

Ceramics, historically defined as refractory, inorganic, solid-state compounds, are known for their high mechanical strength, wear resistance, hardness and thermal and chemical stability. They are less dense than metals, so they possess favourable strength-to-weight ratios relative to other structural materials. In addition, they display a wide range of interesting and useful electrical, magnetic and optical properties. With such characteristics, ceramic powders have been used to fabricate a large number of commercial products, and it is expected that ceramics will serve as key components in many future advanced technology programs including new transportation, communication and health care concepts. As simple as this sounds, before many advanced materials applications can be realized, it is necessary to make significant improvements in the fabrication of ceramic articles from readily available materials, namely powders or new forms such as polymers. This will not be a trivial task.

Until relatively recently, all inorganic oxide ceramics have been prepared as powders and fabricated into articles via classical high-temperature metallurgical techniques.[1] The stringent processing schemes often involved many steps, and the knowledge base for one material often did not transfer to another material. Further, the quantitative properties of a finished product often did not match those of the pure starting material. These shortcomings as well as the need to fabricate complex

architectures at low temperatures have recently stimulated searches for alternative chemical approaches. For example, as early as 1959 Roy[2], suggested that molecular metal alkoxides could be employed as raw materials for metal oxide based ceramics. In most instances, however, coarse particulates were generated during the syntheses, and the powders required further high-temperature processing to obtain useful, uniform monolithic articles. Nonetheless, this early work spawned studies of the chemical polymerization of metal alkoxides that led to the definition of the so-called solution based "sol–gel" process. The sol–gel approach for ambient or near-ambient condition formation of oxides has now been employed to obtain powder, film and fibre forms. This topic has been thoroughly reviewed,[3–7] and a great deal is known about the complex steps involved in molecular-to-ceramic transformation processes for many oxides. In addition, this chemistry and processing are finding their way into commercial utilization.

The synthesis and processing of equally interesting inorganic nonoxide ceramic materials have undergone a similar, although more delayed, development.[8] Prior to 1980, nonoxide ceramics were also obtained as powders from high-temperature reactions of simple, inexpensive raw materials. As found with oxides, these powders typically exhibited variations in compositions, phase homogeneity and purity, grain size and crystallinity. They were found to be useful for some applications; however, their unreliable processing and sintering characteristics made it difficult to obtain useful, high performance finished products with reproducible physical characteristics.

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Clearly, new approaches to the synthesis of non-oxide ceramics were required. In response to these problems, Yajima and coworkers[9] sought to determine if organosilicon compounds could be used to obtain processible (soluble or meltable) carbosilane polymers that, in turn, could be transformed to high-quality SiC forms. They indeed determined that some carbosilanes are good precursors to SiC, and this discovery touched off a rapid development of preceramic polymers that led to new routes to Si_3N_4, B_4C, BN, and AlN.[9-12] It was confirmed that inorganic polymers would not only provide ceramic powders with excellent properties, but more importantly the polymers could be processed into ceramic fibres, coatings, binders and dense or variable porosity bodies. These latter forms could not be obtained by traditional routes. Obviously polymer precursors hold considerable future commercial potential, assuming that production costs can be reduced, and it is expected that many new materials with designed properties will emanate from the emerging field of preceramic polymers.

One area that should benefit greatly from the development of polymer precursors is composite materials. Although most pure ceramics have a number of favourable performance characteristics appropriate for advanced component applications, ceramic composites and solid solutions of two or more pure phases often exhibit dramatically enhanced properties. For example, a number of composites display improved fracture toughness, thermal shock resistance, mechanical strength, microstructure stability and crystallinity properties. In some cases, these materials also display unique electrical, magnetic and optical properties. For many years, composites were obtained by physical mixing of micron-sized powder constituents, followed by traditional powder processing.[1,8] The products were found to be suitable for some applications; however, it is now known that improved properties are realized when fine grain (< 1 micron) powders are employed. Further, it has been discovered that fine powders are difficult to blend while controlling purity and crystallinity, and ultimate composite properties are often not achieved even with submicron constituent powders. As a result, in order to harness the vast potential for these useful materials, alternative synthetic and processing approaches have been sought.

To the solution chemist, it appears obvious that improved control of compositional homogeneity and purity in composite syntheses should be realized by use of single-source precursors, polymers and solution techniques. Indeed, it has been found that mixed metal alkoxides and sol–gel processing provide high-quality metal oxide composites,[13-16] and intense activity in this area is leading to novel materials and properties including ductile and superplastic compositions.[17-22]

Less attention has been given to the formation of advanced, high quality, fine grained, nonoxide composites, yet the literature contains numerous reports on novel properties displayed by nonoxide composites formed even by traditional processing of coarse-grained powders. For example, simple addition of BN powder to Si_3N_4 powders followed by traditional hot pressing produces composites with reduced dielectric constants compared to pure Si_3N_4. It also increases the thermal shock resistance of resulting powder compacts.[23] Subsequent work by Interrante and coworkers,[24] using polymer precursor derived Si_3N_4 combined with BN powders, revealed significant decreases in the activation energy for surface area reduction and inhibition of Si_3N_4 crystallization at 1600°C over pure Si_3N_4. It has also been noted that combination of AlN with SiC provides solid solutions with fine grain sizes, high microstructure uniformity, and improved mechanical properties.[25]

Despite these promising results, it is still necessary to devise improved solution-based synthesis and processing techniques in order to prepare fully homogeneous, nonoxide composites with optimum properties. Very few appropriate single-source precursors for nonoxide ceramics are presently known; however, the large array of nonoxide preceramic polymers offer intriguing alternative synthetic reagents. Some highlights of the recent progress in the application of molecular and polymeric preceramics in homogeneous composite generation are summarized in the following section, and these results clearly indicate that intense study in this area will have beneficial impacts on the design and synthesis of new generations of complex, multifunctional materials.

RECENT RESULTS

Three general approaches utilizing molecular and polymeric preceramics have been followed. In the first method, an inorganometallic or organometallic precursor polymer is combined with a reactive inorganic filler such as a pure, fine-grained metal. With favourable polymer designs, otherwise excessive elemental composition in the polymer over that required to form the ceramic is retained since it combines with the pure metal, giving a second ceramic phase. Obvious benefits of this approach are that ceramic yields are improved and off-gas evolution is reduced. If the metal powder is homogeneously dispersed, then this second ceramic phase should also be highly dispersed, and fine grained,

easily processed powders should result. Seyferth and coworkers[26] have used this approach to prepare several composites whose composition and crystallinity depend greatly on processing conditions including pyrolysis temperature and pyrolysis gas. For example, combination of a toluene solution of polysilazane $[(CH_3SiHNH)_{0.4}(CH_3SiN)_{0.6}]_n$ was sonicated with W powder (W:Si ratio 5:3), and the residue remaining after solvent evaporation was pyrolyzed under Ar at 1500°C. Powder X-ray diffraction (XRD) analysis showed the presence of WC and W_5Si_3 in approximately a 1:1 ratio. Pyrolysis of the precursor mixture in NH_3 at 800°C and then at 1500°C under Ar gave evidence for the formation of only W_5Si_3. It is interesting to note that, with these processing conditions, apparently none of the preceramic polymer is converted to Si_3N_4, which is the primary product of pyrolyses of the polymer under NH_3 in the absence of W. When higher initial ratios of Si were used (W:Si = 1:2), additional ceramic phases (e.g. WSi_2, WC, and SiC) were also obtained under selected processing conditions.

In the same study,[26] Ti and Zr were combined with the polysilazane and pyrolyzed under Ar at 1500°C. With these conditions, mixtures of the stable nitrides, TiN and ZrN, with SiC were formed. Pyrolyses of a polycarbosilane (Nicalon PCS), a known SiC precursor, with Al, Ti, V, Zr, Nb, Ta, and W in a M–Si ratio of 1:1 under Ar at 1500°C gave primarily mixtures of the respective metal carbides and SiC. The polymer/metal filler mixtures were successfully used to fashion near net shape articles. Finally, Seyferth[26] examined reactions of a BN precursor, $B_{10}H_{14} \cdot$ diamine, with Ti, Hf, Mo, W and La. Pyrolyses of these mixtures gave ceramic residues that contained the respective metal borides and amorphous material. Seyferth's initial study demonstrates that reactive polymers have potential; however, further studies will be required to fully characterize the total composition and microstructure of the composites as well as the processibility of the green bodies into useful compacts.

Sneddon and coworkers,[27] in a similar fashion, have combined THF solutions of the BN precursor polyborazylene, $(B_3N_3H_4)_n$, derived from dehydrogenation of molecular borazene $(B_3N_3H_6)$ with Ti powder. Subsequent pyrolysis of the reactive polymer–metal mixture under Ar at 1450°C gave a ceramic residue that was shown to contain TiB_2 and TiN by XRD analysis. The course of the reaction from 800 to 1450°C was also followed by XRD, SEM and TEM analyses, and it was found that the reaction onset was above 1000°C. The grain size of the product obtained at 1200°C was 50–100 nm, and this increased at higher temperatures. The precursor

mixture could be shaped into green bodies, and pyrolysis provided monolithic articles. These processing results are very promising for practical applications, and further studies of the grain size and microstructure evolution and their effect on properties of the final composite are under study.

Another of the limitations in the use of preceramic polymers for the formation of dense articles is the degree of shrinkage and porosity that develops upon pyrolysis of a polymeric green body. It has been suggested that the addition of passive or active fillers might alleviate this problem, and Greil and Seibold[28] have produced a model to predict critical volume fractions for potential fillers. Their work, as well as the chemical studies described above, illustrate the simplicity of the polymer approach as well as benefits that accrue in increased ceramic yields and reduced shrinkage and porosity. Clearly, additional studies in this area are warranted, and the results will likely be practical and useful.

A second approach to polymer-composite synthesis employs the blending of two precursors of the desired composition or copolymerization of two precursors. Interrante and coworkers[29] have described both "hot-drop" pyrolysis and standard pyrolyses of homogeneously mixed polymers in an effort to minimize phase separation. Combinations of an AlN precursor $[Et_2AlNH_2]_3$ with the silicon carbide precursors, vinylic polysilane (VPS), methylhydridopolysilane (MPCS), or hydridopolysilane (HPCS) led to liquids that were pyrolyzed under N_2 at 1000°C.[30–32] The mixtures produce $2H$ AlN/β-SiC or $2H$ SiC/AlN solid solutions depending on reactant ratios, pyrolysis conditions, and annealing conditions. The grain sizes were as large as 500 nm, but most were in the range of 10–50 nm. The interested reader is referred to the original citations for details. Using the same approach, Interrante and coworkers[29] have also blended VPS with $[Et_2AlNH_2]_3$ and pyrolyzed the mixture under NH_3. This results in formation of Si_3N_4AlN composites with grain sizes of 40–80 nm. The crystallinity and phase of the grains varied greatly with processing and annealing conditions. Similarly, mixtures of VPS with polyborazinylamine (PBZA)[33] gave a precursor that, upon pyrolysis, gave Si_3N_4BN composites.[34] It is interesting to note that the crystallization of the Si_3N_4 from the 1:1 mixture was retarded even at 1600°C; however, a 10:1 VPS:PBZA mixture led to significant crystallization after annealing at 1600°C. Finally, Sneddon and coworkers[35] have blended liquid borazine with hydridopolysilazane (HPZ), and pyrolysis of the resulting polymer gave boron containing β-Si_3N_4/β-SiC composites in which the

crystallization is also suppressed by the BN present.

A third approach that has been explored for composite formation involves the synthesis of single-source molecular compounds that contain all the necessary elements of the desired composite. For example, Interrante and coworkers[36] combined cyclotrisilazanes [RR'SiNH]$_3$ (R = Me, R' = Me or vinyl) with Et$_3$Al, and the resulting polymer was pyrolyzed, leaving SiCAlN composites with small grain sizes. The reaction of (EtNH)$_3$B with Et$_2$AlNH$_2$ gave a viscous polymer,[37] and its pyrolysis gave AlN grains (5–10 nm) homogeneously dispersed in a turbostratic BN matrix. In a similar fashion, combination of (EtNH)$_3$B with (Me$_2$N)$_4$Ti gave a solid material that produced partially crystalline TiN (3–6 nm) in a t-BN matrix.[29]

In our own group, we have explored additional examples of the latter two methods, and some progress has been made in understanding some of the stepwise chemistry that takes place in the formation and decomposition of both precursor copolymers and single-source precursor systems. For example, we have examined the reactions of (Me$_3$Si)$_3$Al · OEt$_2$ with NH$_3$ and find that a 1 : 1 reactant ratio produces a single-source dimeric precursor azaalane, [(Me$_3$Si)$_2$AlNH$_2$]$_2$.[38] Pyrolysis of this compound at 300°C leads to a polymer of idealized composition (Me$_3$SiAlNH)$_n$, and further in vacuo pyrolysis at 930°C gives a composite containing SiC and AlN. Further unpublished extensions on this system reveal that heating above 1000°C produces a solid solution of AlN/SiC and the average grain size of the composite formed is < 100 nm. Adjustments in the stoichiometry can be made by using an excess or deficiency of (Me$_3$Si)$_3$Al[39] and the SiC can be converted to Si$_3$N$_4$ or an intermediate silicon carbonitride material by heating the AlN/SiC ceramic in NH$_3$ above 1200°C.

Our group has also been active in developing precursor polymers for BN formation,[40] and that work includes efforts to prepare metal nitride/boron nitride composites. We have reported single-source precursors for BN/MN (M = Ti, V, Zr, Hf, Nb, and Ta) composite formation from the reaction of the little studied azide (N$_3$BNH)$_3$ with thiocyanate salts of the metals.[41] All efforts to date to fully characterize the single-source precursors have been unsuccessful; however, their pyrolysis at 1200°C gives, as shown by XRD analysis, excellent yields of fine grain (10–200 nm) crystalline metal nitrides in a turbostratic BN matrix. A transmission electron micrograph (TEM) for a sample containing crystalline TaN dispersed in t-BN is shown in Fig. 1. Higher resolution TEM for many samples reveals that the surface of each metal nitride is in fact coated with more highly ordered BN, and one example of

this behaviour is illustrated in Fig. 2. The coatings observed here are reminiscent of BN coatings formed from polyborazinylamine (PBZA) decomposition on metal oxides.[42] Further studies of (N$_3$BNH)$_3$ and various metal complexes are under study in our group.

During the course of our development of PBZA polymers as BN precursors, we have prepared several two-point polymers schematically represented by 1.[43] Either passive or reactive groups X can be

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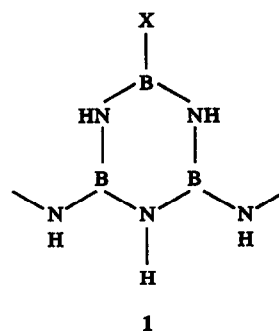
placed on the borazine monomer and subsequently carried into the polymer. Our concept for composite formation has been either to use a group X in the monomer that should decompose directly to a second ceramic phase or use an active group in the monomer that can serve as a coordination site in the polymer for metal ion binding in the polymer.

One example illustrating the first case above involves the formation of a silyl borazine (Me$_3$Si)$_3$SiB(BCl)$_2$(NH)$_3$.[44] It is important to note that most silylboranes with a direct Si—B bond are relatively unstable, and the organyl silyl group should serve as a source of SiC. Indeed, when the monomer is allowed to react with (Me$_3$Si)$_2$NH, a polymer is obtained that, when pyrolyzed, gives fine grain (< 50 nm) composites of homogeneously dispersed SiC/BN. The monomer for this precursor has not been fully characterized; however, a model compound, (Me$_3$Si)$_3$SiB(BMe)$_2$(NMe)$_3$, has been prepared and its crystal structure determined. A view of this molecule is shown in Fig. 3. The results from this study have encouraged further studies of related systems that will be described in future reports from our group.

Some examples illustrating the outcome of "copolymerizations" involving an active group in the polymer are summarized by Scheme 1. We have previously shown that active groups such as H, NH$_2$, and NMe$_2$ can be introduced into the two-point polymer.[43,45] In fact, when the X group is NH$_2$, the two-point polymer rapidly crosslinks, forming a precursor that behaves much like a "three-point" polymer derived from (ClBNH)$_3$ and (Me$_3$Si)$_2$NH. If this NH$_2$ group is intercepted, for example, with

Fig. 1. Transmission electron micrograph of a TaN/BN composite.

Fig. 2. Transmission electron micrograph of a ZrN crystallite coated with crystalline h-BN in a t-BN matrix.
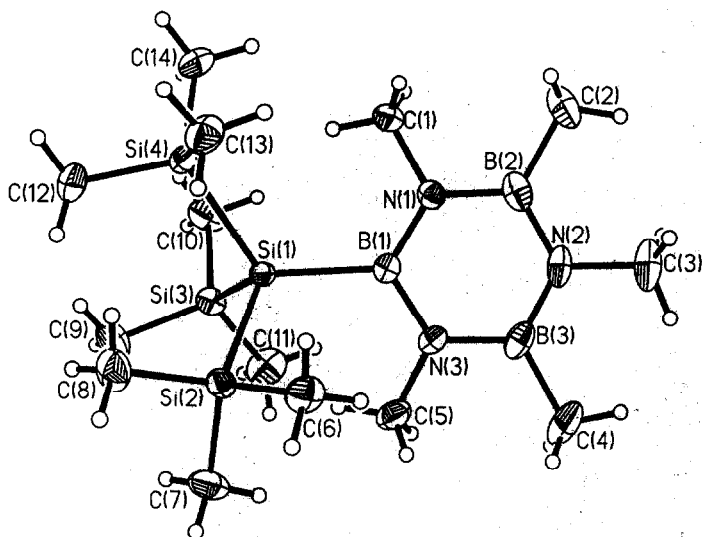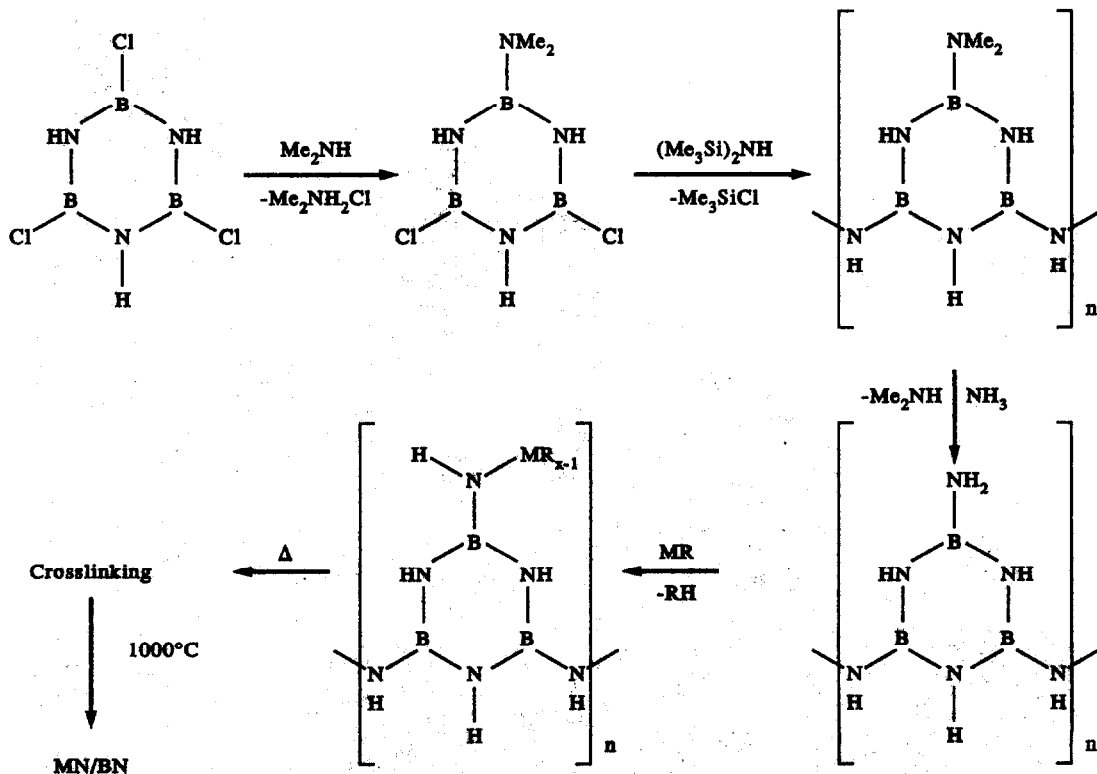
Fig. 3. Molecular structure of $(Me_3Si)_3SiB(BMe)_2(NMe)_3$.

competitive amination or transamination reactions, then products such as illustrated by **2** are likely to be formed. As examples, we have examined reactions of R_3Al (R = Me, Et, i-Bu, Me_3Si) and $M(NMe_2)_4$ (M = Ti, Zr) with the aminated two-point polymer. In each case, the metal reagent is incorporated into the initial polymer structure, as evidenced by the loss of alkane or Me_2NH. Gentle heating of the polymers initiates crosslinking and relatively rigid precursor polymers are obtained. Pyrolysis of these species, usually under NH_3 at 1000°C, gives ceramic residues with high ceramic
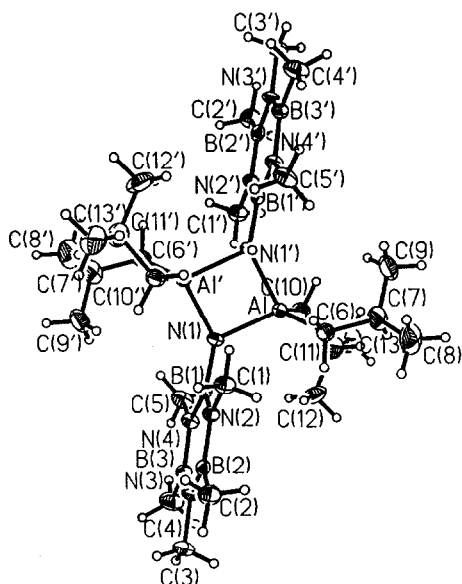

2

Scheme 1.

Fig. 4. Molecular structure of [i-Bu$_2$AlN(H)B(BMe)$_2$(NMe)$_3$]$_2$.

Indeed, the decomposition reactions of metal amides in the presence of a reducing atmosphere provided by NH$_3$ have been studied by several groups under a variety of conditions, and in most cases, metal nitrides are produced.[46]

CONCLUDING REMARKS

As we look to the 21st century, many pressing technological needs are on the horizon, and many people are engaged in efforts to design conceptual devices and processes that will address these needs. Most designs require availability of greatly improved, or even revolutionary, new materials as well as complex construction architectures. At this time, the materials needed are unavailable, and Hondras and Bullock[47] have accurately summarized the states of materials development: ".... materials represent the rate limiting step in the emergence of future technologies and for the competitivity of many existing technologies." Given this situation, it can be seen that materials chemists and engineers hold a crucial key to the continued well-being of our society.

It has been demonstrated already that classically prepared ceramic–ceramic composites are one class of materials that can provide enhanced performance characteristics for some needed devices. Further, early studies, outlined above, of new concepts for preparing and processing these materials through polymeric precursors suggest that continuing studies along these fronts will certainly lead to useful new fabrication possibilities. These results should certainly stimulate the inorganic chemist to explore novel molecular and polymeric concepts for solid state syntheses.
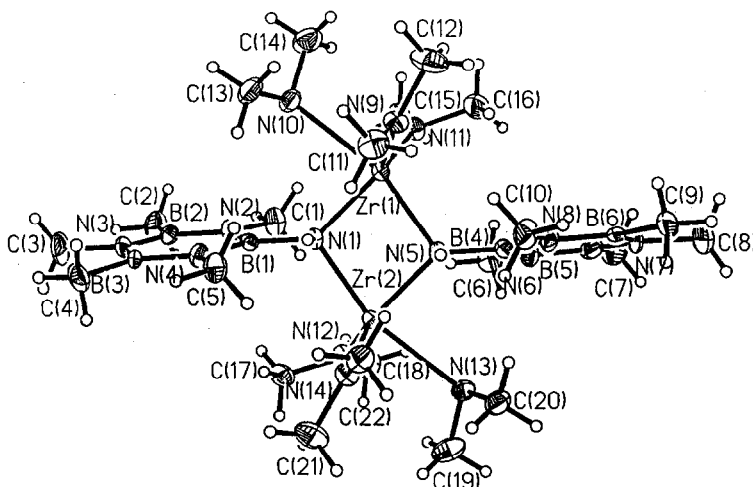
yields that contain fine grain crystalline metal nitrides (AlN, TiN, and ZrN) in a t-BN matrix.

Since the polymers 2 cannot be structurally characterized, model compounds have been prepared from reactions of (H$_2$NB) (BMe)$_2$(NMe)$_3$ and AlR$_3$ and M(NR$_2$)$_4$ reagents. In each case, the expected elimination chemistry takes place, and metal amido products are obtained. The molecular structures of dimeric [i-Bu$_2$AlN(H)B(BMe)$_2$(NMe)$_3$]$_2$ and [(Me$_2$N)$_3$ZrN(H)B(BMe)$_2$(NMe)$_3$]$_2$ are shown in Figs 4 and 5. These model studies are consistent with the formation of species such as 2 in the polymer reactions and with the subsequent decomposition reactions that produce MN/BN composites.

Fig. 5. Molecular structure of [(Me$_2$N)$_3$ZrN(H)B(BMe)$_2$(NMe)$_3$]$_2$.

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