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## CHAPTER 1

# The State of the Art in Boron Polymer Chemistry

**Manoj K. Kolel-Veetil and Teddy M. Keller**

*Advanced Materials Section, Materials Chemistry Branch, Chemistry Division, Naval Research Laboratory, Washington, DC 20375*

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## I. INTRODUCTION

### A. A Brief Historical Perspective on Boron and Its Polymers

Boron (*Buraq* in Arabic/*Burah* in Persian, which is the word for “white,” the color being attributed to borax (sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )) was discovered in 1808 independently by the British Chemist, Sir Humphry Davy, and two French chemists, Joseph Louis Gay-Lussac and Louis Jacques Thenard.<sup>1</sup> They isolated boron in 50% purity by the reduction of boric acid with sodium or magnesium. The Swedish chemist Jons Jakob Berzilius identified boron as an *element* in 1824. The first pure sample of boron was produced by the American chemist William Weintraub in 1909. Boron does not appear in nature in elemental form, but is found in its compounded

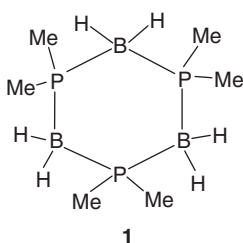
forms of borax, boric acid, colemanite, kernite, ulexite, and borates. In ancient times, compounds of borax ores known as tincal were exported from Tibet. Historically, boron is known to have been used for refining gold and silver in Arabia, for ceramic glazes in China, and for embalming in Egypt. Egyptians are known to have used the salt natron, which contains borates along with other common salts such as sodium bicarbonate, and sodium chloride in the mummification process. Marco Polo is believed to have brought natron to Italy where it was used by the artisans of the time.<sup>2</sup>

The United States and Turkey are the world's largest producers of boron.<sup>1</sup> Economically important sources are from the ores rasorite (kernite) and tincal, which are both found in the Mojave Desert of California, with borax being the most important source there. The famous "20-Mule-Team Borax," now a part of chemistry folklore, originates from the time when teams of 20 mules used to haul colemanite from Furnace Creek in Death Valley 166 miles south to Mojave. Elemental boron in its impure form can be obtained by the reduction of the oxide  $B_2O_3$  by magnesium, and in the pure form by the reduction of  $BCl_3$  by hydrogen on hot filaments.<sup>1</sup>

Boron with an atomic number of 5 is electron deficient, possessing a vacant p orbital (one of the 2p orbitals) making it a good electrophile. In terms of hybridization of atomic orbitals, boron has three  $sp^2$  hybridized orbitals pointing to the vertices of an equilateral triangle with its vacant p orbital positioned perpendicular to the plane of the equilateral triangle containing the  $sp^2$  orbitals. Thus, compounds of boron often behave as Lewis acids, readily bonding with electron-rich substances to compensate for its electron deficiency. Boron, on reaction with hydrogen, is known to form clusters of borohydrides called boranes.<sup>3</sup> Borane clusters, wherein a few of the boron atoms have been substituted by carbon atoms, yield a class of compounds known as carboranes. Boron also exists in "inorganic benzene-like" ring systems such as borazine, boroxine, and triphosphatiborin with nitrogen, oxygen, and phosphorus, respectively. The element boron exists in nature in high abundance both as boron 10 and boron 11 isotopes, with the nucleus of the latter possessing one additional neutron.<sup>2</sup> Boron 10 nucleus is the only *light* element that is capable of binding a slow neutron (or thermal neutron) to yield an excited boron-11 nucleus.<sup>2</sup>

The first reports on the formation of boron polymers were from Alfred Stock in the 1920s on the generation of a boron hydride polymer during his pioneering studies on boron hydride (borane) chemistry.<sup>4</sup> He discovered that fairly complicated compounds analogous to hydrocarbons could be built up from boron and its hydrides. Following Stock's work, Herbert Schlesinger and Anton Burg raised the chemistry of boron hydrides to new heights.<sup>5</sup> Based on the aminoborane adducts ( $R_3N \cdot B_2H_5$ ), with electron deficient bonds (or B—H—B three-centered bonds), obtained from amines such as  $NH_3$  or  $NHMe_2$  and diborane, Burg and co-workers explored the chemistry of similar diborane adducts with phosphine. Phosphine and diborane were found to yield the trimer  $[(CH_3)_2PBH_2]_3$  (**1**) (Fig. 1), which was discovered to be stable when heated to 400°C, with little decomposition, and to reduction by sodium in liquid ammonia.<sup>6</sup> This result, originating from a project sponsored by the Office of Naval Research (ONR), was a serendipitous one, as the initial intent was to make highly water-reactive boron hydride derivatives that might be used to propel underwater torpedos much faster. From then on, ONR extensively supported the development

of stable rubbers containing B—H bonds. Out of such efforts, the carboranosiloxane rubbers, renowned under the tradename DEXSIL, was engineered into existence by Heying and Schroeder at the Olin Laboratories in New Haven, Connecticut.<sup>7</sup> Burg and co-workers discovered that when the  $(\text{CH}_3)_2\text{PBH}_2$  unit was made in the presence of a slight excess of base, a long open-chain compound with as many as 300 repeating units was formed. In anticipation of their high-temperature stability and flame retardancy, the exploration of polyphosphinoboranes, materials based on skeletons of alternating phosphorus and boron atoms, was undertaken in the 1950s and 1960s.<sup>8</sup> However, these pioneering forays could only produce products with low yields and low molecular weights.<sup>9</sup>

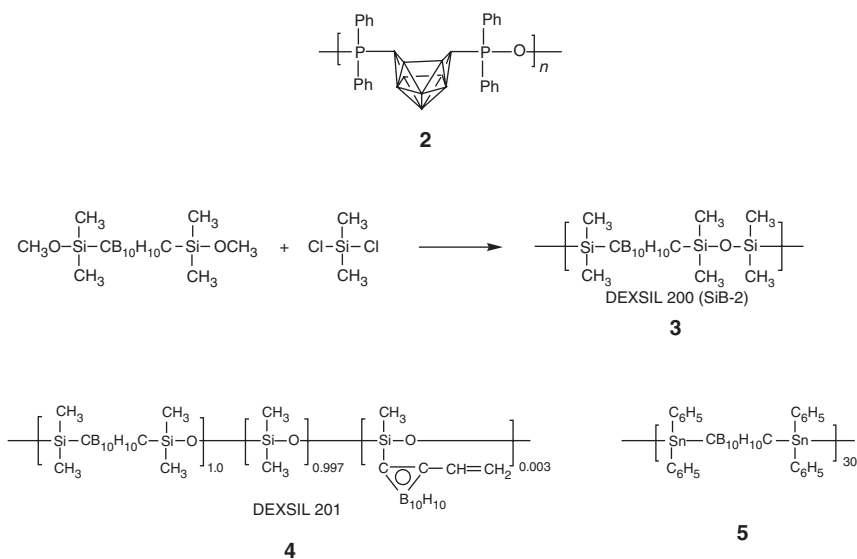


**Figure 1** The triphosphatriborin cyclic product  $[(\text{CH}_3)_2\text{PBH}_2]_3$  (**1**) obtained from  $\text{PMe}_3$  and  $\text{B}_2\text{H}_6$ . (Adapted from ref. 6.)

In their search for thermally stable polymers, the team of Schroeder and Heying at Olin Laboratories synthesized the first polymer (**2**) (Fig. 2) with P—O—P linkages containing the open boron cluster decaborane within the chain architecture (with a molecular weight of ca. 27,000) by the triethylamine-catalyzed condensation reaction between bis(chlorodiphenylphosphine)decaborane and bis(hydroxydiphenylphosphine)decaborane.<sup>10</sup> The selection of boron as the primary element was based both on bond-strength considerations (after Burg's results) and its ability to form appropriate cluster compounds. Simultaneously, they synthesized a P—N=P (phosponitrile) bonded decaborane polymer by the reaction of two difunctional monomers, a diphosphine and a diazide compound derived from diborane. Both of these thermally stable polymers were observed to flow during cross-linking through their dicarborane units. However, these materials were found to be unsuitable for use as molding compounds. Subsequently, in the interest of making elastomeric high-temperature rubbers, the Olin team focused its efforts on the synthesis of silylcarborane systems involving the icosahedral carboranes, *o*-, *m*-, and *p*-carborane.

In Olin's attempts to derivatize dilithiated products of *o*-carborane with chlorosilanes for further reaction with ammonia, it was observed that cyclic compounds, instead of polymers, were produced by the interaction of the substituents on the adjacent carbon atoms in the *o*-carborane units.<sup>11</sup> However, when a linear dimethoxy intermediate of *m*-carborane was reacted as an equimolar mixture with dichlorosilane in the presence of the catalyst  $\text{FeCl}_3$ , the quantitative evolution of  $\text{CH}_3\text{Cl}$  was observed

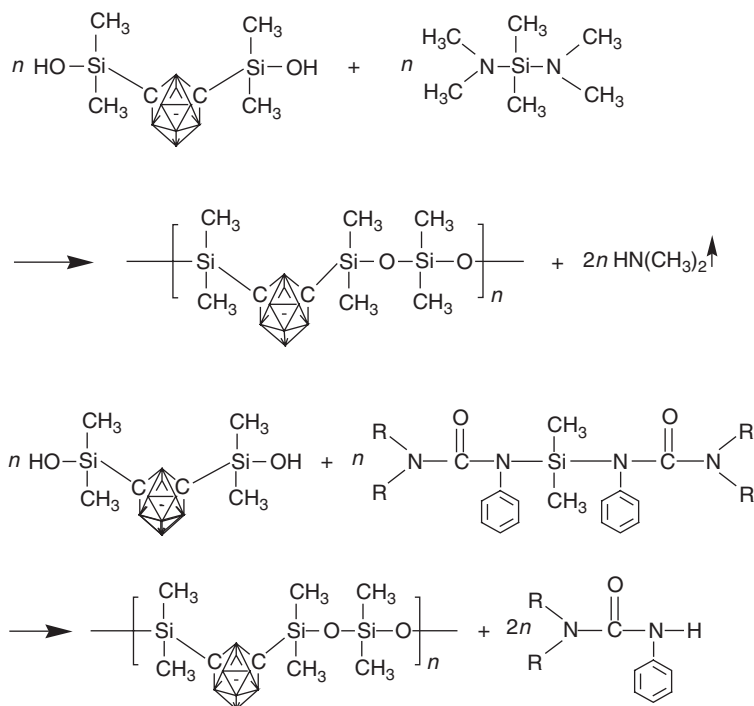
producing a crystalline polymer, which Olin named as DEXSIL 200 (SiB-2) (**3**) (Fig. 2); (M.P. = 151°C).<sup>12</sup> Since the number of repeating units in these polymers was low (5–10 units), some siloxyl moieties with pendant 1-vinyl-*o*-carboranyl groups were introduced in these polymers to improve their curing characteristics, resulting in DEXSIL 201 (**4**) (Fig. 2).<sup>13</sup> DEXSIL 201, upon curing, was found to have a tensile strength of 100 to 150 psi and an elongation of 120 to 250%, both of which were improvable upon addition of selected fillers.<sup>14</sup> Subsequently, it was discovered that carborane polymers (**5**) (Fig. 2) containing tin bridges were amenable to synthesis with higher molecular weights than **3** or **4**. These polymers (with a M.P. of 250–255°C) were produced by the reaction of  $(C_6H_5)_2SnCl_2$  with *m*- $B_{10}H_{10}C_2Li_2$  and contained up to 30 repeating units when formed in Decalin.<sup>15</sup> Continuing its quest for high-temperature polymers, the Olin team attempted the inclusion of *p*-carborane units in these polymers. When the dilithio salt of *p*-carborane was treated with diphenyltin chloride, the polymers were observed to form with an average chain length of only 11 repeating units melting in the 300–400°C range.<sup>16</sup>



**Figure 2** Schematic representations of the Olin polymers: **2** (with —P—O—P— linkages), **3** and **4** (DEXSIL carborane polymers), and **5** (carborane polymers with tin bridges). (Adapted from ref. 7.)

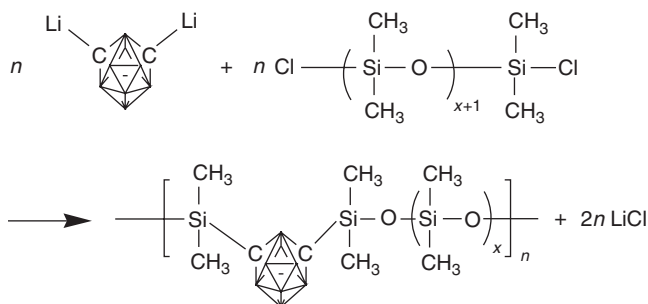
While the Olin efforts on the production of high-temperature polymers were centered mainly on  $FeCl_3$ -catalyzed condensation reactions, subsequent efforts from Union Carbide, Inc. utilized an aminosilane route and a ureidosilane route (Fig. 3) to synthesize carboranylenesiloxane polymers of high molecular weights. Using the former route, the polymer was produced by a condensation reaction between a carborane-disilanol and bis(dimethylamino)dimethylsilane, during which an expulsion of a

dimethylamine by-product occurred.<sup>17</sup> In the latter route, the bis(dimethylamino) dimethylsilane reagent was replaced with a bisureidosilane monomer to yield phenyl urea as the by-product during the polymerization.<sup>18</sup> The aminosilane reaction had the advantage that it did not require a catalyst and was performable between  $-10$  and  $25^{\circ}\text{C}$ . However, the molecular weights of the polymers synthesized by this route seldom exceeded 20,000. The low molecular weights were attributed to the scission of the backbone of the polymer by the dimethylamine by-product. The aminosilane route was abandoned and the ureidosilane route was seriously pursued. In the initial trials of the reaction, where the bisureidosilane monomers were prepared and utilized *in situ*, the molecular weights of the resulting polymers were found to be quite low. At the high polymerization temperature of  $160$ – $170^{\circ}\text{C}$ , the carboranedisilanol underwent self-condensation, thereby causing the molecular weights of the polymers to drop. This self-condensation problem was circumvented by the development of a low-temperature, solution polycondensation reaction, that included the slow addition of the solid carboranedisilanol monomer into a solution of the bisureidosilane.<sup>19</sup> The molecular weights of the polymers obtained by this modified route were as high as 200,000. Subsequently, the synthesis of ultra-high molecular weight (molecular weight of several millions) carboranylenesiloxane polymers was achieved by the Union Carbide team by a modification of the low temperature ureidosilane procedure.<sup>20</sup>



**Figure 3** Reaction schemes for the aminosilane (top) and the ureidosilane (bottom) routes for the synthesis of carboranylenesiloxane polymers. (Adapted from ref. 23.)

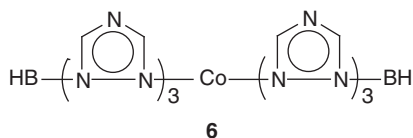
The Union Carbide team also utilized the dilithiocarborane chemistry to produce carboranylenesiloxane polymers by the metal-halogen interchange reaction (Fig. 4) between dilithiocarboranes and dichlorosiloxanes.<sup>21</sup> Polymers with molecular weights up to 52,000 were synthesized by this procedure.



**Figure 4** Reaction scheme for the metal-halogen interchange reaction between dilithiocarboranes and dichlorosiloxanes for the synthesis of carboranylenesiloxane polymers. (Adapted from ref. 23.)

In addition to the icosahedral carboranes, the incorporation of smaller carboranes such as  $\text{C}_2\text{B}_5\text{H}_7$  and/or  $\text{C}_2\text{B}_8\text{H}_{10}$  in carboranylenesiloxane polymers was also achieved by the utilization of their dilithio, diethoxysilyl and dichlorosilyl derivatives in  $\text{FeCl}_3$ -catalyzed polycondensation reactions. A series of homo- and co-polymers were synthesized by this procedure. However, the molecular weights of these polymers were observed to be low, with the highest being 12,500.<sup>22</sup> A more descriptive history of the Olin and the Union Carbide works on carboranylenesiloxane polymers is available in the excellent book on high-temperature siloxane elastomers by Dvornic and Lenz.<sup>23</sup>

During the time of the Olin reports, the first examples of oligomeric boron-bridged (1-pyrazolyl)borate systems appeared from the laboratory of Trofimenko at DuPont Chemicals.<sup>24</sup> He reported the synthesis of poly(1-pyrazolyl)borates (**6**) (Fig. 5) from the reactions of alkali metal borohydrides with the pyrazole ligand. The (1-pyrazolyl)borate ligand was obtained from two pyrazole units when bridged by a  $\text{BR}_2$  unit on one side and by a metal or onium ion on the other. Even though reports



**Figure 5** The first reported poly(1-pyrazolyl)borate (**6**) containing a cobalt bridge. (Adapted from ref. 24.)

of the syntheses of a number of pyrazolyl borate and pyrazabole (a ligand obtained by the bridging of two pyrazole units by two  $BR_2$  units) complexes have appeared in the literature since Trofimenko's account, there are relatively few examples of polymers containing these ligands.

Since these early studies on poly(phosphinoboranes), poly(carboranylensiloxanes) and poly(1-pyrazolyl)borates, the polymer chemistry of boron has burgeoned into an eclectic field that now encompasses areas such as polymeric precursors for high-performance composites and fibers, supramolecular nanomaterials, polymer-supported catalysts for polymeric and organic transformations, therapeutic agents in medicine, optical polymers, and so forth. In a rudimentary sense, these developments in the polymer chemistry of boron may be considered to have been driven by two fundamental characteristics of boron: first, its electronic characteristics; that of its  $\pi$ -delocalizing ability due to the presence of an empty p orbital, and second, its nuclear characteristics; that of its neutron capturing ability due to its natural existence in the form of two isotopes. In addition, a third characteristic of boron, that of its ability to react at high temperatures with oxygen to form a protective intumescent  $B_2O_3$  char, has also contributed to its utilization in high-performance polymers, composites, and fibers, besides other applications.<sup>25</sup>

This review summarizes the significant developments in the area of boron-containing polymers during the past 10 years. The review is divided into three sections, each of which covers a unique group of boron-containing polymers. The first section covers polymers in which boron exists as a backbone element (rather than as part of a ring or a cluster system) or in a pendent group in the polymer. The second section covers polymers wherein boron is present as a part of a ring system. The third section includes polymers where boron exists as a part of a cluster. Within each section, polymers have been grouped in terms of their applications or some other common characteristics such as the presence of a common element (e.g., P, Si, etc.), etc. When a boron polymer deserves inclusion in more than one section, it has been placed in the most appropriate section as deemed by the authors.

## II. RECENT ADVANCES IN BORON-CONTAINING POLYMERS

### A. Polymers Containing Boron Atoms in the Backbone or in Pendent Groups

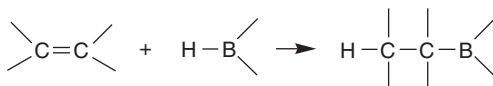
#### *i. $\pi$ -Conjugated Organoboron Polymers Used in Optical and Sensing Applications*

The electron delocalizing capability of a boron atom arising from its empty p-orbital positions it as an ideal candidate for incorporation in conjugated polymers for use in optical and sensing applications. The majority of the examples of boron-atom-containing conjugated polymers have been synthesized via the hydroboration reaction. However, other synthetic procedures have also been utilized.

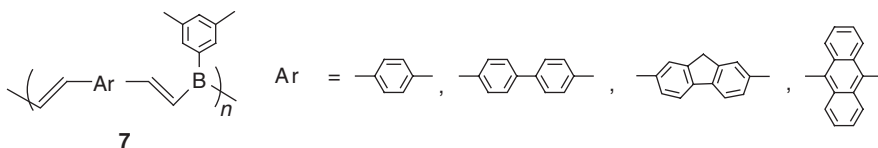


*a. Formed by the Hydroboration Route*

The ubiquitous hydroboration reaction (Fig. 6),<sup>26</sup> which involves the addition of a B—H bond across an organic unsaturation, has been used extensively by researchers for the production of various organoboron polymers, especially for optical [light-emitting diodes (LED), energy storage systems (batteries), nonlinear optical (NLO), etc.] and sensing applications. Chujo and co-workers have utilized this reaction strategy for constructing an impressive library of fluorescent polymers (7) (Fig. 7).<sup>27</sup> A detailed account of their research is present in Chapter 3 of this book. On boron incorporation, the optical and sensing properties of these polymers benefit from the extension of their  $\pi$ -conjugation through the utilization of the reactivity of the vacant p-orbital of the boron atom.<sup>27</sup>

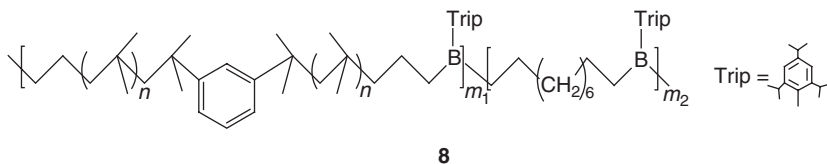


**Figure 6** The hydroboration reaction.



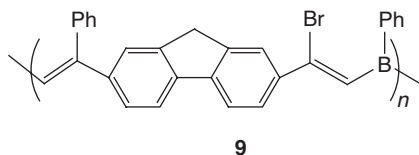
**Figure 7** Some  $\pi$ -conjugated fluorescent organoboron polymers (7) synthesized by the hydroboration polymerization reaction. (Adapted from ref. 27.)

In one of their notable examples, the hydroboration polymerization of low molecular weight allyl-telechelic polyisobutylene with tripylborane (trip = 2,4,6-triisopropylphenyl) was found to yield air-stable organoboron segmented block copolymers. These boron main-chain polymers (8) (Fig. 8), unlike the general ones, were stable to air. The stability was due to the steric hindrance of the bulky tripyl groups preventing oxygen attack of the borons.<sup>28</sup>



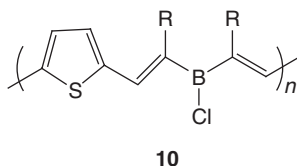
**Figure 8** The air-stable  $\pi$ -conjugated organoboron segmented block copolymer (8) obtained by the hydroboration polymerization of allyl-telechelic polyisobutylene, 1,9-decadiene, and tripylborane. (Adapted from ref. 28.)

In addition to hydroboration, haloboration and phenylboration have also been used in the synthesis of  $\pi$ -conjugated organoboron polymers (**9**)<sup>29</sup> (Fig. 9) and polymers containing B—N bonds.<sup>30</sup>



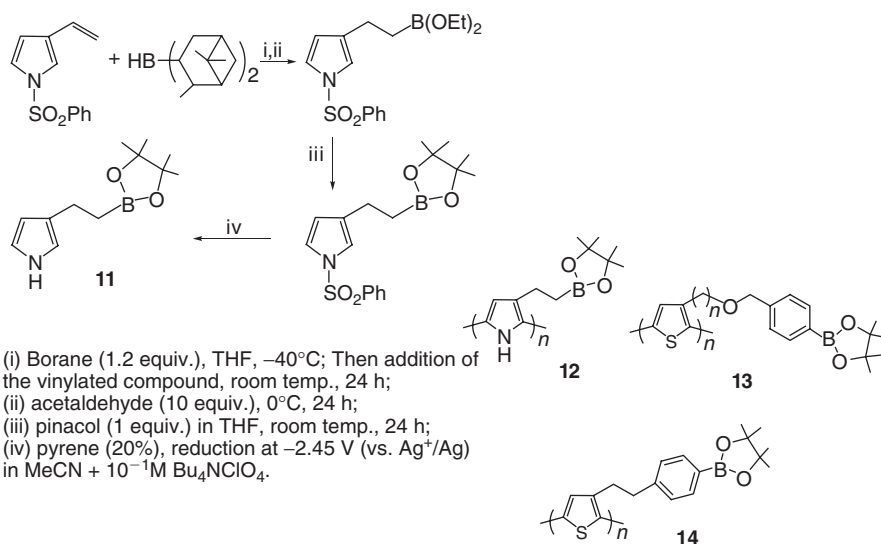
**Figure 9** The  $\pi$ -conjugated organoboron polymer (**9**) produced by haloboration-phenylboration polymerization between 2,7-diethynylfluorene and  $\text{Ph}_2\text{BBr}$ . (Adapted from ref. 29.)

The synthesis of unsaturated polymers (**10**) (Fig. 10) containing boron atoms and thiophene units in the backbone was reported by Corriu and Douglas.<sup>31</sup> Polythiophenes, an important class of conjugated electroactive polymers, are known to have the potential for such applications as energy storage, electrochromic devices and electrochemical sensors.<sup>32</sup> The efficacy of polythiophenes in these applications depends on the nature and extent of their doping, usually with electron acceptors. The Corriu/Douglas polymers, possessing both electron-donor (sulfur) and electron-acceptor (boron) sites, were expected to show interesting properties, since the boron sites with vacant 2p orbitals were available to act as *in situ* electron-acceptor dopants.



**Figure 10** The  $\pi$ -conjugated polythiophene (**10**) containing thiophene units and boron atoms in its backbone. (Adapted from ref. 31.)

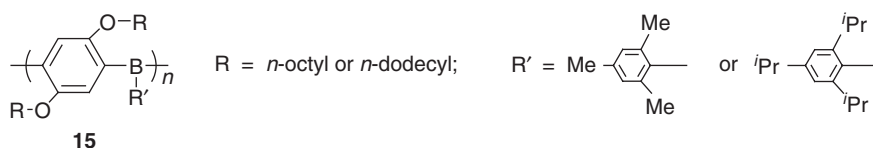
In the area of ion sensing, cation recognition by electrodes containing functionalized redox-active polymers has been an area of considerable interest. Fabre and co-workers have reported the development of a boronate-functionalized polypyrrole as a fluoride anion-responsive electroactive polymer film. The electropolymerizable polypyrrole precursor (**11**) (Fig. 11) was synthesized by the hydroboration reaction of 1-(phenylsulfonyl)-3-vinylpyrrole with diisopinocampheylborane followed by treatment with pinacol and the deprotection of the pyrrole ring.<sup>33</sup> The same methodology was utilized for the production of several electropolymerizable aromatic compounds (of pyrrole (**12**) (Fig. 11), thiophene (**13** and **14**) (Fig. 11), and aniline) bearing boronic acid and boronate substituents as precursors of fluoride- and/or chloride-responsive conjugated polymer.<sup>34</sup>



**Figure 11** The reaction scheme for the polypyrrole precursor (**11**) synthesis (left; top) with reagents and conditions (left; bottom). Representative pyrrole (**12**) and thiophene (**13** and **14**)-based redox-active polypyrroles. (Adapted from refs. 32 and 33.)

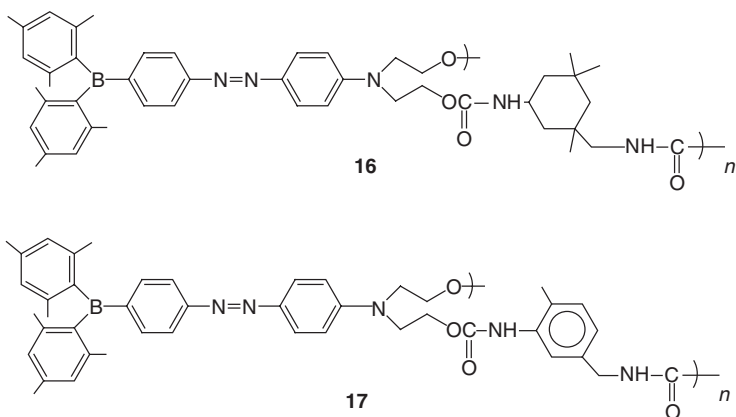
### b. Formed by Other Synthetic Routes

Grignard chemistry was used as an alternative to hydroboration reaction by the Chujo team in its search for new n-type conjugated polymers for utilization in polymer energy storage systems. By this route, the syntheses of  $\pi$ -conjugated poly(*p*-phenylene-boranes) (**15**)<sup>35</sup> (Fig. 12) and poly(ethynylene-phenylene-ethynylene-borane)s were reported.<sup>36</sup>

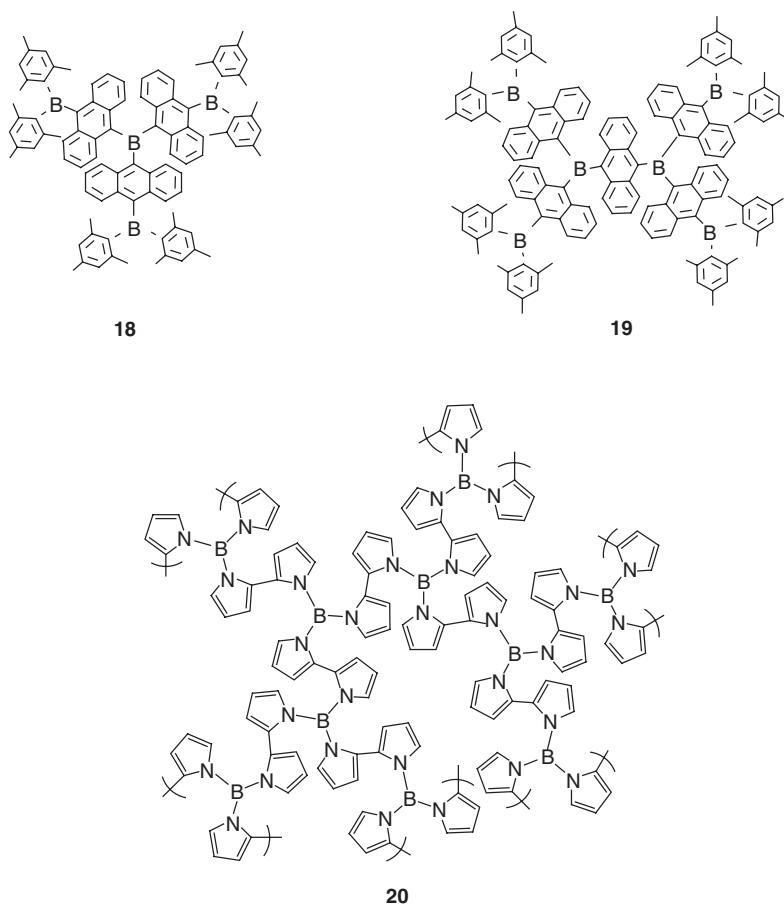


**Figure 12** Some  $\pi$ -conjugated poly(*p*-phenylene-boranes) (**15**). (Adapted from ref. 35.)

NLO materials (**16** and **17**) (Fig. 13) have been obtained from polyurethanes by the incorporation of sidechains with boron chromophores.<sup>37</sup> The dihydroxy ligand of an azobenzene ligand containing a dimesityl boron acceptor was reacted in a polycondensation fashion with the diisocyanate groups of the polyurethanes to yield the desired polymers. Halogen displacement and transmetallation reactions have been utilized in the development of extended  $\pi$ -conjugated systems of tri-9-anthrylborane with dendritic structures.<sup>38</sup> In one (**18**) (Fig. 14) of the novel compounds, three identical



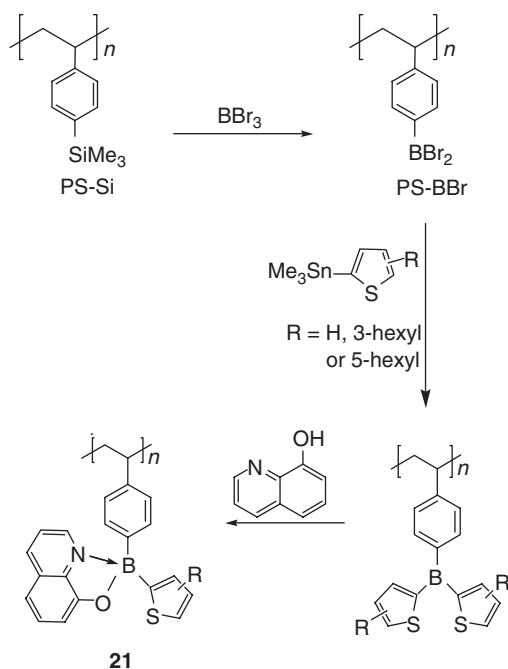
**Figure 13** Boron chromophore-containing polyurethanes (**16** and **17**) for NLO applications. (Adapted from ref. 37.)



**Figure 14**  $\pi$ -Conjugated dendritic polymers (**18** and **19**) obtained from tri-9-anthrylborane. The branched conducting polymer **20** was obtained from tris(*N*-pyrrolyl)borane. (Adapted from refs. 38 and 39.)

$\pi$ -electron systems were introduced onto a planar boron atom, which made it possible to extend the lowest unoccupied molecular orbital (LUMO) over the three  $\pi$ -systems across the vacant p-orbital of boron. The generation of a similar  $\pi$ -extended conducting polymeric system (**20**) (Fig. 14) has been realized by the electrochemical oxidation in THF of tris(*N*-pyrrolyl)borane. The data from pendant group analysis and the number of electrons consumed during electropolymerization suggested the formation of a branched conducting polymer with boron as the diverging center. The conductivity of the polymer film was evaluated to be ca.  $7 \times 10^{-4} \text{ S cm}^{-1}$ .<sup>39</sup>

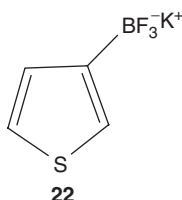
The synthesis of luminescent organoboron quinolate polymers (**21**) (Fig. 15) via a three-step procedure starting from a silylated polystyrene has been communicated. The synthesis was initiated by the highly selective borylation of poly(4-trimethylsilylstyrene) (PS-Si), followed by the replacement of the bromine substituents in poly(4-dibromoborylstyrene) (PS-BBr) with substituted thienyl groups (R = H, 3-hexyl, 5-hexyl). In the final step, the 8-hydroxyquinolato moiety was introduced. The hexyl-substituted polymers efficiently emitted light at 513–514 nm upon excitation at 395 nm.<sup>40</sup>



**Figure 15** Luminescent organoboron quinolate polymers (**21**) produced from silylated polystyrene. (Adapted from ref. 40.)

Several other organoboron polymers have been developed by various synthetic strategies and utilized to construct polymeric sensing systems for cations, dopamine, saccharides, and so on. Fabre and co-workers have reported the preparation of a conjugated trifluoroborate-substituted polythiophene system for sensing cations such as

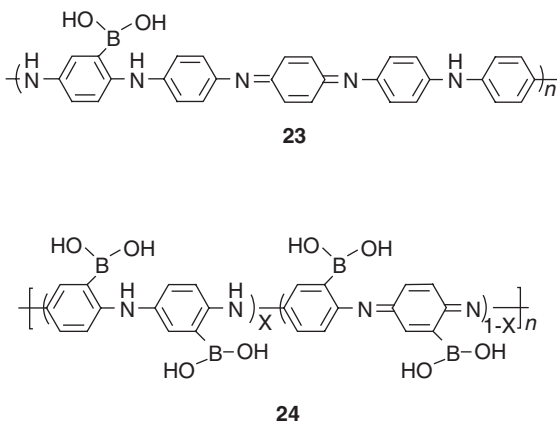
$\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Bu}_4\text{N}^+$ . The monomer **22** (Fig. 16) used for the synthesis of the polymer was produced in one step from 3-thiopheneboronic acid by reacting it with potassium hydrogen difluoride. The electrochemical and UV-visible spectroscopic responses of the polymer were found to be dependent on the nature of the cation.<sup>41</sup>



**Figure 16** Trifluoroborate-substituted thiophene monomer (**22**) used in the synthesis of a conjugated polythiophene system. (Adapted from ref. 41.)

A poly(aniline boronic acid)-based conductimetric sensor for dopamine consisting of an interdigitated microarray electrode coated with poly(aniline boronic acid) has also been developed by the Fabre team. The sensor was found to show a reversible chemoresistive response to dopamine without interference by ascorbic acid from their mixtures.<sup>42</sup>

Boronic acid-containing polyaniline has also been utilized in diabetes-related research. One such polymer (**23**) (Fig. 17) has been observed to exhibit a linear near-infrared optical response to saccharides.<sup>43</sup> The polymer was prepared by the copolymerization of aniline with 3-aminophenylboronic acid using 10 mM  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 1 M HCl. The films were observed to undergo changes in the absorption spectra on addition of saccharides at pH 7.2.



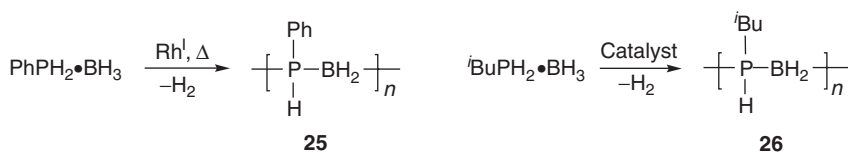
**Figure 17** Boronic acid-containing polyanilines (**23** and **24**) used in the detection of saccharides. (Adapted from refs. 43 and 44.)

Similar boronic acid-containing polyaniline-based potentiometric sensors (**24**) (Fig. 17) have been demonstrated to be effective for the nonenzymatic detection of glucose.<sup>44</sup> The studies on the selectivity of the polymer-bound boronic acid in its complexation reaction toward different sugars ( $\alpha$ -methyl-D-glucoside, D-glucose, and fructose) revealed that for D-glucose, in a pH 7.4 phosphate buffer saline, reversible responses were obtainable within the physiological relevant range of 4–6 mM.

## ii. Boron Polymers Containing P, Si, or Organometallic Units

### a. Boron Polymers Containing P Atoms

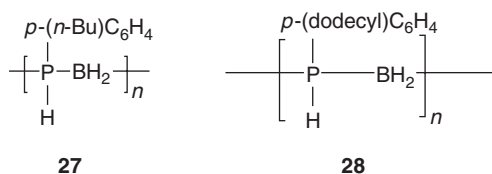
After Burg's and the Olin team's studies on phosphorus-containing boron polymers, new discoveries of boron polymers with phosphorus–boron bonds and an appreciable molecular weight (up to a  $M_w$  of 31,000) had to wait until 1999. Research by Manners and co-workers revealed that the phosphane–borane adduct  $\text{PhPH}_2\cdot\text{BH}_3$  undergoes dehydrocoupling in refluxing toluene to produce an off-white polymeric product poly(phenylphosphinoborane)  $[\text{PhPH-BH}_2]_n$  (**25**) (Fig. 18), when it was carried out (110°C, 14 h) in the presence of a 0.3 mol%  $[\text{Rh}(1,5\text{-cod})_2][\text{Otf}]$  catalyst.<sup>45</sup> This polymer, which could be considered an analog of polystyrene with phosphorus–boron backbone, was obtained as an air- and moisture-stable solid with an absolute weight average molecular weight ( $M_w$ ) of 5600. However, when the polymerization was achieved in the absence of a solvent by heating  $\text{PhPH}_2\cdot\text{BH}_3$  and one of the catalysts from Rh(I) [ $\{\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})\}_2$ , anhydrous  $\text{RhCl}_3$  or  $\text{RhCl}_3$  hydrate (ca. 1 mol % Rh)] at slightly elevated temperatures (3 h at 90°C and 3 h at 130°C), a polymeric product with a higher molecular weight ( $M_w = 31,000$ ) was observed to have formed.



**Figure 18** Syntheses of poly(phenylphosphinoborane)  $[\text{PhPH-BH}_2]_n$  (**25**) and poly(isobutylphosphinoborane)  $[\text{}^i\text{-BuPH-BH}_2]_n$  (**26**) from their respective phosphane–borane adducts. (Adapted from ref. 45.)

In subsequent studies by the Manners team on the catalytic dehydrocoupling of alkyl-substituted phosphine–borane adduct  $\text{}^i\text{-BuPH}_2\cdot\text{BH}_3$ , that were performed under neat conditions at 120°C in the presence of  $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})_2]$ , the phosphinoborane polymer poly(isobutylphosphinoborane)  $[\text{}^i\text{-BuPH-BH}_2]_n$  (**26**) (Fig. 18) was observed to form in 80% yield. When the polymers **25** and **26** were subjected to prolonged heating at elevated temperatures in the presence of a catalyst, insoluble but solvent-swellable gels were obtained, presumably due to light interchain crosslinking through the P–B bonds.<sup>46</sup>

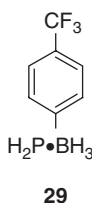
The transition metal-catalyzed synthetic methodology was further expanded by the Manners group to synthesize  $[(p\text{-}n\text{-BuC}_6\text{H}_4)\text{PH-BH}_2]_n$  (**27**) and  $[(p\text{-dodecylC}_6\text{H}_4)\text{PH-BH}_2]_n$  (**28**) (Fig. 19) via the rhodium-catalyzed dehydrocoupling procedure at elevated temperatures (ca. 90–130°C) of the corresponding phosphine–borane adducts.<sup>47</sup> Molecular-weight determinations by gel permeation chromatography (GPC) or light scattering methods revealed that the molecular-weight distributions of the two polymers were significantly broad. The irreproducibility of the molecular weights, owing to high viscosity and facile solidification of the reaction mixture, suggested the need for the development of improved catalysts that were sufficiently active to allow the formation of high molecular-weight polymers in solution.



**Figure 19** Poly(phosphinoborane)s,  $[(p\text{-}n\text{-BuC}_6\text{H}_4)\text{PH-BH}_2]_n$  (**27**) and  $[(p\text{-dodecylC}_6\text{H}_4)\text{PH-BH}_2]_n$  (**28**). (Adapted from ref. 47.)

In an effort to understand the mechanism of these dehydrocoupling reactions, the Manners group undertook further studies of several phosphine–borane adducts. The studies revealed that the dehydrocoupling of phosphine–borane adducts,  $\text{Ph}_2\text{PH}\cdot\text{BH}_3$ , proceeded by a homogeneous mechanism even when the catalysts in question were in the Rh(0) state. However, analogous Rh-catalyzed dehydrocoupling of amine–borane adducts were discovered to proceed via a heterogeneous mechanism involving Rh(0) colloids.<sup>48</sup>

In a recent report, the same group has discussed the influence that the electronic nature of the substituents located on phosphorus in the phosphine–borane adducts might have on both the rate of dehydrocoupling and the polymer properties.<sup>49</sup>  $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})_2]$ -catalyzed dehydrocoupling of the primary phosphine–borane adduct,  $\text{RPH}_2\cdot\text{BH}_3$  ( $\text{R} = p\text{-CF}_3\text{C}_6\text{H}_4$ ) (**29**) (Fig. 20) was observed to proceed at 60°C to yield high molecular-weight polyphosphinoborane polymer  $[\text{RPH-BH}_2]_n$



**Figure 20** The primary phosphine–borane adduct  $\text{RPH}_2\cdot\text{BH}_3$  (**29**) with the highly electron-withdrawing aromatic group  $\text{R} = p\text{-CF}_3\text{C}_6\text{H}_4$ . (Adapted from ref. 49.)

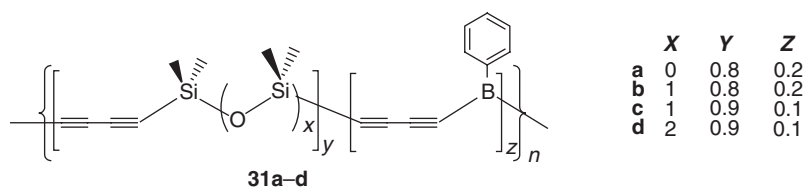


( $M_w = 56,170$ , PDI = 1.67). The electron-withdrawing nature of the fluorinated aryl substituents appeared to have had an important influence on the reactivity, as the dehydrocoupling process was observed to occur efficiently at the mildest temperatures observed with such polymerizations to date.<sup>49</sup>

### b. Silicon-Containing Boron Polymers

The most studied class of boron polymers containing boron–silicon bonds are the carboranylenesiloxane polymers. The history of these polymers was discussed at the beginning of this chapter. The more recent advances in this group of polymers and in silicon-containing borazine and boroxine polymers are discussed in later sections of this chapter. In this section, some remaining groups of silicon-containing boron polymers are discussed.

Sundar and Keller have reported the synthesis of linear boron–silicon–diacetylene polymers (**31**) (Fig. 21) using phenylboron dichloride (PBD) as the source for boron.<sup>50</sup> The compositions of the thermally stable boron–silicon–diacetylene copolymers **31a–d** are summarized in Figure 21. These polymers were observed to possess exceptional thermooxidative stabilities.



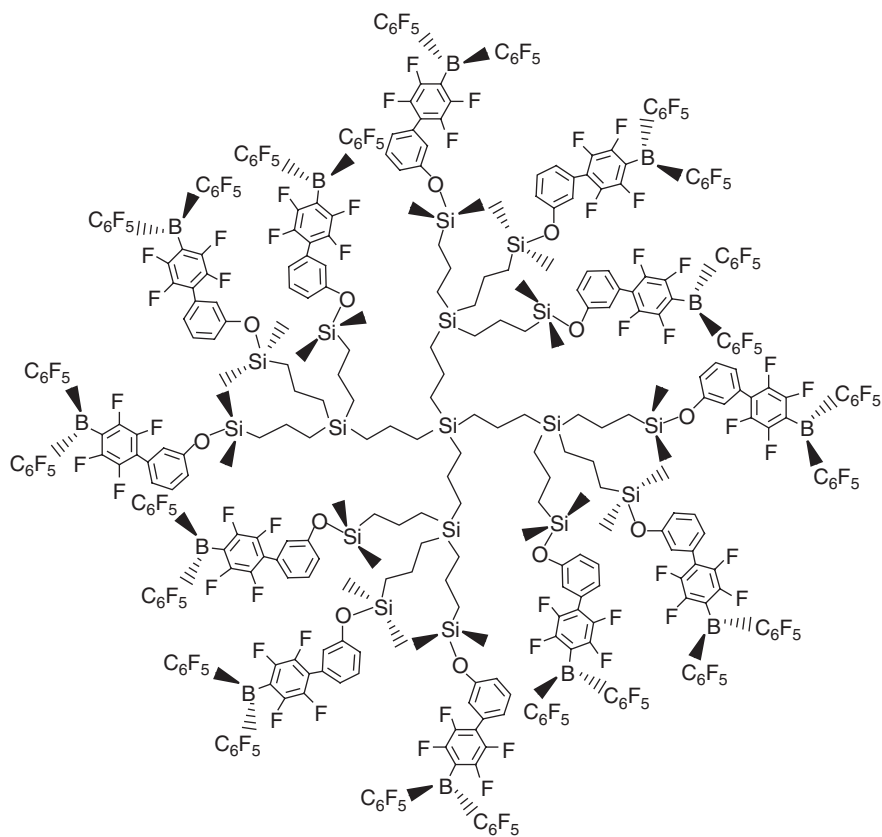
**Figure 21** The linear (boron–silicon–diacetylene) copolymers (**31a–d**) with their respective compositions. (Adapted from ref. 50.)

The synthesis of a variety of lithium ion conducting borosiloxane polymers have been reported.<sup>51</sup> The incorporation of the Lewis acidic boron and silicon into the polymer backbone was expected to facilitate their interaction with anions and thereby increase the  $T_+$  (transference numbers) of the resulting polymers.<sup>52</sup>

Carbosilane dendrimers capped with 4, 8, and 12 (**32**) (Fig. 22) perfluoroarylborane Lewis acids have been synthesized for use as Lewis-acid catalysts for the hydrosilation of acetophenone.<sup>53</sup> The dendrimers were found to be rather effective, exhibiting only slightly inferior activities in comparison to  $B(C_6F_5)_3$ .

### c. Boron Polymers Containing Organometallic Moieties

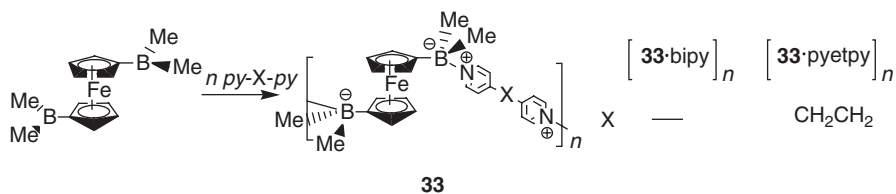
The presence of metals in coordination polymers has been hypothesized to produce interesting electrical, magnetic and optical characteristics as a result of electron delocalization.<sup>54</sup> When an atom such as boron is incorporated in metal-containing coordination polymers, it can conceivably expand the polymer's  $\pi$ -conjugation further by virtue of its empty p-orbital. This property of boron makes it an exciting atom for synthetic manipulations of coordination/organometallic polymers.



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**Figure 22** Carbosilane dendrimeric Lewis-acid catalyst (**32**) capped with perfluoroarylborane Lewis acids. (Adapted from ref. 53.)

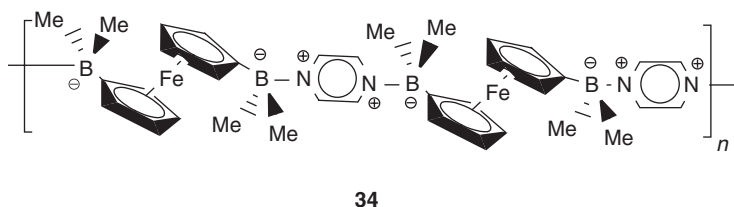
The chemistry of ferrocene compounds appears to have benefited most from the inclusion of boron atoms. Wagner and coworkers have developed coordination polymers with charge-transfer properties from reactions of diborylated ferrocenes (**33**) (Fig. 23) with 4,4'-bipyridine (bipy) or 1,2-bis(4-pyridyl)ethane (pyetpy).<sup>55</sup> The polymer  $[\mathbf{33}\cdot\text{bipy}]_n$  or  $[\mathbf{33}\cdot\text{pyetpy}]_n$  was prepared by layering a one equivalent solution of the corresponding pyridine in  $\text{CH}_2\text{Cl}_2$  over a diborylated ferrocene solution in  $\text{CHCl}_3$ . In the solid state, the polymer  $[\mathbf{33}\cdot\text{bipy}]_n$  exhibited an intense blue to purple color indicative of the charge-transfer reaction between the electron-rich ferrocene moieties and the viologen-like  $\text{R}_3\text{B}-\text{bipy}-\text{R}_3\text{B}$  units. In the  $[\mathbf{33}\cdot\text{pyetpy}]_n$  polymer, the disruption of the extended  $\pi$ -system due to the insertion of an ethylene spacer into the central C—C bond of the bipy ligand was observed to destroy its viologen-like electron accepting ability. As a consequence, it was found to lose its intense color, thereby rendering it yellow in appearance. The solid  $[\mathbf{33}\cdot\text{bipy}]_n$  polymer



**Figure 23** Charge transfer coordination polymers (**33**) obtained from diborylated ferrocenes with 4,4'-bipyridine (bipy) or 1,2-bis(4-pyridyl)ethane (pyetpy) bridges. (Adapted from ref. 55.)

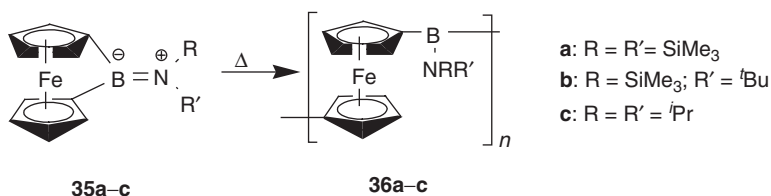
was thermally stable to 240°C under He. However, in toluene, the polymerization was observed to be reversible at 85°C.

Similar polymers (**34**) (Fig. 24) of diborylated ferrocenes linked by pyrazine units were developed that had an unusual dark-green appearance indicative of charge-transfer interactions between the iron centers and the electron-poor pyrazine adduct bridges.<sup>56</sup>

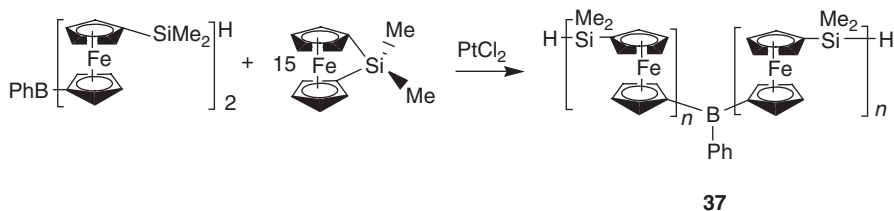


**Figure 24** Charge-transfer coordination polymer (**34**) of diborylated ferrocenes with pyrazine bridges. (Adapted from ref. 56.)

The ring-opening polymerization (ROP) strategy was utilized by Manners and co-workers for the polymerization of boron-bridged [1]ferrocenophanes.<sup>57</sup> The monomers, **35a** ( $R = R' = \text{SiMe}_3$ ), **35b** ( $R = \text{SiMe}_3$ ,  $R' = t\text{-Bu}$ ) and **35c** ( $R = R' = i\text{-Pr}$ ) (Fig. 25), were thermally polymerized in sealed and evacuated Pyrex tubes in the 180–200°C range. While the poly(ferrocenylborane)s **36a** and **36b** were found to be virtually insoluble in common organic solvents, the **35c**-derived low molecular-weight polymer (**36c**) had solubilities in polar organic solvents such as toluene, THF,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ . The ROP enthalpy for **35a** (ca. 95  $\text{kJ mol}^{-1}$ ) was found to be lower than expected and was attributed to the presence of bulky substituents at boron.<sup>58</sup> The Manners team further reported the selective ring-opening reactions of [1]ferrocenophanes with boron halides resulting in the production of functionalized ferrocenylboranes and boron-containing oligo- and poly(ferrocene)s.<sup>59</sup> The transition metal-catalyzed ROP of sila[1]ferrocene in the presence of Si—H functionalized diferrocenylborane was also reported to yield the ferrocene polymer **37** (Fig. 26).



**Figure 25** The ring-opening polymerization of strained boron-bridged [1]ferrocenophanes (**35a-c**) to produce poly(ferrocenylboranes) (**36a-c**). (Adapted from ref. 57.)



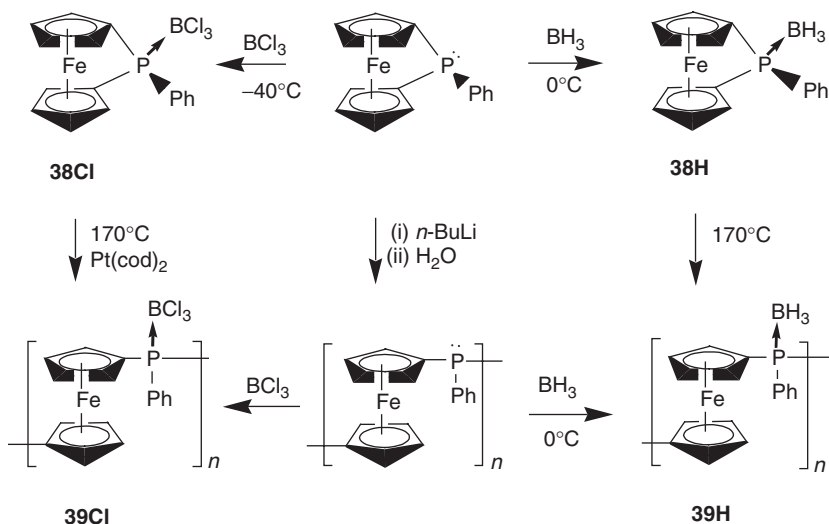
**Figure 26** The transition metal-catalyzed ROP of sila[1]ferrocene in the presence of Si—H functionalized diferrocenylborane to the ferrocene polymer **37**. (Adapted from ref. 59.)

While the boron-bridged [1]ferrocenophanes was observed to undergo polymerization via a transition metal-catalyzed ROP, the phosphorus(III)-bridged [1]ferrocenophanes were discovered to be resistant to a similar polymerization route, presumably due to the ligation of the catalyst by the phosphorus lone pair. However, when the phosphorus lone pair was protected through the formation of a borane adduct  $[(\eta\text{-C}_5\text{H}_4)\text{FeP}(\text{Ph})\text{BX}_3]$  (**38H** (X = H) or **38Cl** (X = Cl)) (Fig. 27), the ROP was observed to proceed either thermally or in the presence of a transition metal catalyst to yield insoluble polymeric products,  $[(\eta\text{-C}_5\text{H}_4)\text{FeP}(\text{Ph})\text{BX}_3]_n$  (**39H** (X = H) or **39Cl** (X = Cl)) (Fig. 27).<sup>60</sup> This approach has the advantage that subsequent deborylation of the poly(ferrocenylphosphine)borane adduct can afford a route to the production of poly(ferrocenylphosphines) with controlled molecular weights. Such materials have potential applications as catalytic materials based on the reactivity of the phosphorus lone pair.<sup>61</sup>

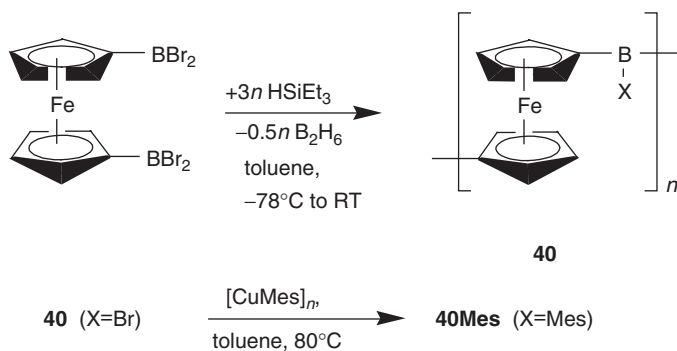
Jakle and Wagner have communicated the synthesis of bromo-substituted, boranediyl-bridged poly(ferrocenylene)s (**40**) (Fig. 28) by the reaction of  $\text{Fc}(\text{BBr}_2)_2$  with three equivalents of  $\text{HSiEt}_3$ . The polymer **40** was transformed into the corresponding mesityl-substituted polymer (**40Mes**) by treating its slurry in toluene with  $[\text{CuMes}]_n$  ( $n = 4, 5$ ).<sup>62</sup>

Ferrocene-bridged tris(1-pyrazolylborate) oligomeric systems have been synthesized by Wagner and co-workers.<sup>62</sup> The examples are described in more detail in the section on pyrazolylborate and pyrazabole polymers in this chapter.

In addition to the ferrocene-derived polymers, there have been reports of a few other metal-containing polymers with incorporated boron atoms. One such polymer



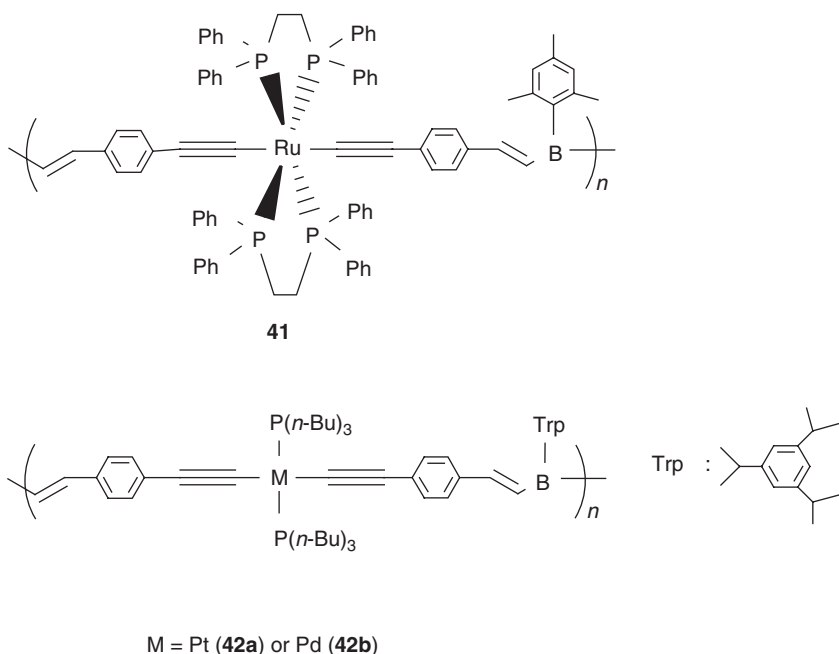
**Figure 27** The protection of the phosphorus lone pair during ROP of a phosphorus(III)-bridged [1]ferrocenophanes by  $\text{BCl}_3$  (**38Cl**) or  $\text{BH}_3$  (**38H**), leading to the production of the poly(ferrocenylphosphines) **39Cl** and **39H**, respectively. (Adapted from ref. 60.)



**Figure 28** Synthesis of bromo-substituted, boranediyl-bridged poly(ferrocenylene)s (**40**) from  $\text{Fc}(\text{BBr}_2)_2$ . (Adapted from ref. 62.)

is the  $\pi$ -conjugated organoboron polymer (**41**) (Fig. 29) containing ruthenium–phosphine moieties that was developed by Chujo and Lavastre by a hydroboration polymerization route.<sup>63</sup> Similar  $\pi$ -conjugated boron polymers (**42a** or **42b**) (Fig. 29) containing Pt or Pd in place of Ru in the polymer backbone have also been developed. The number-average molecular weight of the polymers was determined to be 9000 from gel permeation chromatographic analysis.<sup>63</sup>

Recently, Rauchfuss and co-workers have reported the synthesis of a one-dimensional  $[\text{PhB}(\text{CN})_3\text{Cu}(\text{PCy}_3)_2]$  polymer formed from the reaction between the anionic  $[\text{PhB}(\text{CN})_3]^-$  and  $[\text{Cu}(\text{PCy}_3)_2(\text{NCMe})_x]\text{PF}_6$ .<sup>64</sup>



**Figure 29**  $\pi$ -Conjugated organoboron polymer containing phosphine ligands with Ru (**41**), Pt (**42a**), or Pd (**42b**) in the polymer backbone. (Adapted from refs. 62 and 63.)

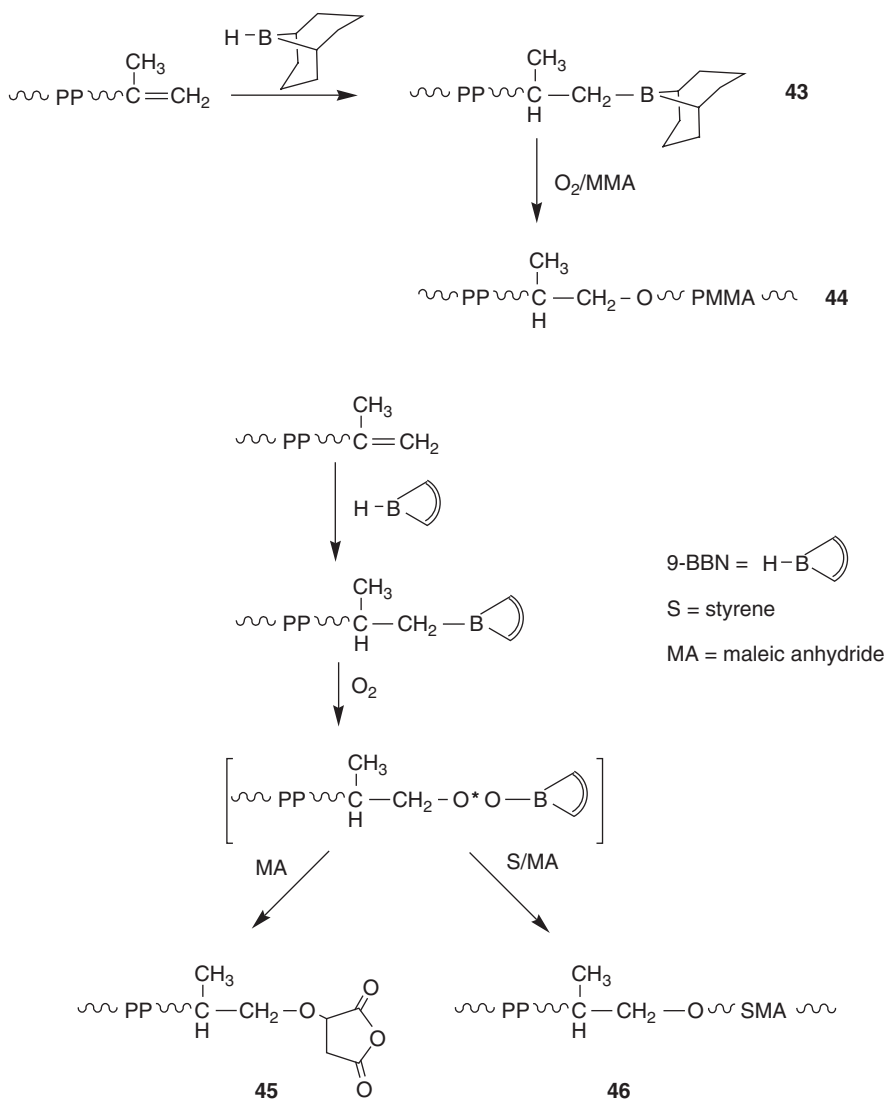
### iii. Organoboron Polymers Used as Catalysts in Organic Transformations

#### a. Boron Ligands/Polymers Used in Olefin Polymerization Reactions

In recent times, boron-containing organic groups have found extensive use as protecting groups for functionalizing olefinic monomers for copolymerization with olefins in the Ziegler–Natta (Z-N) and other metal-catalyzed polymerization reactions. This methodology has been popularized especially by Chung and co-workers.<sup>65</sup> Among the boron ligands, boranes have been particularly effective due to their stability to transition metal catalysts, easy solubility in typical solvents used in Z-N polymerization such as hexane and toluene, and their versatility. In general, a borane-containing olefinic monomer is found to effectively copolymerize with most  $\alpha$ -olefins in the presence of an appropriate catalyst system. The incorporated borane groups in the polyolefins, in turn, function as manipulatable sites for selective functionalization under mild reaction conditions.

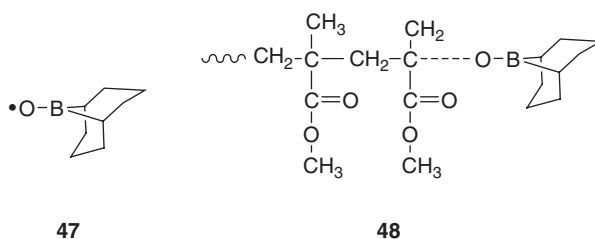
One such reported example is the synthesis of polypropylene-*b*-polymethylmethacrylate (PP-*b*-PMMA) copolymers utilizing metallocene catalysis and the borane chemistry. In the initial step, PP with chain-end olefinic unsaturations was prepared using metallocene catalysts such as Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO. The unsaturation sites were then hydroborated by 9-borabicyclo[3.3.1]nonane (9-BBN) to produce borane-terminated PP (**43**) (Fig. 30), which was selectively oxidized and interconverted to a

polymeric radical. This radical then proceeded to initiate the polymerization to produce diblock copolymers (**44**) (Fig. 30).<sup>66</sup> A similar strategy was used for the synthesis of PP/maleic anhydride (MA) copolymers **45** (single MA unit-terminated PP) and **46** (styrene(S)/MA diblock copolymers of PP) (Fig. 30).<sup>67</sup> MA-modified PP has recently found applications especially in glass fiber-reinforced PP and anticorrosive coatings for metal pipes and containers.<sup>68</sup>



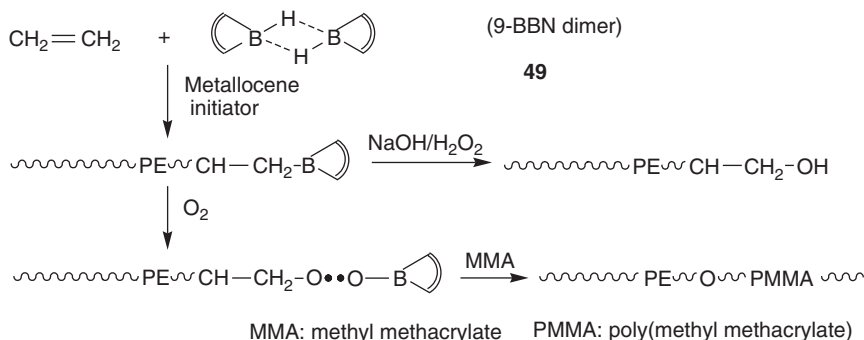
**Figure 30** The hydroboration strategy of chain end olefinic unsaturation in polypropylene with 9-BBN for further conversion into block copolymers via polymer radicals. (Adapted from refs. 66 and 67.)

A radical initiator based on the oxidation adduct of an alkyl-9-BBN (**47**) has been utilized to produce poly(methylmethacrylate) (**48**) (Fig. 31) from methylmethacrylate monomer by a living anionic polymerization route that does not require the mediation of a metal catalyst. The relatively broad molecular weight distribution ( $PDI = (M_w/M_n) \sim 2.5$ ) compared with those in living anionic polymerization cases was attributed to the slow initiation of the polymerization.<sup>69</sup> A similar radical polymerization route aided by **47** was utilized in the synthesis of functionalized syndiotactic polystyrene (PS) polymers by the copolymerization of styrene.<sup>70</sup> The borane groups in the functionalized syndiotactic polystyrenes were transformed into free-radical initiators for the *in situ* free-radical graft polymerization to prepare *s*-PS-*g*-PMMA graft copolymers.



**Figure 31** The radical initiator (**47**) based on the oxidation adduct of an alkyl-9-BBN used for the production of poly(methylmethacrylate) (**48**) from methylmethacrylate monomer by the radical polymerization route. (Adapted from ref. 69.)

A dimeric organoborane chain-transfer agent, the 9-BBN dimer (**49**) (Fig. 32) afforded a very convenient method for the preparation of polyolefins containing a terminal polar group. This first appeared in the literature in 1999.<sup>71</sup> This reagent, which is stable to hydroboration of olefins, incorporates the B-containing group in polyolefins *in situ* during the termination of a metallocene-catalyzed polymerization. The termination of the polymer chains is achieved by quenching the polymer solution with anhydrous/anaerobic MeOH. This borane dimer was utilized in the synthesis of diblock copolymers containing syndiotactic PS and polar polymers.<sup>72</sup>

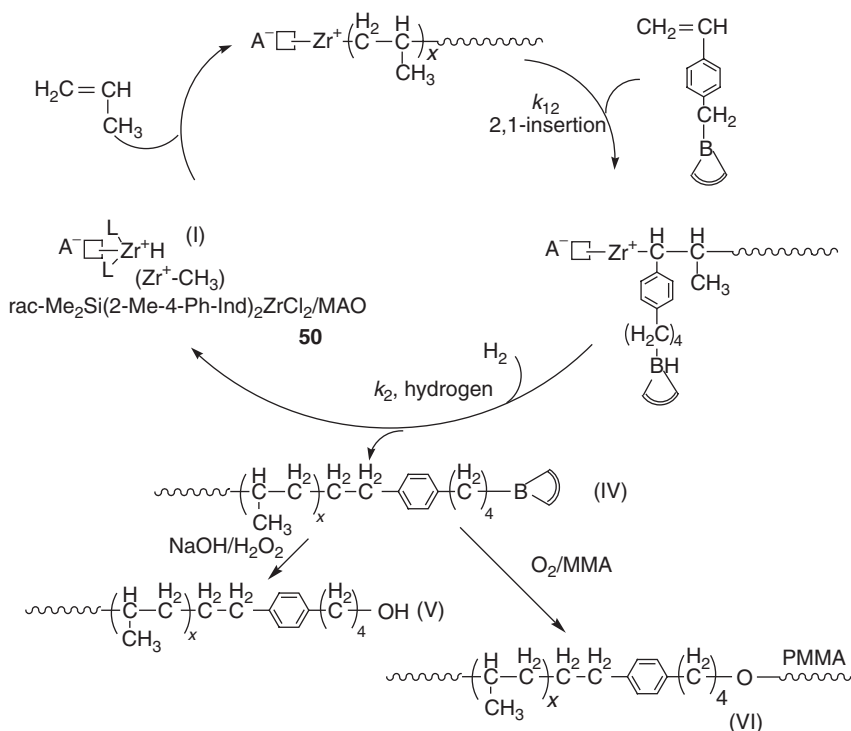


**Figure 32** The dimeric organoborane chain-transfer agent, 9-BBN dimer (**49**), used for the *in situ* incorporation of B-containing group in polyolefins during the termination of a metallocene-catalyzed polymerization. (Adapted from ref. 71.)



The extension of the olefin protection and chain-transfer strategies to the synthesis of a broad range of polyolefin homo- and copolymers has been achieved by the judicious manipulations of borane chain-transfer agents, metallocene catalyst systems, and reaction conditions. The polymers utilized include polyethylene, polypropylene, syndiotactic polystyrene, poly(ethylene-*co*-propylene), poly(ethylene-*co*-1-octene), and poly(ethylene-*co*-styrene). The molecular weight of the borane-terminated polyolefin was found to be proportional to the molar ratio of [olefin]/[borane]. The reactive terminal borane was then converted to various functional groups or selectively oxidized to yield a stable polymeric radical for living free-radical polymerization of desired functional monomers. The preceding steps in effect produced an elegant transformation from a metallocene polymerization to a living free-radical transformation via the borane terminal group. This afforded functional polyolefin diblock copolymers, which ordinarily are difficult to be prepared using conventional initiators.<sup>73</sup>

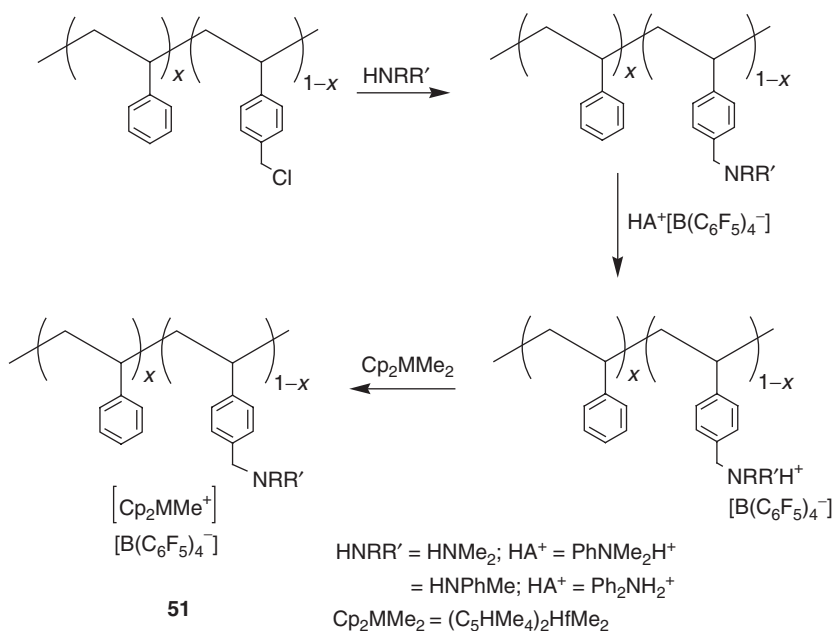
In a recent development, a new process of preparing borane-terminated isotactic polypropylene (*i*-PPs) via an *in situ* chain-transfer reaction was achieved by a styrene/hydrogen consecutive chain-transfer reagent, which avoids the use of a B—H containing chain-transfer agent.<sup>74</sup> This has resulted in the utilization of milder polymerization conditions due to the use of the alkylaluminumoxane cocatalyst (MAO) (**50**) (Fig. 33), which cannot normally be used in the presence of a B—H chain-transferring



**Figure 33** The catalytic mechanism for the production of borane-terminated isotactic polypropylene (*i*-PPs) via *in situ* chain-transfer reaction by a styrene/hydrogen consecutive chain-transfer reagent allowing the utilization of MAO cocatalyst (**50**). (Adapted from ref. 74.)

agent due to ligand exchange reaction between the B—H and the alkyl groups on the aluminum. The undesirable hydroboration of the olefins by the B—H chain-transferring agent during the polymerization can also be avoided by this method.<sup>74</sup>

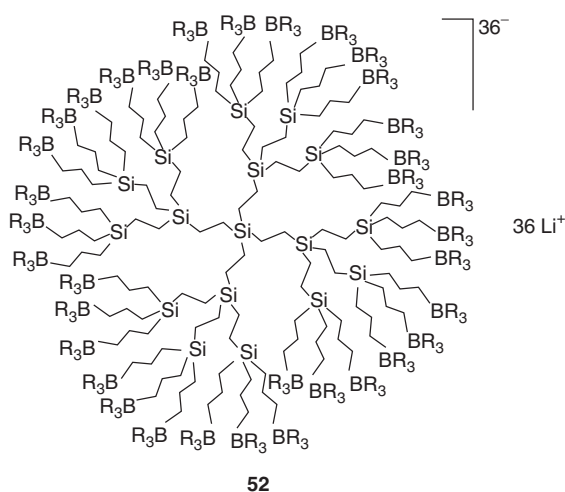
In addition to their use as olefin protecting groups, boron ligands have also been utilized in the modification of polymer-supported metallocene catalysts for olefin polymerization. Roscoe et al. have reported the preparation of metallocene catalysts supported on noninteracting polystyrene to avoid the destructive interaction of highly reactive metallocene catalysts with classic silica-based supports.<sup>75</sup> Supported catalysts (**51**) (Fig. 34) for the polymerization of  $\alpha$ -olefins were prepared by treating lightly cross-linked, chloromethylated polystyrene beads consecutively with a secondary amine, an ammonium salt of a weakly coordinating anion,  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , and a neutral dialkyl metallocene. The copolymerization of ethylene and 1-hexene at 40°C, facilitated by the homogeneously distributed catalytic sites on the support particle, afforded discrete spherical polyolefin beads with a size (0.3 to 1.4 mm) that varied according to the polymerization time.



**Figure 34** A polymer-supported metallocene catalyst (**51**) with a weakly coordinating anion,  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , produced from lightly cross-linked, chloromethylated polystyrene beads for olefin polymerization. (Adapted from ref. 75.)

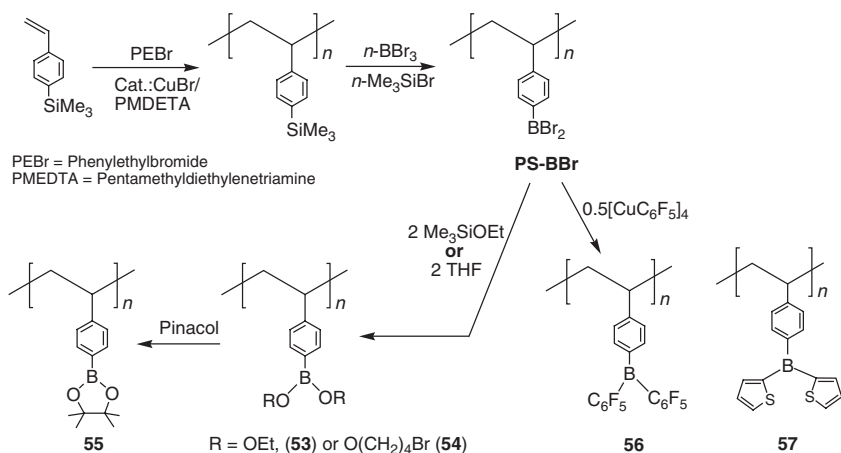
There also have been other reports of polymer-supported catalysts with incorporated boron moieties resulting from multistep polymer modification reactions to incorporate the boron moiety.<sup>76</sup>

It is well known that the nature of the cocatalyst used in the metallocene-catalyzed olefin polymerization has a significant effect on the kinetics of the polymerization. The most important industrial cocatalysts are (MAO),<sup>77</sup> a condensation product prepared from  $\text{AlMe}_3$  and water, and the perfluorophenylborane  $\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>78</sup> Research has recently focused on the design of borane anions, which are even more noncoordinating than  $\text{B}(\text{C}_6\text{F}_5)_3$ . Such cocatalysts are expected to improve the activity and the lifetime of the catalytically active species and to better the chain-termination and chain-transfer reactions as well as regio- and stereoregularity.<sup>79</sup> Nager et al. have recently reported the synthesis of a highly noncoordinating carbosilane dendrimeric polyanion terminated with  $\text{BR}_3$  groups (**52**) (Fig. 35).<sup>80</sup>



**Figure 35** A noncoordinating carbosilane dendrimeric polyanion terminated with  $\text{BR}_3$  groups (**52**) used as a cocatalyst in the metallocene-catalyzed olefin polymerization. (Adapted from ref. 80.)

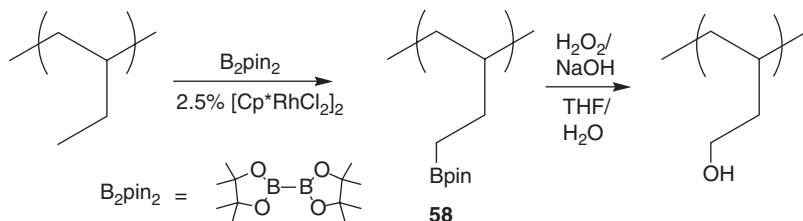
In a series of reports, Jakle and co-workers have reported a new route to organoboron polymers of PS that contained well-defined boron-containing Lewis acids.<sup>81</sup> These acidic polymers have the potential for use as cocatalysts in olefin polymerization and as catalysts in organic syntheses. The initial step in the synthesis involved the production of a dibromoborylated PS (PS-BBr) from the reaction of 4-trimethylsilylstyrene in anisole (50%) by a typical atom-transfer radical polymerization (ATRP)<sup>82</sup> initiated with 2 mol % 1-phenylethyl bromide. PS-BBr was found to readily react with nucleophiles, thereby serving as a precursor to a number of other polymers with boron centers of variable Lewis acidity. When PS-BBr was treated with  $\text{Me}_3\text{SiOEt}$  or tetrahydrofuran (THF), PS-BOEt (**53**) and PS-BOBuBr (**54**) (Fig. 36), were obtained in 90 and 83% yield, respectively. PS-BOEt, on reaction with pinacol, yielded the polymer PS-BPin (**55**) (Fig. 36). The molecular weight and dispersity of PS-BOBuBr were determined by GPC analysis (relative to polystyrene standards) to be 7180 and 1.13, respectively.<sup>81a</sup>



**Figure 36** Organoboron polymers of PS with well-defined boron-containing Lewis acids for use as a cocatalyst in metallocene-catalyzed olefin polymerizations. (Adapted from ref. 81.)

Using the same synthetic strategy, the synthesis of polymeric Lewis acids PS-BAr (**56**) and PS-BTh (**57**) (Fig. 36) were produced by the respective reactions of PS-BBr with pentafluorophenylcopper and trimethylstannylthiophene.<sup>81b,c</sup> The molecular weight and dispersity of the pinacol derivative were determined by GPC methods to be 13,830 and 1.09, respectively.

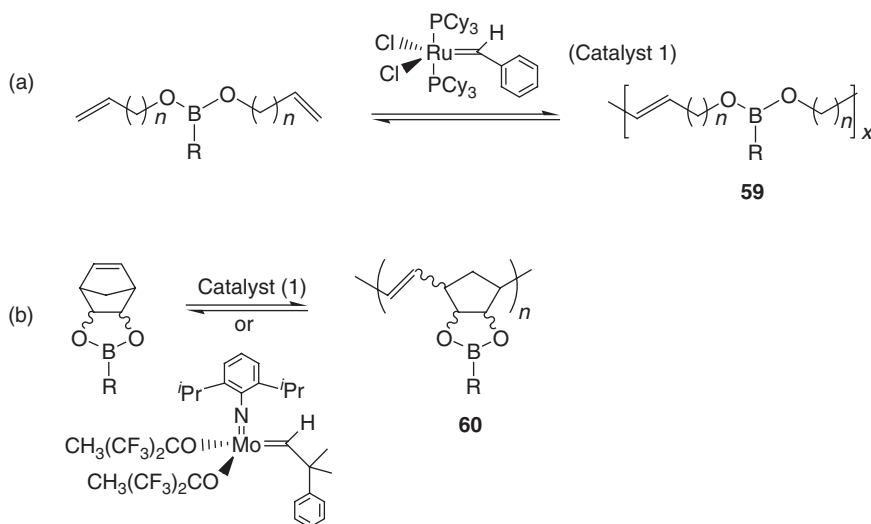
Hartwig and Hillmyer have recently reported the Rh-catalyzed borylation of polyolefins to yield boronate-functionalized polymers (**58**) (Fig. 37) in a single step.<sup>83</sup> The number-average molecular weight of the borylated polymer that was obtained at a B<sub>2</sub>pin<sub>2</sub>:polyethylene ratio of 0.3 was found to be the highest ( $M_n = 52,000$  and PDI = 1.09) among the developed boronate-functionalized polyolefins.



**Figure 37** The boronate-functionalized polymer (**58**) obtained by the Rh-catalyzed borylation of polyolefins. (Adapted from ref. 83.)

Wolfe and Wagener have developed *main-chain* boronate polymers (**59**) (Fig. 38) by the acyclic diene metathesis (ADMET) polymerization of symmetrical  $\alpha,\omega$ -dienes, containing both methyl- and phenyl-substituted boronate functionalities using Mo and Ru catalysts.<sup>84</sup> The ring-opening metathesis polymerization (ROMP) of several norbornene monomers containing methyl- and phenyl-substituted boronates into

unsaturated polymers (**60**) (Fig. 38) has also been achieved. The Ru and the Mo metathesis catalysts were observed to be sensitive to the isomeric form of the norbornene monomer. While the Ru alkylidene generated only the *cis* polymer using the *exo* monomer, the Mo alkylidene was found to produce a completely *trans* polymer from the *endo* monomer. It was discovered that the long-term stability and solution characteristics of both sets of polymers were dramatically influenced by ligand-exchange reactions within the boronate moiety. When the boronates were placed pendent to the main chain, this phenomenon was found to be obviated.

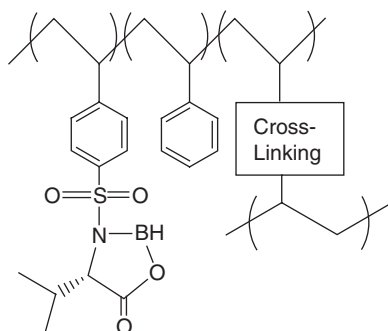


**Figure 38** (a) The ADMET polymerization (using Mo and Ru catalysts) of symmetrical  $\alpha,\omega$ -dienes that yield main-chain boronate polymers (**59**). (b) The ROMP of several norbornene monomers containing methyl- and phenyl-substituted boronates into unsaturated polymers (**60**). (Adapted from ref. 84.)

### b. Organoboron Polymers Used in Other Organic Transformations

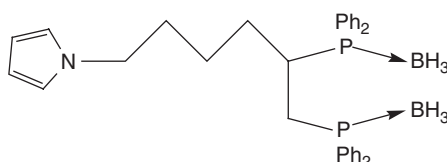
Polymer-supported organoboron catalysts have been finding increasing use in catalytic asymmetric syntheses. The anchoring of catalysts on polymer supports aids in the recycling of the catalysts, which is of great importance in homogeneous catalysis for the development of new industrial processes. Itsuno and co-workers have reported the design of highly enantioselective polymer-supported catalysts (**61**) (Fig. 39) of chiral oxazaborolidinone having different cross-linking structures for use in the Diels–Alder reaction of methacrolein with cyclopentadiene. The polymer-supported catalysts **61** having oxyethylene cross-linkages were found to exhibit better performance in promoting the enantioselective Diels–Alder reaction than their nonpolymeric counterparts.<sup>85</sup>

The development of polypyrroles bearing supported diphosphine ligands protected from oxidation by borane groups has been reported.<sup>86</sup> The polymer was produced by the electropolymerization of 1-(*N*-but-4-yl-pyrrol)-1,2-bis(diphenylphosphinoborane) (**62**) (Fig. 40). These preformed polymeric films lend themselves to the incorporation



61

**Figure 39** The enantioselective polymer-supported catalysts (**61**) of chiral oxazaborolidinone with cross-linking structures for use in the Diels–Alder reaction of methacrolein with cyclopentadiene. (Adapted from ref. 85.)

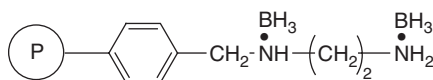


62

**Figure 40** The pyrrole monomer, 1-(*N*-but-4-yl-pyrrol)-1,2-bis(diphenylphosphinoborane) (**62**), used for electropolymerization to yield polypyrroles with diphosphine ligands protected from oxidation by borane groups. (Adapted from ref. 86.)

of palladium, thus generating palladium(0) catalysts that have applications in allylic-catalyzed alkylation reactions.<sup>86</sup>

Devaky and Rajasree have reported the production of a polymer-bound ethylenediamine-borane reagent (**63**) (Fig. 41) for use as a reducing agent for the reduction of aldehydes.<sup>87</sup> The polymeric reagent was derived from a Merrifield resin and a 1,6-hexanediol diacrylate-cross-linked polystyrene resin (HDODA-PS). The borane reagent was incorporated in the polymer support by complexation with sodium borohydride. When this reducing agent was used in the competitive reduction of a 1:1 molar mixture of benzaldehyde and acetophenone, benzaldehyde was found to be selectively reduced to benzyl alcohol.



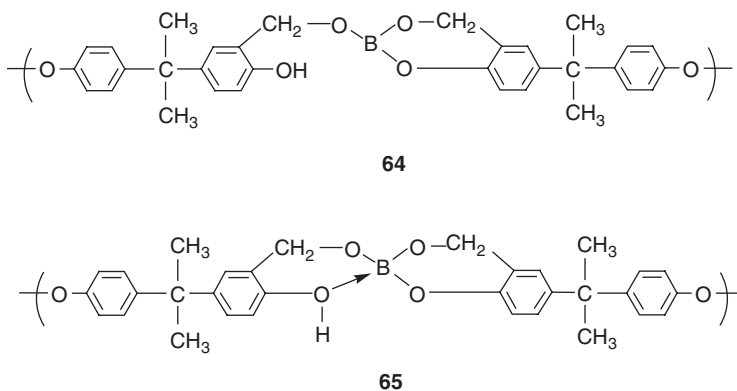
63

**Figure 41** The polymer-bound ethylenediamine-borane reagent (**63**) for use as a reducing agent for the reduction of aldehydes. (Adapted from ref. 87.)

#### iv. Organoboron Polymers that Function as Flame-Retardant Materials

Borates and boric acid have been well known to function as flame retardants, particularly in a synergistic fashion with halogenated polymers and halogen additive polymeric systems.<sup>88</sup> The flame retardancy of boron compounds is known to have its origin in the ability of the compounds to form a surface layer of an intumescent protective char, which acts as a barrier to oxygen, and consequently to the oxidation of carbon.

Recently, several reports of the flame-retardant properties of boron-containing bisphenol-A resins have appeared from Gao and Liu.<sup>89</sup> The synthesis of a boron-containing bisphenol-A formaldehyde resin (**64** and **65**) (Fig. 42) from a mixture of bisphenol-A, formaldehyde, and boric acid, in the mole ratio 1:2.4:0.5, has been reported.<sup>89a</sup> The kinetics of the thermal degradation and thermal stability of the resins were determined by thermal analysis. The analysis revealed that the resin had higher heat resistance and oxidative resistance than most common phenol-formaldehyde resins.

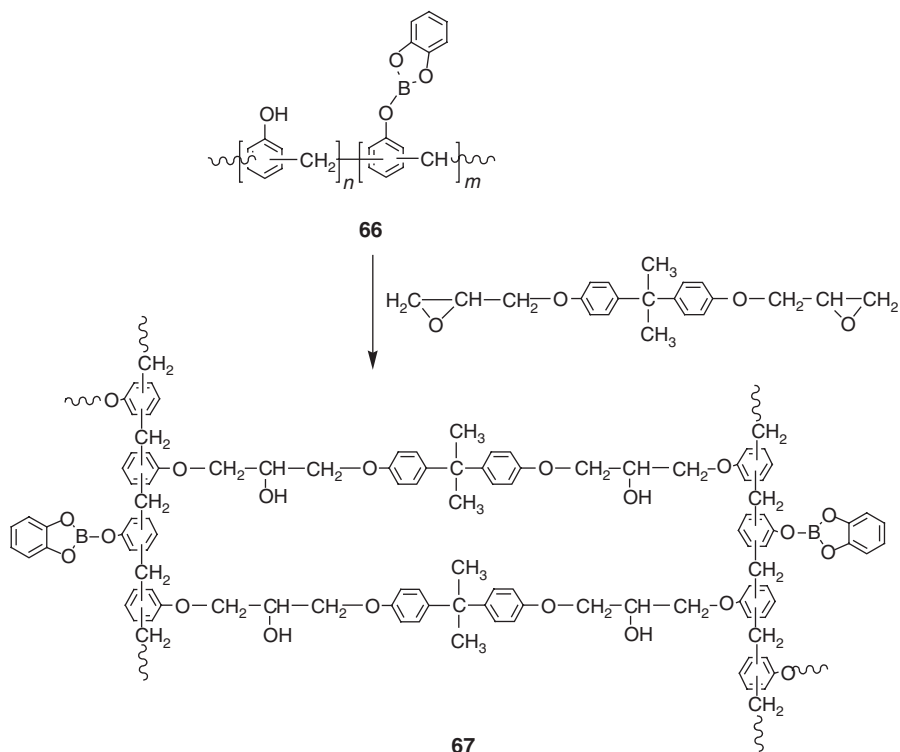


**Figure 42** The boron-containing bisphenol-A formaldehyde resin [**64** and **65** (obtained from **64** on further heat treatment)] produced from a mixture of bisphenol-A, formaldehyde and boric acid, in the mole ratio 1:2.4:0.5. (Adapted from ref. 89.)

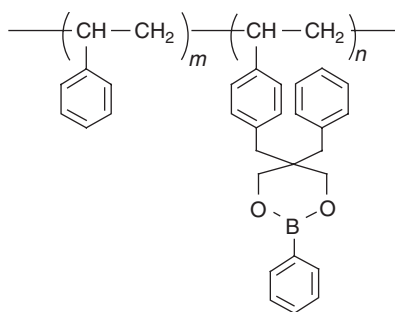
The development of a solvent reaction between triphenyl borate and paraformaldehyde to produce a boron-modified phenolic resin that flowed at usual processing temperatures has been reported.<sup>90</sup>

Cadiz and co-workers have reported the synthesis of a boron-containing Novolac resin (**66**) (Fig. 43) by the modification of the commercially available Novolac (phenolic) resin with different amounts of bis(benzo-1,3,2-dioxaborolanyl)oxide.<sup>91</sup> These modified Novolac resins were further cross-linked (**67**) (Fig. 43) with diglycidyl ether of bisphenol-A. The thermal degradation study of the boron-containing Novolac resin monitored by Fourier transform infrared (FTIR) spectroscopy revealed that they generated boric acid at high temperatures to give an intumescent char that slowed down the thermal degradation of the resin.

The syntheses of a homopolymer and a copolymer (**68**) (Fig. 44) of the boron-containing styrenic monomer, 5-benzyl-2-phenyl-5-(4-vinylbenzyl)-[1,3,3]-dioxaborinane with styrene have been achieved.<sup>92</sup> A similar monomer without boron



**Figure 43** The cross-linking reaction of the boron-containing Novolac resin (**66**) (obtained by the modification of the commercially available Novolac resin) with bis(benzo-1,3,2-dioxaborolanyl)oxide. (Adapted from ref. 91.)



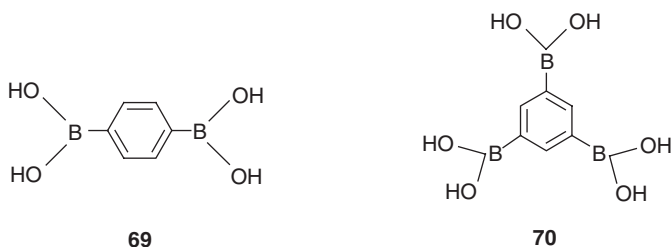
**68**

**Figure 44** The boron-containing styrenic monomer, 5-benzyl-2-phenyl-5-(4-vinylbenzyl)-[1,3,3]-dioxaborinane (**68**) used in the syntheses of a homopolymer and a copolymer with styrene. (Adapted from ref. 92.)



was also prepared and polymerized so that its properties could be compared with the boron-containing polymers. The boron-containing polymers were found to have higher limiting oxygen indices and to give greater char yields than those without boron.

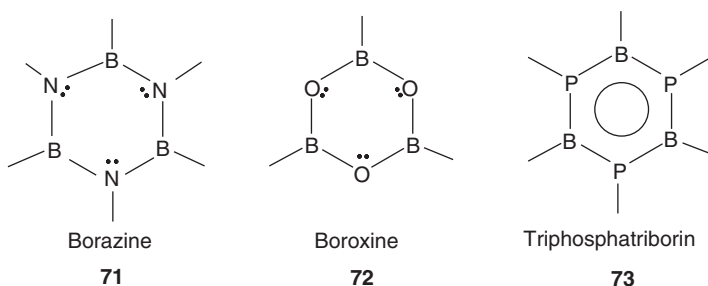
Boronic acids (**69** and **70**) (Fig. 45) with more than one boronic acid functionality are known to form a polymer system on thermolysis through the elimination of water.<sup>93</sup> Specifically, they form a boroxine (a boron ring system) glass that could lead to high char formation on burning. Tour and co-workers have reported the synthesis of several aromatic boronic acids and the preparation of their blends with acrylonitrile-butadiene-styrene (ABS) and polycarbonate (PC) resins. When the materials were tested for burn resistance using the UL-94 flame test, the burn times for the ABS samples were found to exceed 5 minutes, thereby showing unusual resistance to consumption by fire.<sup>94</sup>



**Figure 45** Boronic acids (**69** and **70**) with multiple boronic acid functionalities that form boroxine ring systems on thermolysis through the elimination of water. (Adapted from ref. 93.)

## B. Polymers Containing Boron Ring Systems in the Backbone or in Pendent Groups

The best known boron-containing ring systems are the so-called “inorganic benzenes,” namely, borazine (**71**), boroxine (**72**), and triphosphatiborin (**73**) (Fig. 46), which are isoelectronic and isostructural with benzene. These ring systems are obtained by the interaction of boron with nitrogen, oxygen, and phosphorus, respectively.<sup>4</sup>



**Figure 46** The planar structures of the boron ring systems, borazine (**71**) and boroxine (**72**), with nonexistent aromaticities and of triphosphatiborin (**73**) with an appreciable degree of aromaticity. (Adapted from ref. 95.)

Previous studies on electronic delocalization in borazine, boroxine, and triphosphatriborin in comparison to benzene have indicated that there is no significant aromatic character in borazine, boroxine, or triphosphatriborin.<sup>95</sup> In addition, the borazine and boroxine ring systems were found to possess very similar localized electronic densities.<sup>95</sup> Recent valence bond (VB) theory and ring-current map studies have indicated that in borazine and boroxine there is a localization of lone pairs on the electronegative atoms, nitrogens, and oxygens, respectively, and as a consequence, there is no resonance energy stabilization arising from any Kekule-like structures.<sup>96</sup> However, in the case of triphosphatriborin some benzene-like features were observed in its planar form with a significant contribution to its VB wave function from two Kekule-like structures, resulting in an appreciable resonance energy and a discernible diatropic ring current. The observed resonance stabilization in the planar confirmation of triphosphatriborin was found to be lost when it was allowed to relax to its optimal nonplanar chair conformation.<sup>96</sup> However, in a contrasting report on the calculations of the protonation and methylation energies of  $C_6H_6$  and  $B_3N_3H_6$ , it was claimed that the aromaticity of borazine is about half that of benzene.<sup>97</sup> Even though the debate on the electronic nature of these ring systems is ongoing, their unique and beneficial chemistries have propelled their incorporation, especially that of the borazine ring system, in various polymeric materials.

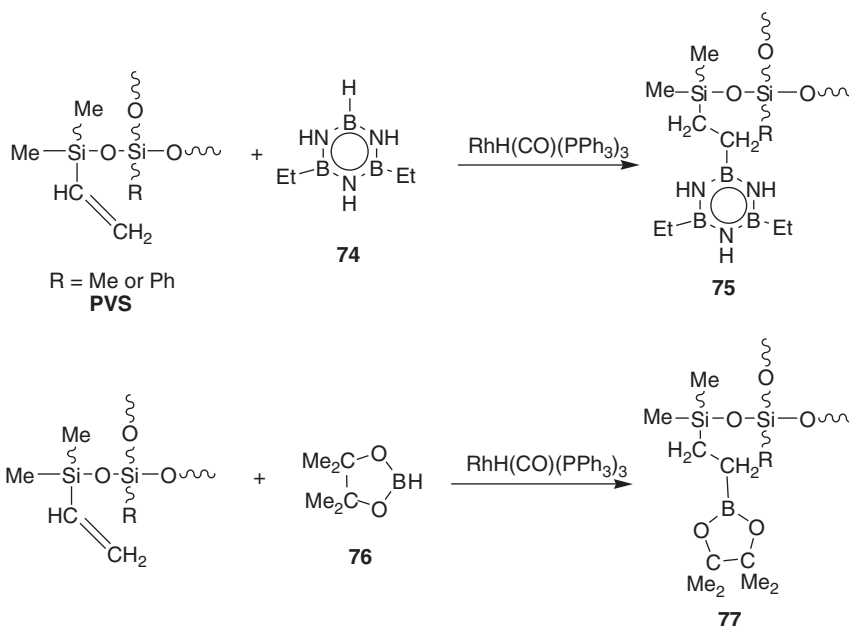
The area of organoboron polymers containing borazine and its derivatives is covered in Chapter 5 of this book by Miele and co-workers. Miele and Bernard also describe the utilization of these polymers in ceramics, fibers, and so on, in Chapter 3 of this book. In this section, the utilization of polymers containing borazine or in some cases the bicyclic boron ligand, 9-BBN, for the production of SiC or Si/C/B fibers is briefly described. Recent advances in polypyrazolylborate or pyrazabole-containing polymers and other boron ring system-derived polymers also have been briefly described.

### ***i. Organoboron Polymers that Contain Borazine or 9-BBN with Utility in the Production of High-Performance Fibers***

#### ***a. SiC-Producing Borazine Polymer Systems***

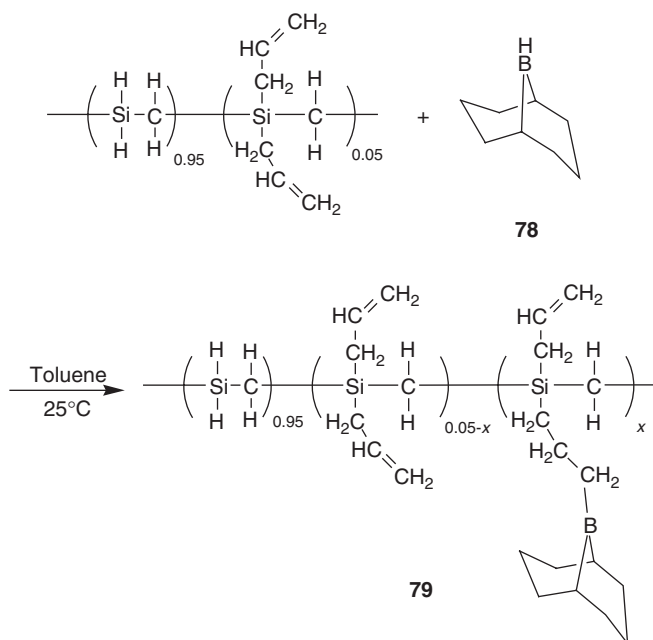
The major impetus for the incorporation of boron in silicon-containing polymers has been the utilization of such polymers in the high-performance fiber industry. The high-performance nonoxide ceramics such as silicon carbide (SiC)<sup>98</sup> and silicon nitride ( $Si_3N_4$ )<sup>99</sup> are conventionally made from polycarbosilanes, polysilazanes, or polycarbosilazanes, respectively. The production of industrial SiC fibers such as NICALON and TYRANNO resulted from the seminal work of Verbeek<sup>100</sup> and Yajima.<sup>101</sup> According to Yajima's strategy, precursor dichlorosilane materials are converted to polysilanes which are in turn converted to polycarbosilanes (PCS) by thermolysis. However, PCS can also be synthesized directly without the mediation of polysilane.<sup>102</sup> The addition of organoborate additive during the thermolysis of polysilane to PCS or during the final pyrolytic conversion to the fiber can improve the mechanical properties of the fiber by decreasing the oxygen and free carbon content and by improving its sintering properties. Additives such as  $B_2H_6$ ,<sup>103</sup>  $BCl_3$ ,<sup>104</sup> or boron vapor<sup>105</sup> have been used in the past toward this goal.

In recent times, polyborazine has been used as an additive to both polysilanes (specifically, polymethylsilane)<sup>106</sup> and PCS<sup>107</sup> separately to improve the yield of oxygen-free SiC fibers. Sneddon and co-workers have reported the use of a borazine, namely, diethylborazine (**74**), for the modification of poly(vinylsiloxane)s (PVS) (Fig. 47) for the production of boron-modified SiC by the RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>-catalyzed reaction of PVS with diethylborazine.<sup>108</sup> The same report also discusses the synthesis of pinacolborane-modified PVS polymers (**77**) (Fig. 47), which happen to be the first examples of a melt-processable poly(borosiloxane) single-source precursor for the formation of small-diameter SiOCB fibers. This synthetic strategy is an alternative way of introducing boron into SiC-producing resins. This is conventionally achieved by the blending of boron-containing materials into the resin before processing or by the treatment of the processed green fibers with a gaseous boron reagent.<sup>108</sup> The pinacolborane product was synthesized by the reaction of PVS with pinacolborane (**76**) (Fig. 47) in the presence of the catalyst RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>. The ceramic chars obtained at 1800°C were found to contain reduced grain growth and more uniform grain distribution compared to the ceramics obtained from unmodified PVS, demonstrating the pronounced effect that the addition of even a small amount of boron (<1%) has had on the ceramic properties of the chars.



**Figure 47** Synthesis of diethylborazine-modified (**75**) (top) and pinacolborane-modified (**77**) (bottom) polyvinylsiloxane polymers. (Adapted from ref. 108.)

Recently, the modification of polycarbosilane polymers with 9-BBN (**78**) (Fig. 48) was reported by the Sneddon group.<sup>109</sup> To improve sintering in SiC ceramics, allylhydridopolycarbosilane (AHPCS) polymers were reacted with 9-BBN at room temperature in toluene. Typical reactions required  $\sim 20$  h for the complete consumption of the 9-BBN ligand. The ceramic yields of the AHPCS-9-BBN polymers (**79**) (Fig. 48) were found to be significantly higher than that of the parent AHPCS polymer due to an additional cross-linking reaction involving the 9-BBN ligand. In addition, the presence of boron was found to increase the density of the ceramic fibers obtained at 1800°C and 2000°C from the BBN-modified polymers compared to those produced from the unmodified polymers.



**Figure 48** Synthesis of 9-BBN-modified allylhydridopolycarbosilane polymers (**79**). (Adapted from ref. 109.)

#### *b. Si/B/C/N-Producing Systems*

The introduction of small amounts of boron into precursors that produce silicon nitride have been known to improve the ceramic yields of silicon nitride and Si—B—C—N ceramics as first reported in 1986.<sup>110</sup> Several reports have appeared in the past couple of years alone that utilize borazine precursors such as 2,4-diethylborazine and other cyclic boron precursors, such as pinacolborane, 1,3-dimethyl-1,3-diaza-2-boracyclopentane, for their reactions with silanes, polysilazanes, and polysilylcarbodiimides for the high-yield production of Si—B—N—C ceramics.<sup>111</sup>

These developments are discussed in depth by Miele and Bernard in Chapter 3 of this book.

### ii. Organoboron Polymers that Contain Boroxine or Triphosphatriborin Ring Systems

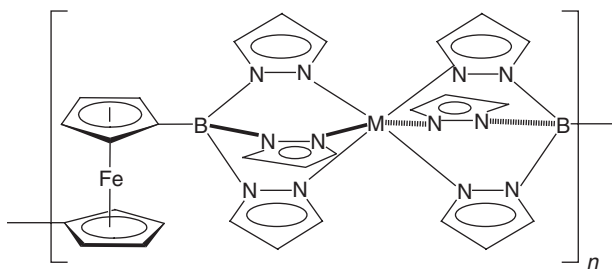
Boroxine ring-containing polymers have found extensive use in the development of polymeric electrolyte materials used in ion-selective transport membranes. Matsumi and Ohno cover this area in Chapter 6 of this book.

There have been no recent examples of polymers that contain the triphosphatriborin ring system.

### iii. Organoboron Polymers that Contain Polypyrazolylborate or Pyrazabole Ring Systems

Over 2000 papers have appeared on the chemistry of polypyrazolylborate/pyrazabole ring systems, but there have only been a few examples of polymers containing these ligands.<sup>112</sup>

Wagner and co-workers have reported the synthesis of ferrocene-bridged tris(1-pyrazolylborate) oligomeric systems (**80**) (Fig. 49).<sup>62</sup> Such polymers are of interest, as they offer a multiplicity of options for tailoring the access space to a metal held by the tris(1-pyrazolylborate) ligand, as well as a means to electronically influence the environment of a transition metal.<sup>113,114</sup>

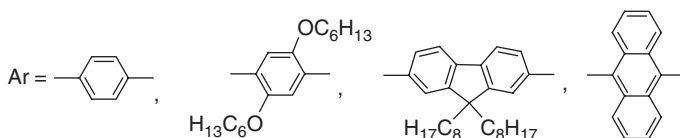
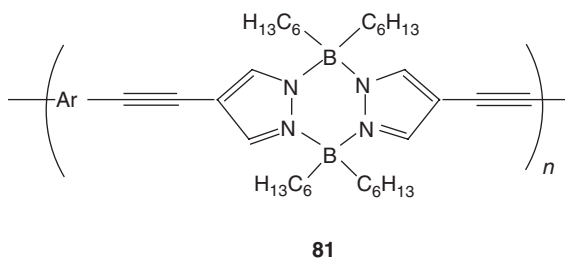


**80**

**Figure 49** Ferrocene-bridged tris(1-pyrazolylborate) oligomeric systems (**80**). (Adapted from ref. 62.)

Pyrazabole ligands have been introduced into fluorescent organoboron polymers (**81**) (Fig. 50) by the Heck-Sonogashira coupling between diyne monomers and pyrazabole derivatives by Chujo and Matsumoto.<sup>115</sup> The number-average molecular weights (9000–34,000) of the polymers obtained by this method were comparatively higher than that of similar polymers obtained from hydroboration reactions.

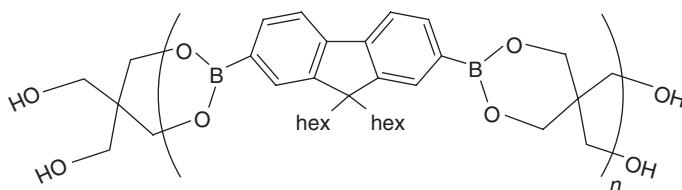
Using the same strategy, new pyrazabole polymers containing electron-withdrawing aromatic units, such as tetrafluorophenylene, pyridinediyl, and nitrophenylene, have also been synthesized in good yields. The number-average molecular weights of the polymers ranged between 2800 and 11,400.<sup>116</sup>



**Figure 50** Fluorescent organoboron polymers (**81**) obtained by Heck–Sonagashira coupling between diyne monomers and pyrazabole derivatives. (Adapted from ref. 115.)

#### *iv. Organoboron Polymers that Contain Other Boron Ring Systems*

Poly(dioxaboralane)s (**82**) (Fig. 51) with controllable molecular weights were reported to be readily obtained through the condensation reaction between 9,9-dihexylfluorene-2,7-diboronic acid and pentaerythritol in toluene with an associated azeotropic removal of water. The molecular weights of the resulting polymers, which ranged between 10,000 and 76,900, were found to depend on the processing conditions of the polymers.<sup>117</sup>



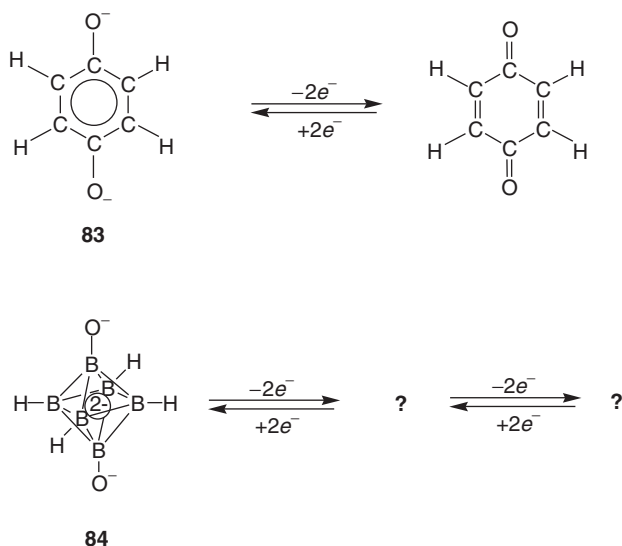
**Figure 51** Poly(dioxaboralane)s (**82**) obtained through the condensation reaction between 9,9-dihexylfluorene-2,7-diboronic acid and pentaerythritol in toluene. (Adapted from ref. 117.)

## **C. Polymers Containing Boron Clusters in the Backbone or in Pendent Groups**

### *i. Monomeric and Polymeric Organic Analogs of Boron Cluster Systems*

The polyhedral clusters of boranes and carboranes are groups of cluster systems that are present ubiquitously in organoboron polymers. As in the case with the

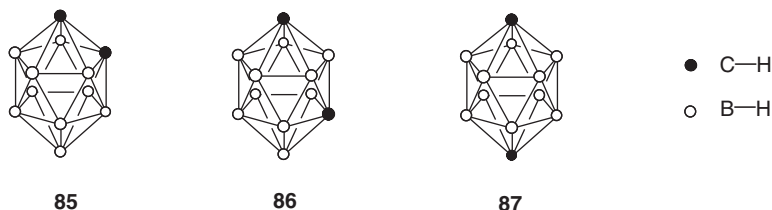
boron ring systems, there have been numerous comparisons of these systems to organic analogs. Recently, Balakrishnarajan and Hoffmann have evaluated the similarities in electronic structures of quinones such as the dioxobenzene dianion (**83**) and polyhedral boranes such as the polyhedral dioxoborane tetraanion (**84**) (Fig. 52)



**Figure 52** The redox equilibria in the compared dioxobenzene dianion (**83**) and dioxoborane dianion (**84**) systems. (Adapted from ref. 118.)

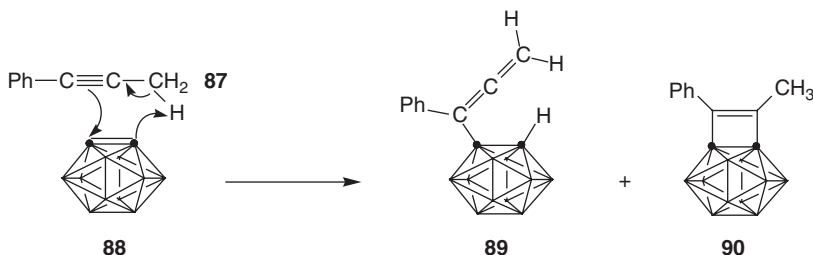
that contain exo multiple bonds.<sup>118</sup> Hybrid Density Functional Theory (DFT) and extended Huckel calculations revealed that the exopolyhedral B—O bond lengths decreased steadily and dramatically when **84** was oxidized in a sequence to its dianion and its neutral form, as has been observed during the oxidation of **83** to the neutral quinone. The carborane cluster systems, which can be represented by the general formula  $C_pB_qH_{p+q}$ , can be thought of as being derived from borane clusters by the substitution of some of their boron atoms by carbon atoms.<sup>119</sup> All of the known carborane clusters fall into three categories, namely, the closo-, nido- and arachno-carboranes, where the first are built of closed polyhedral cages, while the latter two include those carboranes in which the boron-carbon polyhedra resemble the shapes of nest skeletons. The closed-shell structures of the closo-dicarbaboranes are known to contribute to their astonishing chemical inertness, especially to acids, with the 1,2-, 1,7-, and 1,12-dicarpa-closo-dodecaboranes, better known by the more popular names *o*- (**85**), *m*- (**86**) and *p*-carborane (**87**) (Fig. 53), respectively, being the most stable. Carboranes, in general, and icosahedral carboranes, in particular, in their neutral and anionic forms are also known for their exceptional characteristics, such as low nucleophilicity

and high hydrophobicity, in addition to their electron-withdrawing properties having highly polarizable-aromatic character.<sup>25,119</sup> A weak point of carboranes is their susceptibility to alkaline degradation. This weakness, however, applies practically only to the species with adjacent carbon atoms such as *o*-carborane.<sup>25</sup>



**Figure 53** The 1,2-, 1,7-, and 1,12-dicarba-closo-dodecaboranes, better known by the more popular names *o*- (**85**), *m*- (**86**), and *p*-carborane (**87**), respectively. (Adapted from ref. 119.)

Icosahedral carboranes have been described as “superaromatic” due to the optimal occupancy of their 13 bonding molecular orbitals by the 26 framework electrons. They have been known to undergo electrophilic substitution, which is a hallmark of aromatic compounds.<sup>120</sup> Recent reports of the syntheses of carborane analogs of organic aromatic systems have further established this inorganic–organic relationship. Jones and co-workers have reported the reaction of 1,2-dehydro-*o*-carborane with acetylenes that produced the carborane analog of benzocyclobutadiene.<sup>121</sup> 1,2-Dehydro-*o*-carborane (**88**) (Fig. 54), which is obtained from *o*-carborane by treatment with *n*-BuLi and Br<sub>2</sub>, was found to add 3-hexyne to give the product of an ene reaction and with 1-phenyl-1-propyne (**87**) to give the products of both an ene reaction (**89**) and a 2+2 reaction (**90**) similar to the reactivity of benzene (Fig. 54).

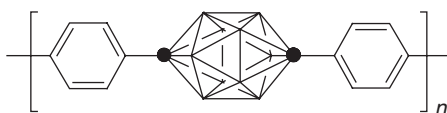


**Figure 54** The ene reaction (**89**) and 2+2 reaction (**90**) products obtained from reaction between 1-phenyl-1-propyne (**87**) and 1,2-dehydro-*o*-carborane (**88**). (Adapted from ref. 121.)

Wade and Williams have reported the synthesis of a carborane-based analog of poly(*p*-phenylene).<sup>122</sup> The rodlike polymer (**91**) (Fig. 55) was prepared by the catalytic



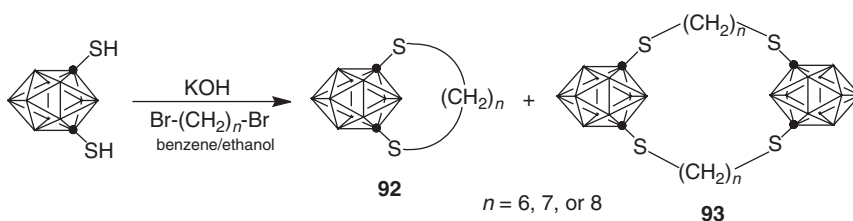
[using Zn and Ni(PPh<sub>3</sub>)<sub>4</sub>] polycondensation of 1,12-bis-(4-chlorophenyl)-1,12-dicarbado-dodecaborane. The aromatic rings in the polymer were found to be effectively coplanar and the torsion angle ( $\Delta$ ) between a carborane cage and its associated aromatic rings was found to be 18°. The polymer was found to yield a very high ceramic yield (ca. 92%) at 1000°C in argon.



91

**Figure 55** The rodlike polymer (**91**) that is the carborane-based analog of poly(*p*-phenylene). (Adapted from ref. 123.)

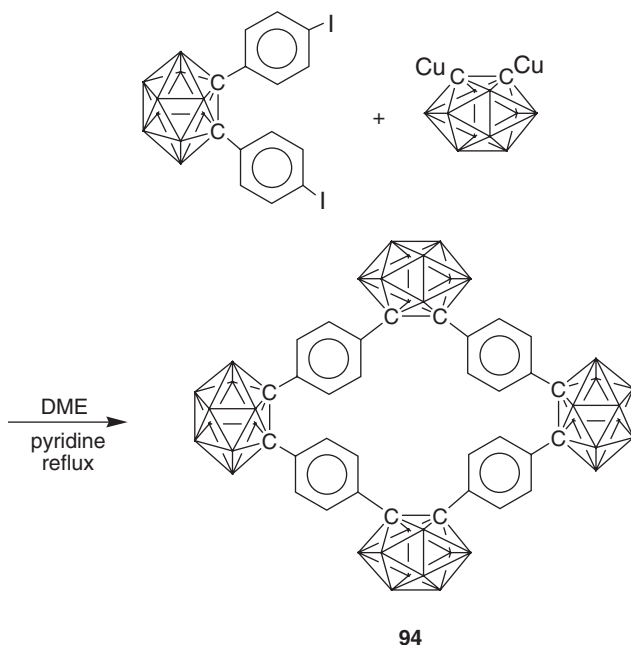
Several reported examples of carboranophane analogs of cyclophanes, compounds obtained by the bridging of 1,4- or 1,3-positions of benzene rings, further emphasize this inorganic–organic analogy. Jones and co-workers have reported the synthesis of carboranophanes starting from *m*-carborane, in which the carbons are in a 1,3-relationship with each other.<sup>123</sup> This compound was converted to the known dithiol, which was further reacted in the presence of KOH in ethanol with 1,*n*-dibromoalkane ( $n = 6, 7, \text{ or } 8$ ) to produce three [*n*]carboranophanes (**92** and **93**) (Fig. 56).



**Figure 56** Two sets of [*n*]carboranophanes (**92** and **93**) derived from the dithiol derivative of *m*-carborane. (Adapted from ref. 123.)

A novel cyclooctaphane (**94**) (Fig. 57) was assembled by the condensation reaction between the C,C'-dicopper(I) derivative of *m*-carborane and 1,2-bis(4-iodophenyl)-*o*-carborane.<sup>124</sup> The macrocycle was found to adopt a butterfly (dihedral angle 143°) confirmation with the *o*-carborane units at the wingtips and the phenylene ring planes roughly perpendicular to the wing planes of the confirmation.

Many other carboracycles and carborands, another group of organic ring systems, have been reported and are discussed in the section on carborane supramolecular chemistry later in this chapter.

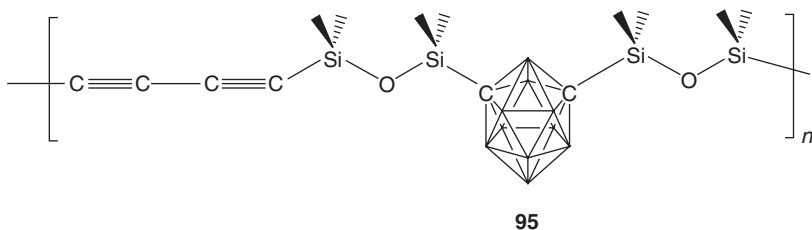


**Figure 57** The cyclooctaphane (**94**) assembled by the condensation reaction between *C,C'*-dicopper(I) derivative of *m*-carborane and 1,2-bis(4-iodophenyl)-*o*-carborane. (Adapted from ref. 124.)

### *ii. Poly(carboranylenesiloxanes) and Related Polymers*

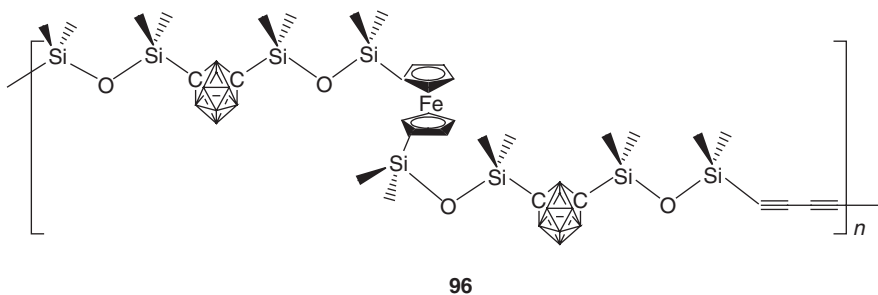
Developments in the chemistry of poly(carboranylenesiloxanes) were sparse in the 1980s following the initial bursts of work from the Olin and the Union Carbide teams. However, there has been renewed interest in this chemistry since the mid-1990s owing especially to the work originating from Keller and co-workers.

A significant development in this area resulted from the inclusion of a thermally cross-linkable diacetylene unit in the backbone of poly(carboranylenesiloxanes).<sup>125</sup> This facilitated the conversion of the starting oligomeric materials into extended networked polymers. Until then, the traditional sites of cross-linking in poly(carboranylenesiloxanes) had consisted of either pendent methyl and vinyl groups on Si atoms of the oligomers, or some reactive sites on the carborane moieties; the chemistry of which was not easily controllable.<sup>25</sup> The inclusion of a diacetylene group in a poly(carboranylenesiloxane) yielded a useful handle to control the extent of curing in the produced networked systems by the selection of appropriate curing temperatures.<sup>125</sup> The first oligomer generated of this kind, **95** (Fig. 58), on complete conversion to a networked system, was found to yield a plastic product. These extremely thermooxidatively stable networked systems exhibited high char yields of ca. 92 and 85% in air and N<sub>2</sub>, respectively.



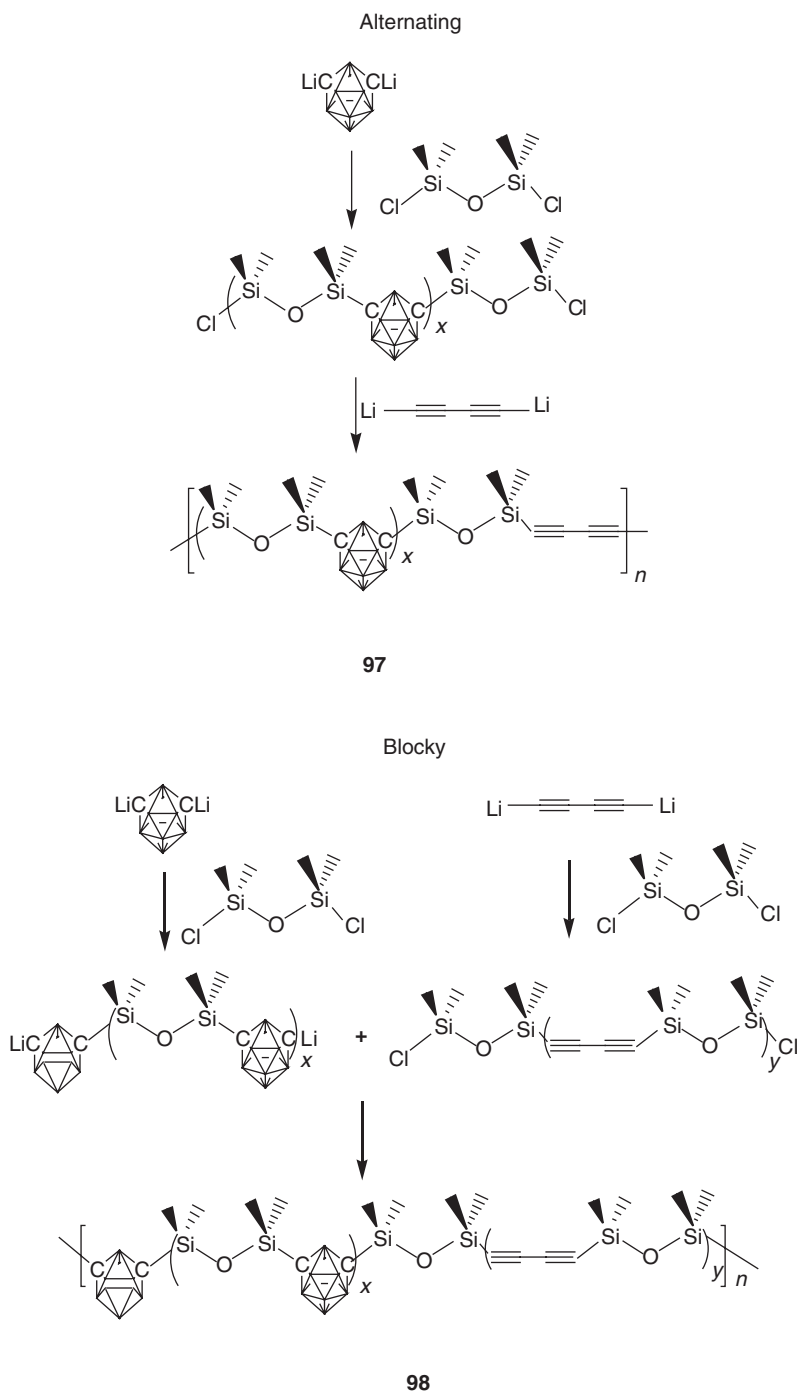
**Figure 58** The carboranylenesiloxane (**95**) containing the cross-linking diacetylene group. (Adapted from ref. 125.)

The inclusion of an organometallic system in these polymers, reported by Houser and Keller, resulted in the synthesis of linear ferrocenyl–carboranylenesiloxyl–diacetylene polymers (**96**) (Fig. 59), which could be deemed as a diacetylene-containing carboranylenesiloxane polymer with some of its carborane groups having been replaced by the bridging ferrocenyl groups.<sup>126</sup> The polymers were produced by the reaction of dilithiobutadiyne with two equivalents of 1,7-bis(chlorotetramethyl-disiloxyl)-*m*-carborane (Dexsil 200 monomer) followed by the treatment with dilithioferrocene-*t*-meda (1 equiv.). The molecular weight of this material was determined to be ca. 10,000 (relative to polystyrene) by GPC, thus accounting for ~10 repeat units of the monomer. On thermal treatment, this oligomer was found to yield an elastomeric material.



**Figure 59** The carboranylenesiloxane (**96**) containing both the organometallic ferrocene moiety and the cross-linking diacetylene group. (Adapted from ref. 126.)

To produce elastomeric materials from **95**, Kolel-Veetil and Keller studied the effects of reducing the concentration of the diacetylene units in **95** on the plasticities of the resulting networks.<sup>127</sup> The ratio (1:2:1) of the carborane, disiloxane, and diacetylene moieties in **95** was altered to 2:3:1, 4:5:1, and 9:10:1, respectively, to produce polymers containing progressively lower amounts of diacetylene units. Two sets of the polymers, one an alternating type (**97**) and the other a blocky type (**98**) (Fig. 60), were synthesized. The networked polymers produced from both the blocky and the alternating sets were found to be slightly elastomeric with  $T_g$  values around

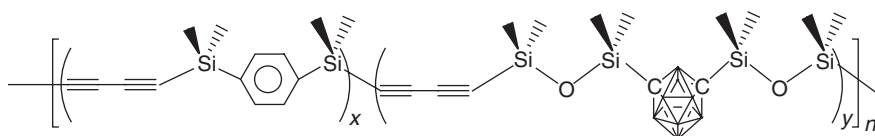


**Figure 60** The synthetic schemes for the diacetylene-diluted (a) alternating (**97**) (left) and (b) blocky poly(*m*-carborane-disiloxane-diacetylene)s (**98**). (Adapted from ref. 127.)

56, 45, and 35°C for the 2:3:1, 4:5:1, and 9:10:1 ratios, respectively, demonstrating the utility of this method for the introduction of elastomeric properties in these materials.

A further improvement in the elasticity of these polymers was realized when the disiloxyl groups in the alternating and blocky type polymers were substituted with the more flexible trisiloxyl groups.<sup>128</sup> The  $T_g$  values of the cured networks produced from the blocky and alternating set of polymers with ratios of 10:9:1, 5:4:1, and 3:2:1 were  $-49$ ,  $-34$ , and  $-27^\circ\text{C}$ , and  $-46$ ,  $-39$ , and  $-30^\circ\text{C}$ , respectively. The thermal stabilities of the cross-linked networks were analyzed thermogravimetrically by heating to  $1000^\circ\text{C}$  in  $\text{N}_2$ . For a given siloxane:carborane:diacetylene ratio, the char yields were discovered to be about 4–6% higher for the blocky type of copolymers when compared to the alternating type of copolymers.

The synthesis of block polymers of diacetylene–silarylene and diacetylene–carboranylenesiloxane polymers (**99a–e**) (Fig. 61) by the polycondensation reaction of 1,4-dilithiobutadiyne with 1,4-bis(dimethylchlorosilyl) benzene and/or 1,7-bis(tetramethylchlorodisiloxane)-*m*-carborane have been reported by Sundar and Keller.<sup>129</sup> These polymers are a hybrid between the carboranylenesiloxane and silarylene-siloxane polymers and have high char yields (up to 85%) at  $1000^\circ\text{C}$  in  $\text{N}_2$  and in air, reflecting the thermal stabilizing effects of the carborane and aromatic units in the polymeric backbone.



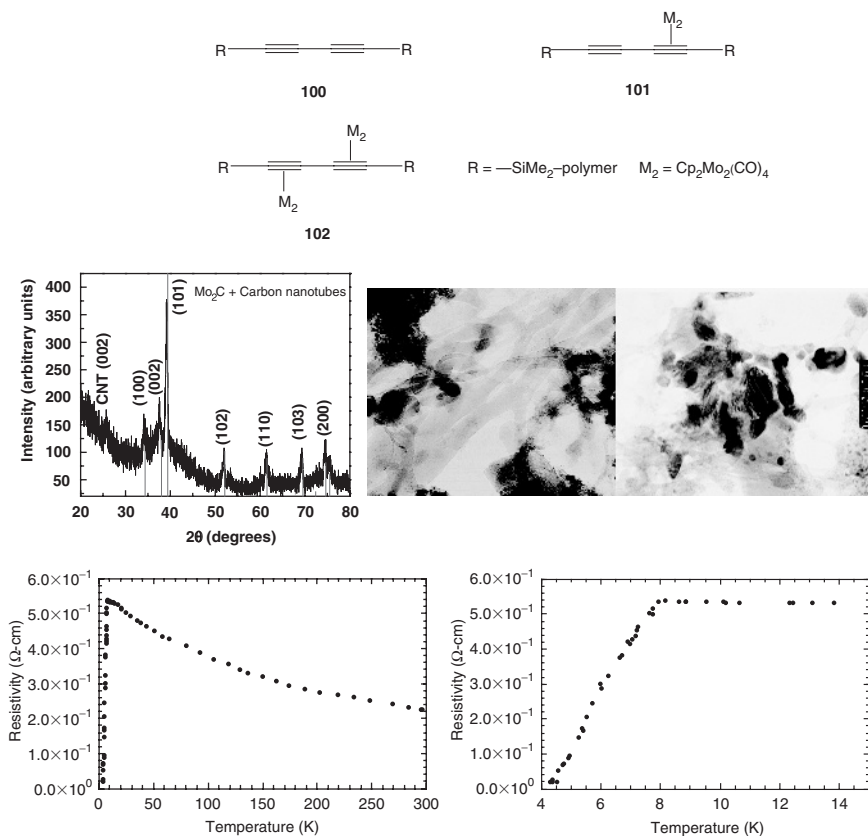
**99a–e**

a:  $x = 1, y = 0$ ; b:  $x = 3, y = 1$ ; c:  $x = 1, y = 1$ ; d:  $x = 1, y = 3$ ; e:  $x = 0, y = 1$ .

**Figure 61** The hybrid silarylene-siloxane/carboranylenesiloxane polymers, **99a–e**. (Adapted from ref. 129.)

In addition to their utility as cross-linking sites, the diacetylene units in **95** have been used for functionalization with organometallic moieties yielding pyrolyzable precursors of nanomaterials with diverse conducting characteristics. In a recent report, Kolel-Veetil and Keller have utilized the substitution reaction of **95** with cyclopentadienylmolybdenum tricarbonyl dimer,  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ , containing labile carbonyl ligands for the production of superconducting nanoparticles of  $\beta\text{-Mo}_2\text{C}$ .<sup>130</sup> When **95** and  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  were reacted at unimolar concentrations in tetrahydrofuran at  $80^\circ\text{C}$ , an oligomeric product mixture containing partially reacted, completely reacted, and unreacted diacetylene groups was observed to form (Fig. 62). The unreacted and partially reacted diacetylene units in the metal-derivatized oligomeric mixture were utilized further for the cross-linking reaction leading to tight cross-linked matrixes in which Mo moieties were spatially confined following the liberation of labile carbonyl and cyclopentadienyl ligands. This Mo-containing

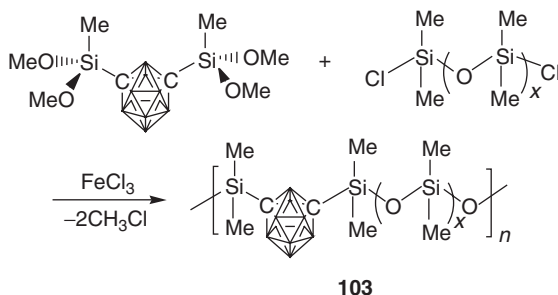
cross-linked network, on pyrolysis to 1000°C, was observed to yield nanoparticles of superconducting  $\beta$ -Mo<sub>2</sub>C nanoparticles ( $T_c = 8$  K) and multiwalled carbon nanotubes in an amorphous matrix of unidentified molybdenum compounds of boron and silicon (Fig. 62). In light of this result, the production of various nanomaterials of metallic carbides, borides, and silicides by the pyrolysis of the appropriate metal derivatives of **95** seems possible.



**Figure 62** The unreacted (**100**), partially reacted (**101**), and completely reacted (**102**) diacetylene group-containing oligomers in the product from the reaction between **95** and  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  (top). The X-ray diffraction spectrum (middle, left), TEM micrographs (middle, right), and conductivity plots (bottom) of the product from the reaction between **95** and  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  after pyrolysis to 1000°C. (Adapted from ref. 130.)

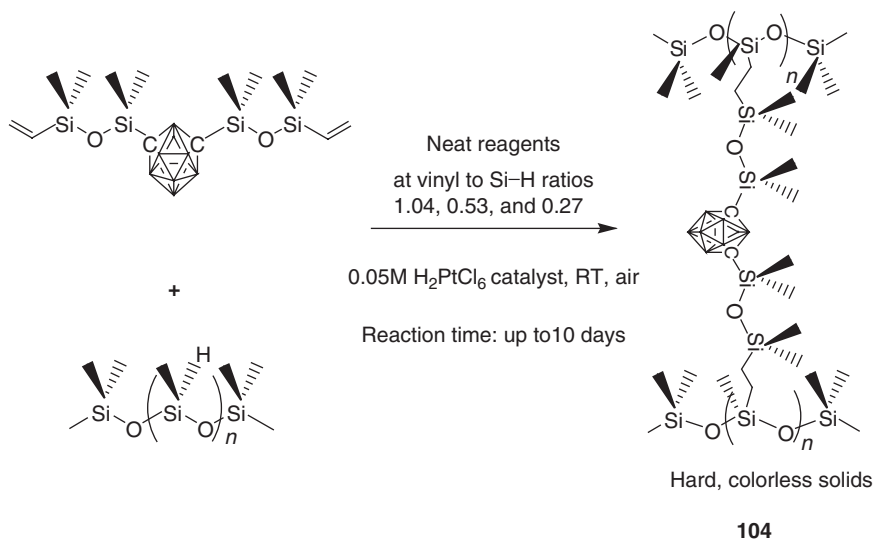
The original  $\text{FeCl}_3$ -catalyzed condensation reaction strategy has been exploited recently by Patel and co-workers for the synthesis of poly(*m*-carborane-siloxane) rubbers (**103**) (Fig. 63) in the reactions between dimethoxy-*m*-carborane terminated monomers and dichlorodimethylsilane.<sup>131</sup> They have also synthesized similar polymers

where Si–Me groups have been substituted either with phenyl or vinyl groups. While the unmodified polymer had some crystallinity, the modified polymers were observed to be amorphous with good elastomeric properties. A detailed account of their research is present in Chapter 2 of this book.



**Figure 63** The poly(*m*-carborane-siloxane) rubbers (**103**) synthesized by the  $\text{FeCl}_3$ -catalyzed condensation reaction between dimethoxy-*m*-carborane terminated monomers and dichlorodimethylsilane. (Adapted from ref. 131.)

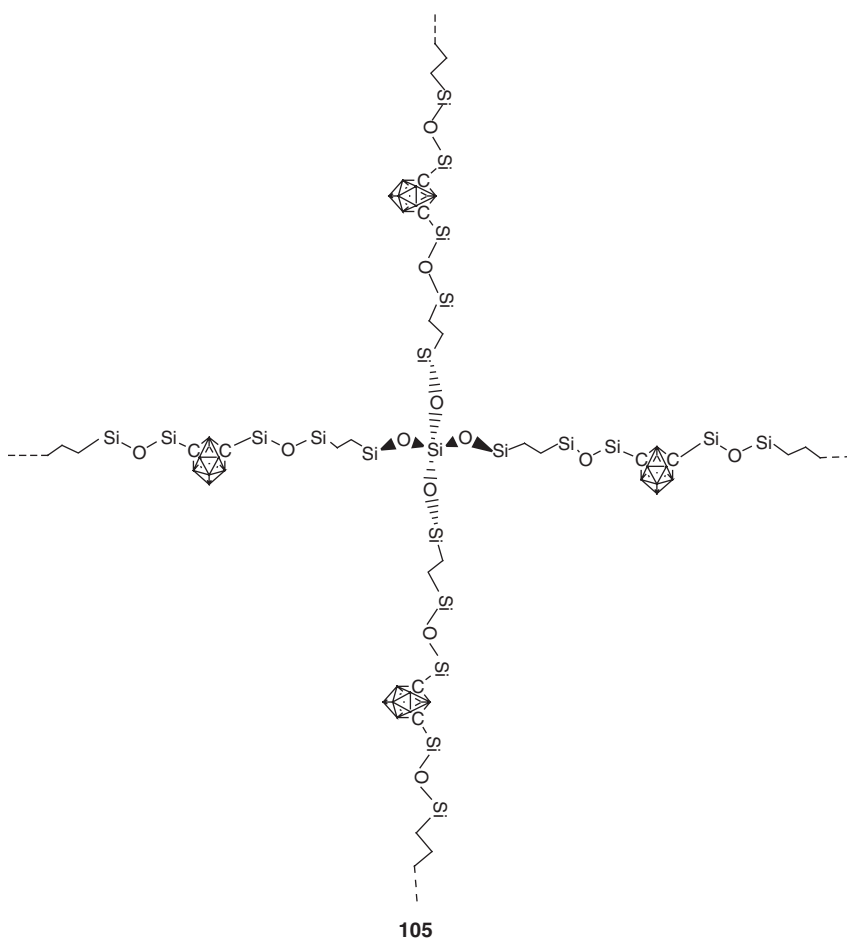
The ubiquitous hydrosilation reaction, popular especially in silicone manufacturing,<sup>132</sup> has been utilized by Houser and Keller for the synthesis of the networked polymers (**104**) (Fig. 64) from the reaction of the 1,7-bis(vinyltetramethyldisiloxy)-*m*-carborane monomer with the polymeric crosslinker, poly(methylhydrosiloxane).<sup>133</sup> The reactions were catalyzed by the Speier's catalyst,  $\text{H}_2\text{PtCl}_6$ . Three samples were



**Figure 64** Hydrosilation reactions between 1,7-bis(vinyltetramethyldisiloxy)-*m*-carborane monomer and the polymeric cross-linker, poly(methylhydrosiloxane), producing hard, colorless networked plastics. (Adapted from ref. 133.)

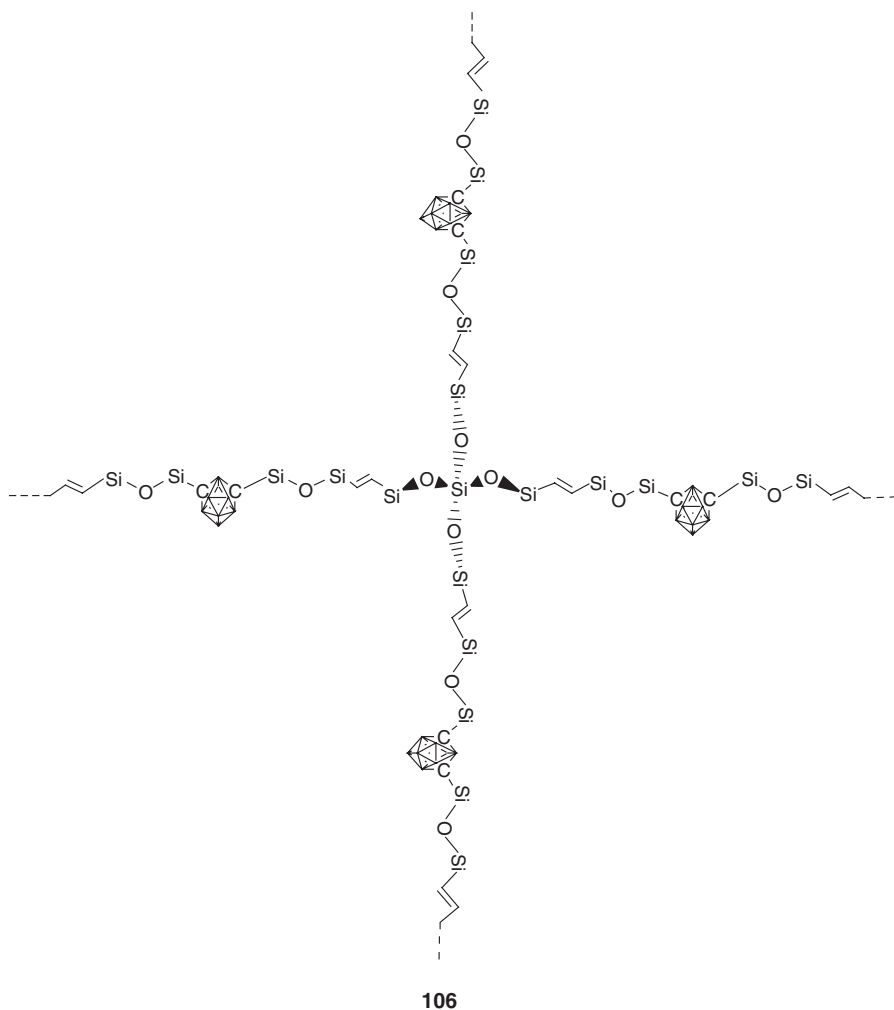
prepared with vinyl (monomer) to Si-H (cross-linker) ratios of 1.04, 0.53, and 0.27. The networked polymers were found to be hard and colorless materials.

Recently, Kolel-Veetil and Keller have modified this system to produce elastomeric networked polymers. The ambient-condition hydrosilation reactions between monomeric vinyl- or ethynyl-terminated carboranylenesiloxane and three different monomeric branched siloxane cross-linkers in hexane yielding these systems were catalyzed by the Karstedt catalyst.<sup>134</sup> The reactions involving the vinyl-carboranylenesiloxane were reported to produce a set of completely hydrosilated networked polymers (**105**) (Fig. 65). In the case of the ethynyl monomer, the reactions were carried out at two different ratios, yielding a partially (**106**) and a com-



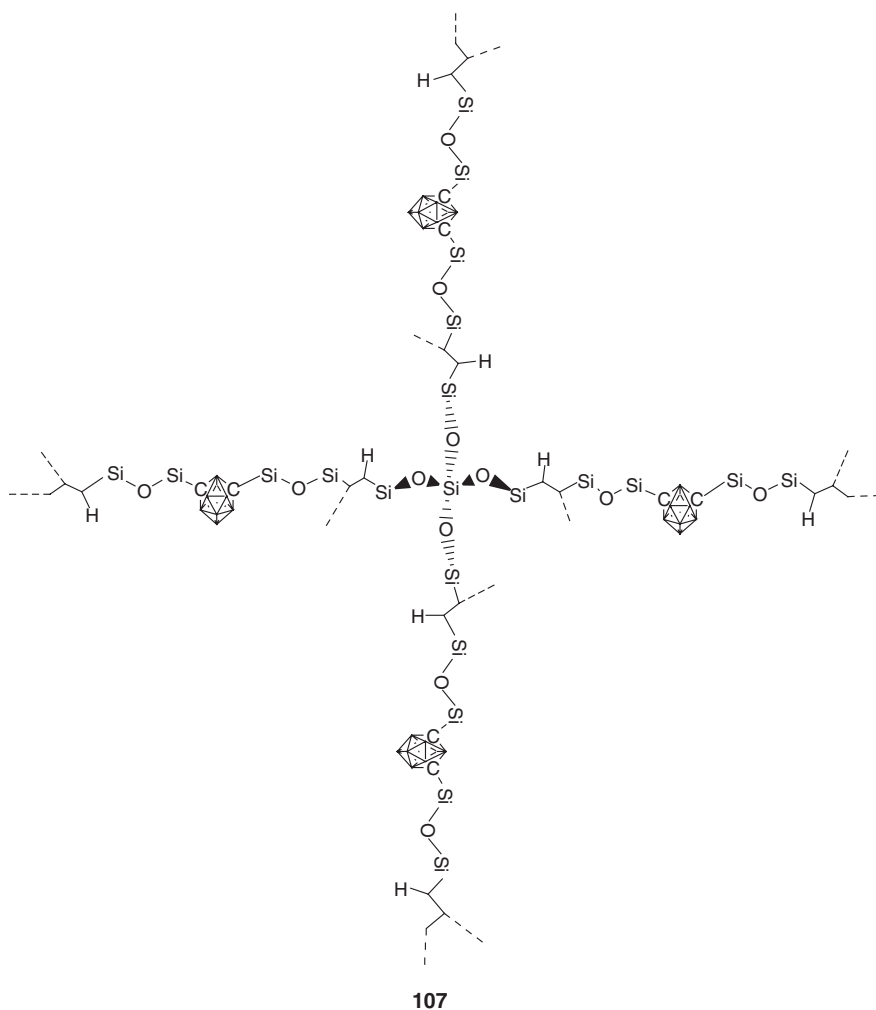
**Figure 65** The hydrosilated networked polymers **105**, **106**, and **107** obtained from Karstedt catalyst-catalyzed hydrosilations involving monomeric vinyl- or ethynyl-terminated carboranylenesiloxane and a branched siloxane cross-linker in hexane. The Si-bound methyl groups have been omitted for clarity. (Adapted from ref. 134.)





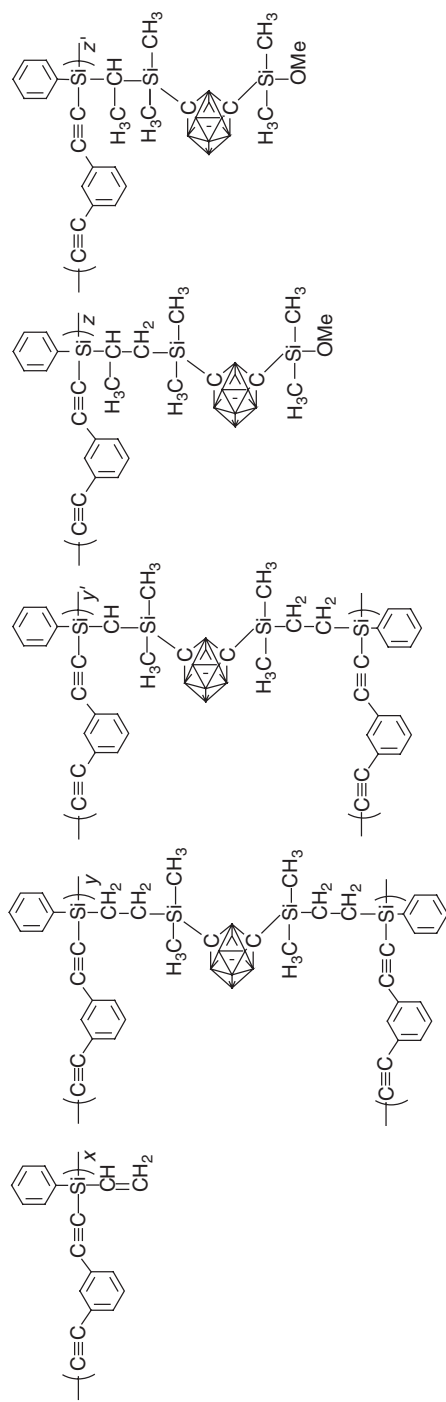
**Figure 65** (Continued)

pletely saturated (**107**) (Fig. 65) set of networked polymers. The Karstedt catalyst was preferred over the Speier's catalyst for its greater activity due to its ability to form finer colloidal Pt particles during the catalyst initiation step.<sup>135</sup> The reactions proceeded rapidly to generate elastomeric networked polymers in contrast to the slow formation of the hard, colorless solid **104**. The flexible and transparent films of the saturated elastomeric networked polymers (**105**) from the vinyl monomer had  $T_g$  values below  $-35^\circ\text{C}$ , while the  $T_g$  values of the films (**106** and **107**) formed from the ethynyl monomers were below  $0^\circ\text{C}$ . Preliminary studies of the three elastomeric products have indicated that the materials retain their elastomeric nature on extended use (3–4 days) in air at a temperature of  $200^\circ\text{C}$ . The clarity of the products was also

**Figure 65** (Continued)

observed to have been maintained during such exposures. At temperatures above 350°C, these materials were observed to lose their clarity, presumably due to further cross-linking reactions of Si-bound methyl groups. The degradation temperature defined as the temperature at 5% weight loss of the material for the three networks was determined to be in the range of 500–550°C.

Ando and co-workers have reported the synthesis of a silyl-carborane hybrid diethynylbenzene-silylene polymer (**108**) (Fig. 66) possessing high thermal stability.<sup>136</sup> The polymer contained Si and  $\text{—C}\equiv\text{C—}$  group in the main chain and *m*-carborane and vinyl groups in the side chain. The 5% weight-loss temperature of the cured polymer in air was over 1000°C as determined by thermogravimetric analysis.



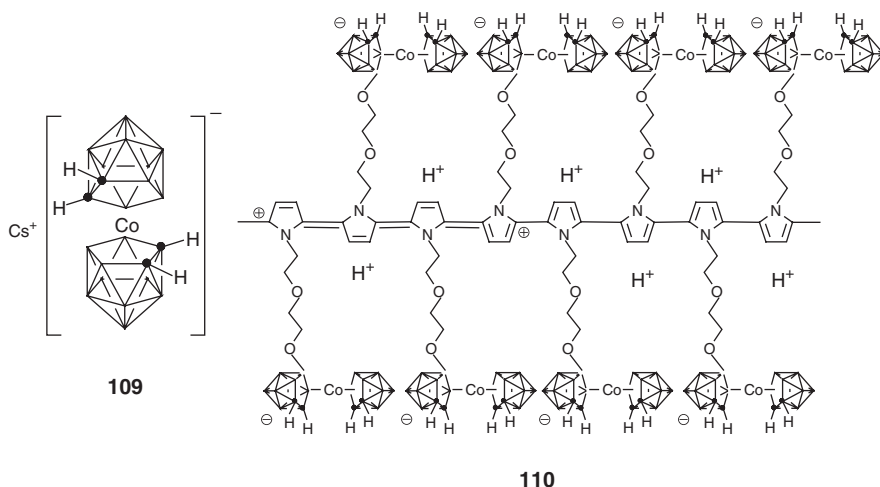
108

**Figure 66** The thermooxidatively stable silyl-carborane hybrid diethynyl/benzene-silylene polymer **108** containing various carbon-carbon unsaturations. (Adapted from ref. 136.)

During heat treatment between 250 and 500°C, the formation of three-dimensional networks by diene and addition reactions of Ph—C≡C, C≡C, and *m*-carborane groups in this system has been characterized by  $^{11}\text{B}$  MQ-MAS NMR and  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS NMR methods.

### iii. Conducting Polymers Containing Carborane Clusters

Carboranes due to their exceptional characteristics in both their neutral and anionic forms have evoked extreme interest in their use as doping agents and covalently bound functionalities in conducting polymers.<sup>137</sup> Teixidor and co-workers have reported the use of an organometallic complex of a carborane  $\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  (**109**) (Fig. 67) as doping agents in organic conducting polymers.<sup>138</sup> The synthesis of the polypyrrole,  $(\text{PPy})[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  polymer, by the electropolymerization of the pyrrole monomer in the presence of **109** has been achieved. On electropolymerization, the carborane clusters were found to be incorporated and uniformly distributed in the PPy polymer. The incorporation of the carborane clusters resulted in a dramatic improvement in the overoxidation threshold (1.25 V) of the polymer when compared to other doping anions (commonly near 0.6 V) such as  $\text{Cl}^-$ ,  $(\text{NO}_3)^-$ , and so on.



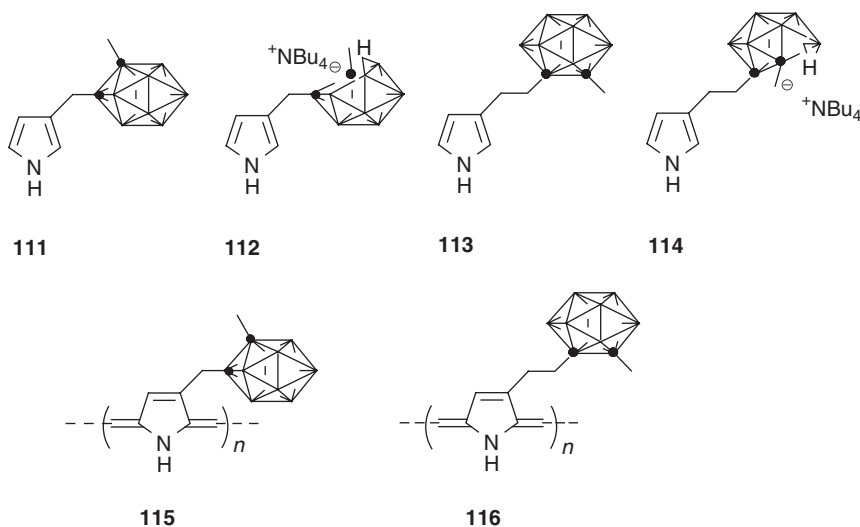
**Figure 67** The cobaltabisdicarbollide  $\{\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  (**109**) that was doped in or covalently bound to a pyrrole monomer to produce conducting polymers (**110** being one of them). (Adapted from refs. 138 and 139.)

The Teixidor team further improved upon this chemistry by covalently linking units of **109** to the polypyrrole monomer prior to electropolymerization.<sup>139</sup> A  $[3,3'-\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  anion was covalently bound to a pyrrole via a spacer through one of its boron atoms by the reaction of the species  $[3,3'-\text{Co}(8-\text{C}_4\text{H}_8\text{O}_2-1,2-\text{C}_2\text{B}_9\text{H}_{10})(1',2'-(\text{C}_2\text{B}_9\text{H}_{11})_2)]^-$  with potassium pyrrole, as functionalization through

its carbon atoms proved impractical due to poor yield of the product. This covalently carborane-bound polymer (**110**) (Fig. 67) did not exhibit overoxidation in the 0–1.8 V range and was found to be better than the noncovalently linked system.<sup>139</sup>

Further studies by this group centered on comparisons of the overoxidation resistance limit (ORL) of polypyrrole materials doped with monoanionic borane clusters  $[B_{12}H_{11}NH_3]^-$  or dianionic borane  $[B_{12}H_{12}]^{2-}$  or carborane  $[Co(C_2B_9H_{11})_2]^{2-}$  clusters. The monoanionic boron clusters were found to offer the highest stability to the PPy doped materials against overoxidation than any other charged dopant. They were also found to be far superior to the dianionic clusters in their ability to impart an ORL rise.<sup>140</sup>

The synthesis of the first covalently attached carborane-containing polypyrrole was reported by Fabre and co-workers.<sup>141</sup> The initial step involved the production of 2-*t*-butoxycarboranylpyrrole from 1-allyl-2-methyl-*o*-carborane by the addition of phenylsulfonyl chloride, followed by oxidation, dehydrochlorination and condensation under Barton–Zard conditions. This product was cleaved and decarboxylated using 2% TFA/THF to produce **111** (Fig. 68) in 70% overall yield. The monomer 3-carboranymethyl-pyrrole (**111**) (**112** being its *nido* version) (Fig. 68) was subsequently electropolymerized to produce the polymer (**115**) (Fig. 68), which exhibited an overoxidation threshold of 1.5 V and a high hyperpolarizability ( $\beta$ ) value.



**Figure 68** The neutral *ortho*- or anionic *nido*-carborane attached pyrrole molecule (**111**, **112**, **113**, and **114**) used in the synthesis of conducting organic polymers **115**, **116**, etc. (Adapted from refs. 141 and 142.)

The Fabre group has further developed the chemistry of covalently attached carborane-containing polypyrrole by synthesizing pyrrole derivatives that are covalently

linked to neutral *ortho*- or anionic *nido*-carborane cage via an ethylene spacer arm attached to the pyrrole molecule [3-(2-methyl-*o*-carboranyl)ethyl-1H-pyrrole (**113**) and **114** (being the *nido* version of **113**)] (Fig. 68) at one of its ring 3-(2-methyl-*o*-carboranyl)ethyl-1H-pyrrole (**113**) carbons.<sup>142</sup> The electrochemical studies under anodic oxidation of both of the polymers (**115** and **116**) (Fig. 68) revealed that while the neutral carborane-containing PPy exhibited conductivity, the anionic derivative caused the passivation of the electrode.

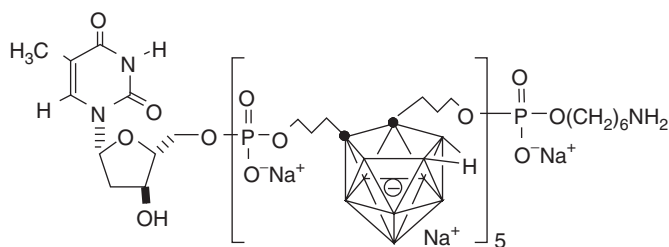
The assembly of a soluble, air-stable, supramolecular structure from the metal-containing porphyrin-carborane moiety  $\{\text{Cp}^*\text{Ir}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}$ , through bridging via nitrogen-based organic spacers has been reported.<sup>143</sup> In the resulting polymeric material,  $\{(\text{Zn-TPyP})[\text{Cp}^*\text{Ir}\{\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]_2 \cdot 6(\text{CHCl}_3)\}_n$ , the strong luminescence of the zinc porphyrin was observed to be completely quenched due to an intramolecular electron transfer between the porphyrin site and the binding cluster in the phthalocyanine site.

#### *iv. Carborane Polymers in Medicine*

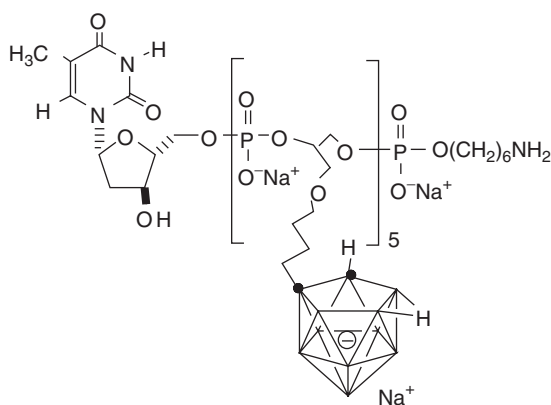
Boron exists in nature in the form of two stable isotopes;  $^{10}\text{B}$  (abundance 19.9%) and  $^{11}\text{B}$  (80.1%), with the latter's nucleus possessing an extra neutron.<sup>2</sup> Boron-10 nucleus is the only *light* element that is capable of binding a slow neutron (or thermal neutron) to yield an excited boron-11 nucleus. This unstable nucleus undergoes fission to form a lithium-7 nucleus and a helium-4 nucleus along with a gamma photon. The neutron-capturing ability of boron has facilitated the use of its boron-10 nucleus for localized treatment of cancers. The use of boron compounds for the treatment of cancer was first proposed by Locher in 1936.<sup>144</sup> In the therapy, known as boron neutron-capture therapy (BNCT), a tumor target is selectively loaded with high concentrations of stable boron-10 ( $^{10}\text{B}$ ) isotope, followed by irradiation with thermal neutrons. The heavy ions ( $^7\text{Li}$ ,  $^4\text{He}$ ) emitted on irradiation have a limited translational path (approximately one cell diameter), and hence, the BNCT-produced cytotoxicity is limited only to the tumor target that contains elevated levels of the  $^{10}\text{B}$  nuclei.

Since the initial discovery by Locher, Hawthorne and co-workers, among others, have pioneered the use of  $^{10}\text{B}$  nucleus in cancer therapy research. Lately, the research in BNCT has centered on the utilization of immunoproteins as vehicles to transport carborane nuclei to targeted cancerous cells. In a recent report, the tethering of oligomeric *nido*-carboranyl phosphodiester to an engineered immunoprotein (a chimeric IgG3 protein) at its exposed cysteine residues was achieved by the coupling of two boron-rich phosphodiester to sulfhydryls (of cysteine) that had been introduced to the  $\text{C}_H2$  domain of the IgG3 protein.<sup>145</sup> The resulting boron-rich immunoconjugates (**117** and **118**) (Fig. 69) were found to have promising *in vitro* and *in vivo* characteristics for boron delivery.

Hawthorne and co-workers have reported the selective uptake of homogeneous fluorescein-labeled *nido*-carboranyl oligomeric phosphate diesters (*nido*-OPDs) by cell nuclei within 2 h after microinjection. The location in the cell of *nido*-OPDs uptake was found to depend on the location of the carboranyl moiety in the *nido*-OPDs. When the carborane cage was located on a side chain attached to the oligomeric



117



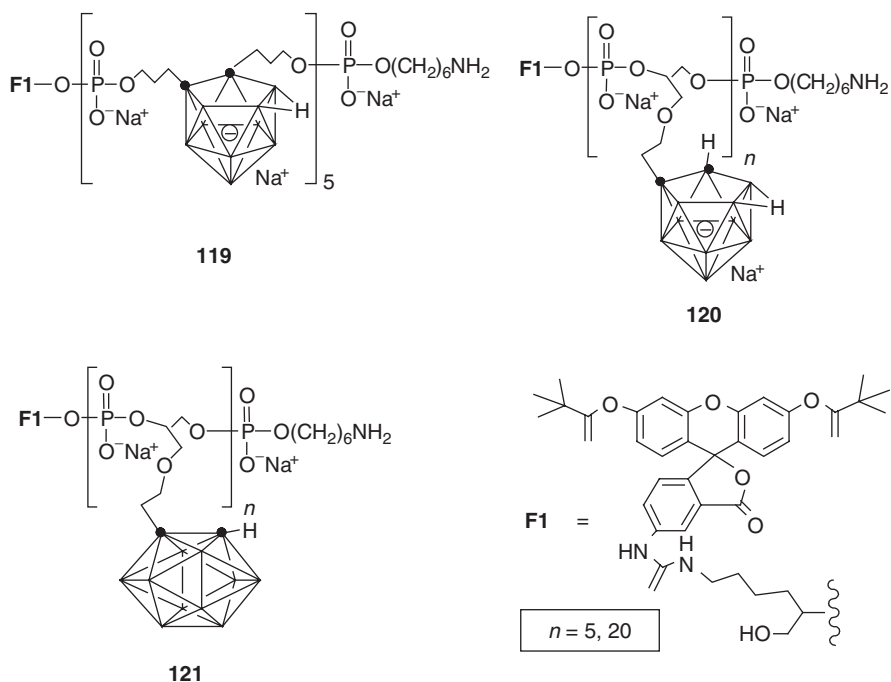
118

**Figure 69** The boron-rich immunoconjugates (**117** and **118**) obtained by the tethering of oligomeric *nido*-carboranyl phosphodiesters to an engineered immunoprotein (a chimeric IgG3 protein). (Adapted from ref. 145.)

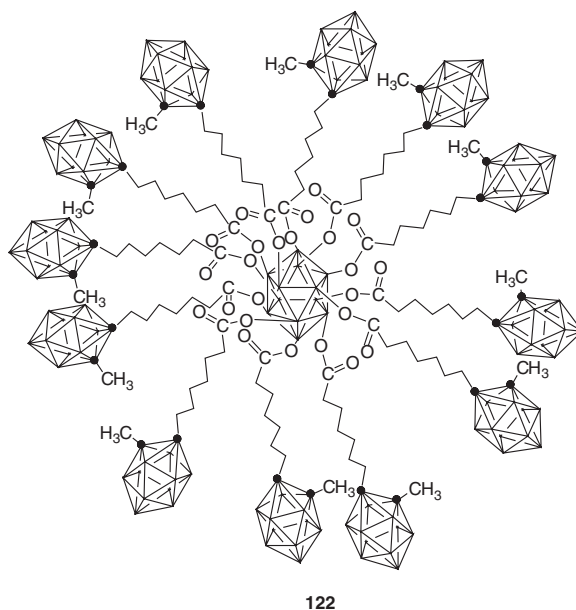
backbone (**120**) (Fig. 70), the *nido*-OPDs were found to distribute between both the cytoplasm and the nucleus. However, when the carborane cage was located along the oligomeric backbone (**119**) (Fig. 70), the *nido*-OPDs were found to remain primarily in the nucleus. In comparative studies, the *ortho*-OPDs (**121**) (Fig. 70) were found to be not as effective as the *nido*-OPDs for boron delivery.<sup>146</sup>

Several dendrimeric borane and carborane systems have been developed for use as boron-delivery agents.<sup>147</sup> *In vitro* tests with a boronated dendrimer-epidermal growth factor bioconjugates indicated that they are endocytosed, resulting in the accumulation of boron in lysosomes.

Thomas and Hawthorne have synthesized unimolecular, nanospherical boron-rich dodeca(carboranyl)-substituted closomers (**122**) (Fig. 71) for their potential application as drug-delivery platforms for BNCT.<sup>148</sup> The substituted closomers were synthesized by reacting carborane acid chloride with the dodecahydroxy dodecaborate closomer in methylene chloride by utilizing a threefold excess of the former in triethylamine. The twelve pendant *closo*-1,2-carborane units in the closomer could



**Figure 70** The fluorescein (F1)-labeled *nido*-OPDs (**119** and **120**) and *ortho*-OPDs (**121**) boron delivery systems. (Adapted from ref. 146.)

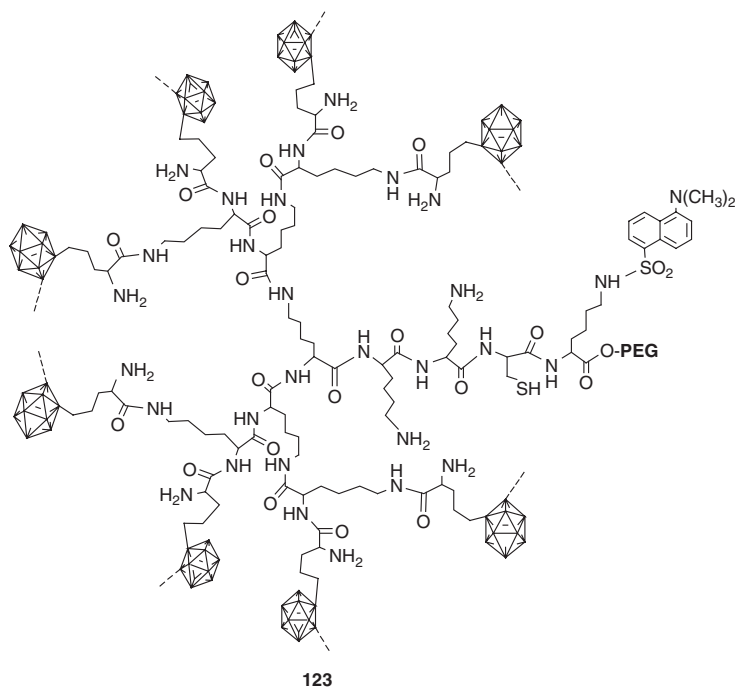


**Figure 71** Nanospherical boron-rich dodeca(carboranyl)-substituted closomers (**122**) with potential for boron delivery in BNCT. (Adapted from ref. 148.)



also be degraded to anionic *nido*-7,8-carborane cages by refluxing with a large excess of CsF in absolute ethanol for 4 days.

Qualmann and Kessels have reported the synthesis of carborane-containing lysine dendrimers (**123**) (Fig. 72), with a better defined number of boron atoms, for use as protein labels in immunocytochemistry using electron microscopic techniques such as electron energy loss spectroscopy (EELS) and electron spectroscopic imaging (ESI).<sup>149</sup>

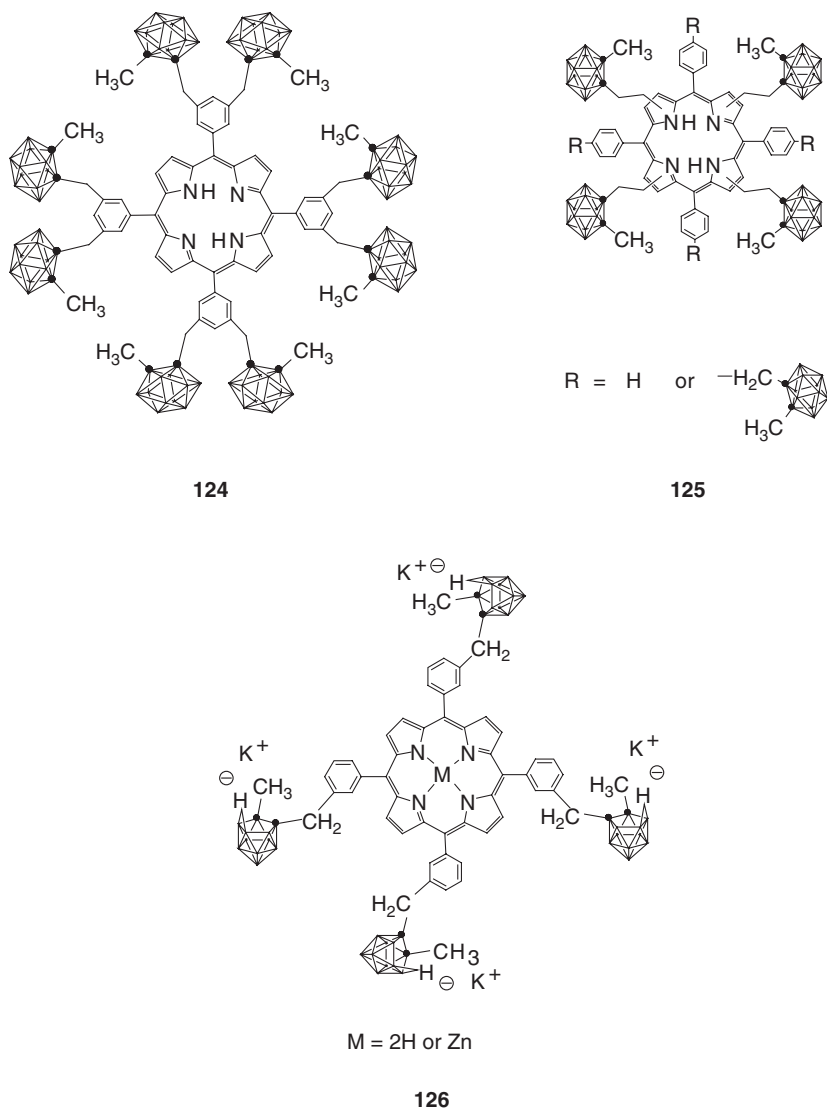


**Figure 72** Carborane-containing lysine dendrimers (**123**), with a defined number of boron atoms, for use as protein labels. (Adapted from ref. 149.)

Several reports of carboranated porphyrins have appeared for utilization in the BNCT of cancer.<sup>150</sup> The examples include both *nido*- (**126**) (Fig. 73) and *closo*-carborane cluster-containing (**124** and **125**) (Fig. 73) materials. Metal-free *nido*-carboranylporphyrins were able to deliver a higher amount of boron to cells than the corresponding zinc complexes.

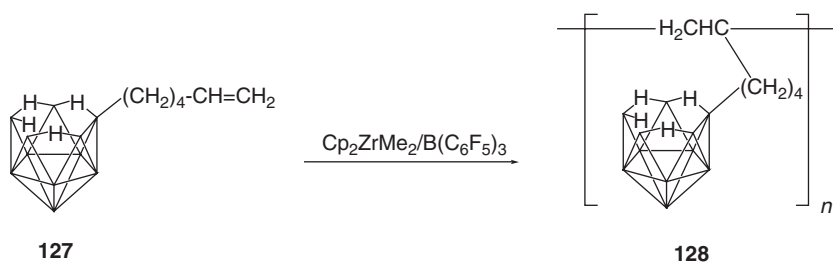
#### *v. Carborane Polymers Used in the Production of High-Performance Fibers*

Carborane-derived polymers have been used in the production of boron carbide ceramic fibers and matrices. Polyhexenyldodecaborane (**128**) (Fig. 74), a dodecaborane-based polymeric material, has been reported to be an ideal source for the production of nanostructured boron carbide materials by new nanoscale templating methods utilizing porous alumina templates having a thickness of 60  $\mu\text{m}$  and a nominal pore



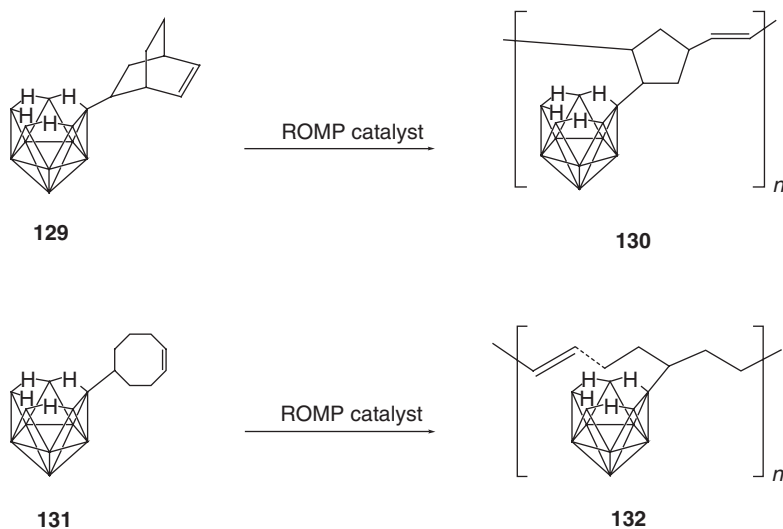
**Figure 73** The *closo*- (**124** and **125**) and *nido*- (**126**) carborane cluster-containing porphyrins for BNCT. (Adapted from ref. 150.)

size of  $\sim 250$  nm.<sup>151</sup> The monomeric building block, 6-hexynyl-decaborane (**127**) (Fig. 74), was constructed from a  $\text{Cp}_2\text{Ti}(\text{CO})_2$ -catalyzed reaction of hexadiene and decaborane. The polymerization was then achieved by employing the  $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$  catalyst.



**Figure 74** The polyhexenyldecaborane (**128**) used in the production of nanostructured boron carbide materials by nanoscale templating methods utilizing porous alumina templates. (Adapted from ref. 151.)

Other monomeric precursors similar to 6-hexynyl-decaborane such as 6-norbornenyl-decaborane (**129**) and 6-cyclooctenyl-decaborane (**131**) (Fig. 75) underwent ROMP in the presence of either first- or second-generation Grubbs catalysts to produce the corresponding poly(norbornenyl-decaborane) (**130**) (Fig. 75) and poly(cyclooctenyl-decaborane) (**132**) (Fig. 75) with  $M_n > 30$  kDa and polydispersities between 1.1 and 1.8.<sup>152</sup> Electrostatic spinning and pyrolysis of poly(norbornenyl-decaborane) was discovered to produce nanoscale, free-standing porous boron-carbide/carbon, ceramic fiber matrices.<sup>153</sup>



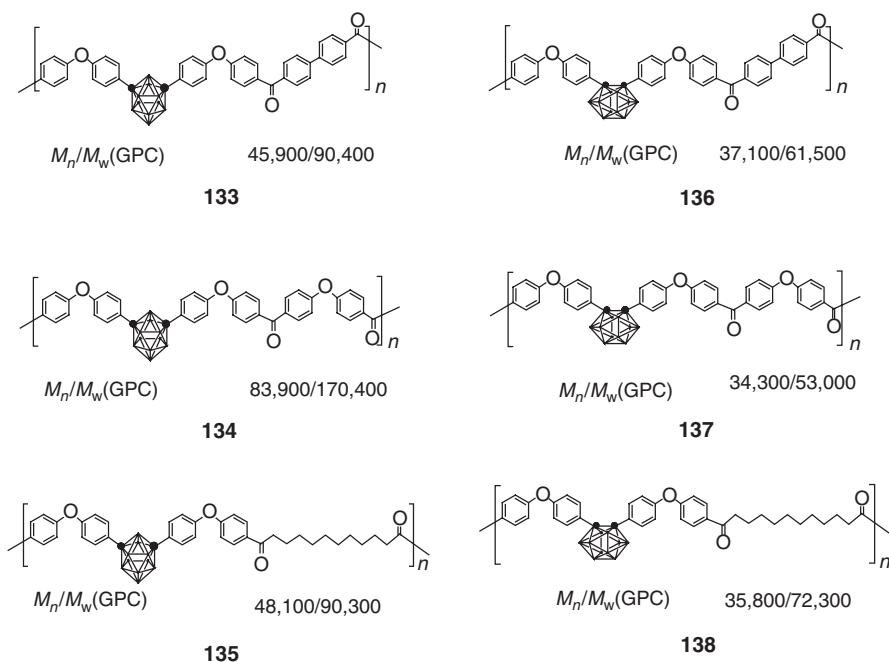
**Figure 75** The conversion of the monomeric precursors, 6-norbornenyl-decaborane (**129**) and 6-cyclooctenyl-decaborane (**131**), by ROMP into poly(norbornenyl-decaborane) (**130**) and poly(cyclooctenyl-decaborane) (**132**). (Adapted from ref. 152.)

The incorporation of decaborane into polycarbosilane-based polymers has been used in the densification of the polymer-derived SiC fibers. Improved densification resulted in the formation of fibers with density as high as 2840 kg/m<sup>3</sup> corresponding to an increase of 89%.<sup>154</sup>

## vi. Miscellaneous Carborane Polymers

### a. Carborane Polymers of Polyetherketones

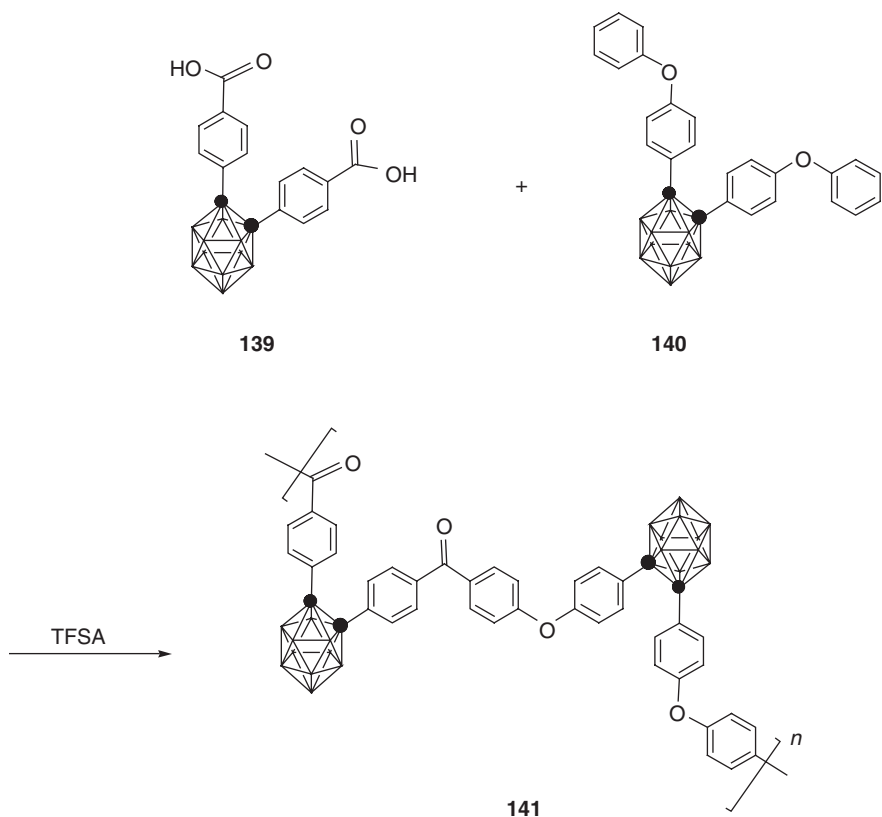
Colquhoun and Wade have reported the synthesis of fire-resistant carborane-containing polyetherketones [**133**, **134**, and **135** (*meta*-derivatives) and **136**, **137**, and **138** (*ortho*-derivatives)] (Fig. 76) from the trifluoromethanesulfonic acid-promoted polycondensation reaction of various bis(4-phenoxyphenyl) derivatives of *meta*- or *ortho*-carborane with aromatic or aliphatic dicarboxylic acids.<sup>155</sup> The weight-average molecular weights of the polymers ranged between 50,000 and 170,000. On thermolysis to 850°C under nitrogen or air, these polymers were observed to lose only 7 or 3% of the weight, respectively, demonstrating their exceptional thermal stability and extreme resistance to combustion.



**Figure 76** Fire-resistant carborane-containing polyetherketones [**133**, **134** and **135** (*meta*-derivatives) and **136**, **137** and **138** (*ortho*-derivatives)]. (Adapted from ref. 155.)

The trifluoromethanesulfonic acid (TFSA)-promoted polycondensation reaction between diarylcarborane dicarboxylic acid (**139**) and diaryl carborane diether

monomer acid (**140**) (Fig. 77) was utilized in the construction of a similar carborane-containing polyetherketone acid (**141**) (Fig. 77) with two ortho-carborane units in a repeating unit.<sup>156</sup> The polymer was found to lose a much smaller proportion of its weight on pyrolysis up to 1000°C compared to conventional aromatic ether-ketones (e.g., ICI's VICTREX).

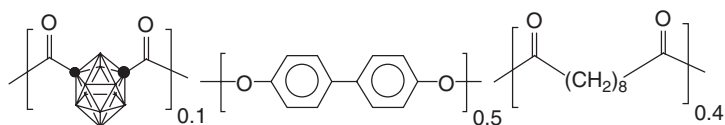


**Figure 77** The trifluoromethanesulfonic acid-promoted polycondensation reaction between diarylcarborane dicarboxylic acid (**139**) and diaryl carborane diether monomer acid (**140**) to yield the polyetherketone acid, **141**. (Adapted from ref. 156.)

A polycondensation reaction of 4,4'-dihydroxybiphenyl, sebacic, and *m*-carboranedicarboxylic acids was reported to produce a carborane-containing polymer (**142**) (Fig. 78) that led to the production of a new columnar phase at elevated temperatures.<sup>157</sup> This new phase was formed in addition to the crystalline and liquid crystalline smectic phases typically formed from only 4,4'-dihydroxybiphenyl and sebacic acids.

#### *b. Carborane Polymers for Use in Catalytic Reactions*

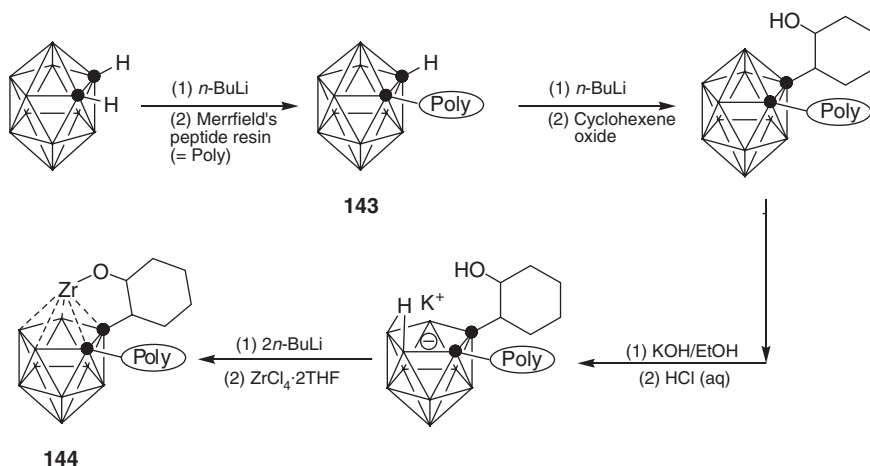
The polymer-supported *o*-carborane, **143**, was utilized further for cage decapitation, deprotonation, and reaction with  $\text{ZrCl}_4 \cdot 2\text{THF}$  to generate a polymer-supported



142

**Figure 78** The carborane-containing polymer (**142**) obtained from the polycondensation reaction of 4,4'-dihydroxybiphenyl, sebacic, and *m*-carboranedicarboxylic acids. (Adapted from ref. 157.)

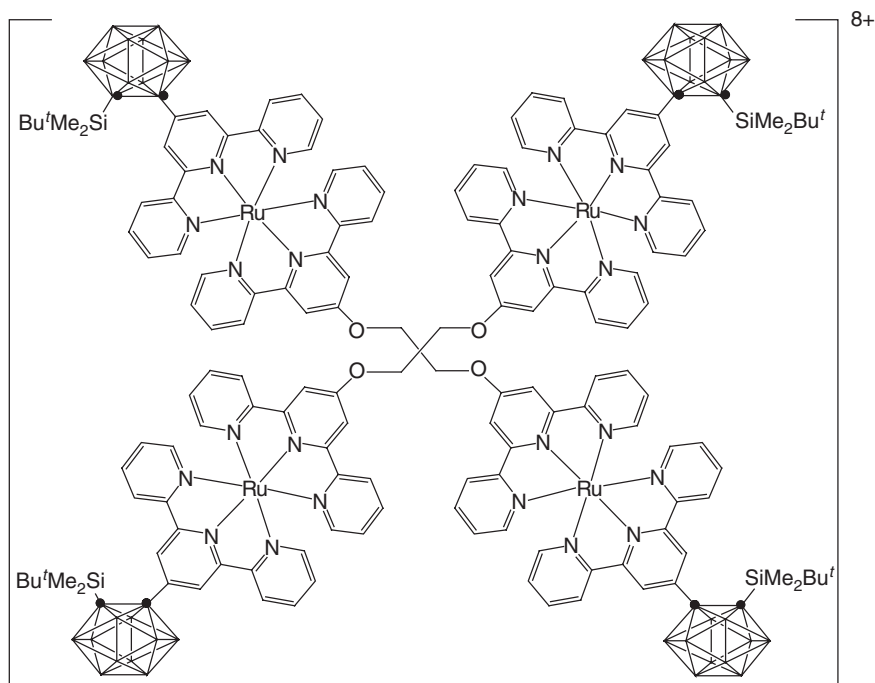
single-site polymerization catalyst (**144**) (Fig. 79). This catalyst was used for the polymerization of ethylene and vinyl chloride in toluene to give high molecular weight polyethylene [ $9.4 \times 10^3$  ( $M_w/M_n = 1.8$ )] and polyvinyl chloride [ $9.4 \times 10^3$  ( $M_w/M_n = 1.8$ )], respectively.<sup>158</sup>



144

**Figure 79** The polymer-supported *o*-carborane (**143**) utilized further for its decapitation, deprotonation and reaction with  $ZrCl_4 \cdot 2THF$  to generate a polymer-supported single-site polymerization catalyst (**144**) for the polymerization of ethylene and vinyl chloride. (Adapted from ref. 158.)

Carborane clusters, consisting of their  $B_{10}H_{10}$  portions, that have been grafted onto the surface of organometallic dendrimers have been reported.<sup>159</sup>  $B_{10}H_{10}$  has been linked to a terpyridine group in a ruthenium complex. The reaction of this complex with a tetra(terpyridine) core afforded a first-generation organometallic dendrimer (**145**) (Fig. 80).



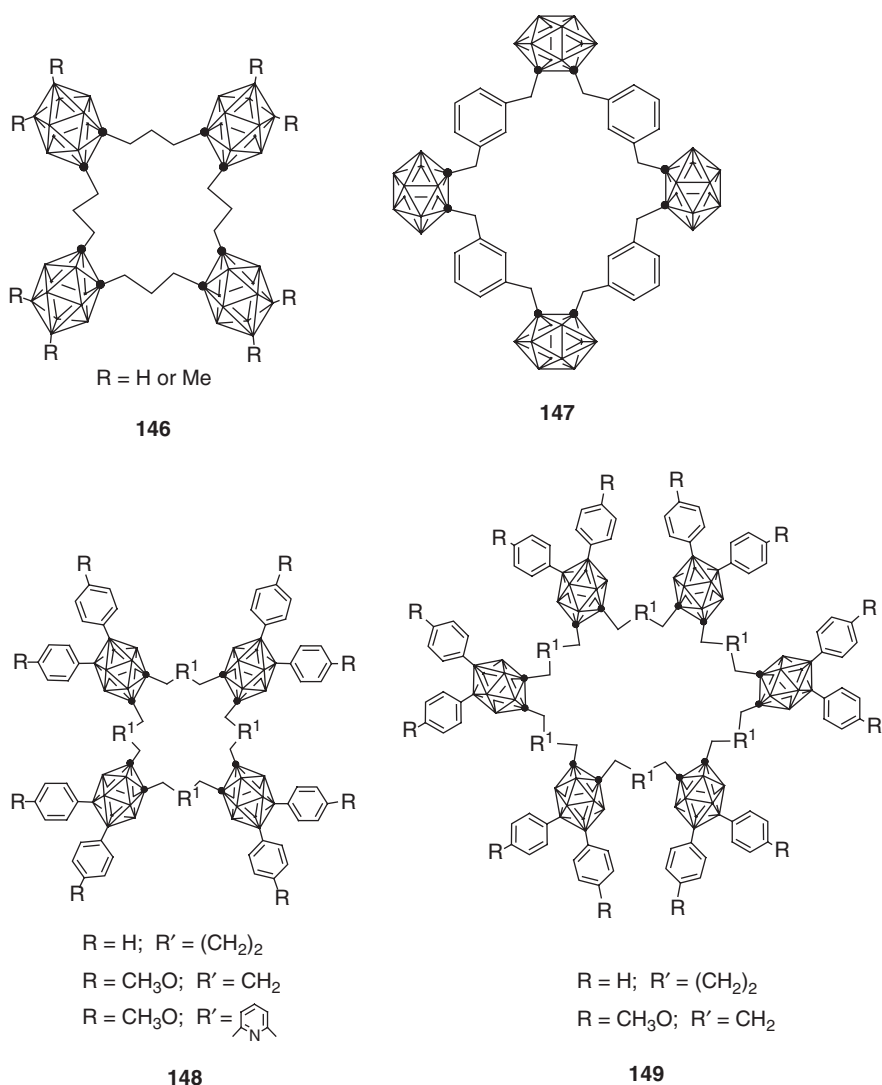
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**Figure 80** A first-generation organometallic dendrimer (**145**) containing grafted carborane clusters on tetra(terpyridine) cores. (Adapted from ref. 159.)

### vii. Carborane Supramolecular Chemistry

The supramolecular chemistry of boron, as with other elements, has witnessed a spectacular explosion in its growth in recent times. Supramolecular chemistry, which deals with the chemistry and collective behavior of organized ensembles of molecules, has obtained one of its perfect assembling tools in the structurally symmetric carborane molecule. The supramolecular architectures produced from carboranes have included such varied examples as carboracycles, mercuracarborands, grid-shaped polymers, and coordination-driven polymers. Hawthorne and co-workers have developed a family of carboracycles (**146**, **147**, **148**, and **149**) (Fig. 81), from carborane icosahedra and bridging organic groups, as alluded to in a previous section, highlighting the suggested carborane–benzene analogy.<sup>160</sup> The organic bridging groups have included 1,3-trimethylene,  $\alpha,\alpha'$ -1,3-xylylene or  $\alpha,\alpha'$ -2,6-lutidylene, among others. These types of nanometer-scaled, structurally well-defined rigid molecules are expected to bridge the gap between discrete molecules and bulk materials.

Carboracycle systems (**150** and **151**) (Fig. 82) with aromatic urea as bridging groups have been constructed by Endo and co-workers.<sup>161</sup> The presence of ureas along with carboranes was expected to be useful for the construction of

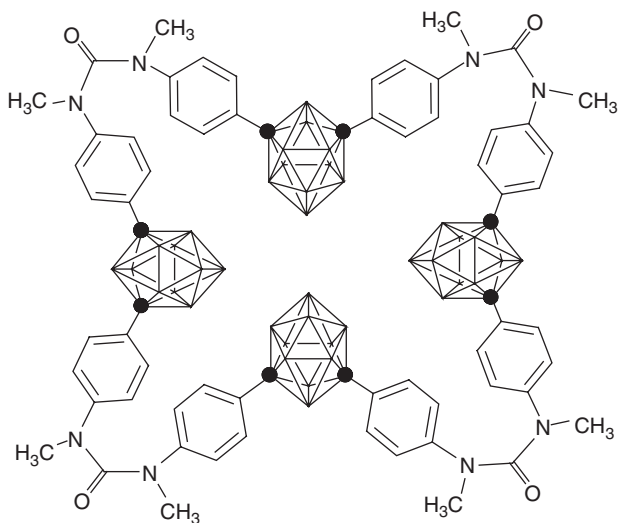
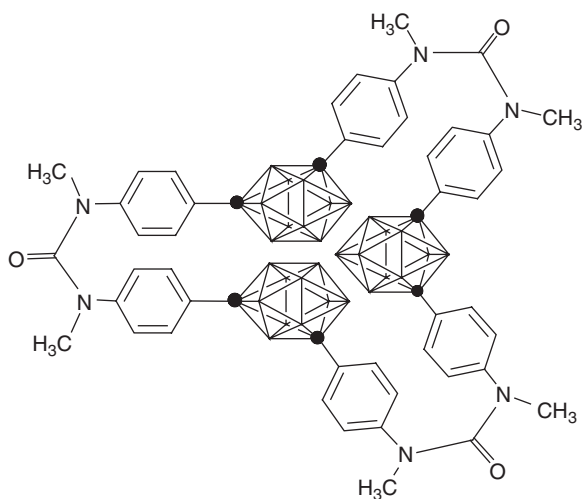


**Figure 81** A few examples (**146**, **147**, **148**, and **149**) from the extensive family of carboracycles. (Adapted from ref. 160.)

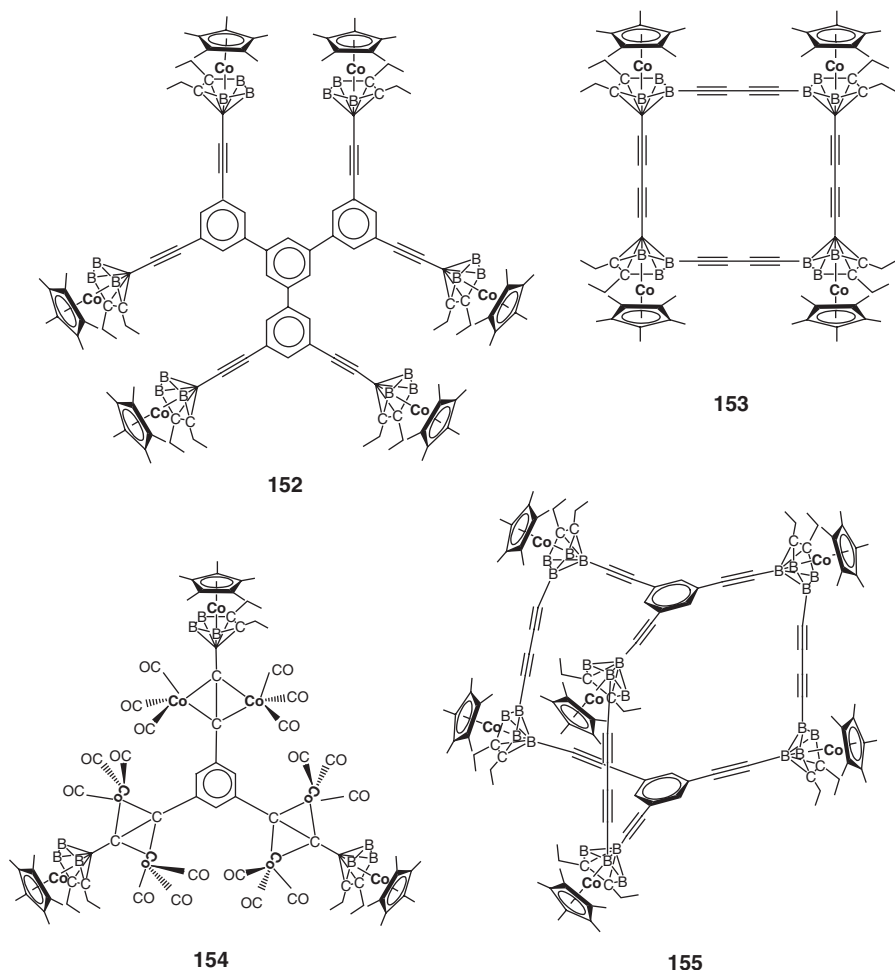
cyclic, layered, or helical molecules with both hydrophobic and hydrogen-bonding characters.

Grimes and co-workers have constructed similar cyclic metallocarborane oligomers with highly symmetric geometries such as squares, triangles, or rectangles for assembling them into extended systems.<sup>162</sup> These symmetric oligomers (**152**, **153**, **154**, and **155**) (Fig. 83) are expected to have useful electronic, optical, magnetic, and catalytic properties along with other properties.





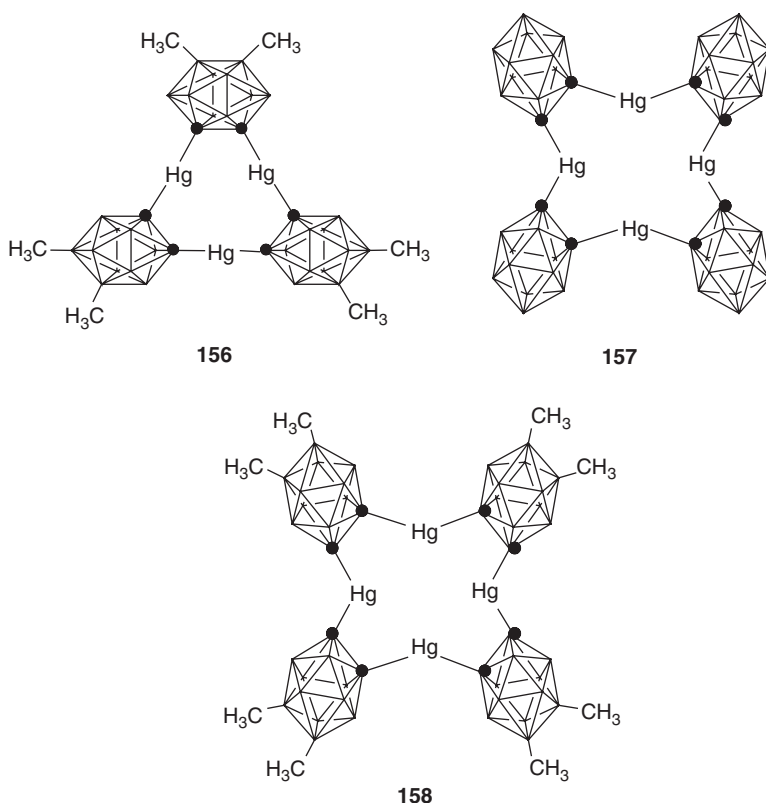
**Figure 82** Carborane systems (**150** and **151**) with aromatic urea as bridging groups. (Adapted from ref. 161.)



**Figure 83** Symmetric cyclic metallacarborane oligomers (**152**, **153**, **154**, and **155**) for assemblage into extended systems. (Adapted from ref. 162.)

Hawthorne and co-workers have also produced a series of macrocyclic Lewis acid hosts called mercuracarborands (**156**, **157**, and **158**) (Fig. 84) with structures incorporating electron-withdrawing icosahedral carboranes and electrophilic mercury centers. They were synthesized by a kinetic halide ion template effect that afforded tetrameric cycles or cyclic trimers in the presence or absence of halide ion templates, respectively.<sup>163</sup> These complexes, which can bind a variety of electron-rich guests, are ideal for catalytic and ion-sensing applications, as well as for the assembly of supramolecular architectures.

A molecular-size construction kit (**159**, **160**, and **161**) (Fig. 85) for the assembly of carborane-containing grid-shaped polymers has been developed by Michl and co-workers.<sup>164</sup> By synthesizing firmly connected, regular two-dimensional grid-shaped

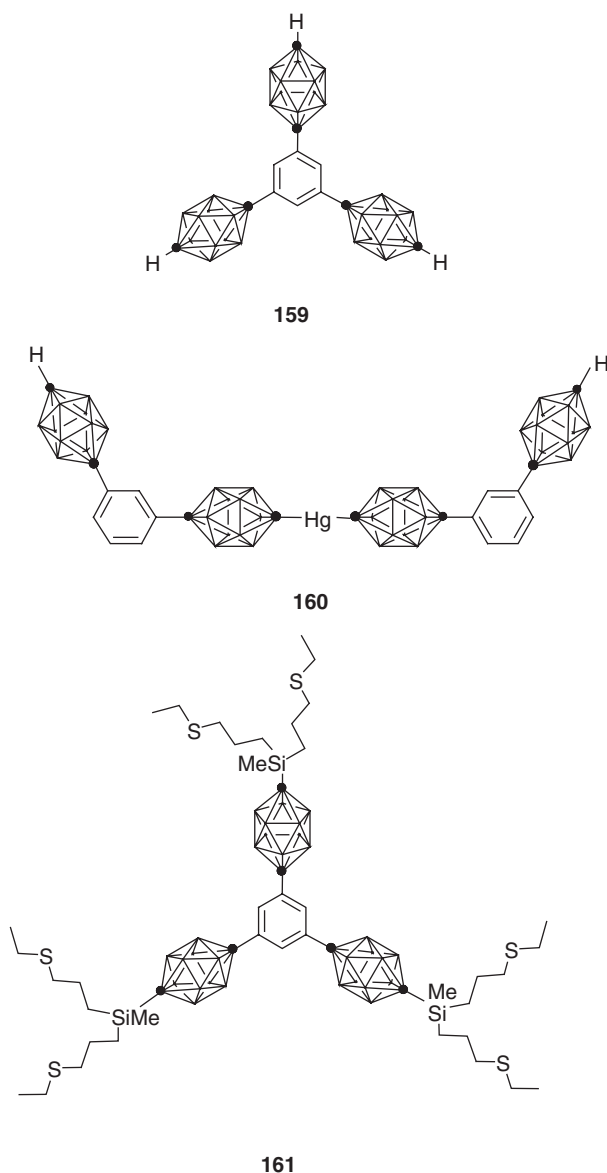


**Figure 84** Macrocyclic mercuracarborands (**156**, **157**, and **158**) with structures incorporating electron-withdrawing icosahedral carboranes and electrophilic mercury centers. (Adapted from ref. 163.)

polymers with a trigonal, square, or hexagonal lattice, it was anticipated that the chance existed for the covalent attachment of additional regular grid layers one at a time on top of the first layer. Thus, as an ultimate goal, the construction of thin layers of materials whose structure is periodic in two wide dimensions and aperiodic in one thin dimension was envisaged for applications in nanotechnology.

Coordination-driven carborane-containing self-assembled polymers (**162**, **163**, and **164**) (Fig. 86) have been reported by Stang et al.<sup>165</sup> Two linear carborane building blocks, 1,12-(4-C≡C(C<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>-*p*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) and 1,12-(*trans*-(Pt(PEt<sub>3</sub>)<sub>2</sub>I)C≡C)<sub>2</sub>-*p*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, were utilized to design and self-assemble five supramolecular complexes (a rectangle, a triangle, a hexagon, and two squares). The coordination originated from interactions of the pyridine ligand's nitrogen atoms and the Pt centers. These systems were expected to have potential applications as host-guest materials, sensors, and catalysts.

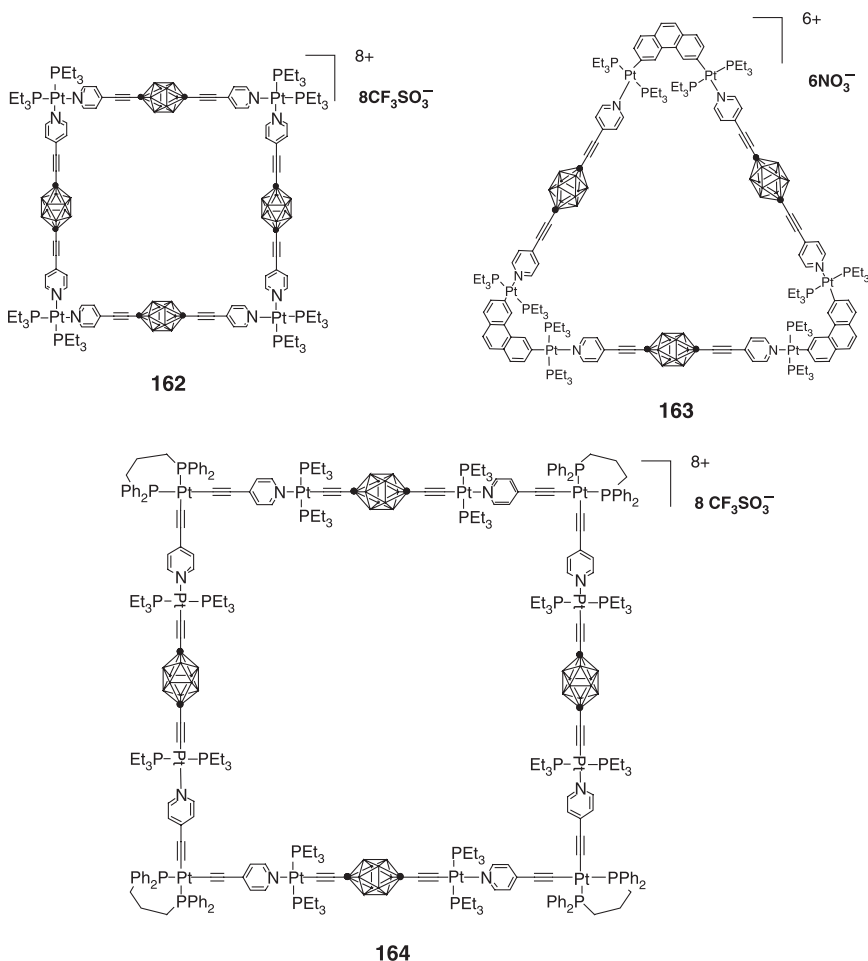
Hardie et al. have utilized the coordination strategy for constructing coordination polymers by mixing silver carborane salts Ag(CB<sub>11</sub>H<sub>12</sub>) (**165**) or Ag[Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]



**Figure 85** Some carborane-containing molecular tools (**159**, **160**, and **161**) in the molecular construction kit for the construction of carborane-containing grid-shaped polymers. (Adapted from ref. 164.)

(**166**) with nitrile ligands (**167**, **168**, **169**, and **170**) (Fig. 87).<sup>166</sup> The coordination originated from B—H···Ag interactions between the silver center and carborane anion.

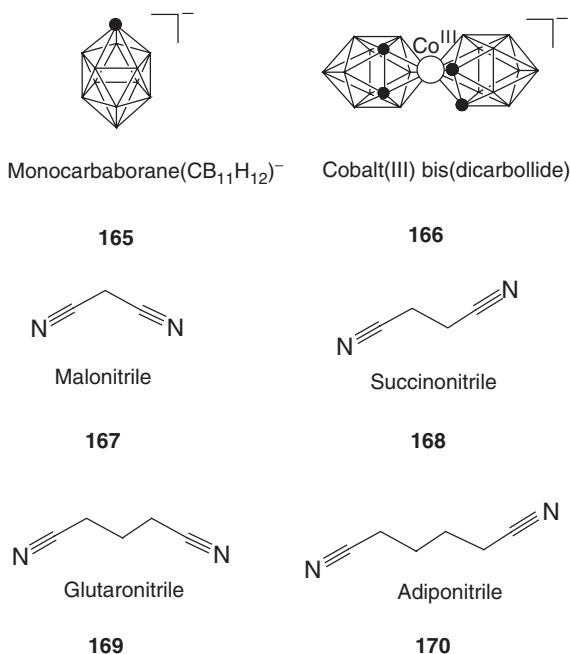
In another example of hydrogen-bond interaction-driven coordination, Teixidor and Lledos have exploited C—H···S—H···H—B hydrogen/dihydrogen-bond



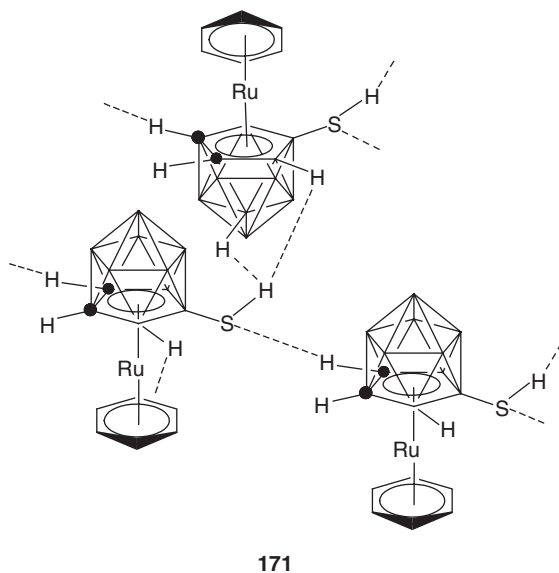
**Figure 86** The coordination-driven carborane-containing self-assembled polymers, **162**, **163**, and **164**. (Adapted from ref. 165.)

interactions between mercaptane and metallacarborane complexes to assemble supramolecular architectures (**171**) (Fig. 88).<sup>167</sup> This is the first instance of the structural elucidation of a S—H ··· (H—B)<sub>2</sub> dihydrogen bond.

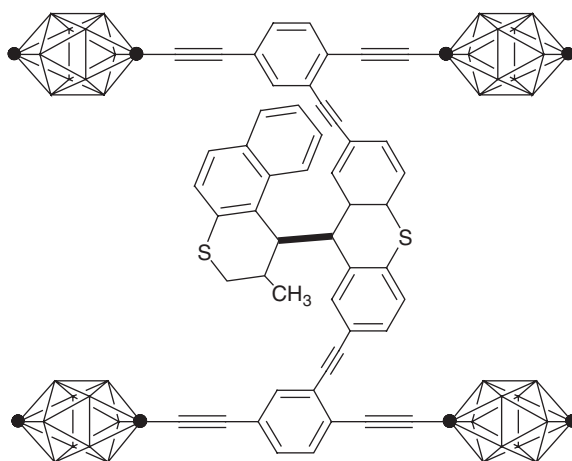
Finally, in a brilliant piece of nanoscale assembly, Tour and co-workers have constructed a “motorized nanocar” structure (**172**) (Fig. 89) that contains a light-activated unidirectional molecular motor and an oligo(phenylene ethynylene) chassis and axle system with four carboranes to serve as the wheels.<sup>168</sup> These authors have demonstrated the rotation of the motor in solution upon irradiation with 365-nm light. This in turn resulted in the turning of the wheels and the movement of the “motorized nanocar” forward. Against its backdrop, it does not seem as a huge leap of faith for one to fathom the construction of a motorized nanotrains and other complex nanostructures in the very near future.



**Figure 87** The silver carborane salts  $\text{Ag}(\text{CB}_{11}\text{H}_{12})$  (**165**) and  $\text{Ag}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$  (**166**), and the nitrile ligands (**167**, **168**, **169**, and **170**) utilized in the construction of coordination polymers. (Adapted from ref. 166.)



**Figure 88** The supramolecular architectures (**171**) assembled by the  $\text{C}-\text{H}\cdots\text{S}-\text{H}\cdots\text{H}-\text{B}$  hydrogen/dihydrogen-bond interactions between mercaptane and metallacarborane complexes. (Adapted from ref. 167.)



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**Figure 89** The “motorized nanocar” structure (**172**) that contains a light-activated unidirectional molecular motor and an oligo(phenylene ethynylene) chassis and axle system with four carboranes to serve as the wheels. (Adapted from ref. 168.)

### III. SUMMARY

Since the pioneering studies of Stocks, Schlesinger, and Burg on the chemistry of borane compounds, the science of boron polymers has blossomed to claim its position among the major polymeric fields, including those of carbon, silicon, and phosphorous. Polymers of boron have now found their niches in virtually every field of chemistry. The only limiting factor for the further unimpeded growth of this polymer field may be the facile and low-cost availability of such boron precursors as carboranes. A concerted effort toward alleviating this deficiency is bound to catalyze even more unique and fascinating polymeric architectural outcomes from this neighbor of carbon.

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