

Boratabenzenes: from chemical curiosities to promising catalysts

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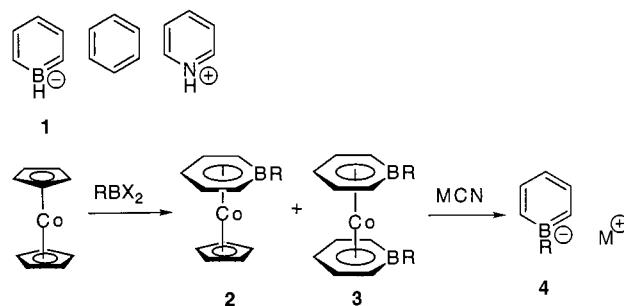
Abstract

Boratabenzenes (**4**) are six π -electron aromatic anions which can serve as versatile ligands towards Zr(IV) and Zr(II). The reaction of **4** with $ZrCl_4$ affords bis(boratabenzene)zirconium(IV) dichlorides (**11**), which on treatment with BuLi and excess PMe_3 give bis(boratabenzene)bis(trimethylphosphine)zirconium(II) (**27**). On activation by excess methylaluminoxane **11** are the catalysts for the polymerization or oligomerization of ethylene. Bridged boratabenzene zirconium dichlorides **19**, **20**, and **21**, which closely resemble the corresponding ansa-zirconocenes, can be similarly activated for polymerization of ethylene. Compound **27** reacts with 1,3-diynes to afford zirconacycles **31** and with acetylene by ring annulation to afford **32**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Boratabenzenes; Catalysts; Aromatic heterocycle

1. Introduction

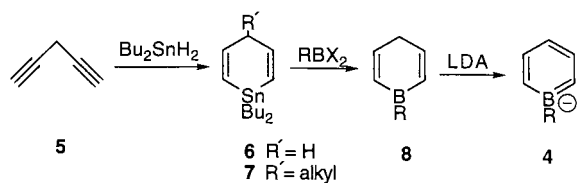
The aromatic heterocycle [1H]-boratabenzene (**1**) is isoelectronic with benzene and pyridinium [1]. However, in comparison with the ubiquitous benzene and pyridine rings, boratabenzenes are rare. Describing them as ‘chemical curiosities’ may even be justified. The first boratabenzene derivative was reported in 1970 by Herberich and coworkers [2]. The reaction of cobaltocene with boron halides leads to the insertion of the boranediyl group into the Cp rings with the production of complexes **2** and **3**. Subsequently it was discovered that complexes **3** could be degraded by treatment with cyanide to produce alkali metal boratabenzenes **4** [3]. The Herberich group, which has remained preeminent in this field, have converted **4** to a large number of main group and transition metal complexes [4].



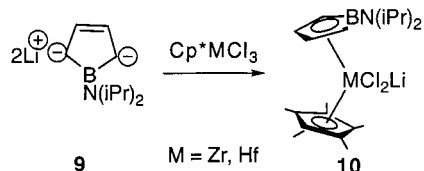
In 1971 we reported a general synthesis for lithium boratabenzenes [5] which can easily be converted to other metal complexes [6]. The hydrostannation of 1,4-pentadiyne **5** with Bu_2SnH_2 affords stannacyclohexadiene **6** which gives boracyclohexadiene **8** on exchange with boron halides. Deprotonation of **8** with base gives the corresponding lithium boratabenzene. This method has been extended to the preparation of more complex boratabenzenes by ourselves [7] and others [8,9]. Recently Herberich has reported a new versatile synthesis of aminoboratabenzenes which is based on the metalation induced ring closure of [bis(dialkylamino)-boryl]pentadienes [10]. Thus boratabenzenes are now available by several routes.

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Since boratabenzenes are six π -electron aromatic anions, they resemble cyclopentadienide. For example, *N,N*-diisopropyl-1-amino-boracyclohexadienes have an acidity in DMSO which is virtually identical to that of cyclopentadiene [11]. Similarly bis(1-methylboratabenzene)iron displays ferrocene-like properties [6]. Although there had been extensive work on boratabenzene complexes of the late transition metals, prior to 1996 no early transition metal derivatives had been reported. In 1994 the Bercaw group prepared several early transition metal complexes of the dianionic diisopropylaminoborollide, e.g. **9** \rightarrow **10** [12]. Since borollide is also isoelectronic with Cp and since early transition metal Cp-complexes are particularly useful in catalysis and in organic synthesis, an exploration of the early metal chemistry of boratabenzene was attractive. Below we summarize our recent work on boratabenzene zirconium complexes.



2. Zirconium(IV) complexes

The reaction of various lithium boratabenzenes (**4**) with ZrCl_4 in ether gives the corresponding bis(boratabenzene)zirconium dichlorides (**11**) in good yields [13,14]. These compounds are yellow to red air-sensitive crystalline solids which can be easily characterized by NMR spectroscopy and X-ray crystallography. The structures of **11**, illustrated in Fig. 1 for **11a** and Fig. 2 for **11c**, generally resemble that of Cp_2ZrCl_2 . The coord-

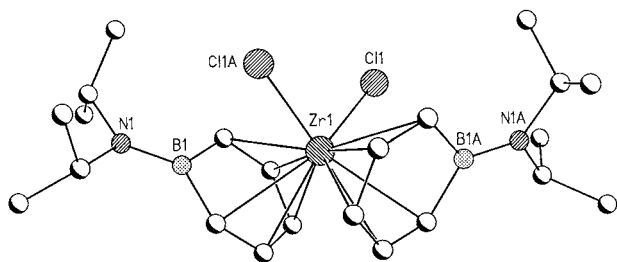


Fig. 1. Molecular structure of **11a**. Some important interatomic distances (Å): B–Zr, 2.980(7); B–N, 1.396(6); C–Zr range 2.58–2.65.

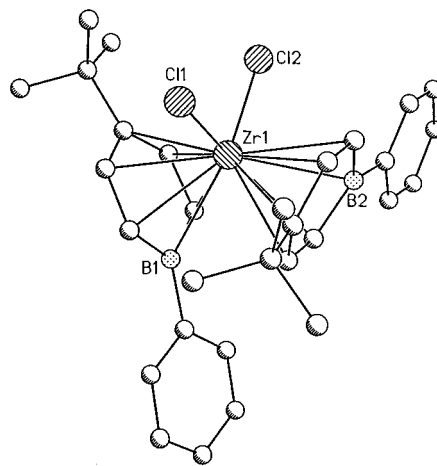
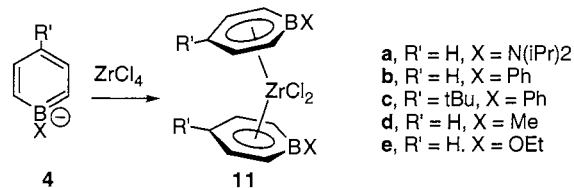


Fig. 2. Molecular structure of **11c**. Some important interatomic distances (Å): B(1)–Zr, 2.826(2); B(2)–Zr, 2.773(3); C–Zr range 2.58–2.66.

ination about Zr is approximately tetrahedral. However, there are marked differences in the juxtaposition of the Zr atom to the boratabenzene rings which depend on the boron substituent.

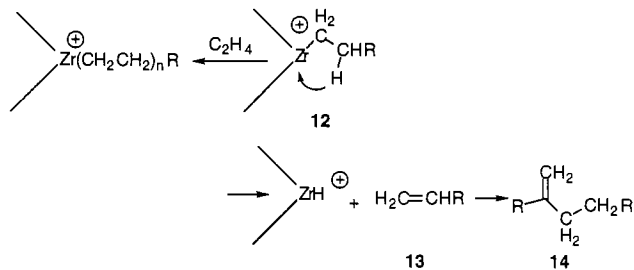


In **11a** the Zr atom slip distorts away from boron so that the B–Zr distance (2.98 Å) is too long for strong bonding. Consequently the diisopropylaminoboratabenzene ring is only η^5 -bound in the manner of the open-metallocenes [15]. The exocyclic nitrogen is strongly π -bound to boron as is indicated by the short B–N distance (1.396 Å) and the sizable barrier to rotation about the B–N bond (18.5 kcal mol⁻¹). It is also likely that this π -donation attenuates the electrophilicity of the Zr atom. When the boron substituent is a poor π -donor as in **11b** and **11c** there is little slip distortion away from boron (Zr–B = 2.80 Å for **11c**) so that the boratabenzene is now η^6 -bound. A similar structure is shown for **11d** (mean Zr–B = 2.82 Å) [16]. The electronic consequence of the poor π -donation to boron is that the Zr atom becomes quite electrophilic.

The chemistry of **11a** and **11b** are also divergent. The addition of excess methylaluminoxane (MAO) to **11a** in hydrocarbon solvents results in a deep red solution which polymerizes ethylene. The polymerization activity slightly exceeds that of MAO activated Cp_2ZrCl_2 . In contrast MAO activated **11b** also reacts rapidly with

ethylene but does not give high molecular weight polyethylene. Instead the products are small oligomers which are largely 2-alkyl-1-alkenes (**14**). The primary products are 1-alkenes (**13**), which subsequently dimerize to form the 2-alkyl-1-alkenes (**14**).

In analogy to the mechanism of metallocene-based homogeneous catalysis of olefin polymerization [17], it seems likely that polyethylene is generated by multiple C_2H_4 insertions into the MAO generated electrophilic Zr species **12a**. However, in the case of **11b** we proposed that **12b** has an enhanced electrophilicity which results in fast β -H elimination to produce 1-alkenes. This limits the chain growth to high molecular weight polyethylene. Bazan and coworkers have subsequently shown that MAO activated **11e** is even more selective affording only 1-alkenes [18].



Obviously the change of the boron substituent has profound effects on ethylene polymerization. The reactivity of the Zr-site seems to be electronically tunable by varying the relatively remote substituent on boron. Since similar changes are not so readily achieved using Cp ligands, it is reasonable to hope that novel electrophilic boratabenzene complexes may find innovative applications complementary to those of Cp-complexes.

Ansa-metallocene based catalysts, e.g. **15** [19], are the most thoroughly investigated Cp-based catalysts [17,20]. The high activity of **15** is apparently due to its rigid open wedge to the metal site, while its stereoselectivity derives from the chirality of the wedge opening. Ansa-metallocenes commonly have bridging groups consisting of CH_2CH_2 , SiMe_2 or CMe_2 , for example, in compounds **16** [21], **17** [22], and **18** [23]. For comparison we have developed syntheses of analogously bridged boratabenzenes **19**, **20**, and **21** [24]. The bridging at C(4) was chosen for ease synthesis. Thus treatment of stannacyclohexadiene **8** with LDA followed by alkylation is regioselective for C(4) [25,26]. Conversion to appropriately 4-substituted boratabenzene proceeds in the same manner as for the parent compound. In a similar manner diisopropylaminoboratabenzene can be directly functionalized at C(4). It is only unfortunate that the symmetrically substituted bridged boratabenzenes **19**, **20**, and **21** are achiral.

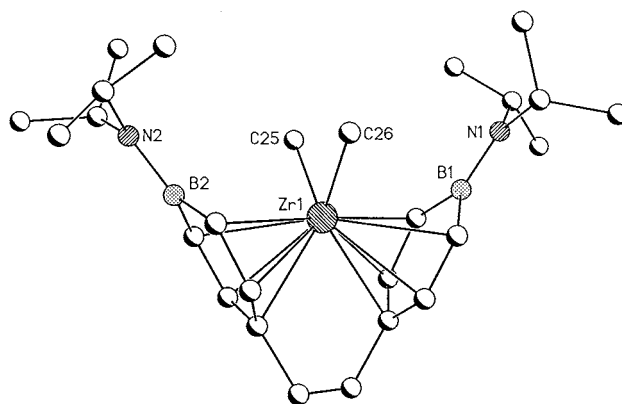
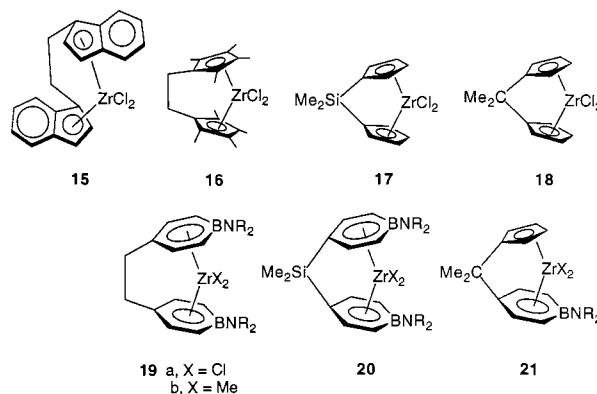


Fig. 3. Molecular structure of the dimethyl derivative of **19**. Some important interatomic distances (Å): B(1)–Zr, 2.909(7); B(2)–Zr, 2.954(7); B(1)–N(1), 1.414(8); B(2)–N(2), 1.437(9); C–Zr range 2.51–2.70.



The structure of the dimethyl derivative **19b** is illustrated in Fig. 3. Both the geometry of the diisopropylaminoboratabenzene rings and their juxtaposition to the Zr atoms of **19** and **21** closely resemble those of **11a**. In the ethylene bridged zirconocene **16** the dihedral angle between the planes of the Cp rings is 57° , while the mean planes of the boratabenzene rings of **19b** intersect at 57.6° . Similarly the Cp ring planes of the Me_2C bridged zirconocene intersect at 72° , while in **21b** the planes of the Cp ring and that of the five carbon atoms of the boratabenzene ring intersect at

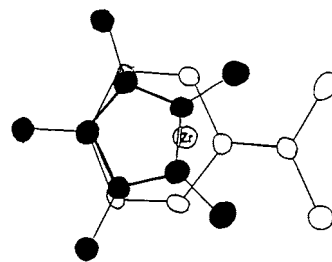


Fig. 4. A superimposition of the bridged tetramethylcyclopentadienyl ring of **16** (dark) on the 4-bridged-*N,N*-diisopropylaminoboratabenzene ring of **19b** (open circles).

70.5°. Thus the wedge openings of the bridged boratabenzenes are nearly the same as those of the corresponding ansa-metallocenes. However, there are important differences in the shape of the six-membered boratabenzene ring versus the five-membered Cp ring. The boratabenzene ring directs its substituents to different regions of space than the Cp. This difference is particularly large for the substituents across the ring from the bridge. See Fig. 4 for a superimposition of the Cp ring of **16** on the boratabenzene ring of **19b**. Clearly in **19b** the bulky diisopropylamino groups encumber the front of wedge to Zr.

When activated by MAO the bridged boratabenzene complexes polymerize ethylene. Under identical conditions the relative reactivity is **21a** > **11a** > **19a** > **20a** (1.3/1.0/0.3/0.1). Qualitatively steric congestion decreases in the series **21a** < **19a** < **20a**. Hence polymerization activity varies inversely with the steric congestion in the front of the wedge. We propose that bridged boratabenzene with bridging groups at other ring positions might be more active. Although bridging at C(4) requires that the boron groups occupy the front of the metal wedge, bridging at other positions would push the boron substituent to the side or rear of the wedge.

Derivatives of **15** have been particularly useful in enantioselective organic synthesis [27]. As yet there are no reports of similar application of chiral boratabenzene complexes. However, there are two separate reports of the preparation of enantiomerically pure boratabenzenes which explicitly discuss their possible use in enantioselective catalysis.

Fu and coworkers have treated boracyclohexadienes **22** with an (*S*)-valinol derived oxazoline to obtain enantiomerically pure boratabenzene **23** [28]. Interestingly the complexation of **23** by Cr(CO)₃ occurs with high diastereoselectivity since the product is largely the single illustrated stereoisomer. Herberich has converted α -pinene derived dienes **25** to the enantiopure lithium (TMEDA) boratabenzene **26** [29]. Conversion of **26** to transition metal complexes has not yet been reported. Obviously this is an area of intense current interest.

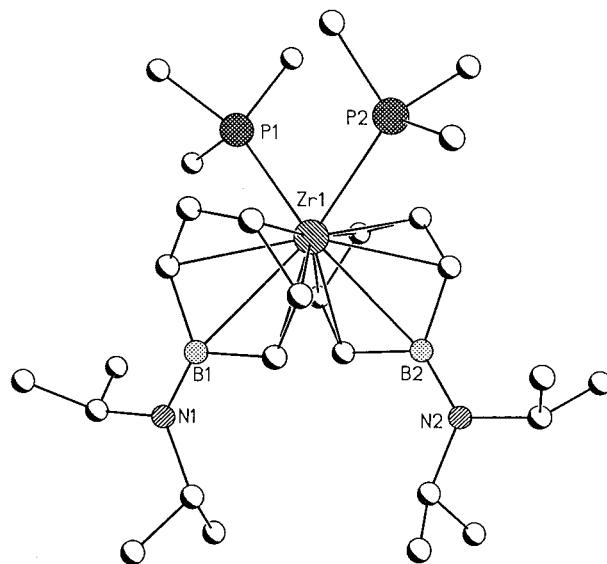
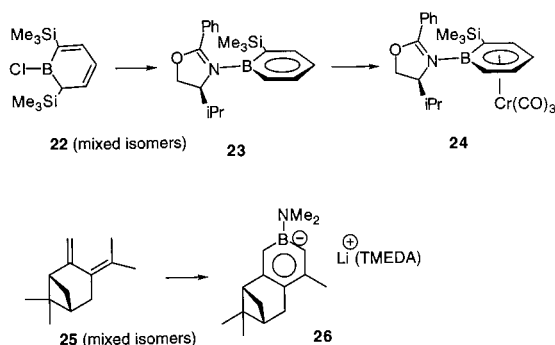
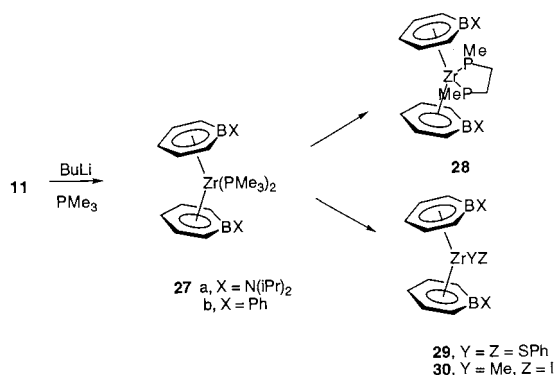


Fig. 5. Molecular structure of **27a**. Some important interatomic distances (Å): Zr–B(1), 2.830(3); Zr–B(2), 2.830(3); Zr–B(1), 2.704(8); Zr–P(2), 2.7323(8); B(1)–N(1), 1.441(4); B(2)–N(2), 1.435(4), Zr–C range 2.44–2.53.

3. Zirconium(II) complexes

Zirconium(II) Cp complexes are particularly useful in organic synthesis [30]. It was of interest to explore the corresponding Zr(II) boratabenzene chemistry. The reaction of **11a** or **11b** with butyllithium in the presence of excess PMe₃ affords the corresponding Zr(II) derivatives **27** in good yields [31]. The structure of **27a** is illustrated in Fig. 5. Comparison with the structure of **11a** (Fig. 1) is instructive. For **27a** the B–Zr bond (2.83 Å) is shorter while the B–N bond (1.44 Å) is longer, indicating a different bonding situation than for **11a**. The boratabenzene ring of **27a** is clearly η^6 -bound to the Zr(II) atom in a similar manner to the η^6 -bonding of the boratabenzene ring to the Zr(IV) of **11c** and **11d**. It may be that the two d-electrons of **27** back bond to boron thereby diminishing the slip distortion. Although structural data are lacking for **27b**, it is likely that Zr atoms are also η^6 -coordinated to its boratabenzene ring. We note here that unlike the Zr(IV) derivatives no important differences have been found for the chemistry of **27a** and **27b**.

Like Cp₂Zr(PMe₃)₂ [32], the trimethylphosphine groups of **27a** exchange under mild conditions. Addition of 1,2-bis(dimethylphosphino)ethane to **27a** affords the chelated derivative **28a**. The reaction of **27a** with Ph₂S₂ splits the S–S bond giving the dithiolated **29a**. Similarly the reaction of **27a** with MeI gives the oxidative addition product **30a**.



The reaction of **27a** or **27b** with 1,3-diyne produces the adduct **31** which can be formulated as metalocycles with three intraring cumulative double bonds [33]. The structure of **31a** is illustrated in Fig. 6. The C–C bonds of the metalocycle moiety are of equivalent length (1.28–1.31 Å) indicative of a cumulene structure, while the diisopropylaminoboratabenzene units are η^5 -bound to Zr indicative of a Zr(IV) species. Although Rosenthal has found that the adduct of bis(*t*-butyl) 1,3-butadiyne with Cp₂Zr is similar to that of **31** [34], most 1,3-diyne-Cp₂Zr complexes have divergent structures [35].

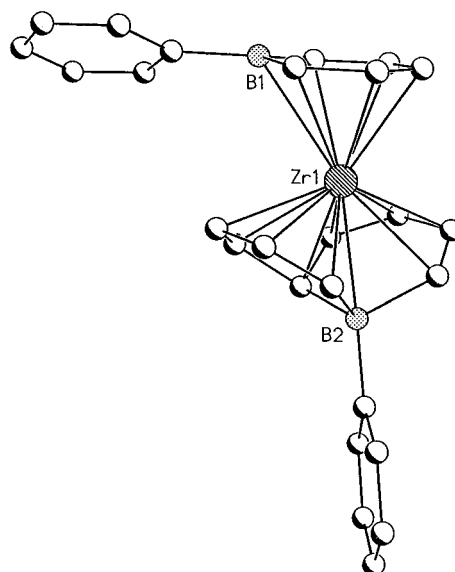
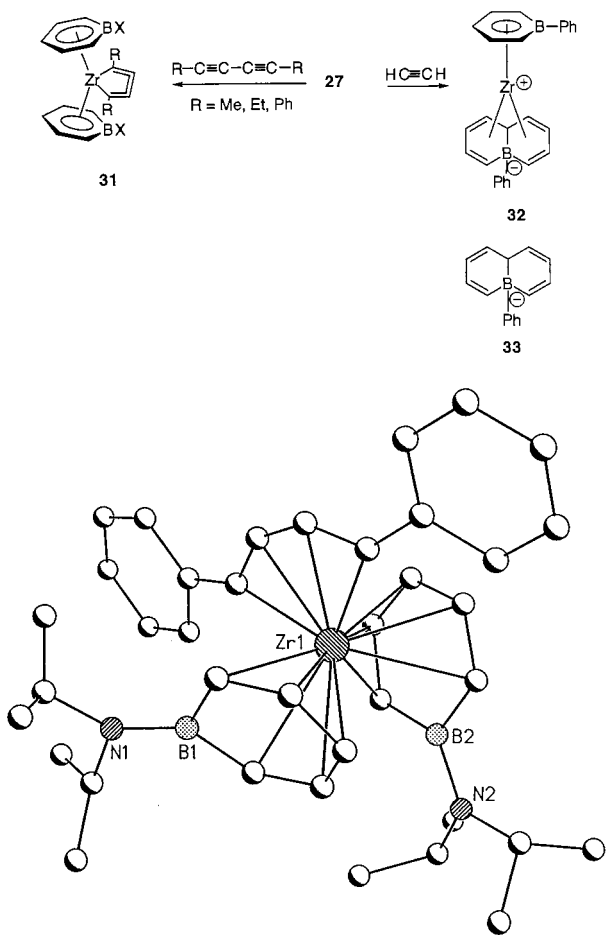


Fig. 7. Molecular structure of **32**. Some important interatomic distances (Å): B(1)–Zr, 2.683(7); Zr–C (boratabenzene) range 2.50–2.55; B(2)–Zr, 2.508(7); Zr–C (dihydroboratanaphthalene) range 2.39–2.50.

The reaction of monoacetylenes with **27** results in an entirely different type of product. For example, acetylene itself reacts rapidly with **27b** to give crystalline adduct **32** in an 78% yield [31]. The crystal structure of **32** (Fig. 7) shows that the two acetylene molecules have added to one of the 1-phenylboratabenzene rings to produce a novel 4a-phenyl-8a-H-4a-boratanaphthalene ligand (**33**). The Zr atom is π -coordinated to the butadiene portions of **33**. The complex is a zwitterion with a formal positive charge on the Zr atom which is balanced by the negative charge on boron. Surely the most unusual feature of **33** is that the bridgehead carbon, formally saturated, is the closest atom to Zr (C–Zr, 2.39 Å). It must be bound, which would make it pentacoordinated. Precedent exists in several electrophilic Cp₂Zr(IV) complexes [36]. We presume that **32** is formed by initial attack at zirconium followed by transfer of the C₄H₄ unit to one of the boratabenzene rings.

4. Future prospects

The pace of research on boratabenzenes has accelerated markedly in the past few years. Work is appearing from four major groups: those of G. Fu at M.I.T., G. Bazan now at U.C. Santa Barbara, G. Herberich at Aachen and ourselves in Ann Arbor. The major interest is in olefin polymerization. Surely we will soon learn how well boratabenzene complexes fulfill their promise as useful catalysts.

Acknowledgements

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