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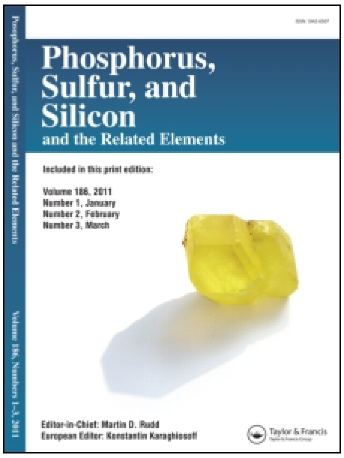

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BORATABENZENE ZIRCONIUM COMPLEXES

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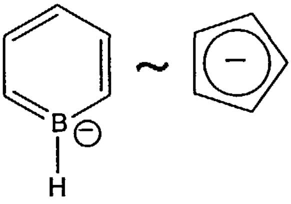
1-Substituted boratabenzenes (**1**) are six π-electron aromatic anions which can serve as surrogates for cyclopentadienyl in important organometallic compounds. The reaction of **1** with $ZrCl_4$ produces bis(boratabenzene) zirconium(IV) dichlorides **3**, which when activated by excess methylaluminoxane react with ethylene to produce either high molecular weight polyethylene or smaller ethylene oligomers, depending upon the substituents at boron. The reaction of **3** with BuLi in the presence of PMe_3 affords the corresponding zirconium(II) complexes (**4**). The reaction of **4** with acetylene involves an unprecedented ring annulation to afford complexes which contain the novel ligand 10H-5-boratanaphthalene.

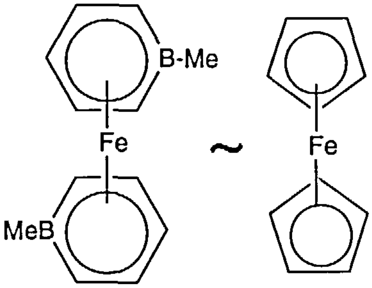
Keywords: Boron Heterocycles; Zirconium Complexes; Polymerization; Agostic Interactions

INTRODUCTION

Although [1H]boratabenzene (**1a**) bears a close structural resemblance to its isoelectronic relative benzene[2], its chemistry is more like that of the anionic cyclopentadienide[3] (Cp). Indeed boratabenzenes can serve as surrogates for Cp in important organometallic compounds. For example, bis(1-methylboratabenzene) iron (**2**) displays ferrocene-like properties.[4] Extensive prior work by the Herberich group from 1970 onwards[3,5], ourselves[4,6] and others[2,7] has involved only boratabenzene derivatives of the later transition metals. Since early transition metal Cp-derivatives, particularly those of Ti and Zr, are useful in catalysis and organic syntheses, we have explored the chemistry of boratabenzene zirconium complexes.[8,9]



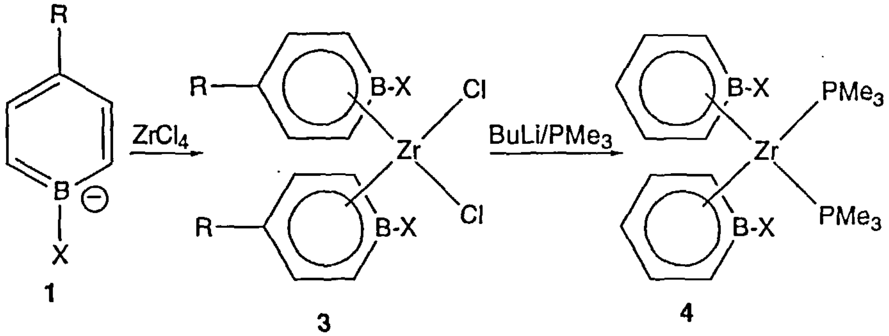
1a



2

ZIRCONIUM(IV) COMPLEXES

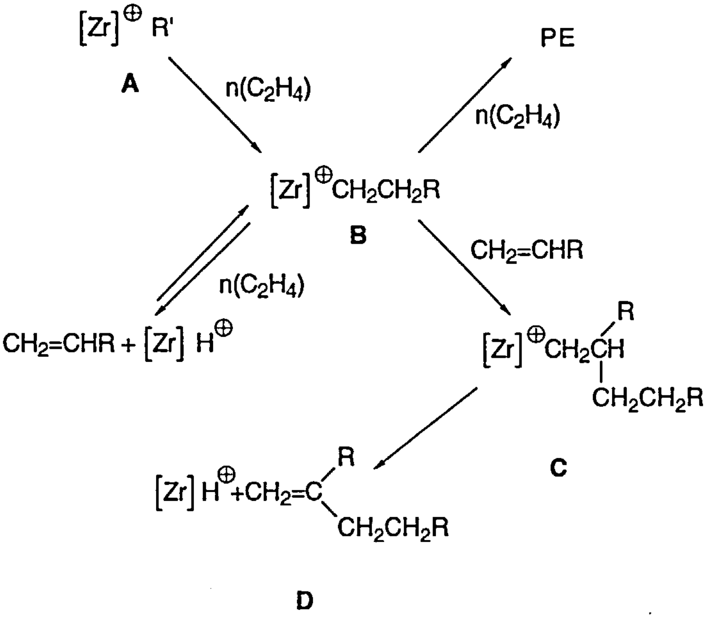
Bis(boratabenzene)zirconium(IV) dichlorides **3** are easily prepared in good yield by the reaction of the corresponding boratabenzene lithium (**1**) with $ZrCl_4$ in ether.[8] The molecular structure of **3b** (Fig. 1) and **3d** each involve a pseudo-tetrahedral coordination about Zr which resembles that of Cp_2ZrCl_2. However the details of the structures depend markedly on the B-substituent. In **3b** there is a strong B-N π-bond which renders the B-Zr interaction antibonding. The consequent slip distortion of Zr away from B (Zr-B, 2.98 Å) makes the diisopropylaminoboratabenzene an η^5-ligand. On the other hand, the phenyl substituent of **3d** is a much poorer π-donor towards B. There is little slip distortion away from B (Zr-B, 2.80 Å) so that the phenylboratabenzene is an η^6-ligand.[9] Since phenylboratabenzene is a poorer donor than Cp, the Zr atoms of **3d** and **3c** should be quite electrophilic.[9,4]



b, X=N(iPr)$_2$, R=H
c, X=Ph, R=H
d, X=Ph, R=tBu

When **3b** is treated with a large excess of methylaluminoxane (MAO), the resulting solutions polymerize ethylene with an activity slightly greater than that of MAO activated Cp_2ZrCl_2. However under identical conditions MAO activated **3c** gives no high molecular weight polyethylene (PE) but only the 2-alkyl-1-alkene oligomers of ethylene.

It seems likely that MAO serves its usual role in all cases.[10] That is methylation at Zr followed by methyl anion extraction to generate a highly electrophilic zirconium cation **A** (Scheme 1). For catalysts derived from Cp_2ZrCl_2 and **3b** this cation undergoes multiple insertion of ethylene to yield propagating alkyl cation **B** and ultimately PE. However we propose that the cation **B** derived from the more electrophilic **3c** undergoes fast β-H elimination of 1-alkenes yielding reactive hydride $[Zr]H^{\oplus}$. This hydride can form more **B** by multiple insertion of ethylene. As the concentration of the 1-alkenes builds up they compete with ethylene for **B**, yielding **C** which leads to the 2-alkyl-1-alkenes **D** by β-H elimination.



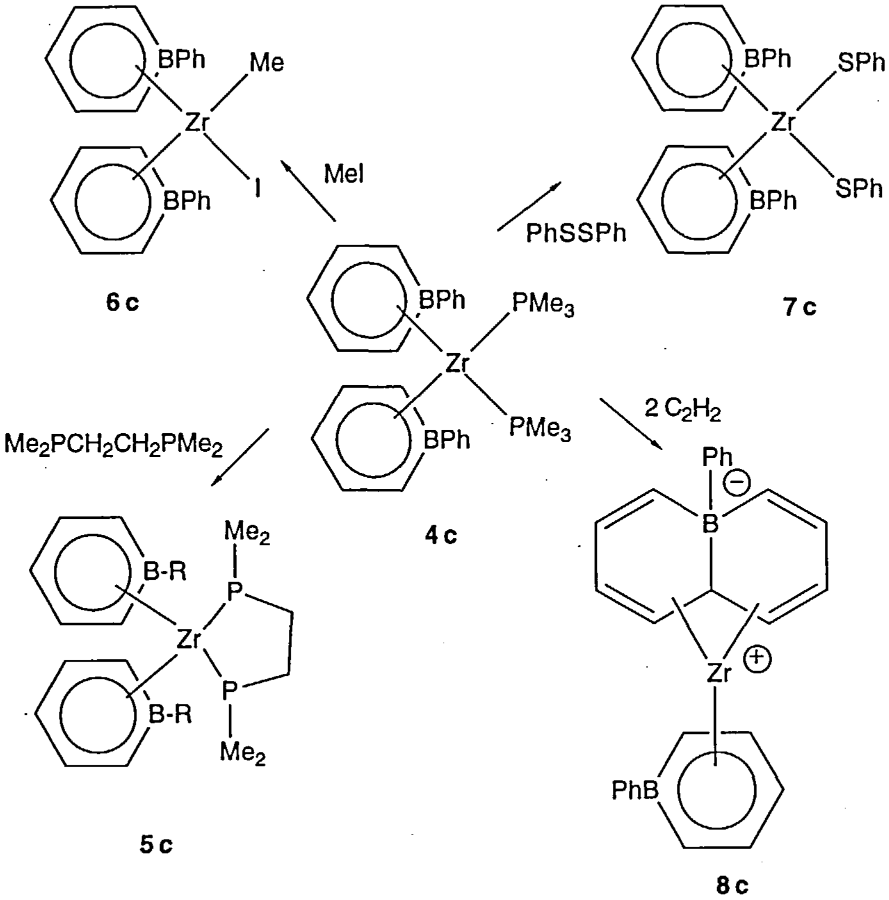
SCHEME 1 Formation of 2-alkyl-1-alkenes (**D**) from MAO activated **3** and ethylene.

These results demonstrate that a change of the boron substituent changes the products of the boratabenzene/zirconium catalyst. Thus boratabenzenes can serve as tunable surrogates for cyclopentadienyl.

ZIRCONIUM(II) COMPLEXES

The reaction of **3** with butyllithium in the presence of excess PMe_3 affords the corresponding zirconium(II) derivatives (**4**). A comparison of the molecular structures of **4b** with **3b** shows that the Zr-B distance (2.83 Å) is much shorter for the Zr(II) compound indicating that the boratabenzene ring is η^6-coordinated. (See Fig. 2). It may be that the two d-electrons of **4b** backbond to B thereby diminishing the slip distortion.

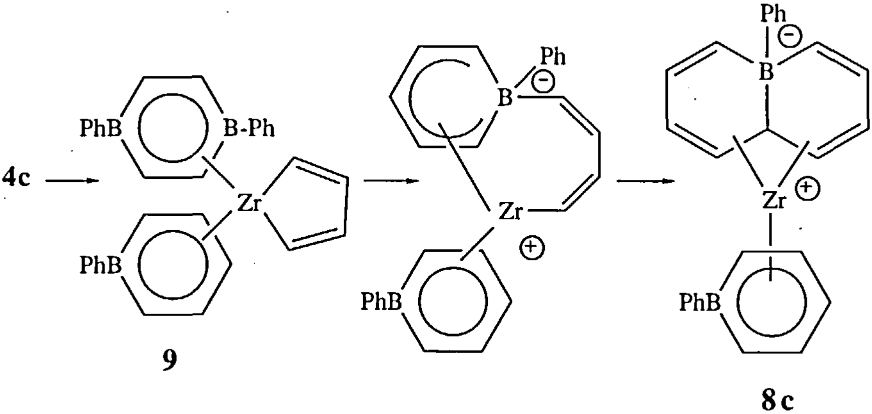
The PMe_3 ligands of **4** are easily displaced under very mild conditions. Treating **4c** with the chelating ligand 1,2 bis(dimethylphosphino)ethane results in the formation of adduct **5c** in 75% yield. The reaction of **4c** with methyl iodide affords the oxidative addition product **6c**, while the reaction with diphenyldisulfide gives the dithiolate **7c**. These reactions are completely analogous to the corresponding reactions of $Cp_2Zr(PMe_3)_2$.[12]



However, the reactions of **4** with acetylenes is extraordinary.

Acetylene reacts rapidly with **4c** to afford adduct **8c** in 78% yield. The molecular structure of **8c** illustrated in Fig. 3 shows that two acetylene units have added to one boratabenzene ring to convert it to the novel 5-phenyl-10H-5-boratanaphthalene ligand. The Zr atom of **8c** remains in the Zr(II) oxidation state with a formal positive charge counterbalancing the negative charge at B(2). The eight non-bridgehead carbon atoms form two butadiene moieties which are coordinated to Zr (Zr-C, 2.40-2.50 Å). The bridgehead carbon (C17) is the closest atom to Zr (2.39 Å) and must be pentacoordinated. Similar pentacoordinated carbon atoms have been found for several related electrophilic Zr(IV) derivatives.[12]

We propose that acetylene initially reacts with **4c** "normally" to produce zirconocycle **9**.[11] An internal alkylation at boron, followed by carbometallation of carbon α to boron would produce **8c**.



9

8c

SCHEME 2 Proposed mechanism for the formation of **8c**.

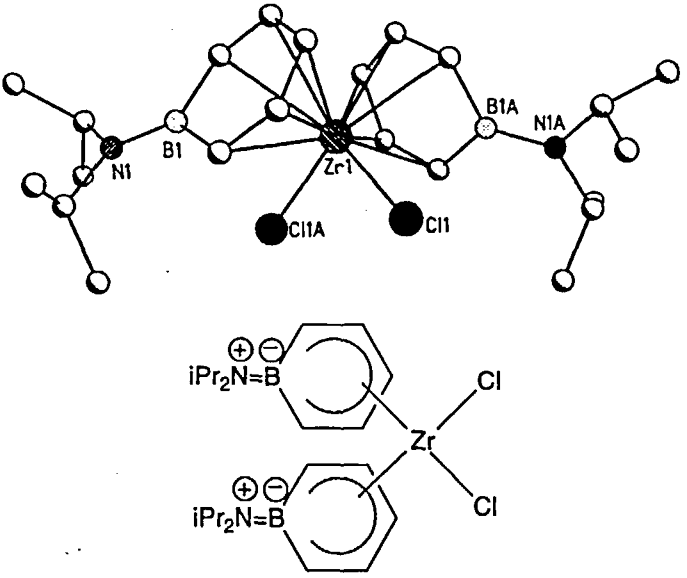


FIGURE 1 The molecular structure of **3b**. Selected interatomic distances (Å); B-Zr, 2.980(7); B-N, 1.396(6), C-Zr, range 2.58-2.65.

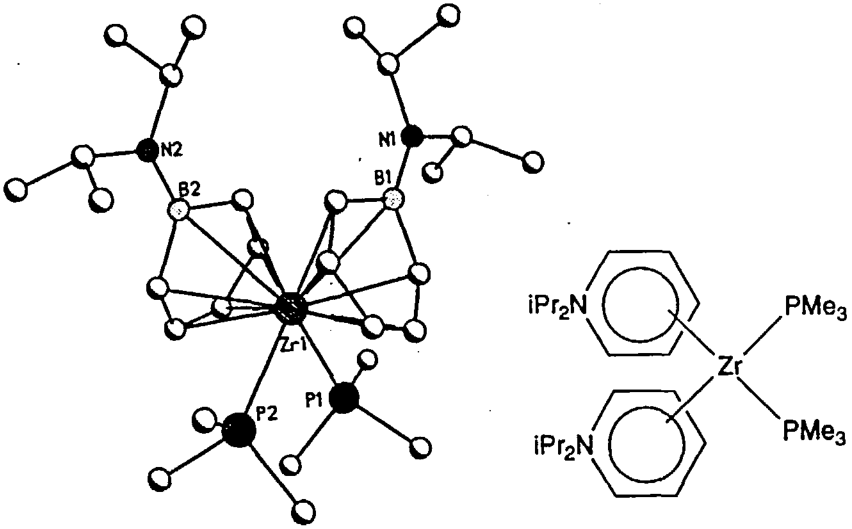
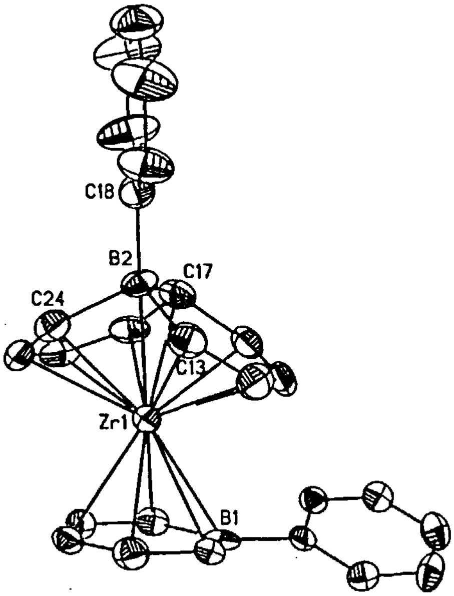
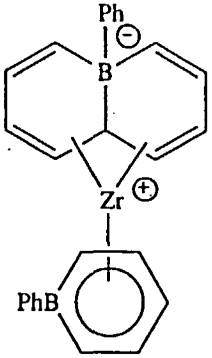


FIGURE 2 The molecular structure of **4b**. Selected interatomic distances (Å): B-Zr, 2.830; B-N, 1.438(3) ave; C-Zr, range 2.49-2.53.





8c

FIGURE 3 The molecular structure of **8c**. Selected interatomic distances (Å): B1-Zr, 2.683(7); B2-Zr, 2.508(7); C17-Zr, 2.390(7); B2-C13, 1.620(10); B2-C17, 1.706(9); B(2)-C(18), 1.624(10); B2-C24, 1.645(10).

Acknowledgments

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References

[1.] E-mail: ajashe@umich.edu

[2.] S. Qiao, D. A. Hoic, and G. C. Fu, *J. Am. Chem. Soc.*, **118**, 6329 (1996).

[3.] G.E. Herberich in *Comprehensive Organometallic Chemistry*, edited by G. Wilkinson, F. G. A. Stone, E. W. Abel (Pergamon, Oxford, 1982) vol. 1, 381; G. E. Herberich and H. Ohst, *Adv. Organomet. Chem.*, **25**, 199 (1986); G. E. Herberich in *Comprehensive Organometallic Chemistry II*, volume editor, C. E. Housecroft (Pergamon, Oxford, 1995) vol. 1, 197.

[4.] A. J. Ashe, III, E. Meyers, P. Shu, T. Von Lehmann and J. Bastide, *J. Am. Chem. Soc.,* **97**, 6865 (1975).

[5.] G.E. Herberich, G. Greiss and H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970).

[6.] A. J. Ashe, III and P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971), A. J. Ashe, III, J. W. Kampf, C. Müller and M. Schneider, *Organometallics*, **15**, 387 (1996).

[7.] S. Qiao, D. A. Hoic and G. C. Fu, *J. Am. Chem. Soc.*, **118**, 6329 (1996).

[8.] G. C. Bazan, G. Rodriguez, A. J. Ashe, III, S. Al-Ahmad and C. Müller, *J. Am. Chem. Soc.*, **118**, 2291 (1996).

[9.] G. C. Bazan, G. Rodriguez, A. J. Ashe, III, S. Al-Ahmad and J. W. Kampf, *Organometallics*, **16**, 2492 (1997).

[10.] For a recent review, see: H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, **34**, 1143 (1995).

[11.] A. J. Ashe, III, S. Al-Ahmad, J. W. Kampf and V. G. Young, Jr., *Angew. Chem., Int. Ed. Engl.*, **36**, in press (1997).

[12.] a) L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, B. Honold and J. Thewalt, *J. Organomet. Chem.*, **320**, 37 (1987); b) K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, **103**, 2687 (1981); c) G. S. Girolami, G. Wilkinson, M. Thornton-Pett and K. M. Hurthouse, *J. Chem. Soc., Dalton Trans.*, 2347 (1984); d) G. Fochi, G. Guidi and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1253 (1953).

[13.] Y. Sun, W. E. Piers and S. J. Rettig, *Organometallics*, **15**, 4110 (1996); R. E. von H. Spence, D. J. Parks, W. E. Piers, M. -A. MacDonald, M. J. Zaworotko and S. J. Rettig, *Angew. Chem., Int. Ed. Engl.,* **34**, 1230 (1995).