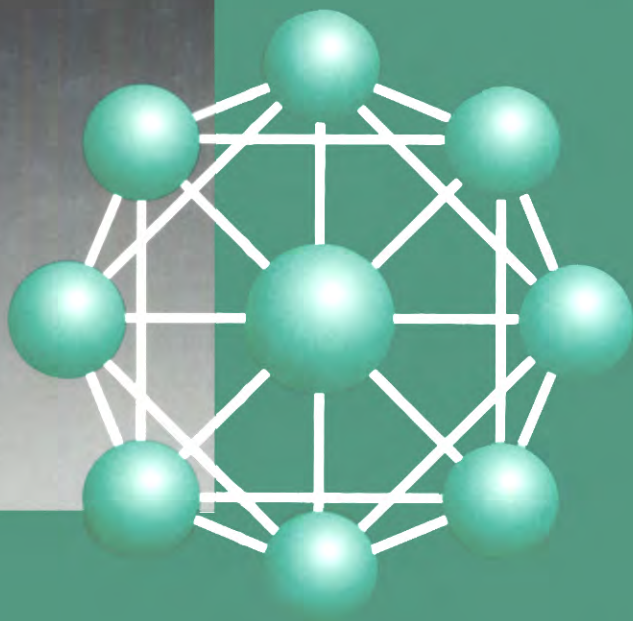




CONTEMPORARY
*boron
chemistry*

edited by M. G. DAVIDSON, A. K. HUGHES,
T. B. MARDER *and* K. WADE

Contemporary Boron Chemistry

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Edited by

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The proceedings of the 10th International Conference on the Chemistry of Boron, IMEBORON X, held at the University of Durham on 11–15 July 1999.

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Preface

This book reports chemistry of boron and its compounds which was presented in lectures given at the Tenth International Conference on Boron Chemistry, IMEBORON X, held at the University of Durham, United Kingdom, 11–15 July 1999. The conference featured 49 invited and 37 contributed lectures as well as 80 poster presentations. In all, over 200 chemists contributed to a truly international meeting with participants representing Australia, Belgium, the Czech Republic, Finland, France, Germany, Hong Kong, India, Ireland, Japan, Korea, Mexico, New Zealand, Poland, Puerto Rico, Russia, Spain, Sweden, Switzerland, the USA as well as the UK.

The invited lecturers included both senior members of the boron chemistry community, who have been important contributors to the field for many years, and younger scientists whose research has already had a significant impact. Topics covered included inorganic and organic compounds as well as polymers and solid-state materials, medicinal aspects and theoretical studies.

Contemporary Boron Chemistry contains 80 reports in nine chapters. Clearly, since much research is interdisciplinary in nature, our decision to include a report in one particular section rather than another was sometimes an arbitrary one. With this caveat in mind, the sections are as follows: Applications to Polyolefin Catalysis; Materials and Polymers; Medicinal Applications; Cluster Synthesis; Carboranes; Metallaboranes; Metallaheteroboranes; Organic and Inorganic Chemistry of Mono- and Di-boron Systems; and Theoretical and Computational Studies.

The continued and evolving significance of boron chemistry to the wider chemical community is illustrated by the broad range of topics covered at IMEBORON X and in this book (*e.g.* boron clusters, metal catalysed boration reactions of organics, synthesis and optical properties of conjugated boron-containing polymers, boron neutron capture therapy, theoretical studies of rare earth borides, weakly coordinating anions, metal boryl and borylene compounds, and boronates as dienophiles to name a few). It is hoped that this book will encourage further interdisciplinary research and new collaborative ventures. With this prospect in mind the editors look forward with optimism to the next IMEBORON meeting to be held in 2002.

Matthew Davidson, Andrew Hughes, Todd Marder and Ken Wade

Durham, January 2000

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The editors thank Janet Freshwater and Sue Askey of the Royal Society of Chemistry for their help and advice in the preparation of this book.

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Professor Stanislav Heřmánek

13th June 1929–16th August 1999



This volume, reporting boron chemistry presented at IMEBORON X in Durham, UK, July 11–15, 1999, is dedicated to the memory of Professor Stan Heřmánek. It was Stan whose vision and enthusiasm for boron chemistry led to the establishment of that series of meetings in 1971, when he and Jaromír Plešek hosted the first IMEBORON meeting in Liblice, Czechoslovakia. In those bleak days, indeed for nearly two more decades, opportunities for meetings and scientific exchanges between researchers separated by the iron curtain were severely limited, and it is to the great credit of scientists like Stan Heřmánek that their efforts to bring about or attend such meetings eventually led to the changed political climate in which such barriers could be dismantled.

Stan Heřmánek was born in Tábor, Bohemia, in 1929, and studied chemistry at Prague Technical University, where he obtained his master's degree in 1952, and then stayed on until 1958 as an assistant to Professor Rudolf Lukeš, one of the leading Czech organic chemists of his day. His young assistant helped with teaching, textbook writing and researches that included borohydride chemistry. Communist purges then required Stan to move to the Research Institute of Natural Drugs in Prague. In 1961, however, he joined what is now the Institute of Inorganic Chemistry of the Czech Academy of Sciences at Řež near Prague, establishing the boron chemistry research group that he led with distinction from 1961 to 1974 and again from 1990 to 1994. This group has been internationally recognised for decades as one of the leading centres of boron chemistry research and, incidentally, its associated commercial laboratory is now one of the best places from which to purchase samples of higher boranes and carboranes. Stan received his Ph.D. from the Technical University at Pardubice in 1966, and much later (1996) was appointed to a chair of chemistry at Charles University (Prague).

At Řež, Stan pioneered a number of approaches to boron hydride research. He developed thin-layer chromatographic methods to separate products, and progressively more sophisticated multinuclear NMR methods to identify new substances. A key early breakthrough, of which he was rightly proud, was his recognition that the kinetics of the thermal gas-phase conversion of diborane into higher boranes, and ultimately decaborane, implied that better yields would be obtained by working at the higher pressures other workers were then avoiding for safety reasons. His success with the production of decaborane in large enough quantities to allow its chemistry to be developed, and higher carborane chemistry to be opened up, proved invaluable to later workers.

A penetrating lateral thinker, Stan also recognised the capacity of carborane icosahedra to transmit electronic effects directly across the cage (antipodal effects), probed using NMR chemical shifts. He also showed how powerful ^{11}B – ^1H coupling constants could be in reflecting the local bonding environment of BH units in boranes. Indeed, he identified various NMR–borane structure correlations of considerable use long before modern IGLO methods were devised. Undaunted by the complexities of borane structures, he demonstrated how localised bond treatments, and sequences of bond cleavages as electron numbers are increased, were powerful aids in rationalising the more open structures of *nido*, *arachno* and *hypho* boranes and carboranes (his ‘seco’ principle). He also developed the solvent extraction of radionuclides using bis(dicarbollide)cobaltate anions.

The value of his contributions was recognised in 1968 by a Czechoslovak Academy of Sciences Award, and most recently by the award of the highly prestigious Heyrovský Medal of the Academy of Sciences of the Czech Republic, a belated tribute to his lifelong achievements recorded in some 200 publications. The intervening years would have been even more productive, and more fully recognised, had he found his politics more in tune with those who then ran his country, but following the brief flirtation of Czechoslovakia in the 1960s with a more open style of government, and the reimposition of a stricter regime, Stan and others found themselves playing more junior roles than before. As Stan himself put it, with his uncanny feeling for the capacity of the English language to express double meanings, ‘having been appointed to a senior position under one regime, I was dis-appointed under its successor’. His ability to play on words even in English, and his endearing modesty, were elsewhere evident in his subtle use of word transposition, as in his deliberate use of the words ‘least, but not last’ in signalling a change of topic in a lecture.

Despite the various set-backs in his career, Stan retained a wonderfully optimistic outlook on life, great enthusiasm for his subject, and an inspirational capacity to infect the young with his own insatiable curiosity to find out more about the fascinating networks of atoms that so enrich borane chemistry. Unselfishly keen to help when hosting conferences in his native country, as at Liblice in 1971 and Bechyně in 1987, a charming, interesting, courteous guest when visiting other countries, he characteristically made light of the problems that his final fatal illness generated. He battled bravely with leukaemia over the last few years of his life, coping so well and making so little of his problems as to lull all of us into thinking that he was winning the battle. It was characteristic of this brave man to show the resilience and determination that allowed him to attend his last IMEBORON meeting in Durham in July 1999, only five weeks before he finally succumbed on August 16th, 1999. It was characteristic of him that at that meeting, he dismissed expressions of concern about himself, endeavouring to behave as if he were in good health, touchingly solicitous of the welfare of his wife Věra, who herself had had to cope with substantial surgery from which she had not fully recovered.

With Stan's death, boron chemistry has lost an original thinker and researcher with the vision to see how much can be achieved by bringing the community together at regular intervals, one who inspired many others with his own great enthusiasm for his subject. His widow and sons Jan and Ivan have lost a wonderful husband and father, and we share that loss. The lives of all who knew him have been enriched by this kind, gentle man.

Applications to Polyolefin Catalysis

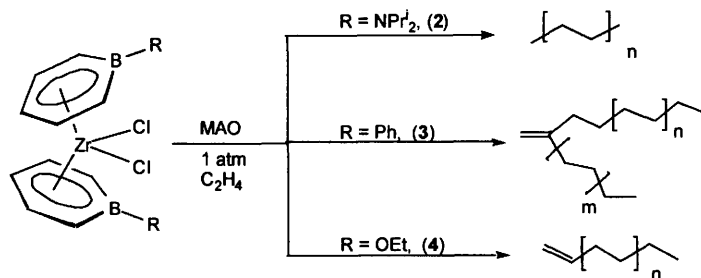
Ethylene Oligomerization and Polymerization Catalysts Supported by Boratabenzene Ligands

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1 INTRODUCTION

The use of the boratabenzene heterocycle as a ligand for transition metal complexes dates back to 1970 with the synthesis of $(C_5H_5B-Ph)CpCo^+$ (**1**) (Cp = cyclopentadienyl).¹ Since boratabenzene and Cp are 6 π electron donors, **1** can be considered isoelectronic to cobaltocenium. Many other transition metal compounds have been prepared that take advantage of the relationship between Cp and boratabenzene.² In 1996, the synthesis of bis(diisopropylaminoboratabenzene)zirconium dichloride $(C_5H_5B-NPr^i_2)_2ZrCl_2$ (**2**) was reported.³ Of particular interest is that **2** can be activated with methylaluminoxane (MAO) to produce ethylene polymerization catalysts with activities similar to those characteristic of group 4 metallocenes.⁴ Subsequent efforts showed that, under similar reaction conditions, $(C_5H_5B-Ph)_2ZrCl_2/MAO$ (**3**/MAO) gave predominantly 2-alkyl-1-alkenes⁵ while $(C_5H_5B-OEt)_2ZrCl_2/MAO$ (**4**/MAO) produced exclusively 1-alkenes.⁶ Therefore, as shown in Scheme 1, it is possible to modulate the specificity of the catalytic species by choice of the exocyclic group on boron.



Scheme 1

Scheme 1 raises two important issues. First, relative to standard metallocenes and **2**/MAO, the boratabenzene catalysts derived from **3** and **4** show enhanced rates of β -hydride elimination. Secondly, the rates of 1-alkene insertion are considerably faster for **3**/MAO relative to **4**/MAO. It would be highly desirable to get a deeper understanding of how the electronic and steric effects of different boratabenzene ligands come together to

dictate the specificity at the metal. Unfortunately, MAO has a poorly defined and complex structure and is used in large excess relative to the organometallic reagent. Well-defined catalysts that offer the possibility of measuring the rates of individual reactions as a function of boratabenzene ligand should be better study subjects for determining reactivity/structure relationships.

Our working hypothesis for the faster rates of β -hydrogen elimination is that the group 4 boratabenzene catalysts are more electron deficient than their Cp-based counterparts. In other words, even though both Cp and boratabenzene are formally monoanionic 6 π electron donors, boratabenzene is a weaker donor. Further, the orbital overlap between boron and its substituent can be strong and should make an impact on the overall charge density on the boratabenzene ring. As the metal becomes more electron deficient, it interacts more strongly with the β -hydrogens in the growing polymer chain. Agostic interactions of this type have previously been observed in the ground state structures of $[\text{CpCo}(\text{L})\text{R}]^+$ (L = phosphine or phosphite, R = alkyl), $\text{Cp}^*\text{ScCH}_2\text{CH}_3$ ⁸ and $(\text{C}_5\text{H}_4\text{Me})_2\text{Zr}(\text{CH}_2\text{CH}_2\text{R})(\text{PMe}_3)^+$ (R = H, Et, SiMe₃, Ph).⁹ Such interactions occur when the C $_{\beta}$ -H bond coordinates to an empty metal-centered MO. We propose that in polymerization reactions, as the β -agostic interaction increases in strength, the molecule approaches the transition state for hydride elimination. It is reasonable to expect that for a closely related family of nearly isostructural propagating species, a decrease in electron density should result in faster rates of β -hydride elimination.

Variations in Zr-B bond distances for complexes of the type $(\text{C}_5\text{H}_5\text{B-R})_2\text{ZrCl}_2$ indicate that the nature of R affects the bonding relationship between zirconium and boratabenzene (Table 1). These data imply that for R = Ph, OEt and Me, the interactions between Zr and B are strong. Boratabenzene with R = NPrⁱ binds in an η^5 -pentadienyl fashion with little overlap between B and Zr. Unfortunately, these metrical parameters do not give sufficient insight into differences in the electron density at the metal. Furthermore, they are measurements of precatalyst structures and it is unclear how they relate to the putative cationic catalytic species.

Table 1. Average Zirconium-Boron Distance for Complexes of the type $(\text{C}_5\text{H}_5\text{BR})_2\text{ZrCl}_2$.

R	Zr-B Distance (Å)
Me (6) ¹⁰	2.814(5)
OEt (4) ⁶	2.826(2)
Ph ¹¹	2.80(3)
NPr ⁱ (2) ³	2.98

In this contribution we discuss how electrochemical measurements and IR spectroscopy may be used to rank electron donating abilities of boratabenzene ligands. We also try to correlate these measurements with the exchange reactions of well-defined zwitterionic compounds of the type $[\text{Cp}^*(\text{C}_5\text{H}_5\text{B-R})\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$.

2 ELECTROCHEMISTRY

The reduction potential of organometallic species can be used as a probe of the electron density at the metal center.¹² An electron poor metal center is more easily reduced than the corresponding electron rich counterpart. As the ability of a ligand framework to donate electron density increases, the reduction potential of the metal center should therefore become more negative. The use of cyclic voltammetry to measure the reduction potentials of boratabenzene complexes of the type $(C_5H_5B-R)_2ZrCl_2$ ($R = NMe_2$ (5), OEt (4), Me (6), Ph (3)) allows us to rank the boratabenzene ligands according to their donating ability (Table 2).¹³ Each of the boratabenzene complexes exhibits a one electron reversible reduction. From this analysis, the observed order of donating ability for (C_5H_5B-R) is: $R = NMe_2 > OEt > Me > Ph$. The measured value for Cp_2ZrCl_2 is listed for comparison and shows that Cp is considerably stronger than any boratabenzene studied thus far.

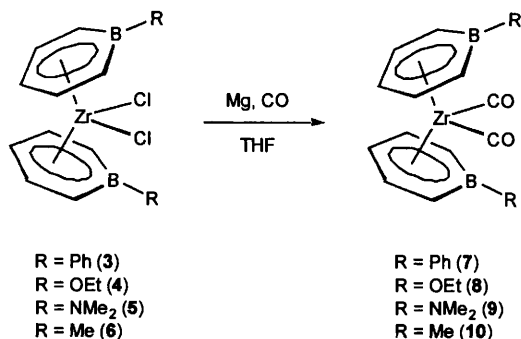
Table 2. Reduction Potentials for $(C_5H_5B-R)_2ZrCl_2$ Complexes vs. SCE.

R	E^0 (V)
NMe_2 (5)	-1.252
OEt (4)	-1.110
Me (6)	-1.034
Ph (3)	-0.954
Cp_2ZrCl_2	-1.70

3 CARBONYL STRETCHING FREQUENCIES

It is well established that increased backbonding from the metal to coordinated CO results in a decrease of the CO stretching frequency.¹⁴ The extent of Zr backbonding to CO in complexes of the type $(C_5H_5B-R)_2Zr(CO)_2$ can therefore be used as a relative measure of electron density at zirconium as a function of R.

The dicarbonyl complexes $(C_5H_5B-R)_2Zr(CO)_2$ ($R = Ph$ (7), OEt (8), NMe_2 (9), Me (10)) can be easily prepared by reductive carbonylation of the corresponding dichlorides (Scheme 2). FT-IR measurements gave values for the symmetric and asymmetric CO stretches as listed in Table 3. Table 3 also includes the $\nu(CO)$ values for the mixed ring complexes $Cp^*(C_5H_5B-R)Zr(CO)_2$ ($R = Ph$ (11), OEt (12), NMe_2 (13), Me (14)) which were prepared from reduction of the $Cp^*(C_5H_5B-R)ZrCl_2$ precursors under an atmosphere of CO. According to these data the ordering of donating ability of (C_5H_5B-R) ligands is: $R = NMe_2 > Me > OEt \sim Ph$. The Cp^* ligand is a considerably stronger donor and it is useful to point out here that all $Cp^*(C_5H_5B-R)ZrCl_2/MAO$ combinations give high molecular weight polyethylene under experimental conditions similar to those in Scheme 1.



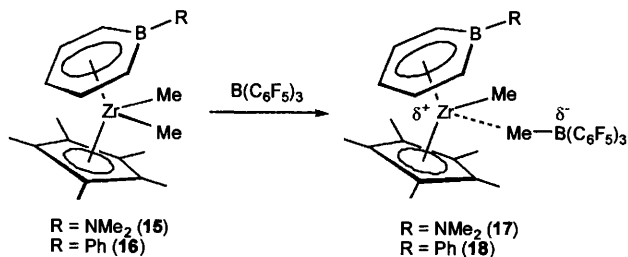
Scheme 2

Table 3. Carbonyl Stretching Frequencies.

Compound	$\nu(\text{CO})$ (cm ⁻¹)
(C ₅ H ₅ B-NMe ₂) ₂ Zr(CO) ₂ (9)	2005, 1955
(C ₅ H ₅ B-Me) ₂ Zr(CO) ₂ (10)	2012, 1964
(C ₅ H ₅ B-OEt) ₂ Zr(CO) ₂ (8)	2017, 1969
(C ₅ H ₅ B-Ph) ₂ Zr(CO) ₂ (7)	2018, 1966
(C ₅ H ₅ B-NMe ₂)Cp [*] Zr(CO) ₂ (13)	1976, 1908
(C ₅ H ₅ B-Me)Cp [*] Zr(CO) ₂ (14)	1981, 1913
(C ₅ H ₅ B-OEt)Cp [*] Zr(CO) ₂ (12)	1982, 1914
(C ₅ H ₅ B-Ph)Cp [*] Zr(CO) ₂ (11)	1987, 1920

4 ZWITTERIONIC SPECIES

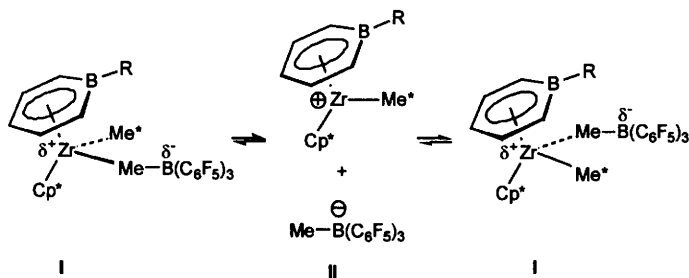
The reaction of Cp^{*}(C₅H₅B-R)ZrMe₂ (R = NMe₂ (15), Ph (16)) with one equivalent of B(C₆F₅)₃ affords the zwitterionic complexes [Cp^{*}(C₅H₅B-R)ZrMe][MeB(C₆F₅)₃] (R = NMe₂ (17), Ph (18)) (Scheme 3).



Scheme 3

The crystal structures of the zwitterionic species **17** and **18** have been obtained and manifest metrical distortions similar to those of the precatalysts **2** and **3**. Compounds **17** and **2** both exhibit long B-Zr distances (2.889(4) Å and 2.98 Å, respectively) as well as shortened N-B bond lengths (1.396(7) Å for both), indicative of B=N double bond character. The structure of **18** displays a shorter Zr-B bond length of 2.770(2) Å.

The variable temperature ^1H NMR spectra of **17** and **18** indicate exchange events similar to those observed by Marks and coworkers for standard metallocenes.¹⁵ In this equilibrium process (Scheme 4), the enantiomeric species represented by I interconvert via a solvent separated ion-pair dissociation/recombination process. It is typically assumed that the highest energy species corresponds to structure II.



Scheme 4

The activation parameters for the exchange reactions of **17** and **18** were determined by a combination of variable-temperature ^1H NMR lineshape analysis¹⁶ and spin saturation transfer experiments.¹⁷ Rate data for **17** were measured over a temperature range of 100 °C. Rates for compound **18** were measured over a 65 °C range. The enthalpy of activation was found to be considerably smaller in the case of **17** (12.2(2) kcal/mol) relative to **18** (17.6(3) kcal/mol). Ion pair dissociation is therefore facilitated by the presence of a lone pair of electrons on the boron substituent. The entropy of activation for **17** is -2.3(6) eu, while that of **18** is 8(1) eu. The more positive entropy of activation measured for **18** may be interpreted as the creation of two independent particles from a closely associated ion pair.

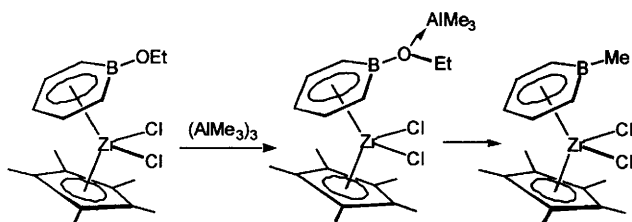
5 DISCUSSION

Electrochemical experiments and IR spectra are clearly consistent with the boratabenzene ligand being a stronger donor when the boron substituent is a dialkylamine group instead of phenyl. The data do not allow a similar unambiguous assessment for the intermediate examples of ethoxy and methyl groups. It is likely that steric factors dictate differences in the reactivity of catalysts containing alkoxy- and alkyl-boratabenzene ligands since their electronic properties are so similar.¹⁸ Ligands based on the Cp framework are considerably stronger donors than boratabenzene derivatives.

The zwitterionic complexes **17** and **18** behave in the expected fashion. In particular, the "typical" boratabenzene distortions observed with neutral zirconium complexes are retained. The exchange process, which requires generation of the ion separated intermediate II in Scheme 4, occurs more readily for R = NMe₂ than for R = Ph. We attribute the faster rates to better stabilization of the positive charge at zirconium by the

more donating aminoboratabenzene ligand. These studies show that the role of the boron substituent in controlling the reactivity at the metal is an inherent feature in boratabenzene complexes.

Less is known about the catalysts formed using MAO. The complex structure of MAO and the large excess that is required for activation do not allow for a careful structure/reactivity correlation similar to that done for **17** and **18**. The effect of ligand structure on the selectivities shown in Scheme 1 remain to be understood. We also note that AlMe_3 forms an adduct with $(\text{C}_5\text{H}_5\text{B-OEt})\text{Cp}^*\text{ZrCl}_2$ via the oxygen atom (Scheme 5). Formation of $(\text{C}_5\text{H}_5\text{B-Me})\text{Cp}^*\text{ZrCl}_2$ ensues after sufficient reaction time.¹⁹ These observations are significant since commercially available MAO can contain up to 35% of $(\text{AlMe}_3)_2$ by weight. The simplicity of structure makes complexes of general composition $[\text{Cp}^*(\text{C}_5\text{H}_5\text{B-R})\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ better candidates for more precise and rational catalyst design.



Scheme 5

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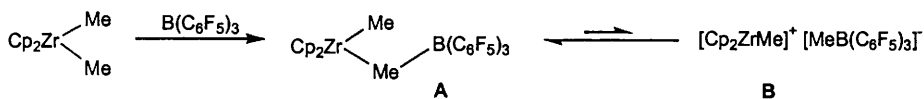
Borate, Boryl and Borole Compounds and their Role in Olefin Polymerisation Catalysis

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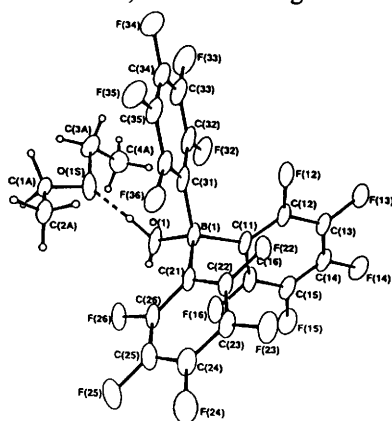
Tris(pentafluorophenyl)borane, a compound first made by Stone et al. in 1963,¹ has in recent years become one of the most widely applied boron reagents, as a highly effective activator for metallocene-based olefin polymerisation catalysts. There are several reasons for this: it is a strong Lewis acid, unlike boron trihalides it is resistant to hydrolysis, and it possesses strong B-C and C-F bonds which make it essentially inert to chemical attack; for example, it can be recovered unchanged from neat elemental bromine.

Due to its Lewis acidity it reacts readily with early transition metal alkyls to give electronically unsaturated, catalytically active species,^{2,3} e.g.:

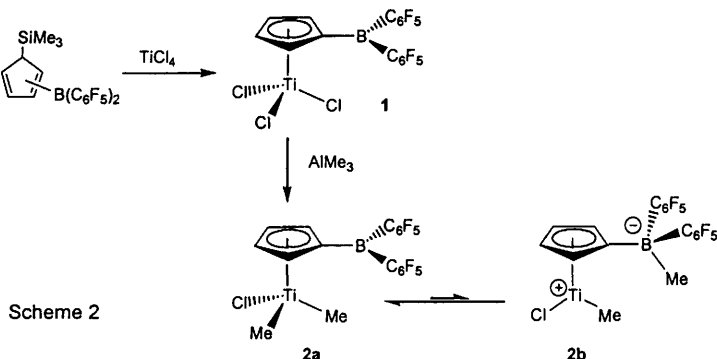


Scheme 1

The Lewis acidity of $\text{B}(\text{C}_6\text{F}_5)_3$ is also apparent in the ready formation of acidic hydrates. The structure of the monohydrate, obtained by recrystallisation from Et_2O containing traces of moisture, is shown in Fig. 1.⁴ It contains one hydrogen-bonded Et_2O molecule.⁵



by the synthesis of the boryl-Cp complex **1**. On treatment with AlMe_3 , **1** readily polymerises ethene, even at low temperatures (-20°C), while $\text{CpTiCl}_3 / \text{AlMe}_3$ mixtures are inactive under these conditions. Although the only identifiable organometallic product in this mixture is **2a**, the catalytic activity can only be explained by assuming an equilibrium between **2a** and the zwitterionic complex **2b** which possesses the vacant coordination site required for ethene bonding and catalysis. The fact that in Scheme 1 the equilibrium with $\text{B}(\text{C}_6\text{F}_5)_3$ is on the side of the zwitterionic product **A**, whereas in Scheme 2 the neutral dialkyl **2a** predominates, illustrates the reduction in Lewis acidity on replacing $\text{B}(\text{C}_6\text{F}_5)_3$ with $\text{Cp-B}(\text{C}_6\text{F}_5)_2$.⁶ A similar reduction in Lewis acidity of borane activators with decreasing electron-withdrawing character of an aryl substituent has recently been found in the series $\text{Ar-B}(\text{C}_6\text{F}_5)_2$, $\text{Ar} = 3,5\text{-F}_2\text{C}_6\text{H}_3 > \text{Ph} > 3,5\text{-Me}_2\text{C}_6\text{H}_3$.⁷



The reaction of **1** with 1 equivalent of LiNHBu^t gives $[\text{Cp}^B\text{TiCl}(\mu\text{-NBu}^t)]_2$ (**3**) as red crystals. There is no interaction between the imino-nitrogen and boron, as evidenced by the ^{11}B NMR chemical shift of **3** (δ 59.9) which is almost identical to that of **1**, (δ 58.9) and $\text{B}(\text{C}_6\text{F}_5)_3$ (δ 60.1, CDCl_3). By contrast, the reaction of **1** with 2 equivalents of LiNHBu^t affords $[\text{Cp}^B\text{TiCl}(\mu\text{-NBu}^t)(\text{H}_2\text{NBu}^t)]_2$ (**4**), where each boron forms an adduct with Bu^tNH_2 (^{11}B : δ -5.0) (equ. 1). The structure of **4** was confirmed by X-ray diffraction

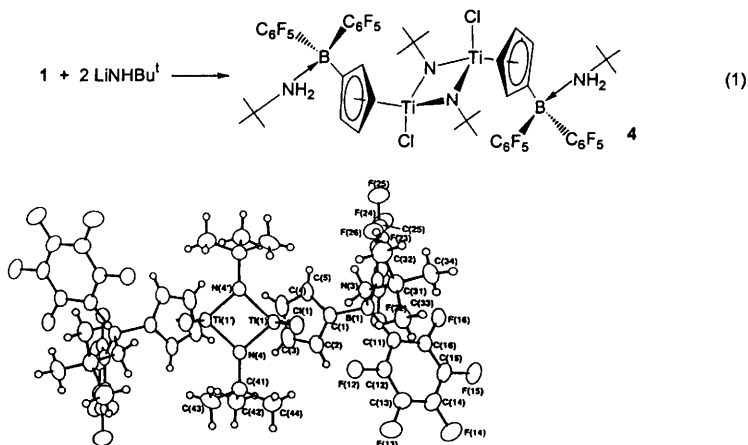


Fig. 2 Molecular structure of **4**.

Different structural motifs are found when **1** is reacted with LiCp or LiInd, to give $(\text{Cp}^{\text{B}})\text{CpTiCl}_2$ (**5**) and $(\text{Cp}^{\text{B}})(\text{Ind})\text{TiCl}_2$ (**6**), respectively.⁸ The spectroscopic data of these complexes are as expected for titanocene dichlorides, except for the ^{11}B NMR resonances which occur at δ 5 ppm, a value indicative of four-coordinate rather than trigonal boron. The assumption of adduct formation is confirmed by the crystal structure of **6** which shows a B-Cl-Ti bridge. The B-Cl bond is relatively short, 2.007(4) Å, and comparable to the terminal B-Cl bond in $[\text{ClB}(\text{C}_6\text{F}_5)_3]^-$ [1.907(8) Å],⁹ whereas the corresponding Ti-Cl(1) bond of 2.4641(9) Å is ca. 6% longer than the terminal Ti-Cl(2) bond of 2.3227(10) Å.

Repeated crystallisation attempts of **5** eventually gave crystals of the $\mu\text{-OH}$ complex **7** which shows a similar bonding pattern, with a short B-O [1.532(3) Å] and a relatively long Ti-O bond (Fig. 3). The Ti-O distance of 2.0437(14) Å is comparable to the n-donor Ti-OH₂ distance in $[\text{Cp}^*\text{Ti}(\text{OH})(\text{OH}_2)]^+\cdot 2\text{THF}$, 2.080(5) Å, whereas the Ti-OH bond in this complex is much shorter, 1.853(5) Å.¹⁰ The structures of **6** and **7** are therefore best described as zwitterionic chloro- and hydroxyborates, respectively, with heteroatom n-donor coordination to the metal atom, as opposed to a donor adduct of a Ti-X ligand to the boryl substituents.

The formation of these Cp-B-X bridges is evidently a consequence of the introduction of a bulky Cp or Ind ligand which forces the boryl substituent into closer proximity to the chloride or hydroxide ligands. This is for example reflected in the X-Ti-C(1) angles which decrease from 87.2° in **1** to 68.4° in **6** and 63.7° in **7** (X = Cl or O).

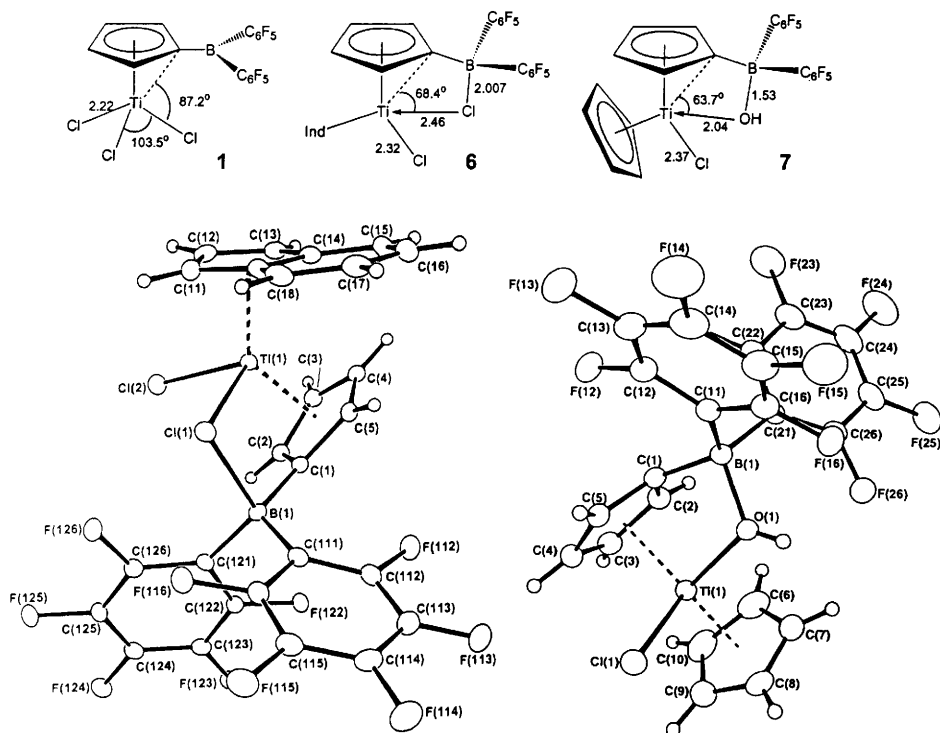
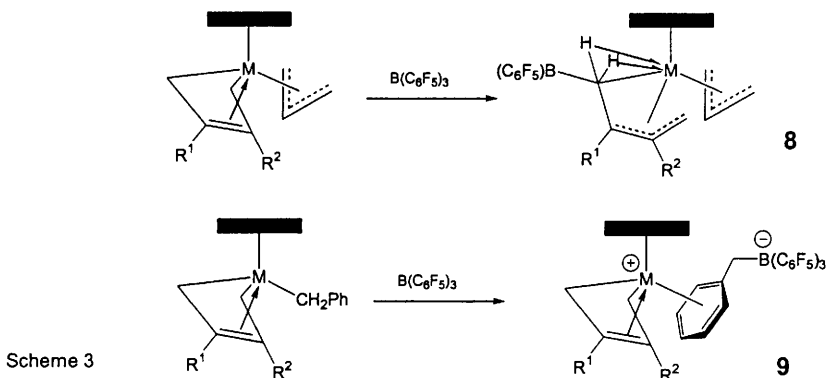


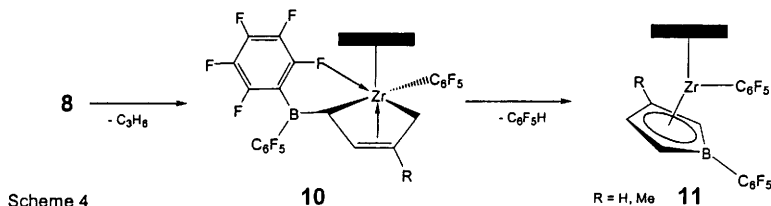
Fig. 3 Molecular structures of **6** (left) and **7**.

2. Boryldiene and Borole Complexes

A different kind of borane reactivity is found in the reaction of $B(C_6F_5)_3$ with η^4 -diene complexes. For example, the borane reacts with $Cp^*M(\eta^3\text{-allyl})(\eta^4\text{-diene})$ selectively under attack at a terminal diene-carbon atom to give the zwitterionic complex **8**; there is no attack at the allyl ligand [$M = \text{Zr or Hf}$, $Cp^* = 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$, diene = 1,3-butadiene, isoprene, or 2,3-dimethylbutadiene].¹¹ On the other hand, the benzyl complexes $Cp^*M(\text{CH}_2\text{Ph})(\eta^4\text{-diene})$ react exclusively by benzyl abstraction to give **9** (Scheme 3).¹² Compounds **8** are stabilised by agostic interactions with the two methylene hydrogen atoms, while **9** forms η^6 -benzylborate zwitterions.



Compound **8** is a stabilised version of the bis(allyl) cation $[Cp^*Zr(allyl)_2]^+$, a 14-electron species isoelectronic to $[Cp_2ZrMe]^+$; as expected, it is an active ethene polymerisation catalyst. It is, however, thermally less stable than the bis-Cp species, depending on the diene substituents R^1 and R^2 . If $R^1 = R^2 = H$, C-H activation takes place even at -60°C , with elimination of propene and concomitant migration of a C_6F_5 substituent from boron to zirconium, to give **10** (Scheme 4). This process constitutes a catalyst deactivation step. Migration of pentafluorophenyl from boron to zirconium or titanium is well known, although it is usually a fairly slow reaction that occurs at room temperature and above.¹³ Analogous C_6F_5 migrations from $Al(C_6F_5)_3$ to Zr are more facile, even in the bis-Cp case.¹⁴



Exposing toluene solutions of **10** in the presence of $AlMe_3$ to 6 bar ethene pressure at 60°C shows initially no gas consumption. However, after an induction period of 8–10 minutes some activity is seen which increases with time, indicative of the formation of a compound capable of catalysing polymerisation. Monitoring the reaction of solutions of **10** by NMR at room temperature over a period of days showed the appearance of a new complex, together with the formation of C_6HF_5 . Clearly another C-H activation reaction

was taking place, with yet another transfer of C_6F_5 from boron to zirconium. The data suggested the formation of the borole complexes **11** ($R = H, Me$) which contain the new borole ligands $C_4H_3RB(C_6F_5)$. The compounds were isolated by addition of diethyl ether as dark red ($R = H$) or deep blue ($R = Me$) ether adducts, $11 \cdot Et_2O$. The structure of $Cp''Zr(C_6F_5)(\eta^5-C_4H_4BC_6F_5)(OEt_2)$ is shown in Fig. 4.¹⁵ The ligand shows an ^{11}B NMR signal at δ 44 (Et_2O -free complex), which is high-field shifted by 10–20 ppm compared to complexes of C_6H_5 -substituted boroles,¹⁶ a consequence of the electron-withdrawing characteristics of C_6F_5 . As a result, the borole ligand is more tightly bound to the metal centre than Cp'' , with shorter average Zr–C distances (2.455 Å, compared to 2.554 Å for Cp'').

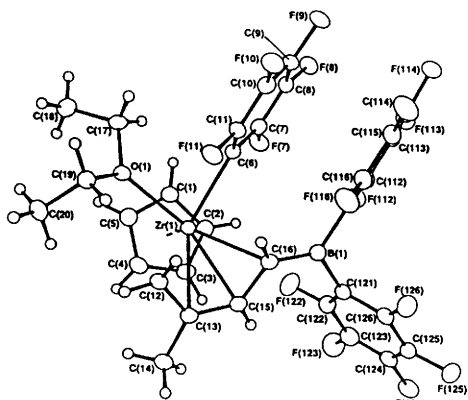


Fig. 4 Molecular structure of $Cp''Zr(C_6F_5)(\eta^5-C_4H_4BC_6F_5)(OEt_2)$ (**11**).

The borole complexes $Cp''Zr(C_6F_5)(\eta^5-C_4H_3RBC_6F_5)$ are 14-electron species and isoelectronic with $[Cp_2ZrMe]^+$; they should therefore show ethene polymerisation activity once the $Zr-C_6F_5$ ligand is exchanged for alkyl. Mixtures of **11** with 28 equivalents of $AlMe_3$ under 6 bar C_2H_4 at 60°C show indeed good polymerisation activity, with a productivity of ca. 1.1×10^5 g PE $\{(\text{mol Zr}) \cdot \text{h} \cdot \text{bar}\}^{-1}$. There is no induction period, and it is clear that the activity observed with **10**/ $AlMe_3$ is due to the slow formation of **11**. There is no improvement in catalytic activity on replacing $AlMe_3$ with methylaluminoxane (MAO).

As neutral species, the adducts $11 \cdot Et_2O$ are very labile and are quantitatively dissociated in C_6D_6 at 25°C. The presence of stoichiometric amounts of ether does therefore not suppress catalytic activity. This is in stark contrast to $[Cp_2ZrMe]^+$ where Et_2O is held strongly and is a potent catalyst poison.

The reaction sequence leading from **8** to **10** and **11** is an interesting demonstration that, under the right conditions, a rather inert compound such as $B(C_6F_5)_3$ can act as a useful synthetic reagent, leading to $-B(C_6F_5)_2$ and $=B(C_6F_5)$ compounds. The transformation $8 \rightarrow 10$ is particularly facile and proceeds in high yield. This sequence is also, to our knowledge, a unique example of “catalyst self-reactivation”: an active catalyst (**8**) undergoes deactivation (**10**) followed by further rearrangement to another active species (**11**).

Subsequent work was directed at exploring the generality of boryldiene and borole formation. Treatment of the readily accessible diene complexes of $(Cp^R)Zr(\text{allyl})(\text{diene})$ ($Cp^R = C_5H_5, C_5H_4SiMe_3, Ind$) with $B(C_6F_5)_3$, followed by stirring under ambient

conditions, readily affords the corresponding boryldiene derivatives $(\text{Cp}^R)\text{Zr}(\text{C}_6\text{F}_5)\{\text{CH}_2\text{C}(\text{Me})\text{CH}_2\text{CHB}(\text{C}_6\text{F}_5)_2\}$ in high yields as deep-red crystalline solids. Unlike the Cp^R and C_5Me_5 analogues^{11,12} they are able to form ether adducts. As the structure of $\text{CpZr}(\text{C}_6\text{F}_5)\{\text{CH}_2\text{C}(\text{Me})\text{CH}_2\text{CHB}(\text{C}_6\text{F}_5)_2\}(\text{OEt}_2)$ (**12**) shows (Fig. 5), the ether is coordinated to the metal, not the boryl moiety.¹⁷ The B-C(16) bond is remarkably short, 1.483(3) Å, and indicates partial B-C double bond character; this might explain the apparently low Lewis acidity of boryldiene ligands.

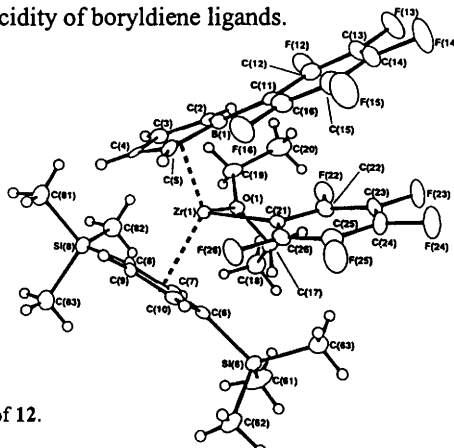
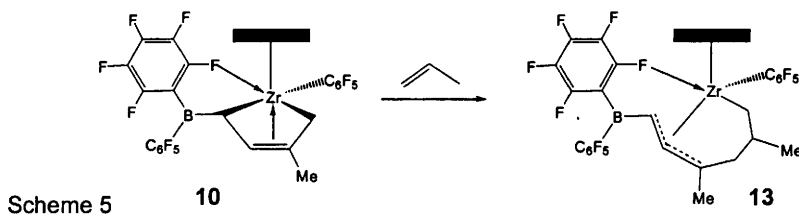


Fig. 5 Molecular structure of **12**.

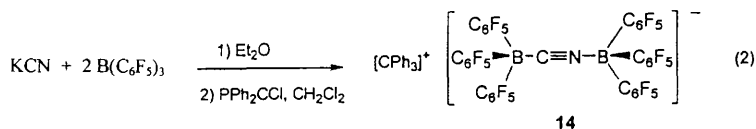
Attempts to generate borole complexes from boryldiene precursors with sterically undemanding Cp ligands under a variety of conditions proved unsuccessful, and only mixtures of decomposition products were obtained. The conversion of **10** into **11** therefore seems to be specific to Cp ligands of high steric hindrance.¹⁸ Cp and indenyl complexes of type **10** do, however, react slowly with propene under insertion to give **13**, with very high regioselectivity (Scheme 5). On prolonged stirring with excess propene, slow polymerisation to atactic materials occurs.



3. New Borate Anions for Olefin Polymerisations

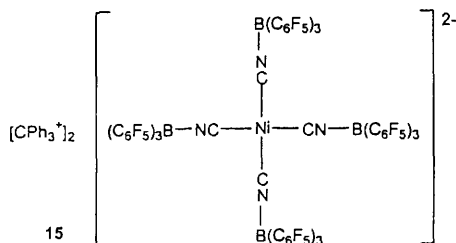
As stated in the Introduction, borates such as $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ play an important role as counteranions to metal alkyl cations in MAO-free polymerisation catalysts. The electronegative C_6F_5 substituents ensure effective delocalisation of the negative charge, and consequently these anions possess extremely low nucleophilicity. We have attempted to reduce the coordinating tendency of borate anions even further by using systems which have less than one negative charge per boron centre. This can be achieved by forming stable adducts between $\text{B}(\text{C}_6\text{F}_5)_3$ and anions X^- , where X can bind more than one $\text{B}(\text{C}_6\text{F}_5)_3$. Thus, complex anions of the type $[\text{X}(\text{B}(\text{C}_6\text{F}_5)_3)_n]^{m-}$ can be envisaged, where $n > m$ and the charge per B is m/n .

Treatment of a suspension of KCN in Et₂O with 2 equivalents of B(C₆F₅)₃ affords K[CN{B(C₆F₅)₃}₂]. Stirring with Ph₃CCl in dichloromethane affords orange crystalline CPh₃[CN{B(C₆F₅)₃}₂] (**14**) in a one-pot procedure (equ. 2).¹⁹

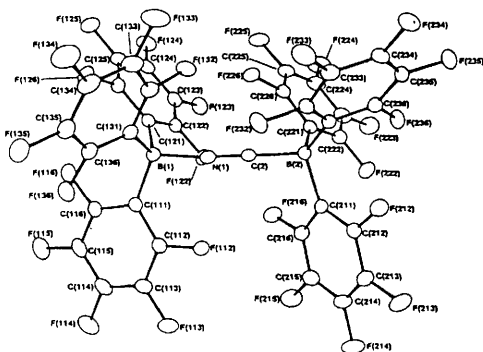


Unlike CPh₃[B(C₆F₅)₄], **14** crystallises readily and is air-stable in the solid state. It has the additional advantage that it can be synthesised without the use of LiC₆F₅, a potentially dangerous compound that has been known to detonate violently on warming above -20°C. It is characterised by two ¹¹B resonances, at δ -11.94 and -21.68. The anion is structurally related to [H₃B-CN-BH₃]⁻²⁰ but has a slightly higher ν_{CN} stretching frequency (2305 vs. 2260 cm⁻¹).

A related type of anion with even more extensively delocalised charges is represented by metal complexes of the isocyanoborate anion. For example, K₂[Ni(CN)₄] reacts with B(C₆F₅)₃ to give colourless K₂[Ni{CNB(C₆F₅)₃}₄], which on treatment with Ph₃CCl gives orange crystalline [CPh₃]₂[Ni{CNB(C₆F₅)₃}₄] (**15**).¹⁹



The structures of **14** and **15** are shown in Figures 6 and 7, respectively.



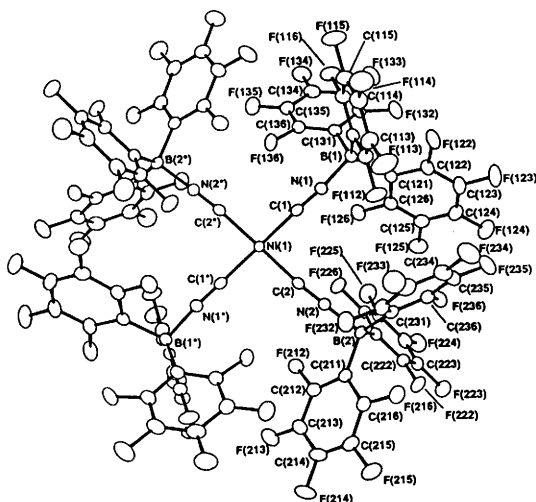


Fig. 7 Molecular structure of $\text{CPh}_3[\text{Ni}\{\text{CNB}(\text{C}_6\text{F}_5)_3\}_4]$ (**15**). Selected bond lengths (Å) and angles (°): Ni-C(1) 1.855(2), B(1)-N(1) 1.574(2), C(1)-N(1) 1.145(2), C(1)-Ni-C(2) 87.15(7), Ni-C(1)-N(1) 176.5(2), C(1)-N(1)-B(1) 174.8(2).

Both **14** and **15** are excellent activators for metallocene polymerisation catalysts. Mixtures of Cp_2ZrMe_2 and **15** in toluene under 1 bar ethene at 25°C gave polymer with a productivity of 1.3×10^6 g PE $\{(\text{mol Zr}) \cdot \text{h} \cdot \text{bar}\}^{-1}$, although some problems were apparent with the comparatively low solubility of **15** in toluene. Solutions of *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ activated with **14** (1:1) under the same conditions gave significantly higher productivities, 18 – 20 $\times 10^6$ g PE $\{(\text{mol Zr}) \cdot \text{h} \cdot \text{bar}\}^{-1}$. Surface films of high molecular weight polyethylene were formed immediately on injection of the activator, suggesting that the polymerisations were probably diffusion limited. Polymerisations were therefore conducted at 7 bar ethene pressure. Some results are collected in Table 1.

Table 1 Ethene polymerisations with *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ /**14**, 7 bar ethene pressure^a

Run	Metallocene, μmol	Activator (μmol)	Temp. [°C]	Time [min]	Polymer yield [g]	Prod. ^b	M_w	M_w/M_n
1 ^c	5.0	14 (1.0)	20	6	21.3	30	204	2.4
2	5.0	14 (1.0)	60	4	96.6	210	n.d.	-
3	1.0	14 (0.2)	60	4	71.1	760	95	2.1
4	5.0	MAO (1000:1)	60	6	74.0	21	n.d.	-
5	$\text{Cp}_2\text{ZrCl}_2^d$	MAO	90	360		283		
6	$\text{Et}(\text{Flu})_2\text{ZrCl}_2^e$	MAO	100	60		352	401	2.1

^a 5 L reactor, 3 L toluene, AlBu^t , 1.0 mmol. Reaction terminated by methanol injection.

^b Catalyst productivity in 10^6 g PE $\{(\text{mol Zr}) \cdot \text{h} \cdot \text{bar}\}^{-1}$.

^c 1 L autoclave, 500 cm³ toluene.

^d Al:Zr ratio 67,000:1, 8 bar ethene. W. Kaminski, M. Miri, H. Sinn and R. Woldt, *Makromol. Chem. Rapid Commun.* 1983, 4, 417.

^e Al:Zr 500:1, 14 bar. H.G. Alt, W. Milius and S.J. Palackal, *J. Organomet. Chem.* 1994, 472, 113.

All reactions showed a considerable exotherm. With 5 μmol *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ activated with 1.0 μmol **14**, the temperature quickly rose from 20 to 60°C, and ethene polymerisation was so rapid that after 2 minutes gas uptake stopped because the autoclave was choked with swollen polymer (Table 1, entry 1). Reducing the maximum concentration of catalytically active zirconocene species to $6.7 \times 10^{-8} \text{ M}$ (entry 3) did not significantly reduce the exotherm; polymerisation was still so rapid that feed gas delivery could not keep pace with gas consumption. The pressure quickly dropped to 2 bar and only recovered when the amount of polymer formed impeded gas take-up. Under these – still mass transport limited – conditions, a productivity figure of $760 \times 10^6 \text{ g PE } \{(\text{mol Zr}) \cdot \text{h} \cdot \text{bar}\}^{-1}$ was recorded. This corresponds to a turnover number of 53,000 s^{-1} , to our knowledge the highest activity for an ethene polymerisation catalyst reported to-date. Data on previous reports of high-activity metallocenes are included for comparison (entries 5 and 6).

The results demonstrate the degree to which ethene polymerisations tend to be mass-transport limited. They also highlight the effect that can be achieved by altering the mode of catalyst activation: a catalyst produced by activating *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2$ with AlBu_3 / **14** proved 36 times more active than the same metallocene activated with MAO under closely comparable conditions.

The results may have implications for catalyst evaluation. Catalyst development has mostly concentrated on ligand design, and in testing catalysts it is usually tacitly assumed that there is a direct relationship between electronic and steric ligand parameters and catalyst activity.²¹ The eventual aim is to arrive at a predictive model that correlates catalyst performance with ligand structure. This can only be achieved if activity data are a function of ligand properties and are not limited by other factors. Our results show that, for certain metallocenes at least, varying the mode of catalyst activation can drastically alter the concentration of active species and thereby result in activity enhancements that are comparable or exceed the effects achievable through ligand modifications. By implication, many catalyst activity values reported in the literature are likely to reflect the limited concentrations of the active species produced, rather than the effect of a particular ligand environment.

Acknowledgement. This work was supported by the Engineering and Physical Sciences Research Council and BP-Amoco Chemicals, Sunbury.

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reflections were collected (Nonius KappaCCD diffractometer, Mo-K α , 150 K). Solved by direct methods (SHELXS-97) and refined by full-matrix least squares (SHELXL-97) on F^2 of all unique data to $R_1 = 0.0726$ (observed data), $wR = 0.1499$ (all data), $S = 1.054$.

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Group 4 Complexes Derived from *o*-Carborane: Catalytic and Luminescent Properties

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1 INTRODUCTION

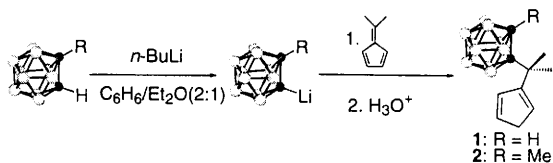
Recent research activity in carborane chemistry has been directed toward expanding the use of carborane clusters in materials science including, among others, molecular recognition systems,¹ display devices,² modular construction systems,³ NLO materials⁴ and special polymers.⁵ Nonetheless, their use in developing functional materials such as olefin polymerization catalysts⁶ and luminescent materials⁷ is still limited.

Olefin transformations are one of the most important reactions in the chemical industry. Among the many factors which influence the performance of homogeneous catalysts for olefin polymerization, the ligand is probably the most important, since it controls the molecular geometry of the catalysts which in turn affects the olefin transformation. Therefore, the development of new ancillary ligands is very critical and is of great interest. In accordance with this point of view, new isopropyl bridged cyclopentadienyl *o*-carboranyl ligands HCpCMe₂CB₁₀H₁₀CH (H₂.1) and HCpCMe₂-CB₁₀H₁₀CMe (H.2) were prepared and their lithiation chemistry was explored. The reactions of lithium salts of **1** and **2** with group 4 halides or mono-Cp* group 4 halides were investigated, affording a set of new group 4 metallocene complexes including rac-(η^5 : η^1 -CpCMe₂CB₁₀H₁₀C)₂M, (η^5 -Cp*)(η^5 : η^1 -CpCMe₂CB₁₀H₁₀C)MCl and (η^5 -Cp*)(η^5 -CpCMe₂CB₁₀H₁₀CR)MCl₂ (M = group 4 metal). Topics discussed in this report include the details of the synthesis, structural characterization, olefin polymerization behavior and luminescent properties of the foregoing new group 4 metallocene complexes derived from *o*-carborane.

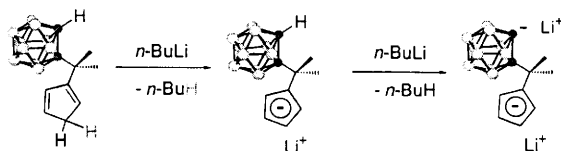
2 SYNTHESIS AND PROPERTIES OF NEW ANCILLARY LIGANDS

New isopropyl bridged cyclopentadienyl *o*-carboranyl ligands H₂.1 and H.2 were prepared as colorless crystalline solids in high isolated yields according to the reaction Scheme 1. The coupled use⁸ of one fold amount of *n*-BuLi and benzene/Et₂O turned out to be efficient compared to the use of LiC₂B₁₀H₁₀SiMe₂(*t*-Bu),⁹ or Li₂C₂B₁₀H₁₀,¹⁰ since the former is unreactive towards 6,6-dimethylfulvene and the latter leads to low yield. The attempted cage degradation of H₂.1 and H.2 with bases such as KOH/EtOH, (*n*-Bu)₄NF or CsF led to the cleavage of the C-C bond between the carborane cage and the isopropyl bridge. However, both ligands can be lithiated. In particular, since the acidities

of the CpH proton and the carborane CH proton are distinctive, H_2I undergoes stepwise lithiation with $n\text{-BuLi}$ as shown in Scheme 2.



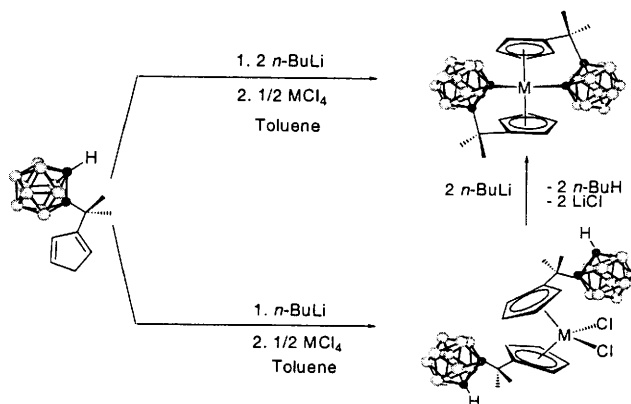
Scheme 1



Scheme 2

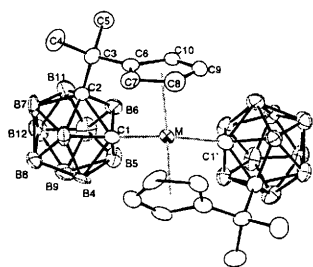
3 HOMOLEPTIC METALLOCENES WITH C_2 SYMMETRY

Treatment of the di-lithium salt of **1**, $\text{Li}_2[\text{CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C}]$, with MCl_4 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) in a 2:1 ratio in toluene affords new group 4 metallocene compounds $\text{rac}(\eta^5\text{-}\eta^1\text{-CpCMe}_2\text{-CB}_{10}\text{H}_{10}\text{C})_2\text{M}$ (**3a** Ti, **3b** Zr, **3c** Hf). Compounds **3**, which are stable in air for an extended period of time, can be also prepared in a stepwise fashion via $(\eta^5\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{CH})_2\text{MCl}_2$ as outlined in Scheme 3.



Scheme 3

The molecular structures of **3** are displayed in Figure 1 and selected geometric parameters are listed in Table 1. The group 4 atoms adopt essentially an η^5 -bonding mode to the Cp rings and an η^1 -bonding mode to the carborane cages. The bent-metalloocene geometry, involving a distorted-tetrahedral arrangement of ligands around the metal with a $\text{Cp}_{\text{cent}}\text{-M-Cp}_{\text{cent}}$ angle in the range of $128\text{--}129^\circ$ and Cl-M-Cl angle between $105.8\text{--}110.8^\circ$, approaches C_2 symmetry, making **3** asymmetric. The isopropyl-bridge of the ligand leads to two possible racemic conformers for **3**. For a given single crystal grown from THF/ether, the X-ray analysis reveals that only one form of racemic conformer exists, presumably leading to the appearance of various luminescent properties (*vide infra*).

**Table 1** Selected bond lengths(Å) and angles (deg)

M	(3a)Ti	(3b)Zr	(3c)Hf
Distances(Å)			
M - C1(avg)	2.306	2.377	2.341
M - cent(avg)	2.057	2.193	2.179
Angles(deg)			
C1 - M - C1'	105.8	110.8	108.6
cent - M - cent'	129.0	128.7	128.0
cent - M - C1(avg)	101.6	99.6	100.2

Figure 1 Perspective view of **3**

The catalytic activity of **3** toward a polar monomer has been tested with methyl methacrylate (MMA) in THF at various temperatures. The polar solvent THF was used for the MMA polymerization, although this is rather unusual in metallocene catalytic systems since retardation of polymerization by THF has been reported in organo-lanthanide systems.¹¹ Polymerization data are summarized in Table 2. The rr triads of 60-70% indicate that the poly(MMA)s produced with **3** are dominantly syndiotactic. The molecular weight distribution of 1.6 ~ 2.1 for the poly(MMA)s obtained with **3b** indicates that this is a single site catalyst. The molecular weight (MW) ranges from 4 - 6 x 10⁴. A decrease of syndiotacticity and an increase of the conversion rate of MMA with an increase of polymerization temperature are observed. For ambient temperature runs, the percentage of monomer conversion increases with the polymerization time while the MW remains constant as expected for single site catalytic systems. Triad tests¹² give 4[mm][rr]/[mr]² values of 0.67 - 0.80 and 2[mm]/[mr] values of 0.12 - 0.24, suggesting that propagation proceeds mainly via a chain-end control mechanism rather than an enantiomorphic site control mechanism. Characteristics of catalysts **3** worthy of mention are their air- and thermal stability and their neutral nature, which makes it unnecessary to use any additional alkylating reagents or cationic center generators such as MAO, AlR₃ and [Ph₃C]⁺[B(C₆F₅)₄]⁻ in MMA polymerization.

Table 2 Polymerization of MMA catalyzed by **3**

Temp(°C)	Time(hr)	% Conv			%rr		
		3a	3b	3c	3a	3b	3c
25	2	1.2	5.4	3.3	67.5	66.7	66.3
25	12	2.3	14	5.2	66.0	66.0	69.4
25	24	3.6	42	30	67.2	65.7	68.1
50	2	5.2	14	14	62.0	63.9	66.0
70	2	5.3	19	25	63.0	60.5	60.6

Polymerization condition : MMA(100 mmol), Catalyst(20 μ mol) in THF(50 ml) solution.

Details of the polymerization mechanism are certainly of considerable interest and remain to be established, but ¹¹B NMR and IR spectral data of well-washed Poly(MMA) may suggest cleavage of a Zr-carboranyl carbon bond, followed by coordination of MMA and subsequent 1,4-addition as the initial steps. Compounds **3** clearly constitute the first examples of the type of Group 4 neutral syndio-rich Poly(MMA) catalysts.

Based on the possible correlation between non-centrosymmetric crystalline systems and the occurrence of mechanoluminescence and/or nonlinear optical effects in those systems, various luminescence properties have been measured for the non-centrosymmetric crystalline systems **3c**. Figure 2 shows photoluminescence (PL) and mechanoluminescence (ML) spectra of crystalline **3c** grown from THF/ether. For the PL measurement, UV radiation with a 340 nm wavelength was used as the photo-excitation source. The optical analysis system for the detection of ML is schematically illustrated in Figure 3. Pressure was applied to the top glass plate, and the resulting emitted light was guided to the spectrograph via an optical fiber. A time-integrated emission spectrum was recorded. Whether the mechanoluminescent behavior of **3c** is elastic or not could not be determined due to our failure to grow sufficiently large single crystals. The maximum of ML at 435 nm is 15 nm red-shifted from the maximum PL peak, indicating that the nature of the excited states for PL and ML is different. The molecular dipole moment for **3b** was calculated using HyperChem and the molecular dipole vector and the net dipole vector in an unit cell are shown in Figure 4. The x and z components of the dipole moment are cancelled due to the crystal symmetric relationship while the y-component of the molecular dipole is aligned along the b-axis to give the net dipole. In addition, the ML of **3c** is different from the characteristic spectrum of dinitrogen gas discharge.¹³ The ML of **3c** can be considered to be a consequence of the deformations which occur during lattice fracture which create local piezoelectricity near the new face of the crystal. In other words, the fracture generates charge separation across the opposing faces of the crack. Then, dielectric break-down discharges eventually lead to the ML.

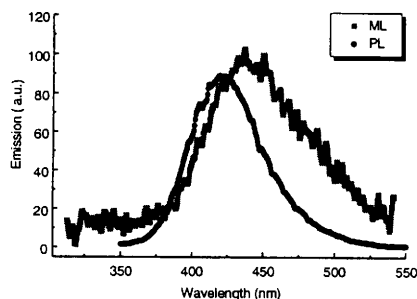


Figure 2 PL and ML of **3c**

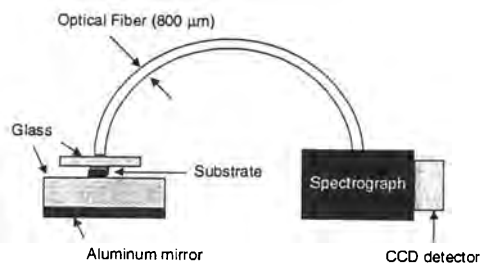


Figure 3 Schematic layout for ML detection

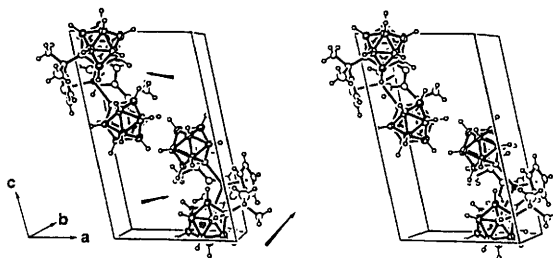


Figure 4 Stereoview of crystal packing diagram showing molecular (small arrow) and net dipole moment (large arrow) vectors for the isostructural systems **3**

Compound **3c** cannot be sublimed, so preliminary studies of the electroluminescence (EL) have been made by incorporating the complex into a charge-transporting polymer of poly(N-vinylcarbazole) (PVK) with various blending concentrations of 0.5–5.0% and using spin-coating technique to fabricate a first-generation LED device. Shown in Figure 5 is the green EL and PL spectra of 3% **3c** in PVK along with a schematic illustration of the device. The PL and EL spectra of the blend system are essentially identical. The PL maximum is at about 530 nm for the blend system and is red-shifted by about 110 nm from the PL maximum for pure **3c**, indicating that the emissive state of the blend system is different from the LUMO of **3c**. The contribution to EL from the PVK is seen at 410 nm for low blending concentrations. The turn on voltage is 16V and a maximum luminescence of 47cd/m² was achieved for 3% **3c** in PVK.

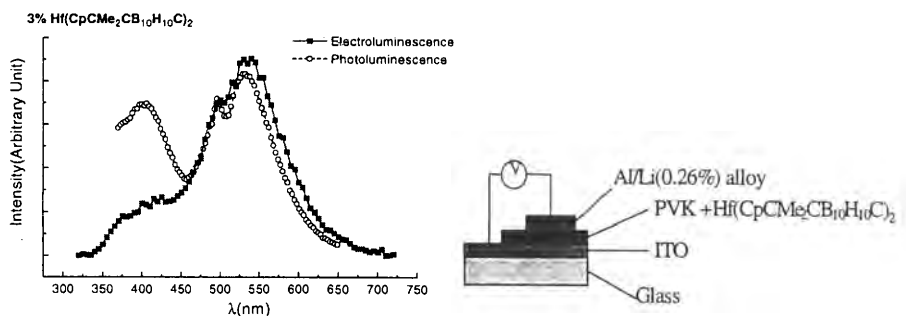
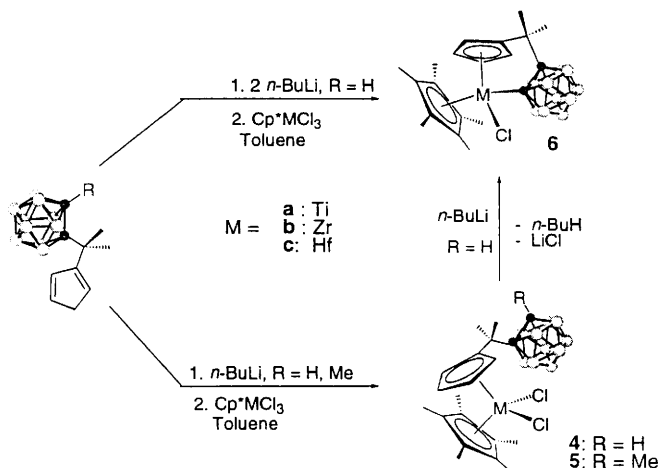


Figure 5 PL and EL spectra of 3% **3c** in PVK and the schematic drawing of the device

4 HETEROLEPTIC METALLOCENES

Three sets of new heteroleptic metallocenes containing the C₂B₁₀ cage unit, (η⁵-Cp*)(η⁵-CpCMe₂CB₁₀H₁₀CR)MCl₂ (M = group 4 metal; R = H, **4**; R = Me, **5**) and (η⁵-Cp*)(η⁵:η¹-CpCMe₂CB₁₀H₁₀C)MCl (**6**) were prepared according to Scheme 4. The facile conversion of **4** to **6** was also observed on reaction with *n*-BuLi. As established by single crystal X-



Scheme 4

ray analyses (Figure 6), the C_2B_{10} cage unit in compounds **6** acts as a σ -donor ligand while in the compounds **4** and **5** it behaves as a part of the substituent to the Cp ring.

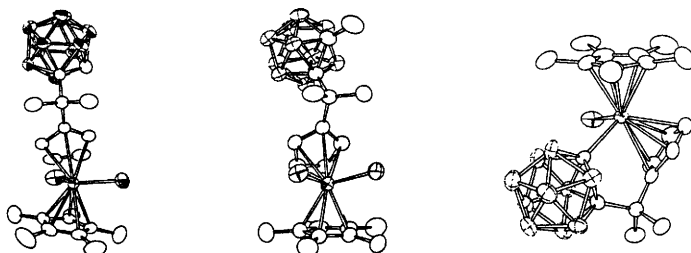


Figure 6 Molecular structures of **4** (left), **5a** (middle) and **6** (right)

Ethylene polymerizations using the catalyst precursors **4**, **5** and **6** ($M = Ti, Zr$) were carried out in the presence of modified methylaluminoxane (MMAO) as co-catalyst at various temperatures and pressures. In all cases, high density polyethylene was obtained, as judged by high T_m values. From the preliminary polymerization data, summarized in Table 3, the followings can be pointed out: (i) as tested with complex **4b**, the activity increases as not only the ethylene pressure, but also the polymerization temperature, increases; (ii) as seen with **4b** and **5b**, the introduction of a methyl group to the carborane cage leads to higher activity; and (iii) comparing compounds **4** and **6**, the latter are more effective and show moderate activity even if they contain one structurally defined active site.

Table 3 Polymerization of ethylene with **4**, **5** and **6**

Cat.	$T_p(^{\circ}C)$	Time(min)	Crude PE(g)	A^c	$T_m(^{\circ}C)^d$
4b	25 ^{a)}	60	0.81	37.5	136.7
	50 ^{a)}	60	2.32	108	140.1
	50 ^{a)}	120	2.65	61.4	140.3
5b	25 ^{a)}	60	1.85	85.9	139.4
5a	25 ^{a)}	60	1.48	115	137.0
6a	25 ^{b)}	30	0.165	30.6	139.2
	50 ^{b)}	30	0.131	24.3	135.6
4a	25 ^{b)}	30	Trace	nd	
	50 ^{b)}	30	0.007	1.3	
6b	25 ^{b)}	30	0.012	2.2	139.7
	50 ^{b)}	30	0.175	32.4	135.9
4b	25 ^{b)}	30	Trace	nd	
	50 ^{b)}	30	0.127	23.5	

^{a)}Polymerization Condition: P(ethylene)= 5 bar; [Cat]= 2.158 mM in Toluene

^{b)}Polymerization Condition: P(ethylene)= 1 bar; [Cat]= 2.158 mM in Toluene

^{c)}Activity = kg PE / (mol Cat $\cdot$ hr) ^{d)}Determined by DSC

The catalytic systems **4a**/MMAO and **5a**/MMAO are also active for propylene polymerization. The polymerization data obtained with a propylene pressure of 5 atm. at

different temperatures are listed in Table 4, and show that syndio-rich high molecular weight polypropylenes are formed. In addition, the resulting polypropylene (PP) does not give a T_m peak in its DSC and its strain-stress curve shows elastomeric characteristics (Figure 7). A triad test gives $4(mm)[rr]/[mr]^2$ values of 0.98–1.32, indicating that the propagation proceeds mainly via a chain-end control mechanism. The catalytic behavior of the **4a**/MMAO system is similar to that of non-substituted analog $Cp^*CpTiCl_2$ but the introduction of a methyl group to the carborane cage (**5a**/MMAO) results in about a 9-fold increase of the activity.

Table 4 Polymerization of propylene catalyzed by **4a**/MMAO and **5a**/MMAO

Cat	Temp (°C)	A ^{d)}	MWD	%rr
4a	25 ^{a)}	8.0	3.24	48.4
	50 ^{a)}	2.2	3.36	42.3
5a	25 ^{a)}	72	2.83	46.6
	50 ^{a)}	18	2.91	48.6
A ^{b)}	25 ^{a)}	7.9	2.02	41.5
B ^{c)}	50 ^{a)}	250	1.9	--

a) Polymerization condition : Propylene 5 atm, Catalyst 10^{-3} mol, MMAO (mol of Al = 1500 x mol of Ti) in 100 ml Toluene, 1 hr, Activity = kg PP / mol Ti·hr·atm

b) **A** : $Cp^*TiCpCl_2$, $2[mm]/[mr] = 0.68$; $4[mm][rr]/[mr]^2 = 1.30$

c) **B** : $C_5Me_4CMe_2IndTiCl_2$

{ 1 atm, 50°C, MAO (mol of Al = 2000x mol of Ti), 1 hr }

d) Activity = kg PP / mol Ti·hr·atm

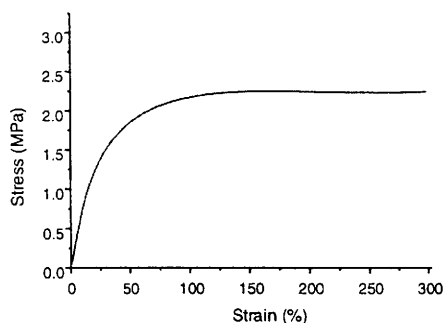
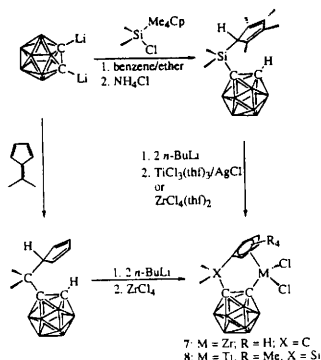


Figure 7 Stress-strain curve of PP

5 CGC DERIVATIVES FROM *o*-CARBORANE

Carborane complexes $Zr(\eta^5\text{-}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)Cl_2$ (**7**) and $M(\eta^5\text{-}\eta^1\text{-}C_5Me_4SiMe_2CB_{10}H_{10}C)Cl_2$ ($M = Ti$, **8**; Zr) of a constrained-geometry catalyst (CGC) type¹⁴ were prepared as outlined in Scheme 5. Species **7** is not stable in solution and undergoes disproportionation to generate compound **3b** and $ZrCl_4$. The stability was improved by the introduction of a $SiMe_2$ bridge to replace the isopropyl unit. The molecular structure of **8** is shown in Figure 8 and clearly shows the CGC nature.



Scheme 5

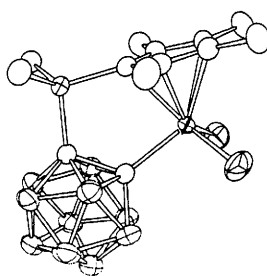


Figure 8 Molecular structure of **8**

6 CONCLUSIONS

The versatile complexation behavior of new *ansa*-type cyclopentadienyl *o*-carboranyl ligands $\text{HCpCMe}_2\text{CB}_{10}\text{H}_{10}\text{CH}$, $\text{HCpCMe}_2\text{CB}_{10}\text{H}_{10}\text{CMe}$ and $\text{HC}_5\text{Me}_4\text{SiMe}_2\text{CB}_{10}\text{H}_{10}\text{CH}$ has been demonstrated, resulting in the synthesis of new classes of group 4 metallocene complexes including novel chiral bis(carboranyl)group 4 complexes. In addition, the functional properties of these new complexes, such as olefin polymerization activity and luminescence, have been measured. Exploratory work on the use of *o*-carborane in developing functional materials continues and appears to be exciting.

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Cationic Metallocenes Derived from Cyclic Organo-hydroborate Metallocene Complexes

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1 INTRODUCTION

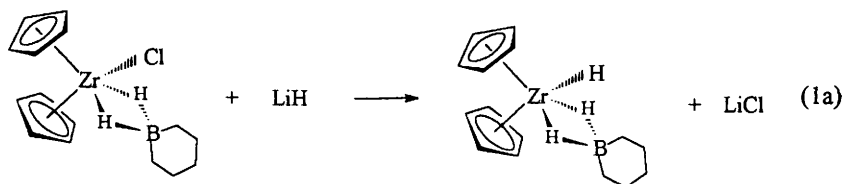
While many metal tetrahydroborate complexes have been prepared and studied,¹ little is known concerning metal organohydroborate chemistry.

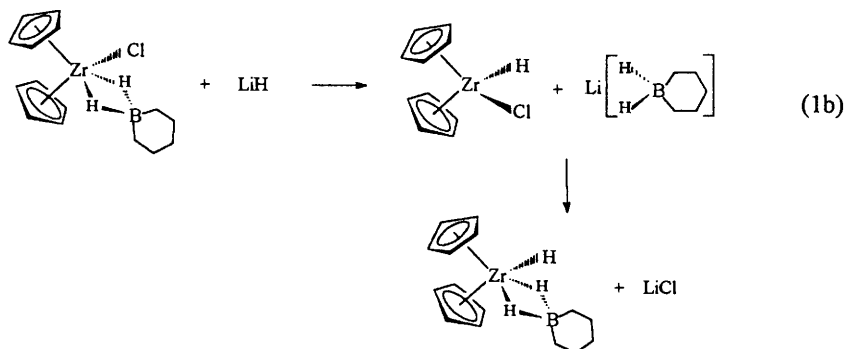
Recently, we investigated the chemistry of $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$, which was prepared earlier.² It is a very good hydride transfer agent. It reduces metal carbonyls to metal carbonyl hydrido carbonylate ions, alkyl halides to alkanes, and ketones and aldehydes to alcohols.³ The driving force for these reduction reactions is the formation of $\text{B}_2(\mu\text{-H})_2(\mu\text{-C}_4\text{H}_8)_2$,⁴ a stable and relatively inert organodiborane. In addition to the hydride transfer ability, an unique ring disproportionation reaction of $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$ was observed in its reactions with zirconocene and hafnocene dichlorides to produce the double hydrogen-bridged cyclopentaborate derivatives $\text{Cp}_2\text{MCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ ($\text{M} = \text{Zr}, \text{Hf}$).⁵ The similar complexes, $\text{Cp}_2\text{MCl}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ ($\text{M} = \text{Zr}, \text{Hf}$),⁶ were also prepared from the reactions of Cp_2MCl_2 ($\text{M} = \text{Zr}, \text{Hf}$) with $[\text{H}_2\text{BC}_5\text{H}_{10}]^-$. This anion simply functions as a bidentate chelating ligand to bond to the metal center.

2 PREPARATION OF $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ AND $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$

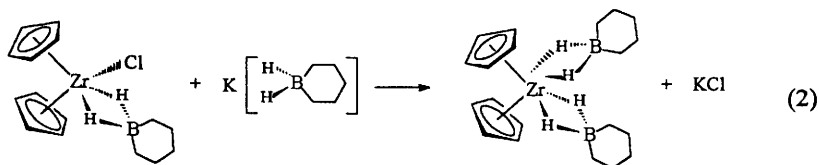
Reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ with LiH produces $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ ⁷ (Reaction (1)). Two parallel reaction pathways might occur. In one pathway, Reaction (1a), nucleophilic displacement of Cl^- by H^- would produce $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ directly. In the second pathway, reaction (1b), the H^- ion could attack the boron atom to cleave the hydrogen bridge system to generate Cp_2ZrClH and $[\text{H}_2\text{BC}_5\text{H}_{10}]^-$, which then react with each other to form $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$. Indeed, $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ was formed in a separate reaction of Cp_2ZrClH with $\text{K}[\text{H}_2\text{BC}_5\text{H}_{10}]$.

The six numbered ring di-substituted complex, $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ ⁷ was prepared



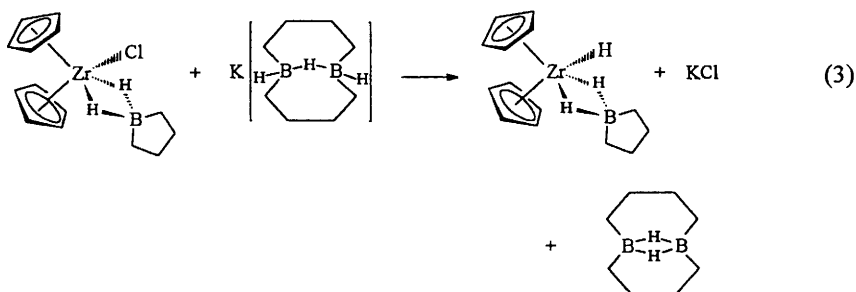


from the reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ with a second mole of $[\text{H}_2\text{BC}_5\text{H}_{10}]^-$ (Reaction (2)). The solid state structure of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ (Fig. 1) indicates each of the two organohydroborate rings connects to the zirconium through two bridge hydrogens.



3 FORMATION OF $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$

The reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ with a second mole of $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$ produces $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ ⁸ (Reaction (3)). For the reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$



with $\text{K}[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]$ two possible products were considered. One product is that actually isolated, $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$, formed through hydride transfer from the organodiborate to zirconium to displace the chloride. The other possible product considered, $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$, but not observed, would have been formed through disproportionation of the organodiborate anion, $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$, as observed in the preparation of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$.⁵ Possible kinetic and thermal factors that resulted in the preferential formation and isolation of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ rather than $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$ were considered. Scheme 1 presents possible pathways for the reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ with $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$. The first step of the reaction might involve the coordination

of $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$ to the zirconium center through a single hydrogen bond. However, the presence of the borocyclopentane ring of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ might sterically prevent or significantly hinder the $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$ anion from approaching the Zr center. Instead, transferring the hydride to zirconium with the breaking of the B-H bond would be more easily achieved.

In order to avoid the problems associated with the disproportionation of $\text{K}[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]$, the anion $\text{Li}[\text{H}_2\text{BC}_4\text{H}_8]$ was chosen as an alternative reagent for the reaction

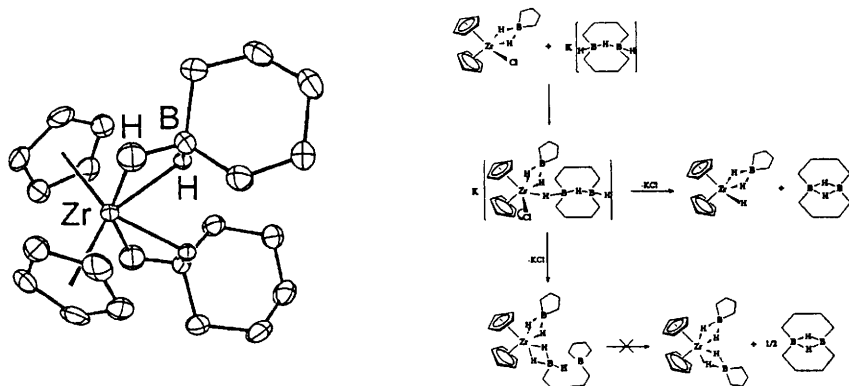


Figure 1 Molecular structure of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$

Scheme I

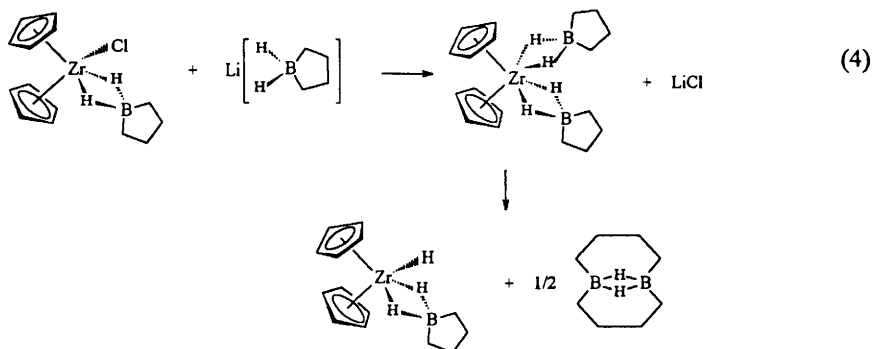
with $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ in an attempt to prepare $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$. This reaction did not yield $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$ but produced $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ as the final isolated product.

Upon reaction of $\text{Li}[\text{H}_2\text{BC}_4\text{H}_8]$ with $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ in THF, time-elapsd $^{11}\text{B}\{^1\text{H}\}$ NMR spectra⁸ showed a new, broad signal at about 28 ppm, which then splits into two overlapping signals at $\delta = 30.2$ and 28.2 ppm, with the intensity of the former larger than the latter. From previous studies, the signal at 28.2 ppm is assigned to $\{\text{B}_2(\text{C}_4\text{H}_8)_2\}$, and the signal at 30.2 ppm corresponds to $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$. If $[\text{H}_2\text{BC}_4\text{H}_8]$ functioned solely as a hydride transfer agent, then $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ and $\{\text{B}_2(\text{C}_4\text{H}_8)_2\}$ would be produced in equal amounts in the ^{11}B NMR spectrum initially. However, the broad signal that initially appears at 28 ppm might indicate the formation of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$. Table 1 presents selected chemical shifts of bis(cyclopentadienyl) zirconium boracyclopentane and boracyclohexane derivatives. The replacement of a boracyclohexane ring by a boracyclopentane ring appears to shift the boron signal of the complex downfield. It is reasonable to assume that the new peak at 28 ppm is due to the formation of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$. However, since the NMR signal diminishes with time, it appears that this compound is unstable and disproportionates into $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ and $\{\text{B}_2(\text{C}_4\text{H}_8)_2\}$ as described in Reaction (4).

While Scheme I suggests that the pathway for the formation of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ is more favorable than that for the formation of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}_2$, based upon steric considerations, consideration of Reaction (4) suggests that this compound is also thermally less stable than $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$.

Table 1 Selected ^{11}B chemical shift (ppm) of cyclic hydroborate complexes

Compd.	δ	Compd.	δ
$\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	16.7	$\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	13.7
$\text{Cp}_2\text{Zr}(\text{CH}_3)\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	20.1	$\text{Cp}_2\text{Zr}(\text{CH}_3)\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	18.2
$\text{Cp}_2\text{Zr}(\text{Ph})\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	22.0	$\text{Cp}_2\text{Zr}(\text{Ph})\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	19.4
$\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	22.1	$\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	19.4
$\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$	30.9	$\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$	28.2
		$\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$	24.6



4 VARIABLE-TEMPERATURE BEHAVIOR OF $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ AND $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$

Intramolecular hydrogen exchange among Cp hydrogens, Zr-H terminal hydride, and Zr-H-B bridge hydrogens was observed in the zirconium hydride complexes, $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ ⁷ and $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$, at elevated temperature.

Proton NMR spectra of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ at elevated temperatures are shown in Figures (2). The two signals of the bridge hydrogens broaden and coalesce as the temperature is raised. During the process, the signal of the terminal hydrogen also broadens into the baseline. The signal of the Cp hydrogens is also broadened at higher temperature. This behavior is independent of the concentration, which suggests an intramolecular hydrogen exchange among Cp hydrogens, Zr-H terminal hydride, and Zr-H-B bridge hydrogens occurred at elevated temperature.

In order to get direct evidence of the hydrogen exchange between Cp hydrogens and other hydrogens, the deuterated complex, $\text{Cp}_2\text{ZrD}\{(\mu\text{-D})_2\text{BC}_4\text{H}_8\}$ was prepared from the reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ with excess LiD (Reaction (5)). The ^2H NMR spectrum of $\text{Cp}_2\text{ZrD}\{(\mu\text{-D})_2\text{BC}_4\text{H}_8\}$ shows terminal deuteride on Zr, and bridge deuteriums (Figure 3(a)). Upon heating this complex at 85 °C for 10 minutes, the intensities of the signals of terminal deuteride and bridge deuteriums decreased and new signals appeared in the Cp region (Figure 3(b)). This result provides the clear evidence of hydrogen exchange in $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$.

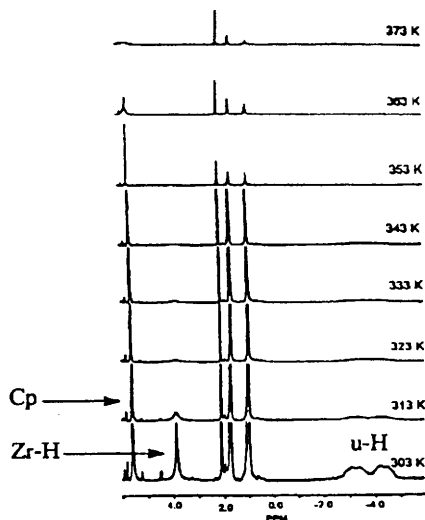
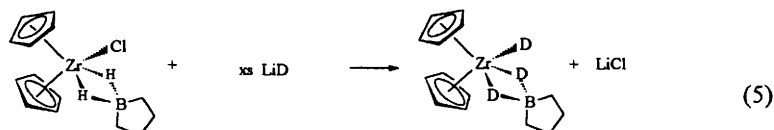


Figure 2 Variable-temperature ^1H NMR spectra of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$



A possible exchange process that involves the Cp hydrogens, Zr-H terminal hydride, and Zr-H-B bridge hydrogens is shown in Scheme II. To account for the

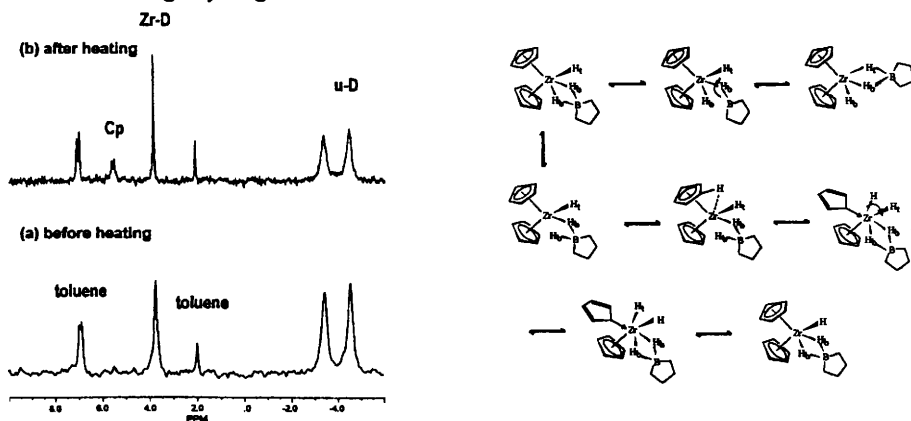


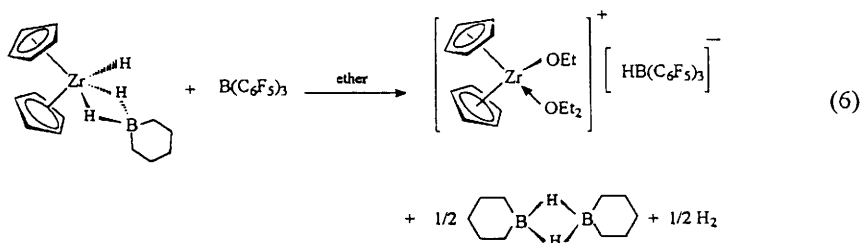
Figure 3 ^2H NMR spectra of $\text{Cp}_2\text{ZrD}\{(\mu\text{-D})_2\text{BC}_4\text{H}_8\}$ in toluene (a) before heating. (b) after heating at 85°C for 10 min.

Scheme II Possible mechanism for the hydrogen exchange of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$

exchange of the terminal hydride, a single hydrogen bridge intermediate with one broken B-H₂ bond is proposed. The exchange of the Cp hydrogens with terminal hydride and bridge hydrogens might involve rearrangement of the bonding of the Cp rings to zirconium, proceeding through $\eta^5 \rightarrow \eta^1 \rightarrow \eta^3$ bonding modes. Line shape analyses of the exchange process for the terminal and bridge hydrogens have been reported.⁹

5 FORMATION OF $[\text{Cp}_2\text{Zr}(\text{OC}_2\text{H}_5)(\text{OC}_4\text{H}_9)][\text{HB}(\text{C}_6\text{F}_5)_3]$ AND $[\text{CpZr}(\text{OC}_4\text{H}_9)(\text{OC}_2\text{H}_5)(\mu\text{-O})\text{C}_2\text{H}_5]_2[\text{HB}(\text{C}_6\text{F}_5)_3]_2$

The ethoxyl substituted cation $[\text{Cp}_2\text{Zr}(\text{OC}_2\text{H}_5)(\text{OC}_4\text{H}_9)]^+$ was formed from the reaction of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in diethyl ether (Reaction (6)) in which $\text{B}(\text{C}_6\text{F}_5)_3$ serves as a hydride abstracting agent. The solid state structure of the cation is shown in Figure (4).



The reaction of $\text{CpZr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_3$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in diethyl ether produces the dication $[\text{CpZr}(\text{OC}_4\text{H}_9)(\text{OC}_2\text{H}_5)(\mu\text{-O})\text{C}_2\text{H}_5]_2^{2+}$ (Reaction (7)), an oxygen bridged dimer (Fig. (5)). "Short" Zr-O distances suggest significant back π bonding.

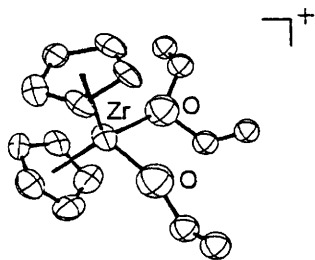
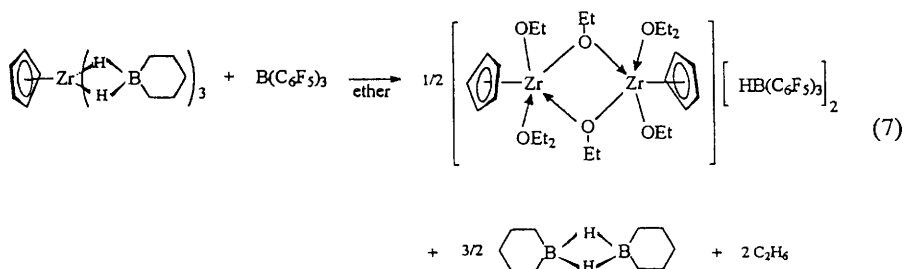


Figure 4 Molecular Structure of $[\text{Cp}_2\text{Zr}(\text{OC}_2\text{H}_5)(\text{OC}_4\text{H}_9)]^+$

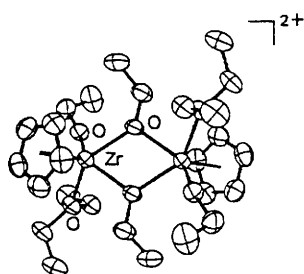
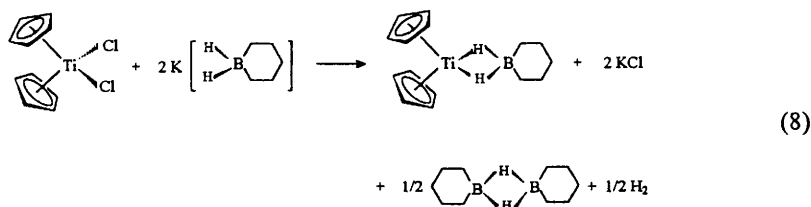


Figure 5 Molecular Structure of $[\text{CpZr}(\text{OC}_4\text{H}_9)(\text{OC}_2\text{H}_5)(\mu\text{-O})\text{C}_2\text{H}_5]_2^{2+}$

6 $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{10}\}$ AND $[\text{Cp}_2\text{Ti}(\text{OC}_4\text{H}_9)_2][\text{HB}(\text{C}_6\text{F}_5)_3]$

The paramagnetic complex $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{10}\}$ was prepared from the reaction of Cp_2TiCl_2 with $\text{K}[\text{H}_2\text{BC}_3\text{H}_{10}]$ (Reaction (8)). In this reaction, titanium was



reduced from oxidation state (IV) to (III). The structure of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{10}\}$ is shown in Figures (6).

$\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{10}\}$ reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ in diethyl ether and produces the ether coordinated cation $[\text{Cp}_2\text{Ti}(\text{OC}_4\text{H}_9)_2]^+$ (Reaction (9)). The solid state structure of $[\text{Cp}_2\text{Ti}(\text{OC}_4\text{H}_9)_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ is shown in Figure (7).

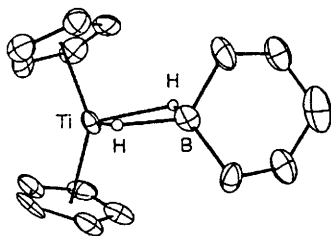
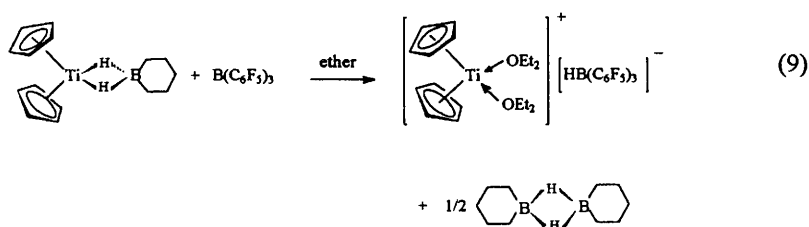


Figure 6 Molecular structure of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{10}\}$

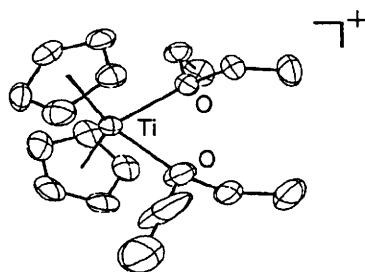


Figure 7 Molecular structure of $[\text{Cp}_2\text{Ti}(\text{OC}_4\text{H}_9)_2]^+$

ACKNOWLEDGMENTS

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Organolanthanide Compounds Bearing Versatile Ligands

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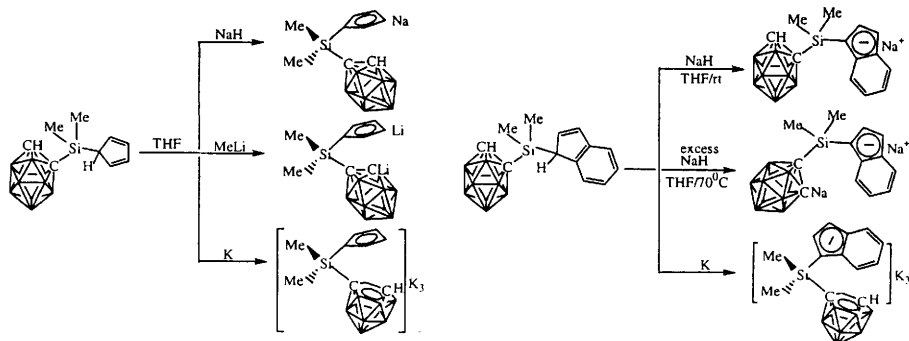
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1 INTRODUCTION

Organolanthanide chemistry has witnessed an explosive growth in the past few decades.¹ The most popular π ligands used in organolanthanide compounds are cyclopentadienyl and its derivatives. As isolobal analogues to the cyclopentadienyl ligand, C_2B_9 ,^{2,3} C_2B_{10} ,⁴ and C_2B_4 ⁵ ligand systems have been successively introduced to lanthanide chemistry, resulting in a new class of organolanthanide compounds. Due to the unique properties of these carborane molecules, the bonding between metal and carboranyl ligands can be varied from 2e-3c σ bonds to η^5 or η^6 bonds depending on the sizes of the bonding faces and the substituents on these faces. There are, however, no definitive reports of mixed-ligand organolanthanide compounds having either a cyclopentadienyl or some other cyclic organic π donor as the companion ligand to a carborane.⁶ We are interested in a new class of versatile ligands that bear both a cyclic organic group and a carborane molecule, in the hope that these molecules would have the advantages of both units and the bridging ligands. Recent findings in our laboratory demonstrate that indeed these versatile ligands not only yield highly versatile organolanthanide compounds, but also prevent disproportionation of the mixed lanthanacarboranes.⁷⁻¹¹

2 LIGAND SYNTHESIS

Treatment of $Me_2Si(Cy)Cl$ with 1 equivalent of $Li_2C_2B_{10}H_{10}$ in toluene/ether at 0°C gave, after hydrolysis, $Me_2Si(Cy)(C_2B_{10}H_{11})$ ($Cy = C_5H_5, C_9H_7$).^{7,10} As expected, these are very



Scheme 1

versatile molecules and can be conveniently converted into the mono-anion, the di-anion, and the tri-anion by treatment with various bases (Scheme 1). It is noteworthy that both MeLi and *n*-BuLi cleave the Si-C(carborane) bond in Me₂Si(C₉H₇)(C₂B₁₀H₁₁), by contrast with Me₂Si(C₅H₅)(C₂B₁₀H₁₁), in which the CH proton of the carborane cannot be deprotonated by NaH, and on the other hand, the Si-C(carborane) bond is not sensitive to either MeLi or *n*-BuLi. These results indicate the effects of the substituents Cy on the acidity of the CH protons of the carborane cage and the stability of the Si-C(carborane) bond.

3 ORGANOLANTHANIDE COMPOUNDS

A wide range of organolanthanide compounds can be generated through the metathesis reaction of lanthanide chlorides with the various anions mentioned above. These compounds include organolanthanide dichloride [η^5 -Me₂Si(Cy)(C₂B₁₀H₁₁)]LnCl₂(THF)₃, mono-chloride [η^5 -Me₂Si(Cy)(C₂B₁₀H₁₁)]₂LnCl(THF)₂, carboranyl [Li(THF)₄][Me₂Si(Cy)(C₂B₁₀H₁₀)]₂Ln], and lanthanacarboranes [η^5 : η^6 -Me₂Si(Cy)(C₂B₁₀H₁₀)]Ln(THF)₂, where the carborane serves as a bulky substituent, a σ ligand, or a π ligand, respectively.⁷⁻¹⁰ The synthetic routes are summarized in Scheme 2.

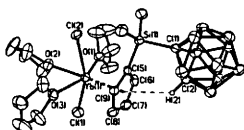


Figure 1 Organolanthanide Dichloride

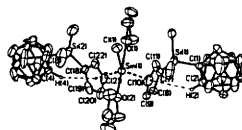


Figure 2 Organolanthanide Monochloride

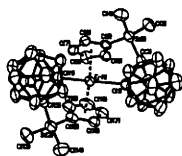


Figure 3 Organolanthanide Carboranyl

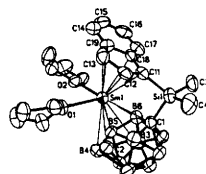
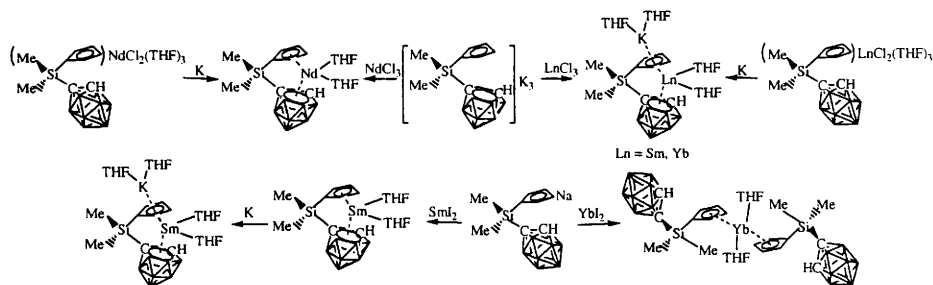


Figure 4 Lanthanacarborane



Scheme 2

It is noteworthy that the reactions between SmI₂ and the mono-anion or the di-anion derived from the above mentioned ligands always lead to the isolation of

organosamarium(III) compounds, indicating that organosamarium(II) compounds of these ligands are extremely reactive.^{8,10} The organoytterbium(II) analogues, however, are stable and well-characterized. Structural information on these compounds can help us to better understand the mechanism of the formation of organosamarium(III) compounds. Schemes 3 and 4 outline the proposed mechanisms for the formation of $[\eta^5:\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$ and $[\text{Na}(\text{THF})_6][\{\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})\}_2\text{Sm}]$, respectively.

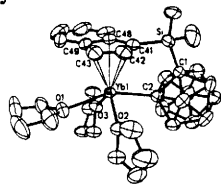
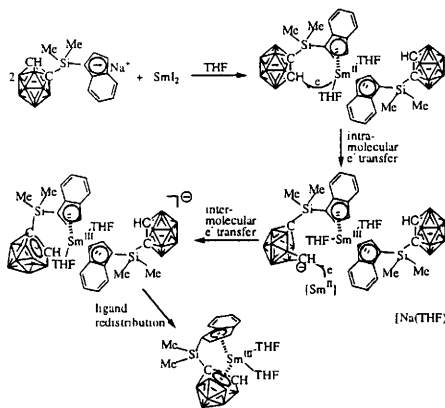


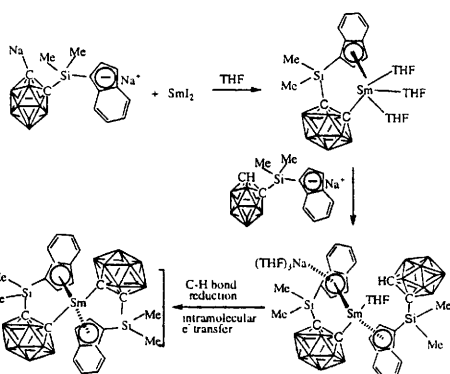
Figure 5 Constrained Geometry Compound



Figure 6 Mixed-ligand Compound



Scheme 3



Scheme 4

4 ORGANOLANTHANIDE CLUSTERS

It has been found that the Si-C(carborane) bond in $\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$ is sensitive to not only organo-lithium reagents such as MeLi and $n\text{-BuLi}$ but also NaNH_2 . Treatment of $\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$ with excess NaNH_2 in THF, followed by reaction with 1 equivalent of LnCl_3 gave tetranuclear and trinuclear organolanthanide clusters of general formulae $[\{(\eta^5:\mu_2\text{-C}_9\text{H}_6\text{SiMe}_2\text{NH})\text{Ln}\}_2(\mu_3\text{-Cl})(\text{THF})_2(\mu_4\text{-NH})]^{11}$ and $[(\eta^5\text{-C}_9\text{H}_6\text{SiMe}_2)_2\text{N}][\mu_2:\mu_2\text{-Me}_2\text{Si}(\text{NH})_2][(\eta^5:\mu_2\text{-C}_9\text{H}_6\text{SiMe}_2\text{NH})(\mu_2\text{-Cl})_2\text{Ln}_3(\text{THF})_3]$.

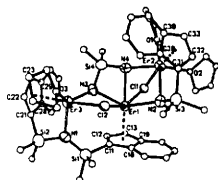


Figure 7 Trinuclear Cluster

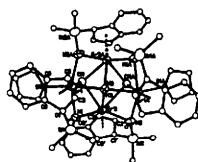
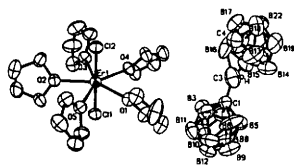


Figure 8 Tetranuclear Cluster

respectively. The type of the clusters is dependent upon the molar ratio of the reactants employed in the reactions. During the course of the reactions, several types of new ligands are generated. It is clear that NaNH_2 serves as both base and nucleophile although the reaction mechanisms are not fully understood.

5 BISCARBORANE MONOANION COMPOUNDS

The sodium salt of the di-anion $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]^{2-}$ undergoes an unprecedented coupling reaction under UV-light to afford a bis-carborane mono-anion compound $[\text{Na}(\text{THF})_x][\mu\text{-CH}(\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-nido-CB}_{10}\text{H}_{11}]$, which on treatment with LnCl_3 in THF produces $[\text{LnCl}_2(\text{THF})_5][\mu\text{-CH}(\text{closo-C}_2\text{B}_{10}\text{H}_{11})\text{-nido-CB}_{10}\text{H}_{11}]$. **Figure 9** Biscarborane Compound. The mechanism of the formation of these compounds is not clear, but may be similar to the Wurtz reaction to some extent.



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