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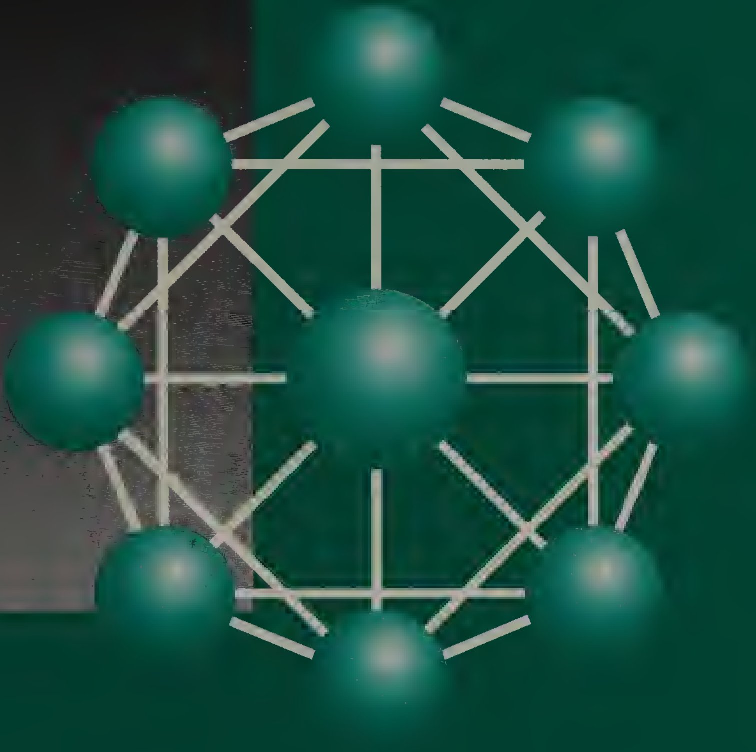

CONTEMPORARY boron chemistry

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

Contemporary Boron Chemistry

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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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Mr Tom Caygill, Dr Wendy Gill, Mr Bill Harris, Mr Tim Heath and Ms Elizabeth Wood

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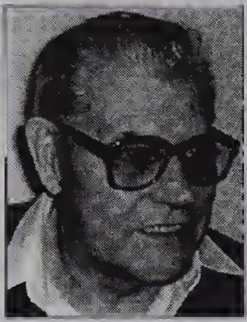
Professor Stanislav Heřmánek

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–^{1}H 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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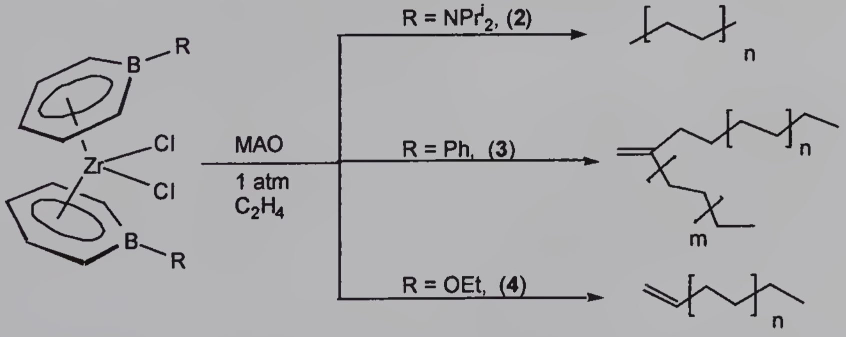
1 INTRODUCTION

The use of the boratabenzene heterocycle as a ligand for transition metal complexes dates back to 1970 with the synthesis of $(C_5H_5B\text{-}Ph)CpCo^+$ (**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 $(C_5H_5B\text{-}NPr^i_2)_2ZrCl_2$ (**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, $(C_5H_5B\text{-}Ph)_2ZrCl_2$/MAO (**3**/MAO) gave predominantly 2-alkyl-1-alkenes[5] while $(C_5H_5B\text{-}OEt)_2ZrCl_2$/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 $[CpCo(L)R]^+$ (L = phosphine or phosphite, R= alkyl)[7], $Cp^*{}_2ScCH_2CH_3$[8] and $(C_5H_4Me)_2Zr(CH_2CH_2R)(PMe_3)^+$ (R = H, Et, $SiMe_3$, Ph).[9] Such interactions occur when the C_β-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 $(C_5H_5B\text{-}R)_2ZrCl_2$ 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 = $NPr^i{}_2$ 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 $(C_5H_5BR)_2ZrCl_2$.*

R	Zr-B Distance (Å)
Me (**6**)[10]	2.814(5)
OEt (**4**)[6]	2.826(2)
Ph[11]	2.80(3)
$NPr^i{}_2$ (**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 $[Cp^*(C_5H_5B\text{–}R)ZrMe][MeB(C_6F_5)_3]$.

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 $(C_5H_5B\text{-}R)_2ZrCl_2$ (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 $(C_5H_5B\text{-}R)$ 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.

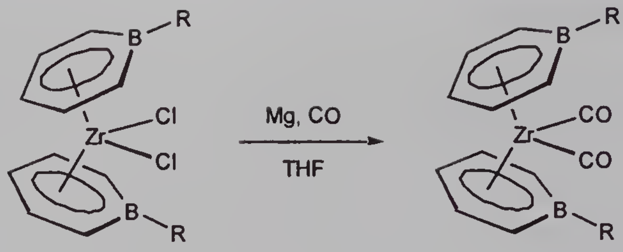
Table 2. *Reduction Potentials for $(C_5H_5B\text{–}R)_2ZrCl_2$ Complexes vs. SCE.*

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 $(C_5H_5B\text{–}R)_2Zr(CO)_2$ can therefore be used as a relative measure of electron density at zirconium as a function of R.

The dicarbonyl complexes $(C_5H_5B\text{–}R)_2Zr(CO)_2$ (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 ν(CO) values for the mixed ring complexes $Cp^*(C_5H_5B\text{–}R)Zr(CO)_2$ (R = Ph (**11**), OEt (**12**), NMe_2 (**13**), Me (**14**)) which were prepared from reduction of the $Cp^*(C_5H_5B\text{–}R)ZrCl_2$ precursors under an atmosphere of CO. According to these data the ordering of donating ability of $(C_5H_5B\text{–}R)$ ligands is: R = NMe_2 > Me > OEt ~ Ph. The Cp* ligand is a considerably stronger donor and it is useful to point out here that all $Cp^*(C_5H_5B\text{–}R)ZrCl_2$/MAO combinations give high molecular weight polyethylene under experimental conditions similar to those in Scheme 1.



R = Ph (**3**)
R = OEt (**4**)
R = NMe$_2$ (**5**)
R = Me (**6**)

R = Ph (**7**)
R = OEt (**8**)
R = NMe$_2$ (**9**)
R = Me (**10**)

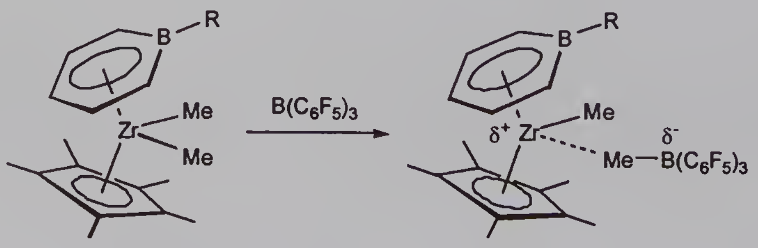
Scheme 2

Table 3. *Carbonyl Stretching Frequencies.*

Compound	ν(CO) (cm^{-1})
$(C_5H_5B\text{-}NMe_2)_2Zr(CO)_2$ (**9**)	2005, 1955
$(C_5H_5B\text{-}Me)_2Zr(CO)_2$ (**10**)	2012, 1964
$(C_5H_5B\text{-}OEt)_2Zr(CO)_2$ (**8**)	2017, 1969
$(C_5H_5B\text{-}Ph)_2Zr(CO)_2$ (7)	2018, 1966
$(C_5H_5B\text{-}NMe_2)Cp^*Zr(CO)_2$ (**13**)	1976, 1908
$(C_5H_5B\text{-}Me)Cp^*Zr(CO)_2$ (**14**)	1981, 1913
$(C_5H_5B\text{-}OEt)Cp^*Zr(CO)_2$ (**12**)	1982, 1914
$(C_5H_5B\text{-}Ph)Cp^*Zr(CO)_2$ (**11**)	1987, 1920

4 ZWITTERIONIC SPECIES

The reaction of $Cp^*(C_5H_5B\text{–}R)ZrMe_2$ (R = NMe_2 (**15**), Ph (**16**)) with one equivalent of $B(C_6F_5)_3$ affords the zwitterionic complexes $[Cp^*(C_5H_5B\text{–}R)ZrMe][MeB(C_6F_5)_3]$ (R = NMe_2 (**17**), Ph (**18**)) (Scheme 3).



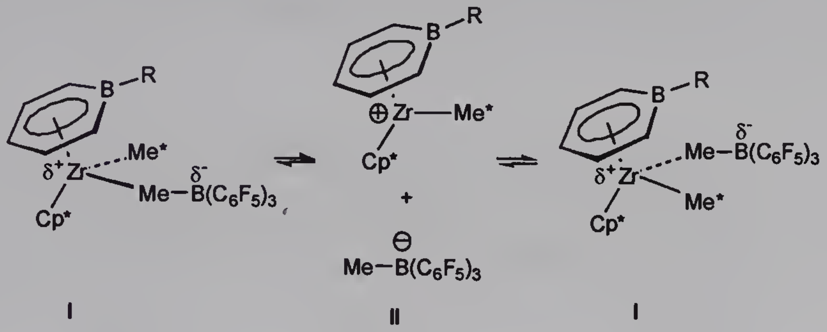
R = NMe$_2$ (**15**)
R = Ph (**16**)

R = NMe$_2$ (**17**)
R = Ph (**18**)

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 ^{1}H 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

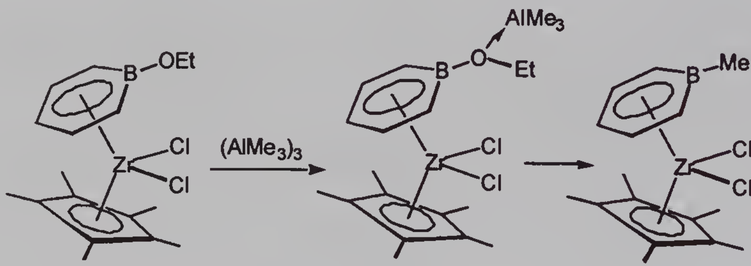
The activation parameters for the exchange reactions of **17** and **18** were determined by a combination of variable-temperature ^{1}H NMR lineshape analysis[16] and spin saturation transfer experiments.[17] Rate data for **17** were measured over a temperature range of 100 °C. Rates for compound **18** 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 = NMe_2 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 $(C_5H_5B\text{-}OEt)Cp^*ZrCl_2$ *via* the oxygen atom (Scheme 5). Formation of $(C_5H_5B\text{-}Me)Cp^*ZrCl_2$ ensues after sufficient reaction time.[19] These observations are significant since commercially available MAO can contain up to 35% of $(AlMe_3)_2$ by weight. The simplicity of structure makes complexes of general composition $[Cp^*(C_5H_5B\text{–}R)ZrMe][MeB(C_6F_5)_3]$ better candidates for more precise and rational catalyst design.



Scheme 5

References

1. (a) G. E. Herberich, G. Greiss and H. F. Heil, *Angew. Chem. Int. Ed. Engl.*, 1970, **9**, 805. (b) G. E. Herberich and H. Ohst, 'Advances in Organometallic Chemistry', Academic Press, New York, 1986, Vol. 25, p. 199.
2. For general reviews on boratabenzene complexes see: (a) G. E. Herberich, 'Comprehensive Organometallic Chemistry II', E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, Vol. 1, p. 197. (b) A. J. Ashe III, S. Al-Ahmad and X. G. Fang, *J. Organomet. Chem.*, 1999, **581**, 92.
3. G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and C. Müller, *J. Am. Chem. Soc.*, 1996, **118**, 2291.
4. (a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1143. (b) 'Ziegler Catalysts', G. Fink, R. Mülhaupt and H. H. Brintzinger, Springer-Verlag, Berlin, 1995. (c) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem. Int. Ed. Eng.,* 1999, **38**, 429. (d) M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
5. G. C. Bazan, G. Rodriguez, A. J. Ashe III, S. Al-Ahmad and J. W. Kampf, *Organometallics*, 1997, **16**, 2492.
6. J. S. Rogers, G. C. Bazan and C. K. Sperry, *J. Am. Chem. Soc.*, 1997, **119**, 9305.
7. G. F. Schmidt and M. Brookhart, *J. Am. Chem. Soc.*, 1985, **107**, 1443.
8. B. J. Burger, M. E. Thompson, W. D. Cotter and J. E. Bercaw, *J. Am. Chem. Soc.*, 1990, **112**, 1566.

9. R. F. Jordan, P. K. Bradley, N. C. Baenziger and R. E. LaPointe, *J. Am. Chem. Soc.*, 1990, **112**, 1289.
10. G. E. Herberich, U. Englert and A. Schmitz, *Organometallics*, 1997, **16**, 3751.
11. These data are from the structure of (4-Bu^t-$C_5H_4BPh)_2ZrCl_2$. See reference 5.
12. a) J. D. L. Holloway and W. E. Geiger Jr., *J. Am. Chem. Soc.*, 1979, **101**, 2038. (b) M. F. Lappert, C. J. Pickett, P. I. Riley and P. I. W. Yarrow, *J. Chem. Soc., Dalton Trans.*, *1981*, 805. (c) R. G. Finke, G. Gaughan and R. Voegeli, *J. Organomet. Chem.*, 1982, **229**, 179. (d) P. G. Gassman, D. W. Macomber and J. W. Hershberger, *Organometallics*, 1983, **2**, 1471.
13. G. C. Bazan, W. D. Cotter, Z. J. A. Komon, R. A. Lee and R. J. Lachicotte, submitted.
14. D. J. Sikora, D. W. Macomber and M. D. Rausch, *Adv. Organomet. Chem.*, 1986, **25**, 317.
15. (a) P.A. Deck and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 6128. (b) P. A. Deck, C. L. Beswick and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1772.
16. J. Sandstrøm, 'Dynamic NMR Spectroscopy', Academic Press, New York, 1982.
17. S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, 1963, **39**, 2892.
18. R. A. Lee, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1998, **120**, 6037.
19. J. S. Rogers, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1999, **121**, 1288.

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

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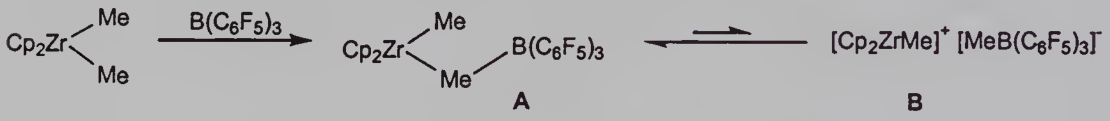
Tris(pentafluorophenyl)borane, a compound first made by Stone et al. in 1963,[1] has in recent years become one of the most widely applied boron reagents, as a highly effective activator for metallocene-based olefin polymerisation catalysts. There are several reasons for this: it is a strong Lewis acid, 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 $B(C_6F_5)_3$ 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]

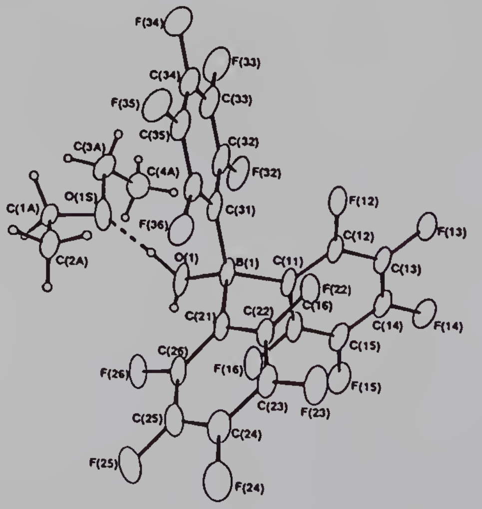
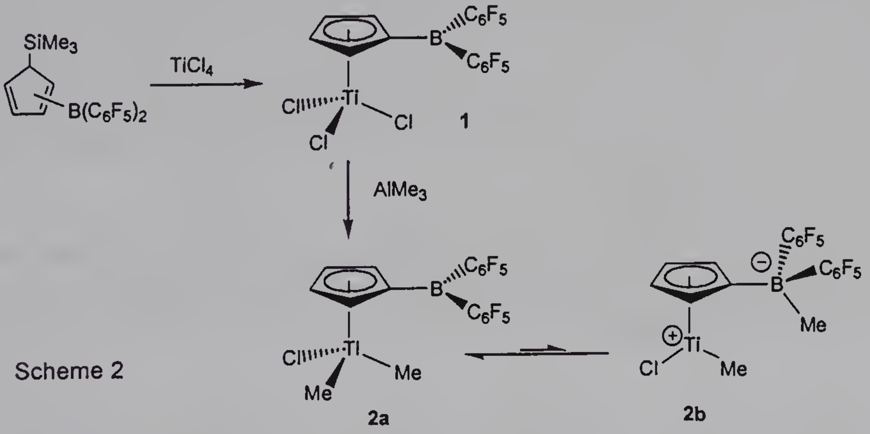


Fig. 1 Selected bond lengths (Å) and angles (°): B-O(1) 1.566(4), B-C(11) 1.652(4), B-C(21) 1.625(5), B-C(31) 1.621(6), O(1)-B-C(11) 104.9(2), O(1)-B-C(21) 109.9(3), O(1)-B-C(31) 104.1(3), C(11)-B-C(21) 107.7(3), C(11)-B-C(31) 114.7(3), C(21)-B-C(31) 115.1(3).

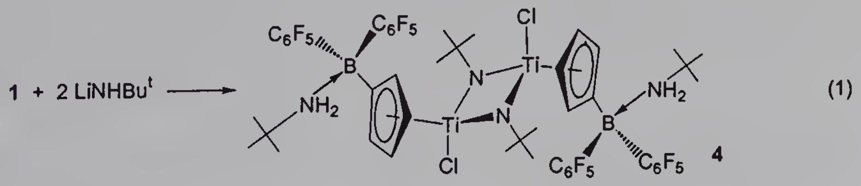
1. Boryl-Cp Complexes

The active species in $B(C_6F_5)_3$-activated metallocene catalysts is an ion pair, consisting of an electron-deficient cation, such as $[Cp_2ZrMe]^+$, stabilised by a weakly coordinating anion, here $[MeB(C_6F_5)_3]^-$. One aspect of our research recently has been the attempt of building the Lewis acidic activator function into the metallocene precursor complex, in an effort to synthesise "self-activating" systems. The principle is illustrated 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 $CpTiCl_3$ / $AlMe_3$ 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 $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ with $Cp\text{-}B(C_6F_5)_2$.[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 $Ar\text{-}B(C_6F_5)_2$, $Ar = 3,5\text{-}F_2C_6H_3 > Ph > 3,5\text{-}Me_2C_6H_3$.[7]



Scheme 2

The reaction of **1** with 1 equivalent of $LiNHBu^t$ gives $[Cp^BTiCl(\mu\text{-}NBu^t)]_2$ (**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 $B(C_6F_5)_3$ (δ 60.1, $CDCl_3$). By contrast, the reaction of **1** with 2 equivalents of $LiNHBu^t$ affords $[Cp^BTiCl(\mu\text{-}NBu^t)(H_2NBu^t)]_2$ (**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



(1)

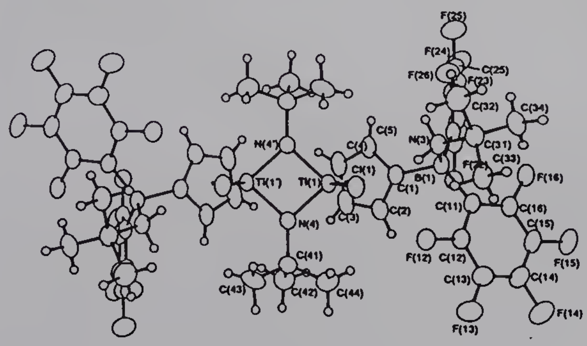
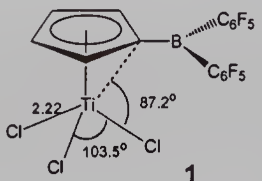


Fig. 2 Molecular structure of **4**.

Different structural motifs are found when **1** is reacted with LiCp or LiInd, to give $(Cp^B)CpTiCl_2$ (**5**) and $(Cp^B)(Ind)TiCl_2$. (**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 $[ClB(C_6F_5)_3]^-$ [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 μ-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-OH_2 distance in $[Cp^*{}_2Ti(OH)(OH_2)]^+\cdot 2THF$, 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).



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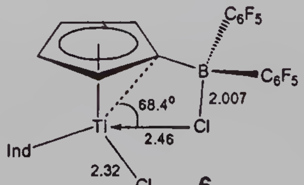

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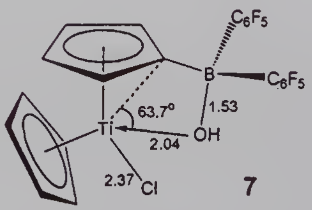

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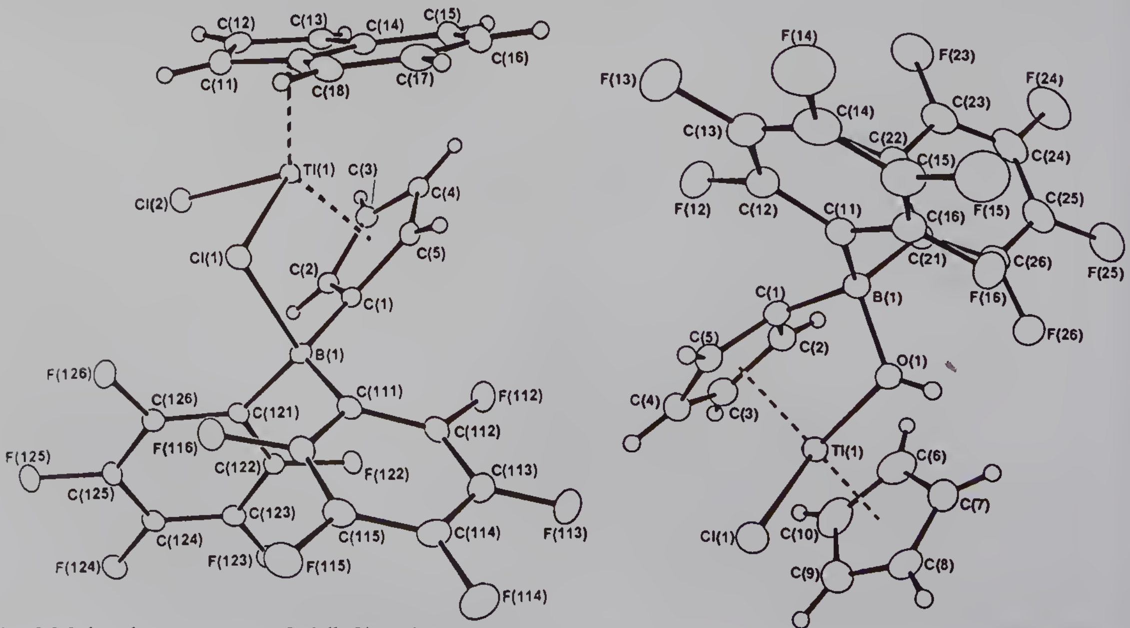
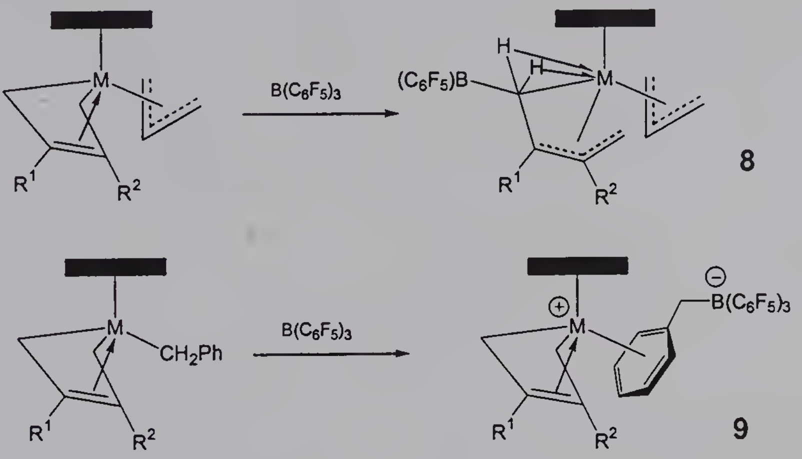


Fig. 3 Molecular structures of **6** (left) and **7**.

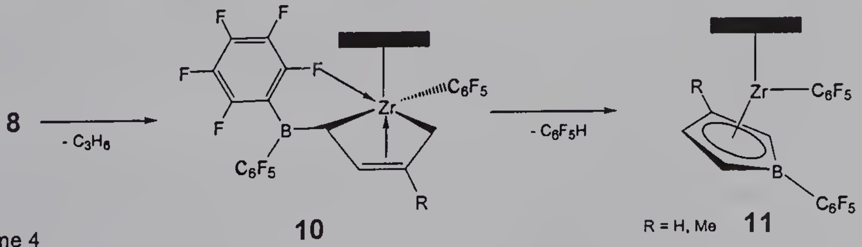
2. Boryldiene and Borole Complexes

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(η^3-allyl)(η^4-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 = Zr or Hf, Cp” = 1,3-$C_5H_3(SiMe_3)_2$, diene = 1,3-butadiene, isopene, or 2,3-dimethylbutadiene].[11] On the other hand, the benzyl complexes Cp”M(CH_2Ph)(η^4-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.



Scheme 3

Compound **8** is a stabilised version of the bis(allyl) cation $[CpZr(allyl)_2]^+$, 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]



Scheme 4

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**·Et_2O. The structure of Cp”Zr(C_6F_5)(η^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”).

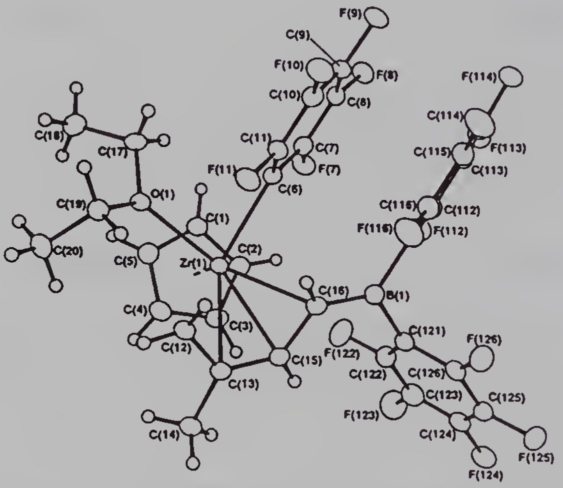


Fig. 4 Molecular structure of Cp”Zr(C_6F_5)(η^5-$C_4H_4BC_6F_5$)(OEt_2) (**11**).

The borole complexes Cp”Zr(C_6F_5)(η^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**·Et_2O are very labile and are quantitatively dissociated in C_6D_6 at 25°C. The presence of stoichoimetric 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(allyl)(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 $(Cp^R)Zr(C_6F_5)\{CH_2C(Me)CH_2CHB(C_6F_5)_2\}$ in high yields as deep-red crystalline solids. Unlike the Cp" and C_5Me_5 analogues[11,12] they are able to form ether adducts. As the structure of $CpZr(C_6F_5)\{CH_2C(Me)CH_2CHB(C_6F_5)_2\}(OEt_2)$ (**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.

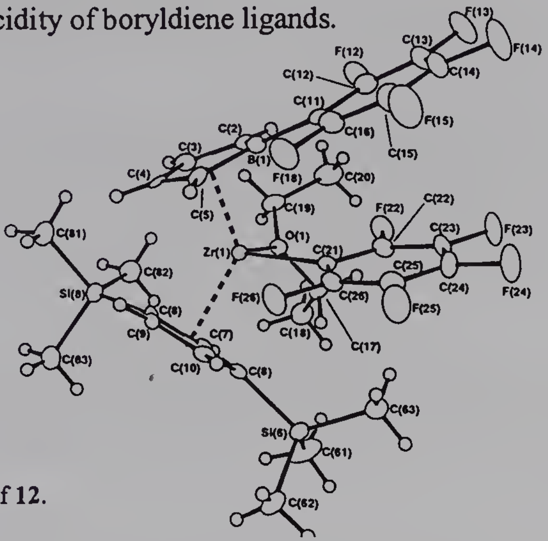
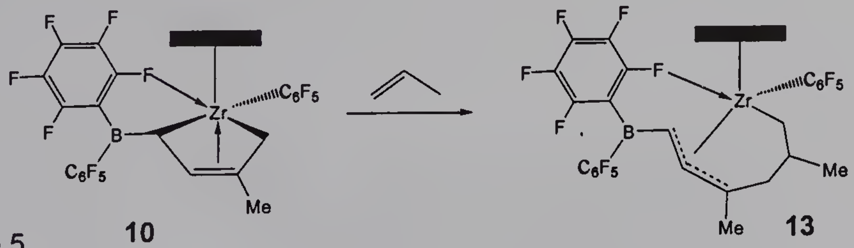


Fig. 5 Molecular structure of **12**.

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.

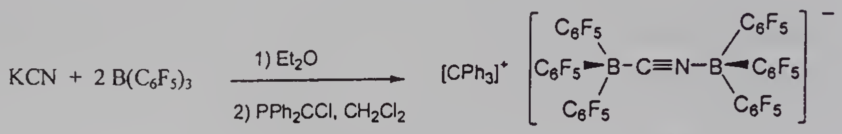


Scheme 5

3. New Borate Anions for Olefin Polymerisations

As stated in the Introduction, borates such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ 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 $B(C_6F_5)_3$ and anions X^-, where X can bind more than one $B(C_6F_5)_3$. Thus, complex anions of the type $[X(B(C_6F_5)_3)_n]^{m-}$ can be envisaged, where n>m and the charge per B is m/n.

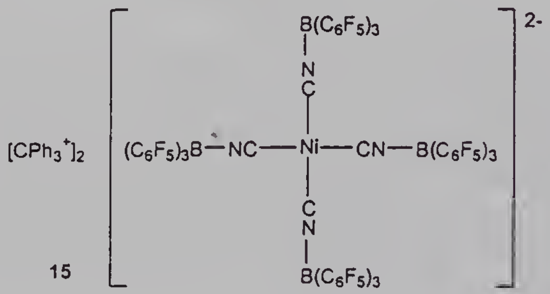
Treatment of a suspension of KCN in Et_2O with 2 equivalents of $B(C_6F_5)_3$ affords $K[CN\{B(C_6F_5)_3\}_2]$. Stirring with Ph_3CCl in dichloromethane affords orange crystalline $CPh_3[CN\{B(C_6F_5)_3\}_2]$ (**14**) in a one-pot procedure (equ. 2).[19]



14 (2)

Unlike $CPh_3[B(C_6F_5)_4]$, **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 LiC_6F_5, a potentially dangerous compound that has been known to detonate violently on warming above -20°C. It is characterised by two ^{11}B resonances, at δ -11.94 and -21.68. The anion is structurally related to $[H_3B\text{-}CN\text{-}BH_3]^-$ [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, $K_2[Ni(CN)_4]$ reacts with $B(C_6F_5)_3$ to give colourless $K_2[Ni\{CNB(C_6F_5)_3\}_4]$, which on treatment with Ph_3CCl gives orange crystalline $[CPh_3]_2[Ni\{CNB(C_6F_5)_3\}_4]$ (**15**).[19]



15

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

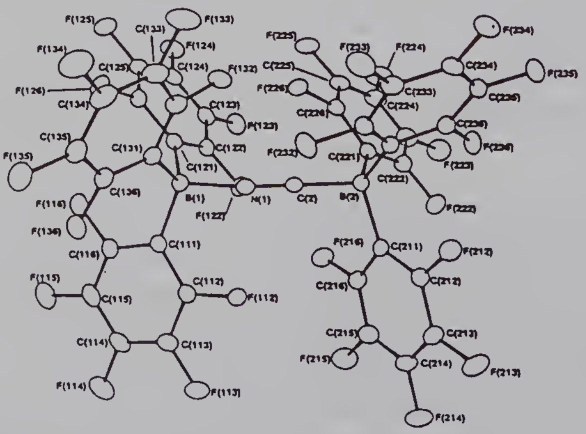


Fig. 6 Molecular structure of $CPh_3[CN\{B(C_6F_5)_3\}_2]$ (14). Selected bond lengths (Å) and angles (°): N(1)-B(1) 1.593(2), C(2)-B(2) 1.583(2), N(1)-C(2) 1.144(2), B-C(111) 1.636(2), C(2)-N(1)-B(1) 173.55(14), N(1)-C(2)-B(2) 174.50(14).

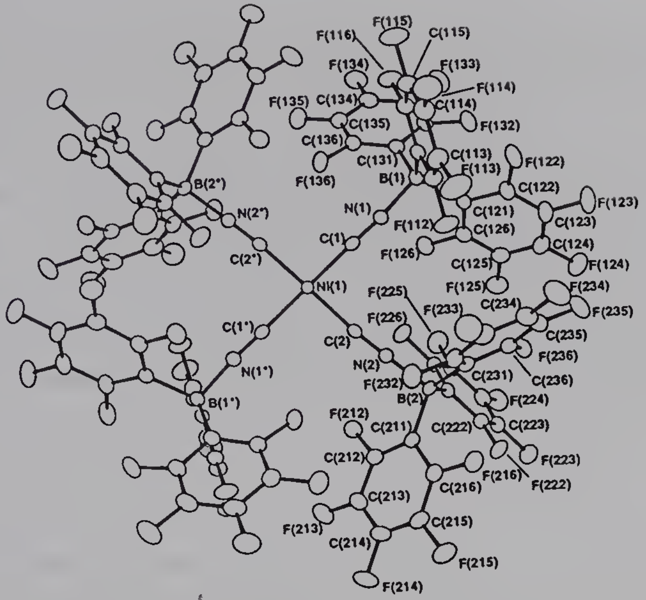


Fig. 7 Molecular structure of $CPh_3[Ni\{CNB(C_6F_5)_3\}_4]$ (**15**). Selected bond lengths (Å) and angles (°): Ni-C(1) 1.855(2), B(1)-N(1) 1.574(2), C(1)-N(1) 1.145(2), C(1)-Ni-C(2) 87.15(7), Ni-C(1)-N(1) 176.5(2), C(1)-N(1)-B(1) 174.8(2).

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 $\{(\text{mol Zr})\cdot h\cdot \text{bar}\}^{-1}$, although some problems were apparent with the comparatively low solubility of **15** in toluene. Solutions of *rac*-$Me_2Si(Ind)_2ZrMe_2$ activated with **14** (1:1) under the same conditions gave significantly higher productivities, 18 – 20 x 10^6 g PE $\{(\text{mol Zr})\cdot h\cdot \text{bar}\}^{-1}$. 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*-$Me_2Si(Ind)_2ZrMe_2$ /**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	Cp_2ZrCl_2[d]	MAO	90	360		283		
6	$Et(Flu)_2ZrCl_2$[e]	MAO	100	60		352	401	2.1

[a] 5 L reactor, 3 L toluene, $AlBu^i_3$ 1.0 mmol.. Reaction terminated by methanol injection.

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

[c] 1 L autoclave, 500 cm^3 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*-$Me_2Si(Ind)_2ZrMe_2$ activated with 1.0 µmol **14**, the temperature quickly rose form 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 6.7×10^{-8} *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 760×10^6 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*-$Me_2Si(Ind)_2ZrMe_2$ with $AlBu^i_3$ / **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.

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References

1. A.G. Massey, A.J. Park and F.G.A. Stone, *Proc. Chem. Soc. [London]*, 1963, 212; A.G. Massey and A.J. Park, *J. Organomet. Chem.* 1964, **2**, 245; J.L.W. Pohlmann and F.E. Brinckmann, *Z. Naturforsch. B*, 1965, **20b**, 5.
2. X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.* 1991, **113**, 3623.
3. Reviews: M. Bochmann, *Topics in Catal.* 1999, **7**, 9; L. Luo and T.J. Marks, *ibid.*, 1999, **7**, 97; W.E. Piers, Y. Sun and L.W.M. Lee, *ibid.*, 1999, **7**, 133.
4. S. O'Hara and M. Thornton-Pett, unpublished results. *Crystal data:* $C_{22}H_{12}BF_{15}O_2$, M = 604.13, monoclinic, $P2_1/a$, $a = 14.5073(14)$, $b = 12.3193(9)$, $c = 14.896(2)$ Å, β = 117.061(9)°, V = 2370.7(5) Å^3, Z = 4, D_c = 1.693 g cm^{-3}. 3936 independent

reflections were collected (Nonius KappaCCD diffractometer, Mo-Kα, 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), $S = 1.054$.

5. The trihydrate, $B(C_6F_5)_3 \cdot H_2O \cdot 2H_2O$, has recently been reported: A.A. Danopoulos, J.R. Galsworthy, M.L.H. Green, S. Cafferkey, L.H. Doerrer and M.B. Hursthouse, *Chem. Commun.* 1998, 2529.
6. R. Duchateau, S.J. Lancaster, M. Thornton-Pett and M. Bochmann, *Organometallics,* 1997, **16**, 4995.
7. P.A. Deck, C.L. Beswick and T.J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1772.
8. S.J. Lancaster, S. Al-Benna, M. Thornton-Pett and M. Bochmann, manuscript in preparation.
9. B.E. Bosch, G. Erker, R. Fröhlich and O. Meyer, *Organometallics* 1997, **16**, 5449.
10. M. Bochmann, A.J. Jaggar, L.M. Wilson, M.B. Hursthouse and M. Motevalli, *Polyhedron* 1989, **8**, 1838.
11. G. Jiménez Pindado, M. Thornton-Pett, M. Bouwkamp, A. Meetsma, B. Hessen and M. Bochmann, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 2358; G. Jiménez Pindado, M. Thornton-Pett, and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 3115.
12. G. Jiménez Pindado, M. Thornton-Pett, M. B. Hursthouse, S. J. Coles and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1999, 1663.
13. See for example: R. Gomez, M.L.H. Green and J.L. Haggit, *J. Chem. Soc., Dalton Trans.*, 1996, 939; X. Yang, C.L. Stern and T.J. Marks, *J. Am. Chem. Soc.* 1994, **116**, 10015; V.K. Dioumaev and J.F. Harrod, *Organometallics* 1997, **16**, 2798; J.D. Scollard, D.H. McConville and S.J. Rettig, *Organometallics* 1997, **16**, 1810.
14. M. Bochmann and M.J. Sarsfield, *Organometallics* **1998**, *17*, 5908.
15. G. Jiménez Pindado, Simon J. Lancaster, M. Thornton-Pett, and M. Bochmann, *J. Am. Chem. Soc.* 1998, **120**, 6816.
16. G.E. Herberich, B. Hessner, W. Boveleth, H. Lüthe, R. Saive and L. Zelenka, *Angew. Chem. Int. Ed. Engl.* 1983, **22**, 1024; G. E. Herberich, T. Carstensen, N. Klaff and M. Neuschütz, *Chem. Ber.* 1992, **125**, 1801; G.E. Herberich, H.J. Eckenrath and U. Englert, *Organometallics* 1997, **16**, 4292 and 4800.
17. G. Jiménez Pindado, M. Corradi, M. Thornton-Pett and M. Bochmann, unpublished results.
18. The formation of borole complexes from boryldiene precursors has also been observed for C_5Me_5 complexes but could not be isolated: B. Hessen, personal communication.
19. S.J. Lancaster, D.A. Walker, M. Thornton-Pett and M. Bochmann, *Chem. Commun.*, in press.
20. R.C. Wade, E.A. Sullivan, J.R. Berschield and K.F. Purcell, *Inorg. Chem.* 1970, **9**, 2146.
21. H.G. Alt and E. Samuel, *Chem. Soc. Rev.* 1998, **27**, 323; G.J.P. Britovsek, V.C. Gibson and D.F. Wass, *Angew. Chem. Int. Ed.* 1999, **38**, 429.

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

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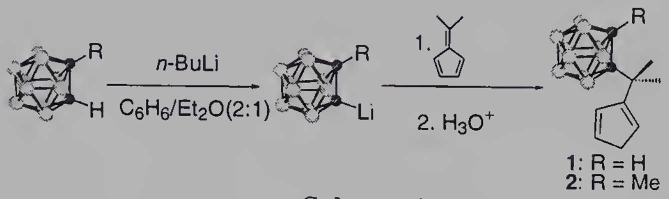
1 INTRODUCTION

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 materials[4] and special polymers.[5] Nonetheless, their use in developing functional materials such as olefin polymerization catalysts[6] and luminescent materials[7] is still limited.

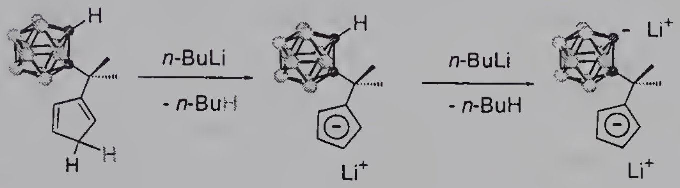
Olefin transformations are one of the most important reactions in the chemical industry. Among the many factors which influence the performance of homogeneous catalysts for olefin polymerization, the ligand is probably the most important, since it controls the molecular geometry of the catalysts which 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 $HCpCMe_2CB_{10}H_{10}CH$ (H_2.**1**) and $HCpCMe_2$-$CB_{10}H_{10}CMe$ (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-$(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2M$, $(\eta^5\text{-}Cp^*)(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)MCl$ and $(\eta^5\text{-}Cp^*)(\eta^5\text{-}CpCMe_2CB_{10}H_{10}CR)MCl_2$ (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 H_2.**1** and H.**2** were prepared as colorless crystalline solids in high isolated yields according to the reaction Scheme 1. The coupled use[8] of one fold amount of n-BuLi and benzene/Et_2O turned out to be efficient compared to the use of $LiC_2B_{10}H_{10}SiMe_2$(t-Bu),[9] or $Li_2C_2B_{10}H_{10}$,[10] since the former is unreactive towards 6,6-dimethylfulvene and the latter leads to low yield. The attempted cage degradation of H_2.**1** and H.**2** with bases such as KOH/EtOH, (n-Bu)$_4$NF 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_2.**1** undergoes stepwise lithiation with *n*-BuLi as shown in Scheme 2.



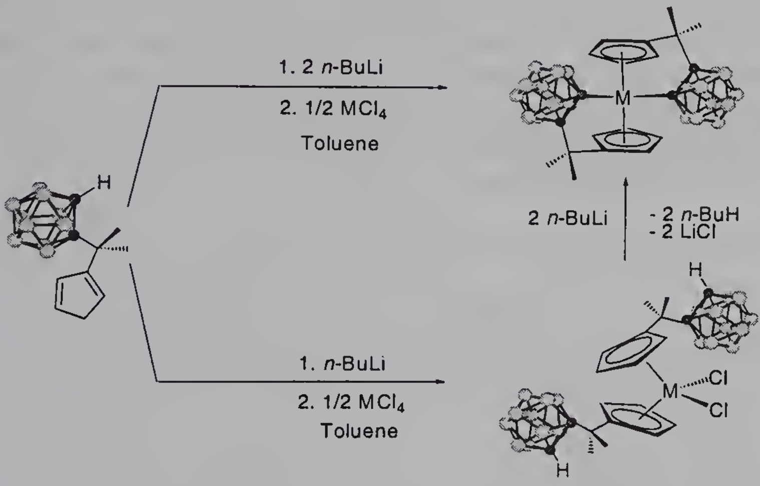
Scheme 1



Scheme 2

3 HOMOLEPTIC METALLOCENES WITH C_2 SYMMETRY

Treatment of the di-lithium salt of **1**, $Li_2[CpCMe_2CB_{10}H_{10}C]$, with MCl_4 (M = Ti, Zr, Hf) in a 2:1 ratio in toluene affords new group 4 metallocene compounds rac-(η^5:η^1-$CpCMe_2$-$CB_{10}H_{10}C)_2M$ (**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 (η^5-$CpCMe_2CB_{10}H_{10}CH)_2MCl_2$ 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-metallocene geometry, involving a distorted-tetrahedral arrangement of ligands around the metal with a Cp_{cent}-M-Cp'_{cent} angle in the range of 128-129° and Cl-M-Cl' angle between 105.8-110.8°, 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).*

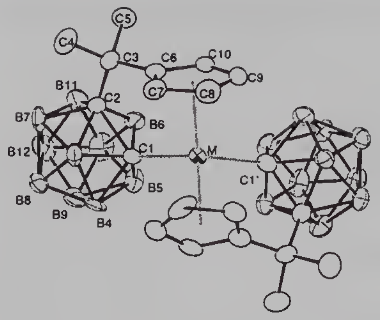


Figure 1 *Perspective view of 3*

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

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 10^4. 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 tests[12] 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 regents or cationic center generators such as MAO, AlR_3 and $[Ph_3C]^+[B(C_6F_5)_4]^-$ 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 ^{11}B 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.

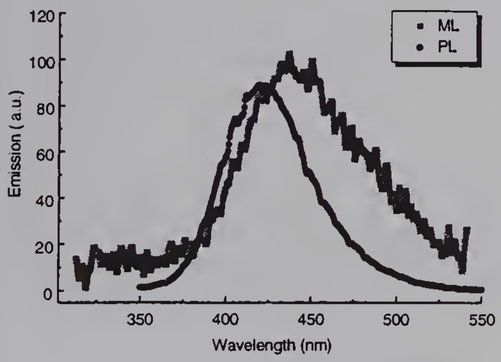


Figure 2 *PL and ML of 3c*

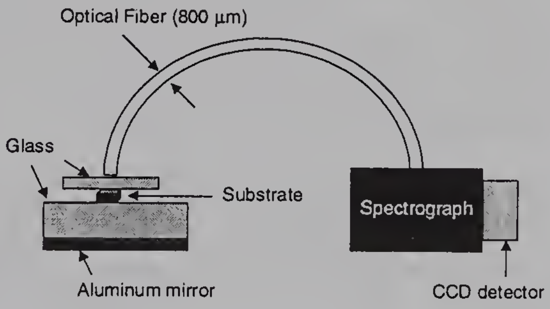


Figure 3 *Schematic layout for ML detection*

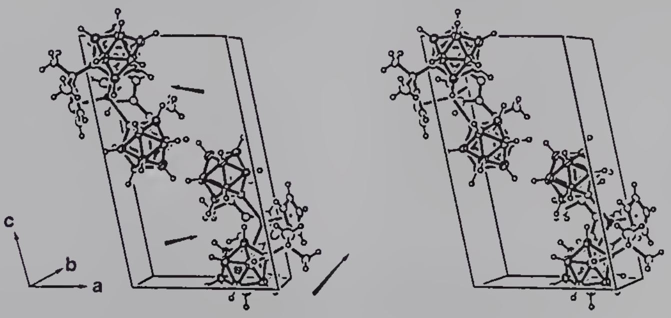


Figure 4 *Stereoview of crystal packing diagram showing molecular (small arrow) and net dipole moment (large arrow) vectors for the isostructural systems 3*

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/m^2 was achieved for 3% **3c** in PVK.

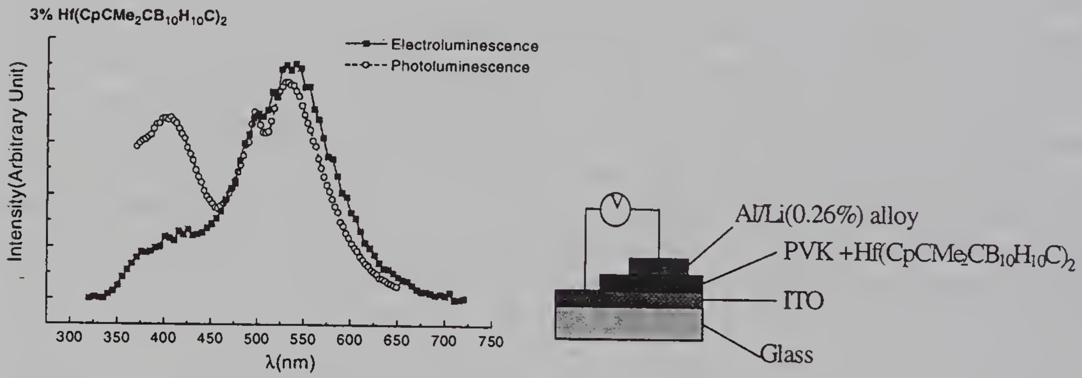
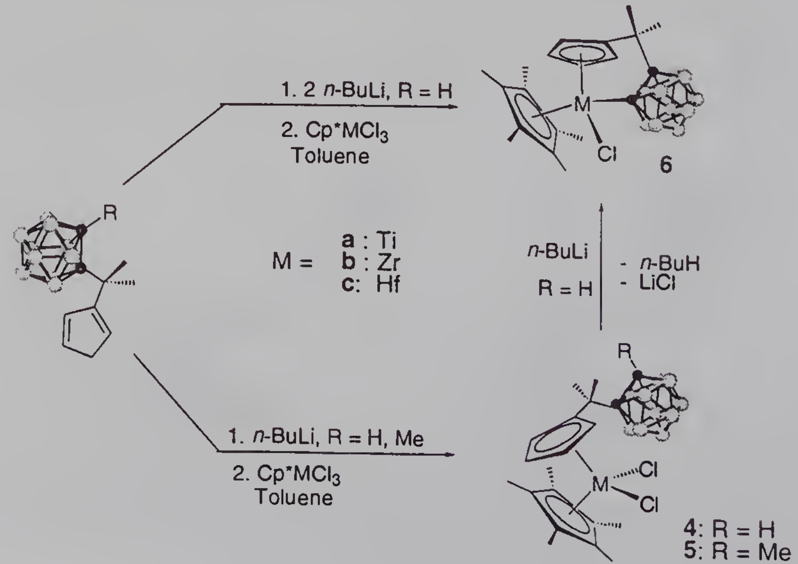


Figure 5 *PL and EL spectra of 3% 3c in PVK and the schematic drawing of the device*

4 HETEROLEPTIC METALLOCENES

Three sets of new heteroleptic metallocenes containing the C_2B_{10} cage unit, $(\eta^5\text{-Cp*})(\eta^5\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{CR})\text{MCl}_2$ (M = group 4 metal; R = H, **4;** R =Me, **5)** and $(\eta^5\text{-Cp*})(\eta^5{:}\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})\text{MCl}$ **(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.

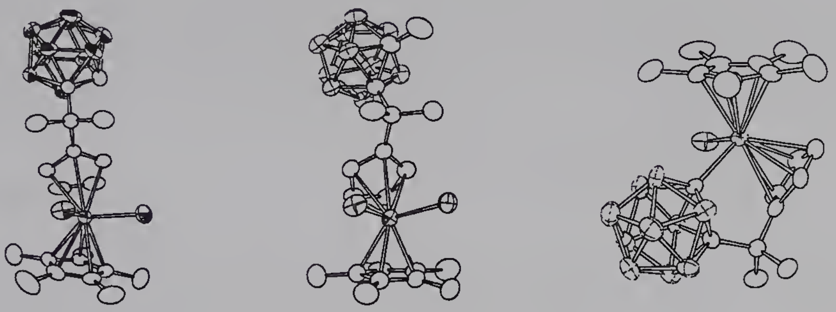


Figure 6 *Molecular structures of* *4* *(left),* *5a* *(middle) and* *6* *(right)*

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.	Tp(°C)	Time(min)	Crude PE(g)	A[c]	Tm(°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• 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 Tm 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(℃)	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^{-5}mol, MMAO (mol of Al = 1500 x mol of Ti) in 100 ml Toluene. 1hr, 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** : $C_5Me_4CMe_2IndTiCl_2$
{1atm, 50℃, MAO (mol of Al = 2000x mol of Ti), 1hr}

d) Activity = kg PP / mol Ti•hr•atm

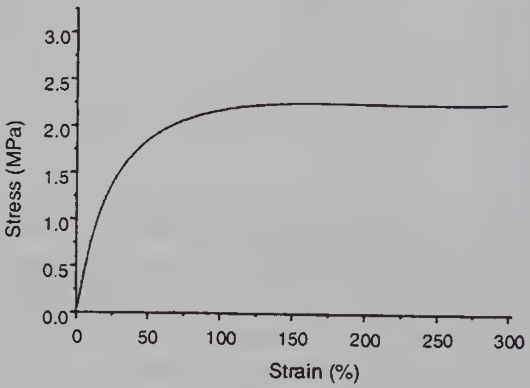
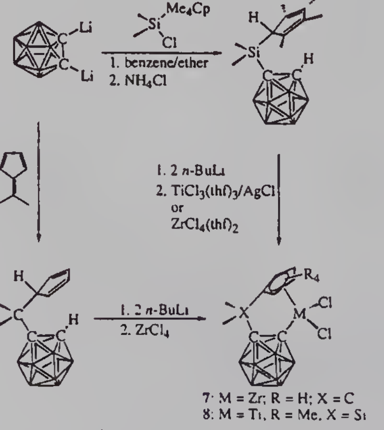


Figure 7 *Stress-strain curve of PP*

5 CGC DERIVATIVES FROM *o*-CARBORANE

Carborane complexes Zr(η^5:η^1-CpCMe$_2$CB$_{10}$H$_{10}$C)Cl$_2$ (**7**) and M(η^5:η^1-C$_5$Me$_4$SiMe$_2$CB$_{10}$H$_{10}$C)Cl$_2$ (M = Ti, **8**; Zr) of a constrained-geometry catalyst (CGC) type[14] 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

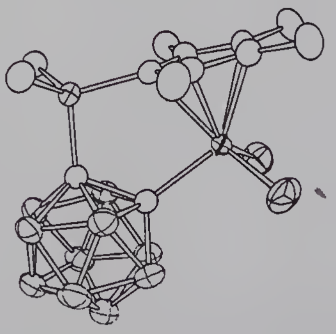


Figure 8 *Molecular structure of 8*

6 CONCLUSIONS

The versatile complexation behavior of new *ansa*-type cyclopentadienyl o-carboranyl ligands $HCpCMe_2CB_{10}H_{10}CH$, $HCpCMe_2CB_{10}H_{10}CMe$ and $HC_5Me_4SiMe_2CB_{10}H_{10}CH$ 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.

References

1. (a) I. H. A. Badr, M. Diaz, M. F. Hawthome, L. G. Bachas, *Anal.Chem.*, 1999, **71,** 1371. (b) M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.*, 1997, **30,** 267. (c) M. F. Hawthorne, A. Varadarajan, C. B. Knobler, S. Chakrabarti, R. J. Paxton, B. G. Beatty, F. L. Curtis, *J. Am. Chem. Soc.*, 1990, **112,** 5365. (d) M. F. Hawthorne, A. Varadarajan, C. B. Knobler, S. Chakrabarti, R. J. Paxton, B. G. Beatty, F. L. Curtis, J. *Am. Chem. Soc.*, 1990, **112,** 5365. (e) H. Hatanaka, W. H. Sweet, K. Sano, F. Ellis, *Pure Appl. Chem.*, 1991, **63,** 373.
2. (a) S. Lee, J. Mazurowski, G. Ramseyer, P. A. Dowben, *J. Appl. Phys.*, 1992, **72,** 4925. (b) S. Lee, P. A. Dowben, *Appl. Phys.*, 1994, **A58,** 223. (c) D, Byun, S. D.Hwang, P. A. Dowben, F. K. Perkin, F. Filips, N. J. Ianno, *Appl. Phys. Lett.*, 1994, **64,** 1968. (d) S. D. Hwang, D. Byun, N. J. Ianno, P. A. Dowben, H. R. Kim, *Appl. Phys. Lett.*, 1996, **68,** 1495. (e) R K. Perkins, R. A. Rosenberg, S. Lee, P. A. Dowben, *J. Appl. Phys.*, 1991, **69,** 4103.
3. (a) M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 1993, **32,** 950. (b) H. M. Colquhoun, P. L. Herbertson, K. Wade, I. Baxter, D. J. Williams, *Macromolecules,* 1998, **31,** 1694. (c) C. Mazal, A. J. Paraskos, J. Michl, *J. Org. Chem.*, 1998, **63,** 2116.
4. (a) K. Base, M. T. Tierney, A. Fort, J. Muller, M. W. Grinstaff, *Inorg. Chem.*, 1999, **38,** 287. (b) W. Fendrich, J. E. Harvey, P. Kaszynski, *Inorg. Chem.*, 1999, **38,** 408.
5. (a) A. G. Douglass, K. Czuprynski, M. Mierzwa, P. Kaszynski, *J. Mater Chem.*, 1998, **8(11),** 2391. (b) A. G. Douglass, K. Czuprynski, M. Mierzwa, P. Kaszynski, *Chem. Mater,* 1998, **10**, 2399.
6. (a) D. J. Crowther, D. C. Swenson, R. F. Jordan, *J. Am. Chem. Soc.*, 1995, **117,** 10403. (b) D. E. Bowen, R. F. Jordan, *Organometallics,* 1995, **14,** 3630. (c) R. Uhrhammer, D. J. Crowther, J. D. Olson, D. C. Swenson, R. F. Jordan, *Organometallics,* 1992, **11,** 3908.
7. (a) Y Hamada, *IEEE Trans. Elec. Dev.*, 1997, **44,** 8, 1208. (b) S. Miyata, H. S. Nalwa, *Organic Electroluminescent Materials and Devices,* 1997.
8. R. N. *Grimes, Carboranes;* Academic Press: New York, 1970.
9. F. A. Gomez, S. E. Johnson, M. F. Hawthorne, *J. Am. Chem. Soc.* 1991, **113,** 5915.
10. F. A. Gomez, M. F. Hawthorne, *J. Org. Chem.* 1992, **57,** 1384.
11. H. Yasuda, H. Tamai, *Prog. Polym. Sci.* 1993, **18**, 1097.
12. J. A. Ewen, *J. Am. Chem. Soc.* 1984, **106**, 6355.
13. (a) H. Longchambon, *Bull. Soc. Fr Mineral Cristallogr.*, 1925, **48**, 130. (b) M. C. Hoff, C. E. Boord, *J. Am. Chem. Soc.*, 1950, *72*, 2770.
14. Dow Chemical Co. European Patent 0416815A2,1990.

Cationic Metallocenes Derived from Cyclic Organohydroborate Metallocene Complexes

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1 INTRODUCTION

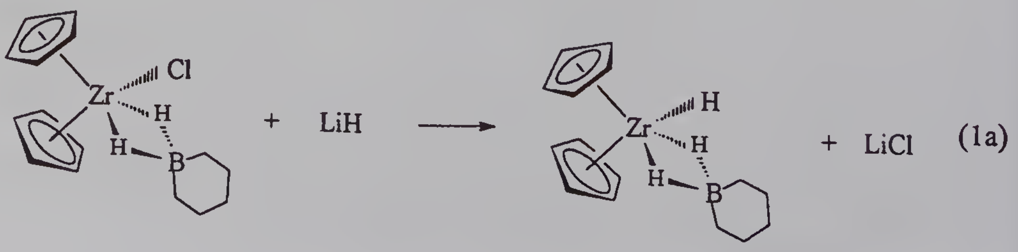
While many metal tetrahydroborate complexes have been prepared and studied,[1] little is known concerning metal organohydroborate chemistry.

Recently, we investigated the chemistry of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, 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 $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$,[4] a stable and relatively inert organodiborane. In addition to the hydride transfer ability, an unique ring disproportionation reaction of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ was observed in its reactions with zirconocene and hafnocene dichlorides to produce the double hydrogen-bridged cyclopentaborate derivatives $Cp_2MCl\{(\mu\text{-}H)_2BC_4H_8\}$ (M = Zr, Hf).[5] The similar complexes, $Cp_2MCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ (M = Zr, Hf),[6] were also prepared from the reactions of Cp_2MCl_2 (M = Zr, Hf) with $[H_2BC_5H_{10}]^-$. This anion simply functions as a bidentate chelating ligand to bond to the metal center.

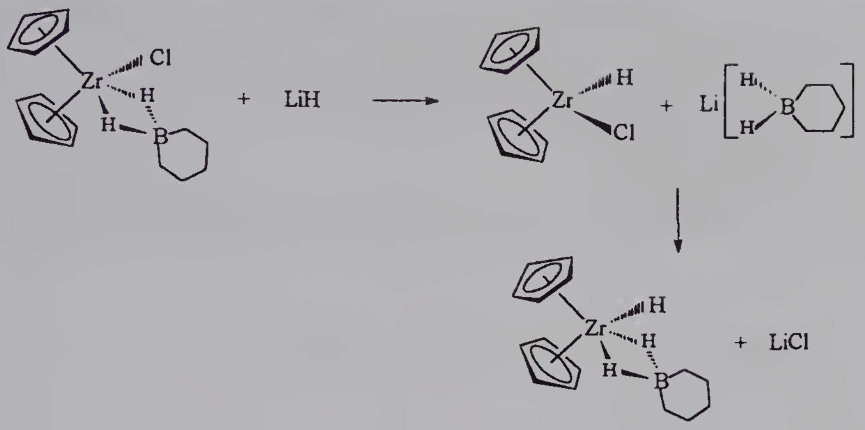
2 PREPARATION OF $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ AND $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$

Reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ with LiH produces $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$[7] (Reaction (1)). Two parallel reaction pathways might occur. In one pathway, Reaction (1a), nucleophilic displacement of Cl^- by H^- would produce $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ 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 $[H_2BC_5H_{10}]^-$, which then react with each other to form $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$. Indeed, $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ was formed in a separate reaction of Cp_2ZrClH with $K[H_2BC_5H_{10}]$.

The six numbered ring di-substituted complex, $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$[7] was prepared

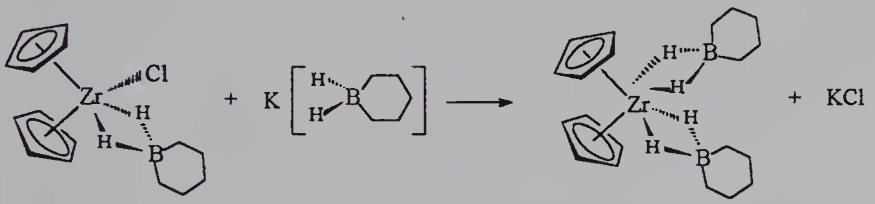


(1a)



(1b)

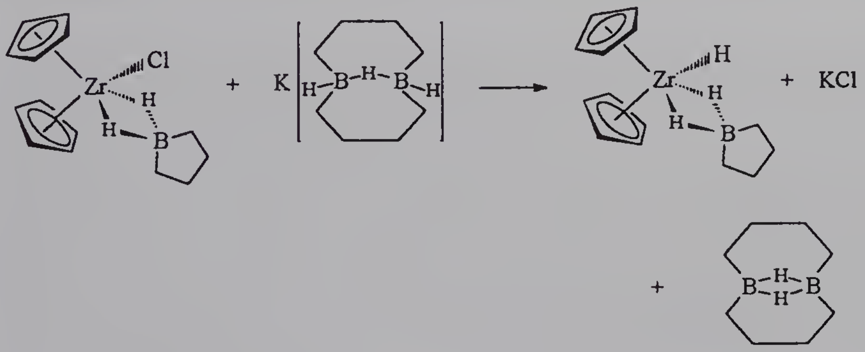
from the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ with a second mole of $[H_2BC_5H_{10}]^-$ (Reaction (2)). The solid state structure of $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$ (Fig. 1) indicates each of the two organohydroborate rings connects to the zirconium through two bridge hydrogens.



(2)

3 FORMATION OF $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$

The reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with a second mole of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ produces $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$[8] (Reaction (3)). For the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$



(3)

with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ two possible products were considered. One product is that actually isolated, $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, formed through hydride transfer from the organodiborate to zirconium to displace the chloride. The other possible product considered, $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$, but not observed, would have been formed through disproportionation of the organodiborate anion, $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, as observed in the preparation of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$.[5] Possible kinetic and thermal factors that resulted in the preferential formation and isolation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ rather than $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$ were considered. Scheme 1 presents possible pathways for the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$. The first step of the reaction might involve the coordination of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ to the zirconium center through a single hydrogen bond. However, the presence of the borocyclopentane ring of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ might sterically prevent or significantly hinder the $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ 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 $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$, the anion $Li[H_2BC_4H_8]$ was chosen as an alternative reagent for the reaction with $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ in an attempt to prepare $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$. This reaction did not yield $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$, but produced $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ as the final isolated product.

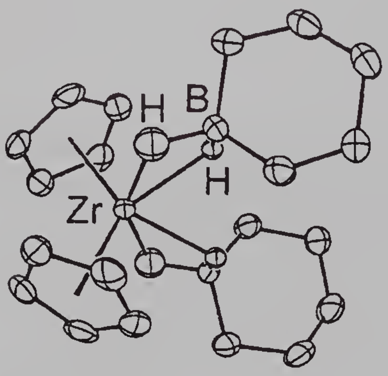
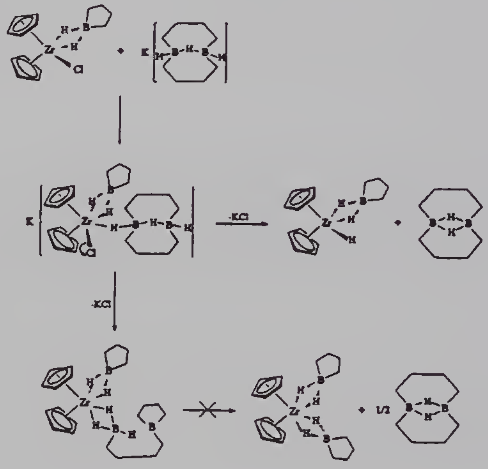


Figure 1 *Molecular structure of* $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$



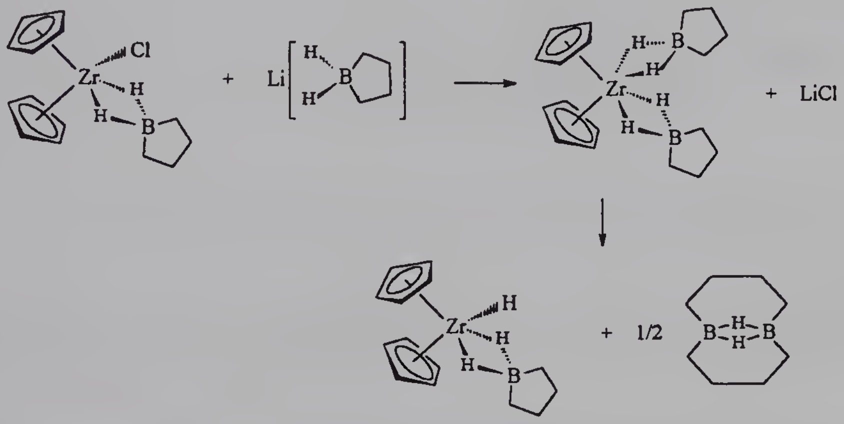
Scheme I

Upon reaction of $Li[H_2BC_4H_8]$ with $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ in THF, time-elapsed $^{11}B\{^1H\}$ NMR spectra[8] 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 $\{B_2(C_4H_8)H_2\}$, and the signal at 30.2 ppm corresponds to $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$. If $[H_2BC_4H_8]^-$ functioned solely as a hydride transfer agent, then $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ and $\{B_2(C_4H_8)H_2\}$ 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 $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$. 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 $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$. However, since the NMR signal diminishes with time, it appears that this compound is unstable and disproportionates into $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ and $\{B_2(C_4H_8)H_2\}$ as described in Reaction (4).

While Scheme I suggests that the pathway for the formation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ is more favorable than that for the formation of $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$, based upon steric considerations, consideration of Reaction (4) suggests that this compound is also thermally less stable than $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$.

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

Compd.	δ	Compd.	δ
$Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$	16.7	$Cp_2ZrCl\{(\mu-H)_2BC_5H_{10}\}$	13.7
$Cp_2Zr(CH_3)\{(\mu-H)_2BC_4H_8\}$	20.1	$Cp_2Zr(CH_3)\{(\mu-H)_2BC_5H_{10}\}$	18.2
$Cp_2Zr(Ph)\{(\mu-H)_2BC_4H_8\}$	22.0	$Cp_2Zr(Ph)\{(\mu-H)_2BC_5H_{10}\}$	19.4
$Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_4H_8\}$	22.1	$Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_5H_{10}\}$	19.4
$Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$	30.9	$Cp_2ZrH\{(\mu-H)_2BC_5H_{10}\}$	28.2
		$Cp_2Zr\{(\mu-H)_2BC_5H_{10}\}_2$	24.6



(4)

4 VARIABLE-TEMPERATURE BEHAVIOR OF $Cp_2ZrH\{(\mu-H)_2BC_5H_{10}\}$ AND $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$

Intramolecular hydrogen exchange among Cp hydrogens, Zr-H terminal hydride, and Zr-H-B bridge hydrogens was observed in the zirconium hydride complexes, $Cp_2ZrH\{(\mu-H)_2BC_5H_{10}\}$[7] and $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$, at elevated temperature.

Proton NMR spectra of $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$ 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, $Cp_2ZrD\{(\mu-D)_2BC_4H_8\}$ was prepared from the reaction of $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ with excess LiD (Reaction (5)). The ^2H NMR spectrum of $Cp_2ZrD\{(\mu-D)_2BC_4H_8\}$ 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 $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$.

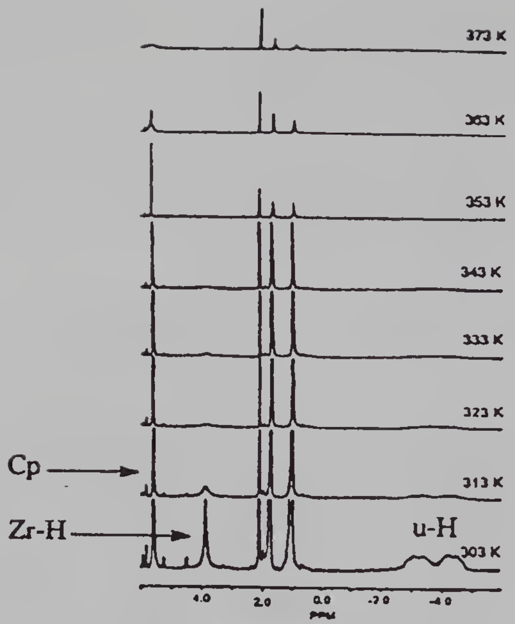
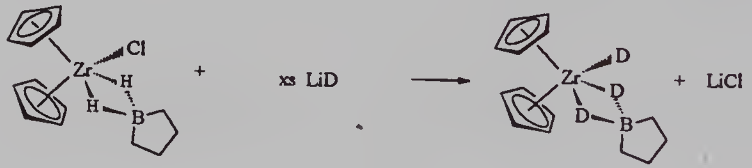


Figure 2 *Variable-temperature ^1H NMR spectra of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$*



(5)

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

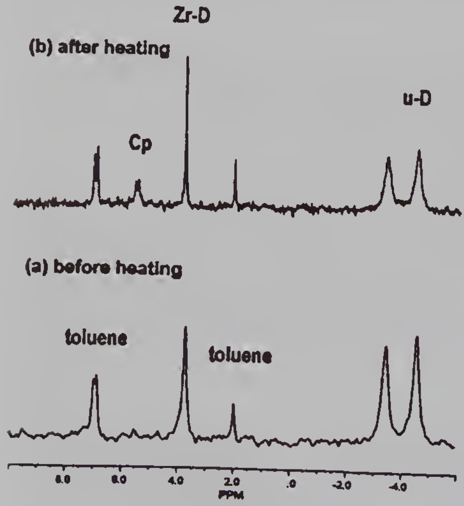
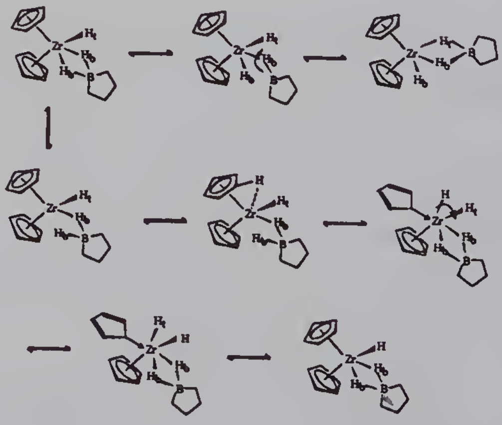


Figure 3 *^2H NMR spectra of $Cp_2ZrD\{(\mu\text{-}D)_2BC_4H_8\}$ in toluene (a) before heating. (b) after heating at 85 °C for 10 min.*

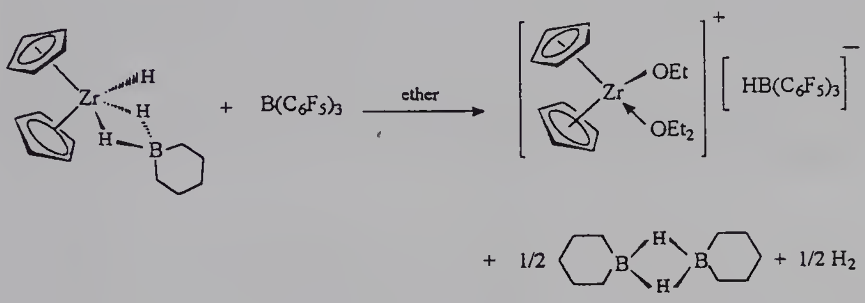


Scheme II *Possible mechanism for the hydrogen exchange of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$*

exchange of the terminal hydride, a single hydrogen bridge intermediate with one broken B-H_b 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 $\eta^5 \rightarrow \eta^1 \rightarrow \eta^5$ bonding modes. Line shape analyses of the exchange process for the terminal and bridge hydrogens have been reported.[9]

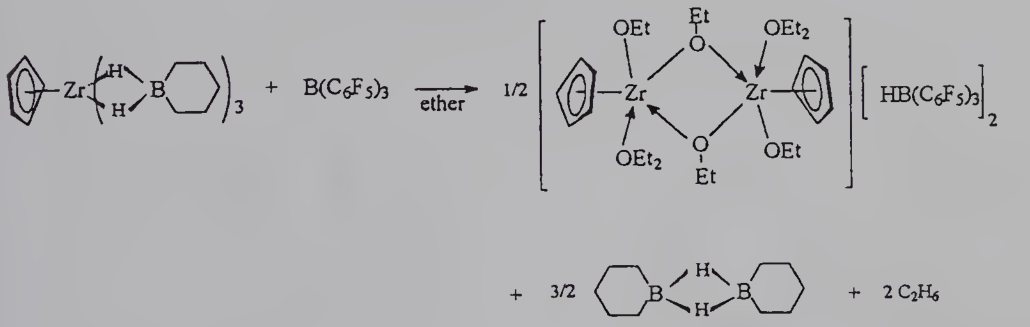
5 FORMATION OF $[Cp_2Zr(OC_2H_5)(OC_4H_{10})][HB(C_6F_5)_3]$ AND $[CpZr(OC_4H_{10})(OC_2H_5)(\mu\text{-}O)C_2H_5]_2[HB(C_6F_5)_3]_2$

The ethoxyl substituted cation $[Cp_2Zr(OC_2H_5)(OC_4H_{10})]^+$ was formed from the reaction of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ with $B(C_6F_5)_3$ in diethyl ether (Reaction (6)) in which $B(C_6F_5)_3$ serves as a hydride abstracting agent. The solid state structure of the cation is shown in Figure (4).



(6)

The reaction of $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ with $B(C_6F_5)_3$ in diethyl ether produces the dication $[CpZr(OC_4H_{10})(OC_2H_5)(\mu\text{-}O)C_2H_5]_2^{2+}$ (Reaction (7)), an oxygen bridged dimer (Fig. (5)). "Short" Zr-O distances suggest significant back π bonding.



(7)

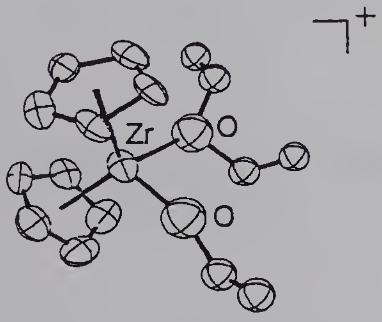


Figure 4 *Molecular Structure of* $[Cp_2Zr(OC_2H_5)(OC_4H_{10})]^+$

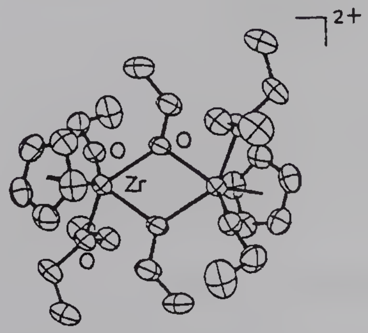
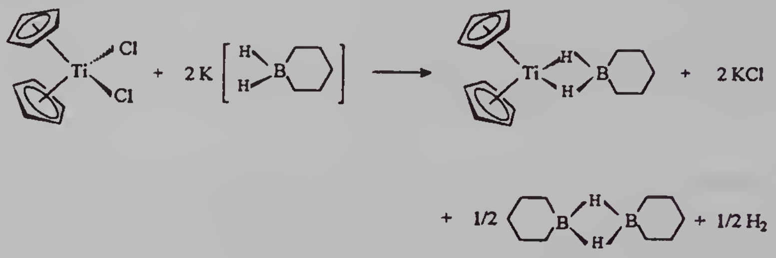


Figure 5 *Molecular Structure of* $[CpZr(OC_4H_{10})(OC_2H_5)(\mu\text{-}O)C_2H_5]_2^{2+}$

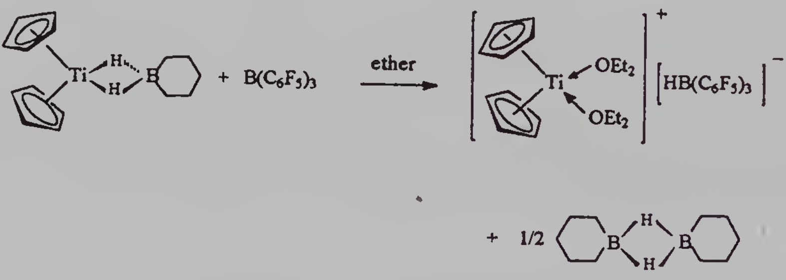
6 $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ AND $[Cp_2Ti(OC_4H_{10})_2][HB(C_6F_5)_3]$

The paramagnetic complex $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ was prepared from the reaction of Cp_2TiCl_2 with $K[H_2BC_5H_{10}]$ (Reaction (8)). In this reaction, titanium was reduced from oxidation state (IV) to (III) The structure of $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ is shown in Figures (6).



(8)

$Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$ reacts with $B(C_6F_5)_3$ in diethyl ether and produces the ether coordinated cation $[Cp_2Ti(OC_4H_{10})_2]^+$ (Reaction (9)). The solid state structure of $[Cp_2Ti(OC_4H_{10})_2][HB(C_6F_5)_3]$ is shown in Figure (7).



(9)

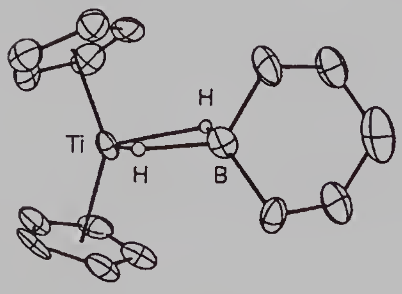


Figure 6 *Molecular structure of* $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$

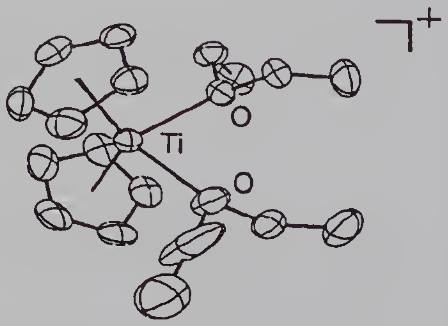


Figure 7 *Molecular structure of* $[Cp_2Ti(OC_4H_{10})_2]^+$

ACKNOWLEDGMENTS

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References

1. (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (b) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. Compounds with Bonds between a Transition Metal and Boron. In *Comprehensive Organometallic Chemistry* ; Wilkinson, G.; Stone, F. G. A,; Abel, E. W.; Eds,; Pergamon Press Inc., New York, 1982; pp 879-945. (c) Barton, L.; Srivastava, D. K. Metallaboranes in *Comprehensive Organometallic Chemistry* ; Wilkinson, G.; Abel, E. W.; Stone, F. G. A.; Eds,; Pergamon Press Inc., New York, 1995; pp 275-372.
2. (a) Clayton, W. R.; Saturnino, D. J.; Corfield, P. W. R.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1973**, 377. (b) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063.
3. Shore, S. G.; Liu, J.; Jordan, G. T., IV; Liu, F. -C.; Meyers, E. A.; Gaus, P. L. Cyclic Organohydroborate Anions as Hydride Transfer Agents in Reactions with Organic and Organometallic Compounds. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: London, 1997; pp 84-91.
4. Young, D. E.; Shore, S. G. *J. Am. Chem. Soc.* **1969**, *91*, 3497.
5. (a) Jordan IV, G. T.; Liu, F. -C.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 5597. (b) Jordan IV, G. T.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1087.
6. Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 496.
7. Liu, F. -C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293.
8. Liu, F. -C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 2169.
9. Chow, A.; Liu, F. -C.; Fraenkel, G.; Shore, S. G. *Magn. Reson. Chem.* **1998**, *36*, S145.

Organolanthanide Compounds Bearing Versatile Ligands

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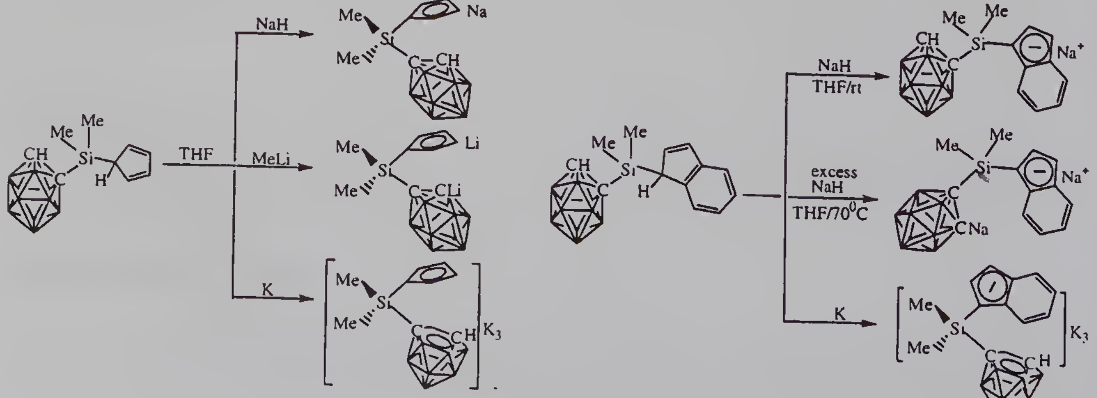
1 INTRODUCTION

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 $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$, by contrast with $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$, 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 $[\eta^5\text{-}Me_2Si(Cy)(C_2B_{10}H_{11})]LnCl_2(THF)_3$, mono-chloride $[\eta^5\text{-}Me_2Si(Cy)(C_2B_{10}H_{11})]_2LnCl(THF)_2$, carboranyl $[Li(THF)_4][Me_2Si(Cy)(C_2B_{10}H_{10})]_2Ln]$, and lanthanacarboranes $[\eta^5{:}\eta^6\text{-}Me_2Si(Cy)(C_2B_{10}H_{10})]Ln(THF)_2$, 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.

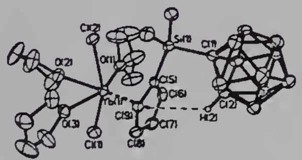


Figure 1 *Organolanthanide Dichloride*

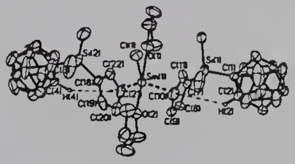


Figure 2 *Organolanthanide Monochloride*

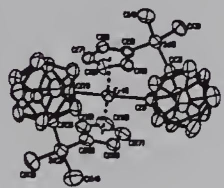


Figure 3 *Organolanthanide Carboranyl*

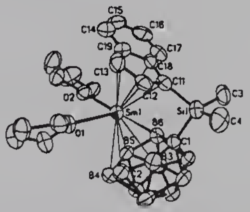
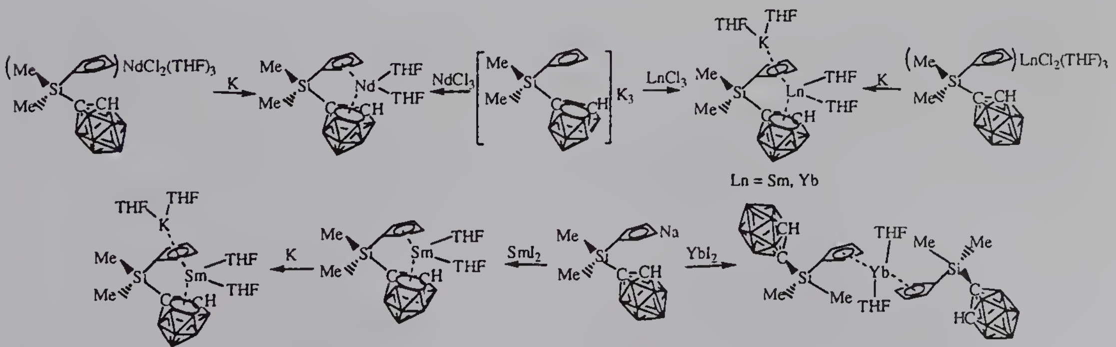


Figure 4 *Lanthanacarborane*



Scheme 2

It is noteworthy that the reactions between SmI_2 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 $[\eta^5{:}\eta^6\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})]Sm(THF)_2$ and $[Na(THF)_6][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{11})\}_2Sm]$, respectively.

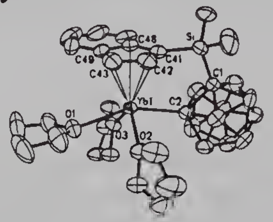
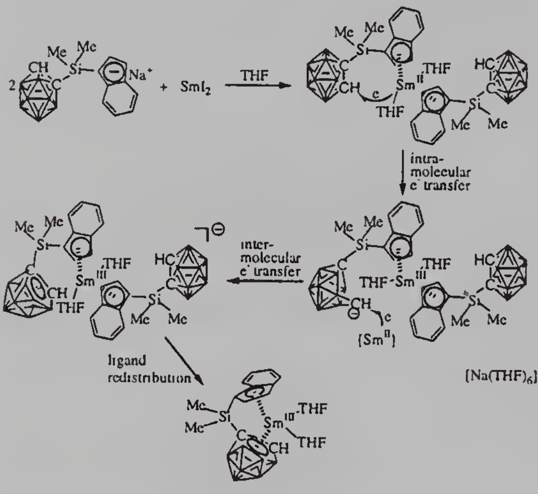
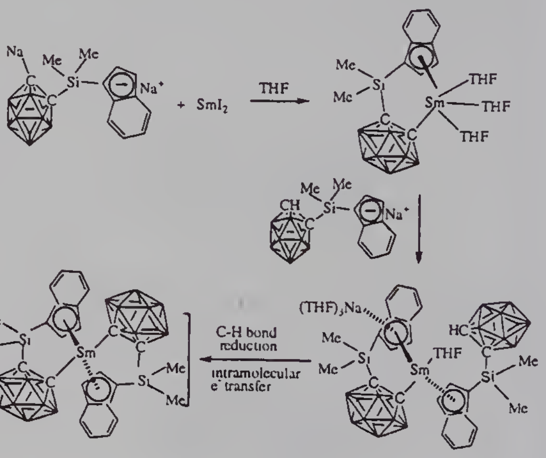


Figure 5 *Constrained Geometry Compound*

Figure 6 *Mixed-ligand Compound*



Scheme 3



Scheme 4

4 ORGANOLANTHANIDE CLUSTERS

It has been found that the Si-C(carborane) bond in $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ is sensitive to not only organo-lithium reagents such as MeLi and *n*-BuLi but also $NaNH_2$. Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with excess $NaNH_2$ in THF, followed by reaction with 1 equivalent of $LnCl_3$ gave tetranuclear and trinuclear organolanthanide clusters of general formulae $[\{(\eta^5{:}\mu_2\text{-}C_9H_6SiMe_2NH)Ln\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)$[11] and $[(\eta^5\text{-}C_9H_6SiMe_2)_2N][\mu_2{:}\mu_2\text{-}Me_2Si(NH)_2](\eta^5{:}\mu_2\text{-}C_9H_6SiMe_2NH)(\mu_2\text{-}Cl)_2Ln_3(THF)_3$,

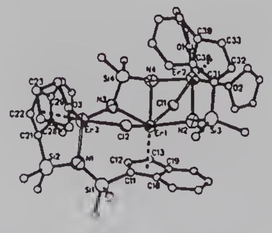


Figure 7 *Trinuclear Cluster*

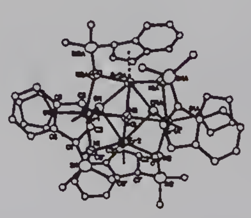


Figure 8 *Tetranuclear Cluster*

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 $[Me_2Si(C_9H_6)(C_2B_{10}H_{10})]^{2-}$ undergoes an unprecedented coupling reaction under UV-light to afford a bis-carborane mono-anion compound $[Na(THF)_x][\mu\text{-CH-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}$, which on treatment with $LnCl_3$ in THF produces $[LnCl_2(THF)_5][\mu\text{-CH-}(\textit{closo}\text{-}C_2B_{10}H_{11})\text{-}\textit{nido}\text{-}CB_{10}H_{11}]$. The mechanism of the formation of these compounds is not clear, but may be similar to the Wurtz reaction to some extent.

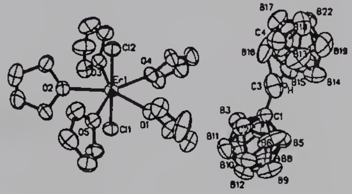


Figure 9 *Biscarborane Compound*

Acknowledgment. We thank the Hong Kong Research Grants Council (Earmarked Grant CUHK 4183/97P) for financial support.

1. For reviews, see: H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95,** 865; F. T. Edelmann, *Comprehensive Organometallic Chemistry II,* eds, E. W. Abel, F. A. G. Stone and G. Wilkinson, Pergamon, Oxford, 1995, Vol. 4, p. 11.
2. M. J. Manning, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.*, 1988, **110,** 4458; M. J. Manning, C. B. Knobler, R. Khattar, M. F. Hawthorne, *Inorg. Chem.*, 1991, **30,** 2009.
3. Z. Xie, Z. Liu, K. Chiu, F. Xue, T. C. W. Mak, *Organometallics,* 1997, **16,** 2460.
4. R. Khattar, C. B. Knobler, S. E. Johnson, M. F. Hawthorne, *Inorg. Chem.*, 1991, **30,** 1970; R. Khattar, M. J. Manning, C. B. Knobler, S. E. Johnson, M. F. Hawthorne, *Inorg. Chem.*, 1992, **31**, 268.
5. A. R. Oki, H. Zhang, N. S. Hosmane, *Angew. Chem. Int. Ed. Engl.*, 1992, **31,** 432; N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang, J. A. Maguire, *Organometallics,* 1996, **15,** 626; N. S. Hosmane, Y. Wang, H. Zhang, J. A. Maguire, M. McInnis, T. G. Gray, J. D. Collins, R. K. Kremer, H. Binder, E. Waldhör, W. Kaim, *Organometallics,* 1996, **15,** 1006; N. S. Hosmane, Y. Wang, H. Zhang, A. R. Oki, J. A. Maguire, E. Waldhör, W. Kaim, H. Binder, R. K. Kremer, *Organometallics,* 1995, **14,** 1101*;* N. S. Hosmane, D. Zhu, H. Zhang, A. R. Oki, J. A. Maguire, *Organometallics,* 1998, **17,** 3196; N. S. Hosmane, H. Zhang, L. Jia, T. J. Colacot, J. A. Maguire, X. Wang,. N. S Hosmane, K. A. Brooks, *Organometallics,* 1999, **18,** 516.
6. A. K. Saxena, N. S. Hosmane, *Chem. Rev.*, 1993, **93,** 1081.
7. Z. Xie, S. Wang, Z. Zhou, F. Xue, T. C. W. Mak, *Organometallics,* 1998, **17**, 489.
8. Z. Xie, S. Wang, Z. Zhou, T. C. W. Mak, *Organometallics,* 1998, **17,** 1907.
9. Z. Xie, S. Wang, Z. Zhou, T. C. W. Mak, *Organometallics,* 1999, **18,** 1641.
10. Z. Xie, S. Wang, Q. Yang, T. C. W. Mak, *Organometallics,* 1999, **18**, 2420.
11. Z. Xie, S. Wang, Q. Yang, T. C. W. Mak, *Organometallics,* 1999, **18,** 1578.

Aluminoxanes via Boron Compounds

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1 INTRODUCTION

In 1960 Vandenberg[1] observed for the first time the positive influence of water on the activity of organoaluminum catalysts in the polymerization of organic monomers. As this activity achieved its maximum for Al to H_2O molar ratios of 1:1 or 2:1 he postulated aluminoxanes $(RAlO)_n$ or dialuminoxanes $(R_2AlOAlR_2)_n$ as the active catalytic species. Since that time, many people have worked in this field trying to prepare aluminoxanes and/or dialuminoxanes, to explore their properties and most of all to determine the structures of these compounds.

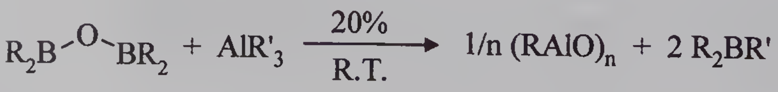
The most widely used method of synthesis of aluminoxanes is the partial hydrolysis of alkylaluminums, and water in various phases is used for this reaction.[2-6] Some have used water in hydrates.[7,8] All these reactions have one big disadvantage: despite the very mild conditions of the reaction (low temperature, high dilution) these reactions are unselective and always lead to mixtures of aluminoxanes and dialuminoxanes. The separation and isolation of defined species is usually very difficult.

We have used borylated water (water in which protons are replaced by BR_2 groups) - so called ”organoboron water” - in the reaction with aluminum alkyls. This works similarly but the reactions are more convenient. Apart from this ”organoboron water” also some borinic, boronic or even boric acids have been used for this reaction.

1.1 “Organoboron water” R_2BOBR_2

We have used Et_2BOBEt_2 or $(9\text{-BBN})_2O$ as a source of water in reactions with aluminum alkyls R_3Al (R = Me, Et, Bu^i). The molar ratios of reagents were 1:1 and 1:2, respectively.

1.1.1 The 1:1 system. In the reaction of 1 equivalent of R_2BOBR_2 with 1 equivalent of AlR'_3 in toluene one obtains aluminoxane and mixed trialkylborane as the by-product according to Equation 1:



$$R_2B^{\diagup O \diagdown}BR_2 + AlR'_3 \xrightarrow[R.T.]{20\%} 1/n\,(RAlO)_n + 2\,R_2BR' \qquad (1)$$

As dialkylaluminum hydroxides R'_2AlOH have been postulated as the intermediates in the partial hydrolysis of organoaluminums, we thought initially that the corresponding R'_2AlOBR_2 species would be the intermediates in the reaction with R_2BOBR_2. Traces of such a compound were isolated from the reaction mixture and identified by MS. Later on we succeeded in the synthesis of a series of B-O-M type compounds (M = Al, Ga, In).[9]

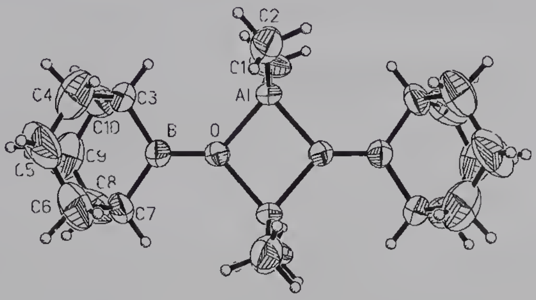
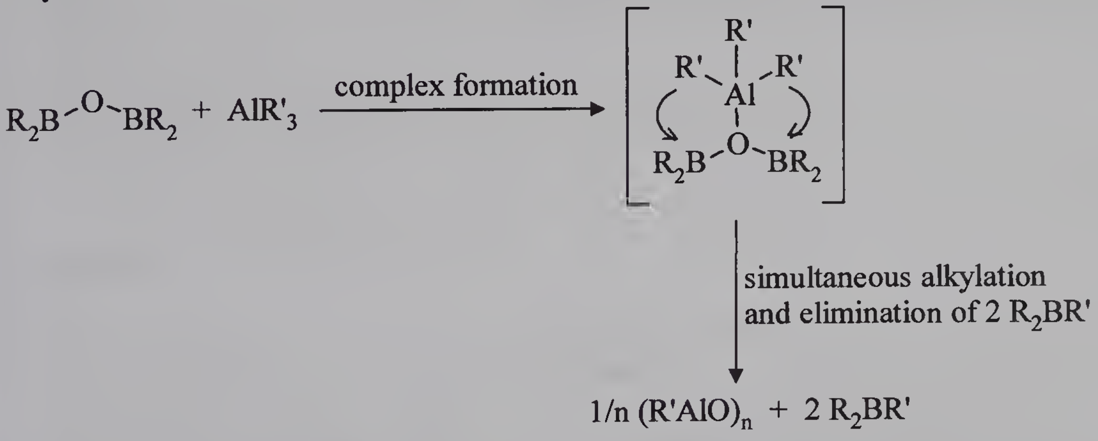


Figure 1 *Molecular structure of* $[9\text{-BBN-}9\text{-OAlMe}_2]_2$

However, we now think that the formation of aluminoxane $(RAlO)_n$ does not involve the intermediate formation of B-O-Al species. Rather, we assume a mechanism in which a complex is formed in the first step and this complex decomposes by intramolecular alkylation of both boron atoms according to the following scheme:



Scheme 1

As the final product one obtains aluminoxane, $(R'AlO)_n$, which can be isolated by removal of the solvent and the by-product R_2BR'.

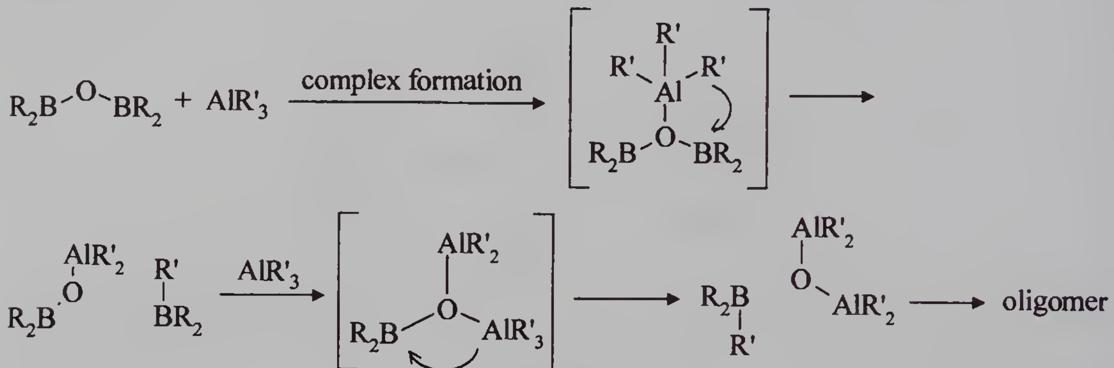
1.1.2 The 1:2 system. In the reaction of diboroxane with aluminum alkyl in a 1:2 molar ratio one obtains dialuminoxane and mixed trialkylboranes as the by-products according to Equation 2:

$$R_2B{-}O{-}BR_2 + 2\ AlR'_3 \xrightarrow[\text{R.T.}]{20\%} 1/n\ (R'_2AlOAlR'_2)_n + 2\ R_2BR' \qquad (2)$$

$$n = 2, 3$$

Dialuminoxanes obtained in this reaction have been determined to have dimeric or trimeric structures depending on the substituent (Bu^i or Et) on aluminum.

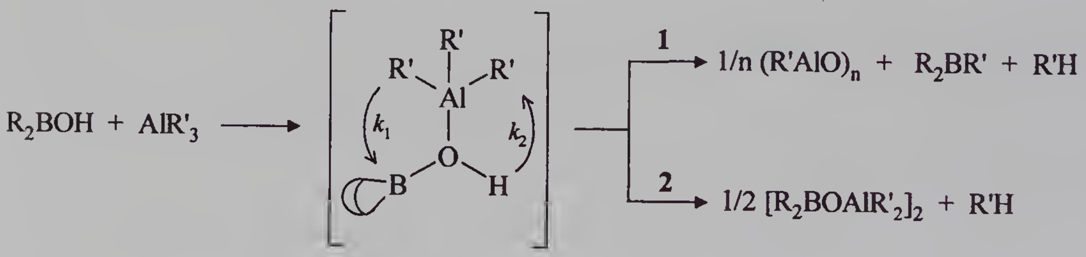
We assume a mechanism in which the first step is a complex formation as in the 1:1 system. But in the 1:2 system only one intramolecular alkylation occurs with formation of R_2B-O-AlR'_2 species. This species forms the next complex with the next AlR'_3 molecule present in the system and under elimination of the second R_2BR' molecule the $R'_2AlOAlR'_2$ system is formed, which oligomerizes according to the scheme:



Scheme 2

1.2 Borinic acids R_2BOH

Et_2BOH, 9-(OH)-9-BBN and Mes_2BOH were used in reactions with aluminum alkyls. These reactions proceeded according to Scheme 3:



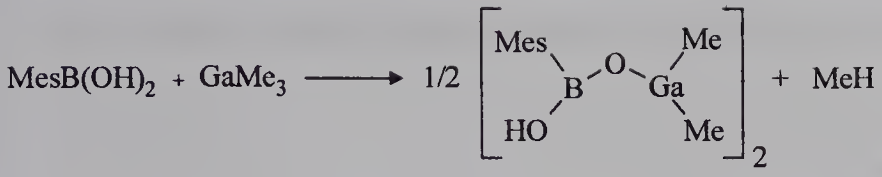
$k_1 \approx k_2$ however $k_1 < k_2$

Scheme 3

The products of these reactions depend strongly on the bulk of the alkyl groups bonded to aluminum and boron. For example, if there is a small alkyl group attached to the boron atom, pathway **1** is the main route for all R' = Me, Et, Bu^i groups attached to the aluminum atom. If there is a bulky substituent on the boron atom (e.g. R = Mes) then **2** is the main route, independent of the substituent on aluminum.

1.3 Boronic acids $RB(OH)_2$

Mesitylboronic acid was used in reactions with group 13 metal alkyls. The expected B-O-M species was obtained only for M = Ga, according to the reaction in Equation 3. This is possibly due to the properties of Me_3Ga, in which only one methyl group is used in the protonolysis reaction.


(3)

1.4 Boric acid $B(OH)_3$

Very recent results of this reaction with aluminum alkyls allow us to suggest the following reaction equation:

$$B(OH)_3 + 3\ AlR_3 \xrightarrow[100°C]{\text{toluene}} BR_3 + 3\ HR + 3/n\ \underset{\text{soluble oligomers}}{(RAlO)_n} \qquad (4)$$

This reaction requires elevated temperature, probably due to a heterogeneous first step. The subsequent steps occur much more quickly, probably by step-by-step protonolysis of Al-R bonds and final intramolecular elimination of the BR_3 molecule and formation of the aluminoxane.

1.5 Conclusions

- Some boron compounds containing oxygen are good oxygen sources in reactions with aluminum alkyls to form aluminoxanes and dialuminoxanes
- Reactions conditions are more convenient by comparison with the previously used hydrolytic methods
- Of special importance is R_2BOBR_2 ("organoboron water") which:
  - works like water but more selectively and does not require very mild conditions;
  - is soluble in hydrocarbons;
  - provides easy to isolate by-products.

References

1. E. J. Vandenberg, *J. Polym. Sci.*, 1966, **47,** 486.
2. G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, E. J. Larikov, A. F. Zhigach, *Zh. Obshch. Khim.*, 1969, **34,** 3435.
3. A. Storr, K. Jones, A. W. Laubengayer, *J. Am. Chem. Soc.*, 1968, **90,** 3173.
4. M. Bolesławski, S. Pasynkiewicz, A. Kunicki, J. Serwatowski, *J. Organomet. Chem.*, 1976, **116,** 285.
5. M. Bolesławski, J. Serwatowski, *J. Organomet. Chem.*, 1983, **254,** 159.
6. S. Pasynkiewicz, M. Bolesławski, A. Kunicki, J. Serwatowski, *Patent Pol.*, 1979, 102 562, *C.A.*, **92**: P22595z.
7. G. A. Razuvaev, Y. A. Sangalov, Y.Y. Nelkenbaum, K.S. Minskier, *Izv. Akad. Nauk SSSR*, 1975, **11,** 2547.
8. M. R. Mason, J. M. Smith, S. G. Bott, A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115,** 4971.
9. R. Anulewicz-Ostrowska, S. Luliński, J. Serwatowski, *Inorg. Chem.* 1999, accepted.

Highly Fluorinated *closo*-Borane and -Carborane Anions

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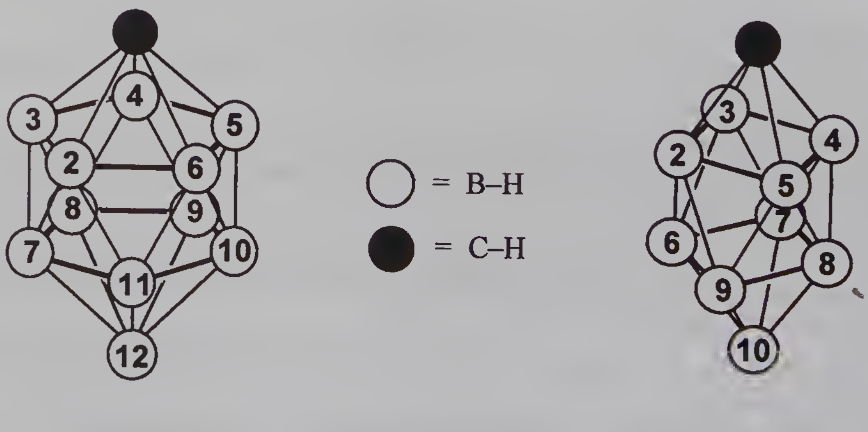
1 INTRODUCTION

Monocarborane monoanions, especially derivatives of $CB_{11}H_{12}^-$, are among the best superweak anions available today.[1–5] They are extremely weakly coordinating *and* possess extraordinary chemical, electrochemical, and thermal stability. Important examples include 7,8,9,10,11,12-$CB_{11}H_6X_6^-$ (abbreviated $CB_{11}H_6X_6^-$; X = F,[6] Cl,[7,8] Br,[7,9] and I[5]), 1-Me-$CB_{11}Cl_{11}^-$,[10] $CB_{11}(Me)_{12}^-$,[11] $CB_{11}(CF_3)_{12}^-$,[12] and 1-R-$CB_{11}F_{11}^-$ (R = H, Me, Et, Bn).[13,14] We have been developing synthetic strategies for the polyfluorination of $CB_{11}H_{12}^-$ and the related carborane ion $CB_9H_{10}^-$.[6,13–19] The use of liquid anhydrous HF (LAHF) or F–TEDA (F–TEDA = 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane bis (tetrafluoroborate)) as fluorinating agents has resulted in regioselective fluorinations, producing partially fluorinated carborane anions in high yields and with high isomeric purity such as 12-$CB_{11}H_{11}F^-$,[15,16] 7;12-$CB_{11}H_{10}F_2^-$,[15,16] 7,8,9,10,11,12-$CB_{11}H_6F_6^-$,[6] 6-$CB_9H_9F^-$, 6,8-$CB_9H_8F_2^-$,[16,17] 6,7,8,9-$CB_9H_6F_4^-$,[18] and 6,7,8,9,10-$CB_9H_5F_5^-$.[19] The numbering schemes for $CB_{11}H_{12}^-$ and $CB_9H_{10}^-$ are shown below, and a complete list of the fluorocarborane anions prepared by us during 1995 and 1999 is given in Table 1. In addition to these anions, we have also prepared new fluorinated derivatives of *closo*-borane and -heteroborane anions, including 1- and 2-$B_{10}H_9F^{2-}$, 1,10-$B_{10}H_8F_2^{2-}$, 2-, 7-, and 12-$AsB_{11}H_{10}F^-$, 7,12-$AsB_{11}H_9F_2^-$, and 7,9-$EB_{11}H_9F_2^-$ (E = As, Sb, Bi).[6,16,17]



$CB_{11}H_{12}^-$ $CB_9H_{10}^-$

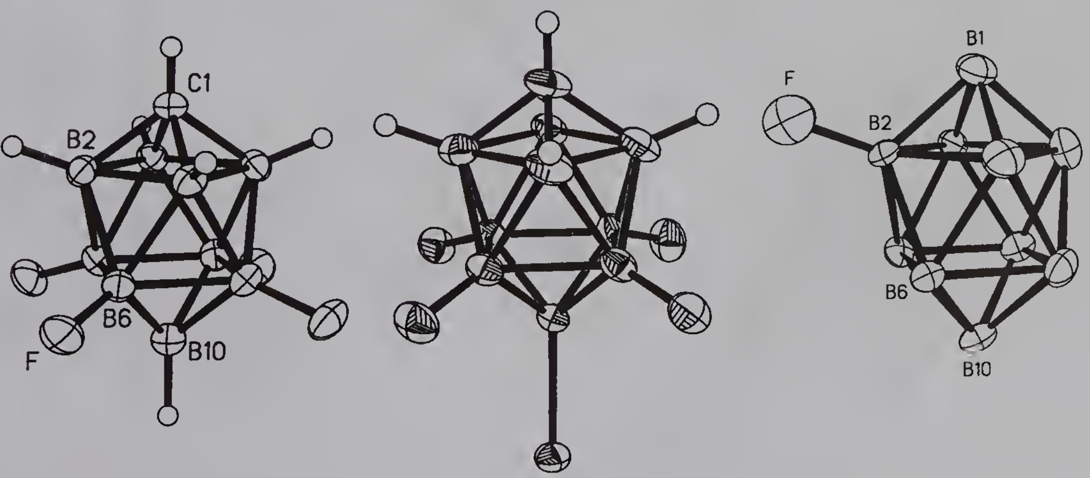
Table 1 *New Fluorocarborane Anions Prepared in Our Labs*

$12\text{-}CB_{11}H_{11}F^-$
$7\text{-}CB_{11}H_{11}F^-$
$7,12\text{-}CB_{11}H_{10}F_2^-$
$2,12\text{-}CB_{11}H_{10}F_2^-$
$7,9,12\text{-}CB_{11}H_9F_3^-$
$7,8,10,12\text{-}CB_{11}H_8F_4^-$
$7,8,9,10,11,12\text{-}CB_{11}H_6F_6^-$
$2,7,8,9,10,12\text{-}CB_{11}H_6F_6^-$
$1,12\text{-}CB_{11}H_2F_{10}^-$
$1\text{-R-}CB_{11}F_{11}^-$ (R = H, Me, Et, CH_2F, CHF_2, CF_3, CH_2Cl, *n*-Bu, CH_2Ph, $CH_2CH{=}CH_2$)
$1\text{-}CB_{11}F_{11}^{2-}$
$CB_{11}F_{12}^-$

$6\text{-}CB_9H_9X^-$ (X = F, Cl, Br, I)
$6,8\text{-}CB_9H_8X_2^-$ (X = F, Cl, Br, I)
$6,7\text{-}CB_9H_8X_2^-$ (X = F, Cl, Br, I)
$6,7,8\text{-}CB_9H_7F_3^-$
$6,7,8,9\text{-}CB_9H_6F_4^-$
$6,7,8,9\text{-}CB_9F_4\text{-}10\text{-}X^-$ (X = Br, I, OH, $NHCOCH_3$)
$6,7,8,9,10\text{-}CB_9H_5F_5^-$
$2,6,7,8,9\text{-}CB_9H_5F_5$
$1\text{-H-}CB_9F_9^-$

2 RESULTS AND DISCUSSION

The structures of some of the 10-vertex fluoroanions are shown in Figure 1.[6,16,18] It can be seen that the regioselectivity of B–H → B–F transformations can be controlled, at least to some extent. For example, when $6,7,8,9\text{-}CB_9H_6F_4^-$ was heated to 260°C in LAHF, only 8% of the desired isomer $6,7,8,9,10\text{-}CB_9H_5F_5^-$ was formed; the isolated product contained 92% of the isomer $2,6,7,8,9\text{-}CB_9H_5F_5^-$. However, when $6,7,8,9,10\text{-}CB_9H_5F_5^-$ was treated with F–TEDA in acetonitrile at 60°C in the presence of trifluoroacetic acid, 98% of $6,7,8,9,10\text{-}CB_9H_5F_5^-$ and only 2% of $2,6,7,8,9\text{-}CB_9H_5F_5^-$ were isolated. The structure of $6,7,8,9,10\text{-}CB_9H_5F_5^-$ is shown in Figure 2.[19]



$6,7,8,9\text{-}CB_9H_6F_4^-$ $6,7,8,9\text{-}CB_9H_5F_4\text{-}10\text{-}I^-$ $2\text{-}B_{10}H_9F^{2-}$

Figure 1 *Structures of three 10-vertex fluoroborane and -carborane anions.*

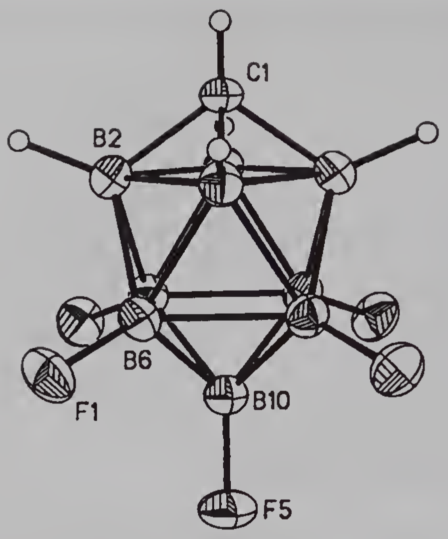
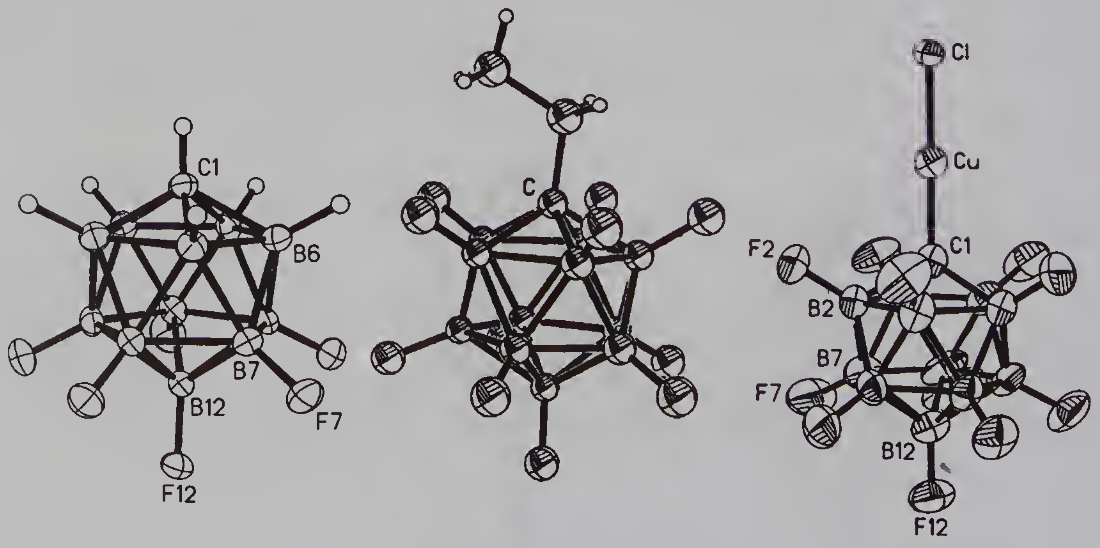


Figure 2. *Structure of* $6,7,8,9,10\text{-}CB_9H_5F_5^-$ *(*PPh_4^+ *salt).*

The structures of some of the 12-vertex fluoroanions are shown in Figure 3.[6,13,14] The structure of $1\text{-Et-}CB_{11}F_{11}^-$ is interesting in that the esd's on the B–F bond distances are small enough that one can conclude that the upper-belt B–F distances are significantly shorter than the lower-belt or antipodal B–F bonds distances, in harmony with recent DFT calculations.[20]



$7,8,9,10,11,12\text{-}CB_{11}H_6F_6^-$ $1\text{-Et-}CB_{11}F_{11}^-$ $1\text{-CuCl-}CB_{11}F_{11}^{2-}$

Figure 3 *Structures of three 12-vertex fluorocarborane anions.*

Several new cationic metal complexes have been isolated with the 1-Et-$CB_{11}F_{11}^-$ anion, including $\{Ag(\mu^3\text{-}\eta^2\text{-}CHPh_3)^+\}$, $Cu(CO)_4^+$, $(\eta^6\text{-}C_6H_6)Rh(CO)_2^+$, and $Rh(CO)_4^+$. The first three of these have been structurally characterized and are shown in Figure 4.

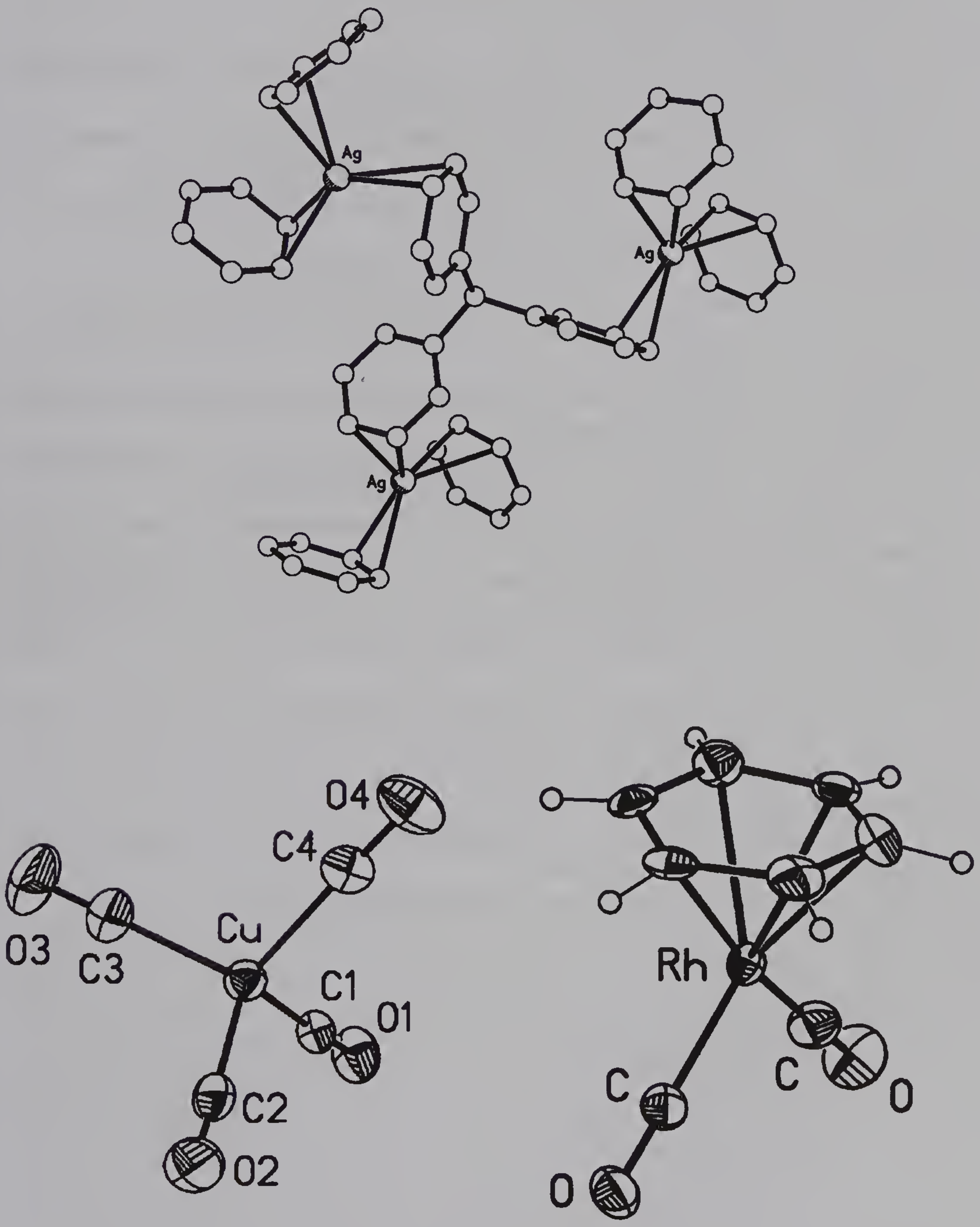


Figure 4 *New cationic complexes isolated with the 1-Et-$CB_{11}F_{11}^-$ superweak anion*

References

1. C. A. Reed, *Accounts Chem. Res.*, 1998, **31**, 0000.
2. A.J . Lupinetti and S. H. Strauss, *Chemtracts–Inorg. Chem.*, 1998, **11**, 565.
3. R. Dagani, *Chem. Eng. News*, *May 4* (1998), 49.
4. S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927.
5. J. Plešak, *Chem. Rev.*, 1992, **92**, 269.
6. A. J. Lupinetti, S. V. Ivanov, S. M. Ivanova, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, manuscript in preparation.
7. T. Jelínek, J. Plešak, S. Heřmánek, and B. Štíbr, *Coll. Czech. Chem. Commun.*, 1986, **51**, 819.
8. Z. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi, and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 2922.
9. Z. Xie, R. Bau, and C. A. Reed, *Inorg. Chem.*, 1995, **34**, 5403.
10. Z. Xie, C.-W. Tsang, F. Xue, and T. C. W. Mak, *Inorg. Chem.*, 1997, **36**, 2246.
11. B. T. King, Z. Janoušek, B. Grüner, M. Trammell, B. C. Noll, and J. Michl, *J. Am. Chem. Soc.*, 1996, **118**, 3313.
12. J. Michl and B. T. King, Abstracts of Meeting, 12th European Symposium on Fluorine Chemistry, Berlin, 1998, Abstract B10.
13. S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *J. Am. Chem. Soc.*, 1998, **120**, 4224.
14. S. M. Ivanova, S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *Inorg. Chem.* 1999, **38**, 0000.
15. S. V. Ivanov, A. J. Lupinetti, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *Inorg. Chem.*, 1995, **34**, 6419.
16. S. V. Ivanov, A. J. Lupinetti, K. A. Solntsev, and S. H. Strauss, S. H. *J. Fluorine Chem.*, 1998, **89**, 65.
17. S. V. Ivanov, J. J. Rockwell, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *Inorg. Chem.*, 1996, **35**, 7882.
18. S. V. Ivanov, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, manuscript in preparation.
19. S. V. Ivanov, S. M. Ivanova, S. M. Miller, O. P. Anderson, K. A. Solntsev, and S. H. Strauss, *Inorg. Chim. Acta*, in press.
20. D. K. McLemore, D. A. Dixon, and S. H. Strauss, *Inorg. Chim. Acta*, in press.

Materials and Polymers

A New Class of π-Conjugated Organoboron Polymers

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1. INTRODUCTION

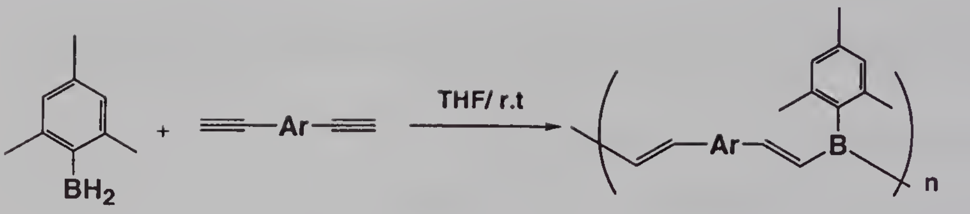
There has been a great deal of interest in the construction of π-conjugated systems for a number of years. Because of their unusual optical or electrochemical behavior and potential importance for light emitting diodes, light harvesting systems and energy storage systems and so on, versatile types of such polymers have been reported so far. However, for the future development of the organic electronic devices, it appears indispensable to search for π-electron deficient n-type π-conjugated polymers 1) that are appropriate for electron transport material or negative electrode.

In this viewpoint, incorporation of the boron atom in the π-conjugated system should be an attractive approach, since the resulting polymer can be regarded as a polymer homolog of triphenylborane 2a) or trimesitylborane 2b) that are known as good electron acceptors. Here is described the synthesis of novel organoboron π-conjugated polymers by polyaddition using well-known hydroboration reaction or polycondensation via Grignard reagents.

2. HYDROBORATION POLYMERIZATION OF AROMATIC DIYNES 3)

The synthesis of π-conjugated organoboron polymer was first examined by hydroboration polymerization of aromatic diynes with mesitylborane (Scheme 1). The conjugative interaction between vinyl group and boron atom has been investigated by the spectral properties of low molecular weight vinylborane derivatives. In the early studies, it was found that these spectroscopic data such as ^{11}B-NMR and absorption maxima were in accordance with the calculated results using Hückel MO theory, which suggested considerable conjugative overlap of the π-orbitals of the vinyl groups with the p-orbital of boron atom. 4) Therefore, the polymers prepared are expected to show characteristics as novel n-type conjugated polymers owing to extension of π-conjugated length via the vacant p-orbital of the boron atom and high electron affinity of the organoboron unit.

A series of π-conjugated organoboron polymers were successfully prepared by simple polyaddition between aromatic diynes and mesitylborane in a dry THF solution (Table 1). The polymerization preceeded smoothly at room temperature without catalyst to afford the corresponding polymers whose *Mn* were in the range of several thousands.



1 2 3

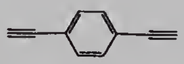
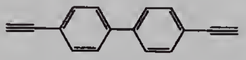
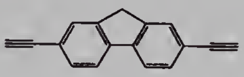
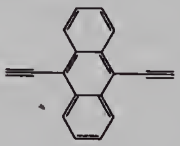
Scheme 1

The optical data of the organoboron polymers are summarized in Table 2. In the UV-vis spectra of the organoboron polymers, an effective extension of π-conjugation length via the empty p-orbital of the boron atom was indicated from the observation of their absorption maxima in the visible region (Figure 1). The every polymer exhibited blue light emission in a strong intensity upon irradiation with ultraviolet light.

In order to obtain theoretical support for the extension of π-conjugation via the boron atom, theoretical calculation based on self-consistent-field crystal orbital method was carried out. From the results, it was suggested that a considerable amount of π-electrons were delocalized on the boron atom in accord with the observation.

Third order non-linear optical properties of organoboron polymers were also investigated by degenerate four waves mixing method, as represented in Table 3. [Light sourse; Nd:second harmonic generation of YAG laser; 532 nm, pulse width 7 ns, intensity, 1MW/cm^2) after casting diglyme solutions of <u>3a</u> and <u>3c</u> onto ITO glass respectively.

Table 1. Hydroboration Polymerization of Aromatic Diynes Using Mesitylborane. [a)]

Diynes		<u>1</u>/<u>2</u>	Mn [b)]	Mw/Mn [b)]	Yield (%) [c)]
	(<u>2a</u>)	1.17	6500	2.5	71
	(<u>2b</u>)	1.27	5100	2.1	95
	(<u>2c</u>)	1.24	2800	1.5	71
	(<u>2d</u>)	1.22	1300	1.3	67

a) Reactions were carried out in THF at r.t. b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into MeOH.

Table 2. Optical Properties of Organoboron Polymers <u>3a</u>-<u>3d</u>

polymers	UV λ_{max} [a)] (nm)	ε [a)]	PL λ_{max} [a), b)] (nm)
<u>3a</u>	399	8470	441
<u>3b</u>	390	17700	440
<u>3c</u>	350, 390, 407	9670, 10230, 10800	455
<u>3d</u>	364, 383, 405	3520, 5360, 6120	412, 436, 462

a) Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at r.t. b) Excited at 350nm.

During the measurement, phase conjugate waves (Figure 2) of fairly high intensities were observed in an ocilloscope. Unusually high values of optical 3rd order non-linear susceptibility were observed for <u>3a</u> and <u>3c</u>. The value for <u>3a</u> amounts to more than thousand times higher than that of all-trans polyacetylene.

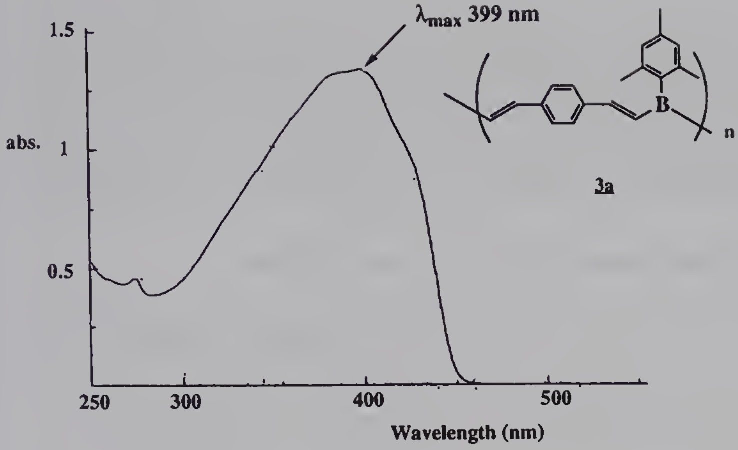


Figure 1. UV-vis Spectrum of 3a (in CHCl$_3$, at r.t)

Table 3. 3rd Order Non Linear Optical Property of Organoboron Polymers

sample	3a	3c
$\chi^{(3)}$ (e.s.u.)	6.87×10^{-6}	3.56×10^{-7}

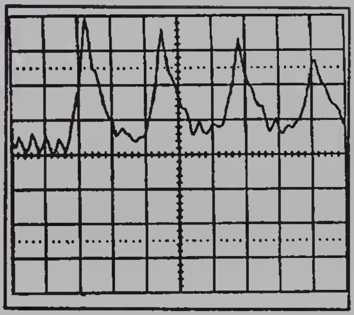
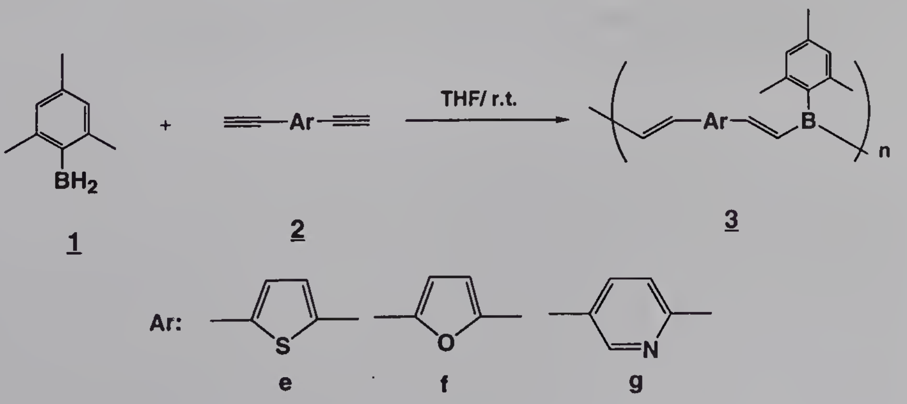


Figure 2. Phase Conjugate Wave of 3a

3. HYDROBORATION POLYMERIZATION OF HETEROAROMATIC DIYNES [5)]

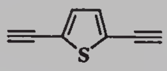
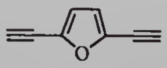
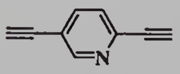
Synthesis of donor-acceptor type π-conjugated polymers was next examined by hydroboration polymerization between heteroaromatic diynes and mesitylborane (Scheme 2). Generally, incorporation of donor-acceptor pair into conjugated system is an interesting subject in view of achieving the narrow band gap or improved 3rd order non-linear-optical properties, due to the charge transferred structure in their backbone [6)]. The hydroboration polymerization between heteroaromatic diynes and mesityborane proceeded smoothly at room temperature without complex formation, probably because of the relatively low Lewis acidity of boron atom in mesitylborane due to the π-electron donation to the vacant p-orbital of boron atom.



Scheme 2

The results of the polymerization of various heteroaromatic diynes and optical data of the resulting polymers are summarized in Table 4. The polymer prepared from 2,5-diethynylpyridine showed a relatively red-shifted absorption maximum, possibly due to some charge transfer in the ground state. In the fluorescence emission spectra of these polymers (Figure 3), visible green or white emission was observed. The large Stokes shift and the broad emission peak implies that an energy transfer is taking place in the excited states.

Table 4. Hydroboration Polymerization between Various Heteroaromatic Monomers and Mesitylborane. a)

Run	2		1/2	*Mn* b)	*Mw/Mn* b)	Yield (%) c)	λ_{max} (abs.) d)	λ_{max} (emission) e)
1		(2e)	1.27	3000	1.6	58	350	488
2		(2f)	1.03	3000	2.0	57	356	495
3		(2g)	1.21	2900	1.6	36	450	416, 495, 593

a) Reactions were carried out in THF at room temperature. b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into MeOH (runs 1-2) or n-hexane (run 3). d) In chloroform at room temperature. e) In chloroform at room temperature. Excitation wavelength was 350 nm.

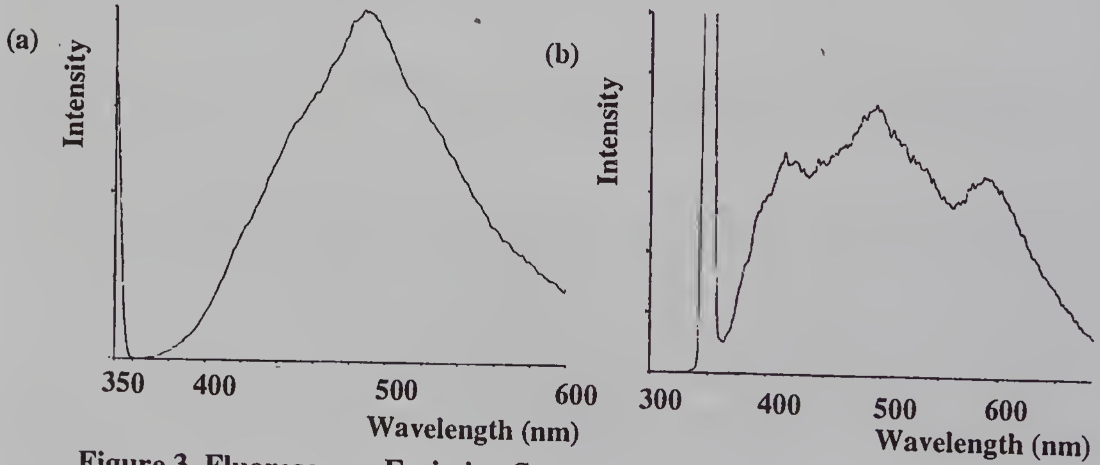
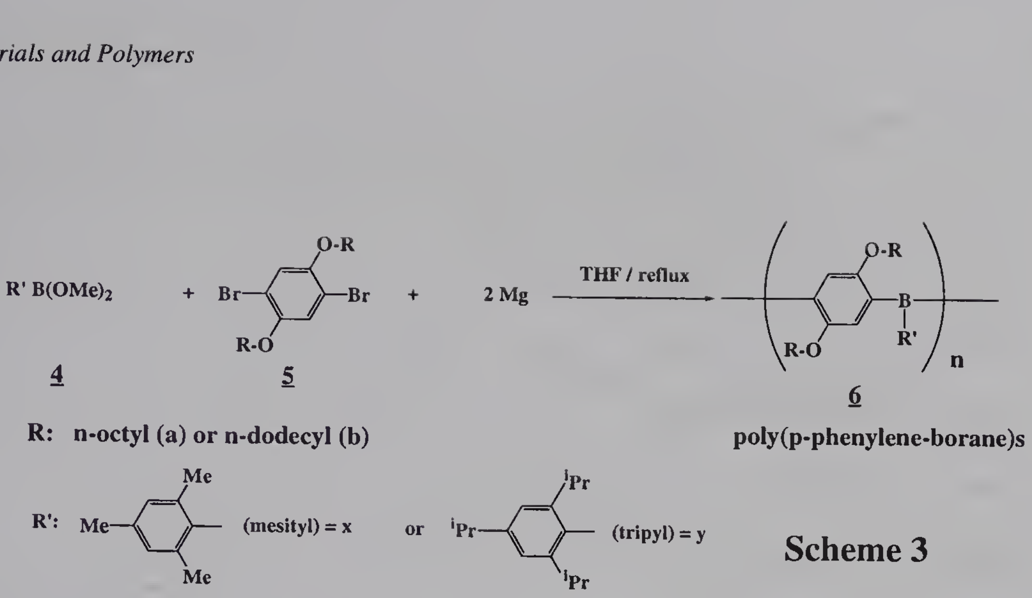


Figure 3. Fluorescence Emission Spectra of 3e (a) and 3g (b) in $CHCl_3$ at r.t.

4. NOVEL POLY(PHENYLENE-BORANE)S (PPB)S 7)

Heteroatom-including polyphenylenes such as poly(phenylene-oxide) (PPO), poly(phenylene-sulfide) (PPS) and polyaniline (PANI) are industrially very important as engineering plastics or electronic materials. These polymers exhibit excellent mechanical property and high stability. Here, we examined the synthesis of novel poly(phenylene-borane)s (PPB)s by polycondensation between di-Grignard reagents and aryldimethoxyborane. This provides a novel methodology for the preparation of organoboron conjugated polymers as a useful alternative to hydroboration polymerization.



Scheme 3

The polymerization between di-Grignard reagents and aryldimethoxyborane was carried out under nitrogen atmosphere, as depicted in Scheme 3 to give the corresponding polymers in excellent yields. For instance the polymerization using tripyldimethoxyborane and 2,5-didodecyloxy-1,4-dibromobenzene gave the polymer whose *Mn* was estimated to be 3000 from the GPC measurement (THF, PSt standards) (Table 5).

The optical data of the PPBs are listed in Table 6. In the UV-vis spectrum of <u>**6by**</u>, the absorption maximum was observed at 367 nm (Figure 4). The bulky tripyl group substituent does not seem to retard the expansion of π-conjugation. When the dilute chloroform solutions of the polymers were irradiated with UV light, intense visible blue-green emissions were observed.

The air stability of PPB (<u>**6by**</u>) was examined by an air-bubbling experiment. After the vigorous air-bubbling of the THF solution of <u>**6by**</u> for 24h, no significant decrease in *Mn* was observed from the GPC measurements. The relatively high thermal stability is also expected due to the absence of a retro-hydroboration (β-elimination) process during their thermal degradation. These characteristics of PPBs might allow their application for various electronic devices.

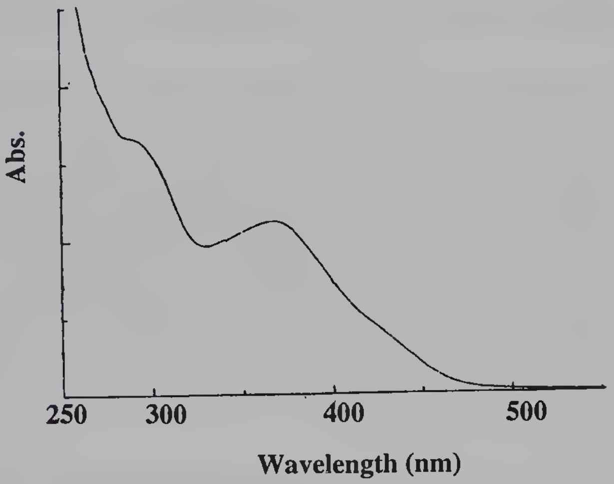


Figure 4. UV-vis Absorption Spectrum of <u>6by</u> (in $CHCl_3$ at r.t.)

Table 5. Polymerization of <u>5b</u> with Various Borane Reagents. [a]

Borane	<u>4</u>/<u>5b</u>	conc. (M) [b]	*Mn* [c]	*Mw*/*Mn* [c]	yield (%) [d]
<u>4x</u>	1.10	0.2	2200	1.1	77
<u>4y</u>	1.04	0.67	3000	1.2	99

a) The reactions were carried out under nitrogen atomosphere at 80°C. b) Concentration of <u>5</u>. c) GPC (THF), polystyrene standards. d) Isolated yields after washing with methanol.

Table 6. Optical Properties of Poly(p-phenylene-borane)s.

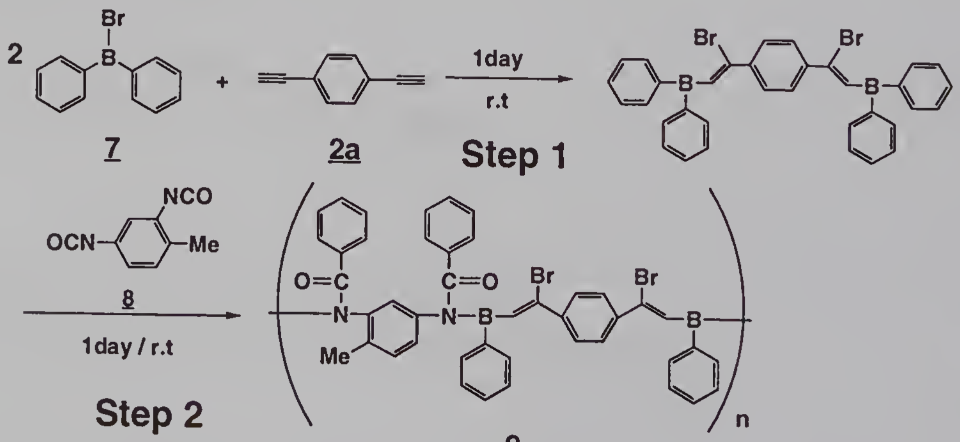
polymers	UV λ_{max} [a] (nm)	ε [a]	PL λ_{max} [a), b] (nm)
6ax	359	2240	496
6ay	365	2510	481
6bx	359	1780	477
6by	367	1820	487

a) Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at r.t. b) Excited at 350nm.

5. FULLY AROMATIC ORGANOBORON POLYMERS BEARING MONOMERIC IMINOBORANE IN THEIR MAIN CHAIN [8)]

Poly(iminoborane)s $[(\text{-BR=N-})_n]$ are a potential π-conjugated polymers, since boron-nitrogen bonds possess the double bond like nature owing to pπ-pπ interaction [9)]. However, these materials are not fully characterized so far [10)]. In order to incorporate the monomeric B-N bond into the conjugation path, we examined an alternating boration copolymerization between diisocyanates and diynes making use of different reactivity between haloboration and phenylboration reactions.

As depicted in Scheme 4, the treatment of 1,4-diethynylbenzene with 2eq. of diphenylbromoborane (selective haloboration) and the subsequent reaction with 1eq. of tolylene-2,4-diisocyanate (phenylboration polymerization) gives the corresponding alternating copolymers.



Scheme 4

The extent of unit alternation was clearly monitored by ^{11}B-NMR measurement. In the ^{11}B-NMR spectrum of alternating copolymer (Figure 5), the chemical shift of the main peak was located in the almost middlepoint (29.2 ppm) between those of both polymers prepared from diisocyanates or diynes, respectively. This indicates the highly alternating nature of this polymerization system. However, efficient extension of π-conjugation is prevented because of the presence of cross-linked structure (0.55 ppm, diamidoalkenylborane) which is formed by further phenylboration.

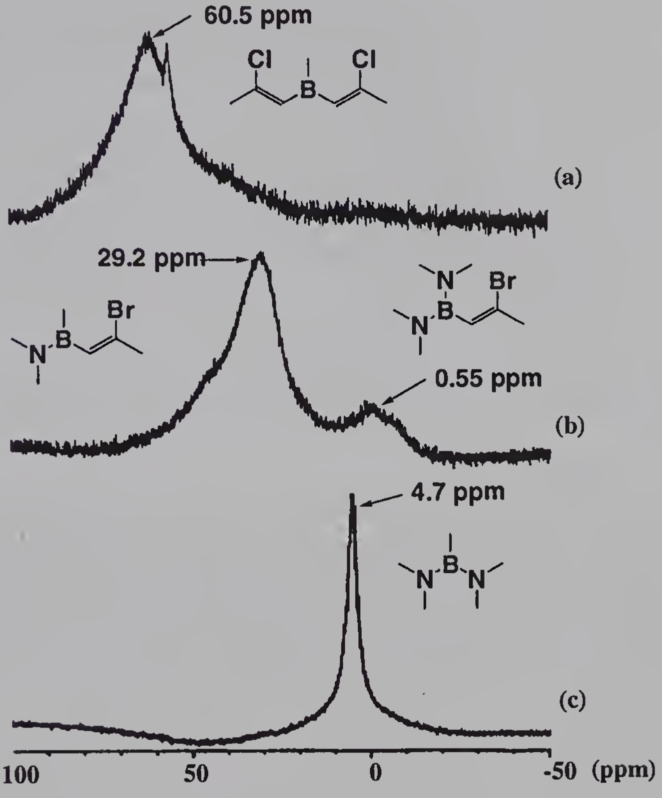
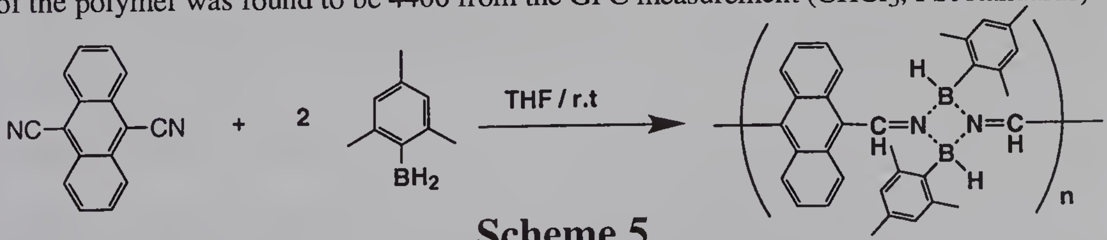


Figure 5. ^{11}B-NMR Spectra of Organoboron Polymers Prepared by Boration Polymerization.
(a)-Haloboration Polymerization between $PhBCl_2$ and 2a.
(b)-Haloboration-Phenylboration Alternating Copolymerization between 2a and 8a Using 7.
(c)-Haloboration-Phenylboration Polymerization between $PhBCl_2$ and Diisocyanotohexane.

6. HYDROBORATION POLYMERIZATION OF 9,10-DICYANOANTHRACENE (DCA) 11)

A fully aromatic poly(cyclodiborazane) was prepared by hydroboration polymerization between DCA and mesitylborane. Since DCA is a highly fluorescent compound and widely used as a photocatalyst, the obtained polymer is expected to act as a novel type of electron transport material or polymer photocatalyst. The polymerization was carried out as Scheme 5, by adding a slight excess amount of mesitylborane (in THF) to a THF suspension of DCA at room temperature, and stirring the reaction mixture for 12h. The *Mn* of the polymer was found to be 4400 from the GPC measurement ($CHCl_3$, PSt standards).



Scheme 5

In the UV-vis absorption spectrum ($CHCl_3$, at r.t.), DCA shows three strong absorption bands at 377, 402 and 426 nm (Figure 6a). Interestingly, the spectrum of the polymer had only one broad band at 406 nm (Figure 6b). This might be due to some conjugative interaction or stronger solvation due to improved solubility. The fluorescence emission spectra were also recorded for both DCA and the polymer. In the spectrum of DCA, two sharp emission peaks were observed at 437 and 461 nm, in the blue region. In the case of the polymer, a relatively broad emission was observed in the green region (494 nm).

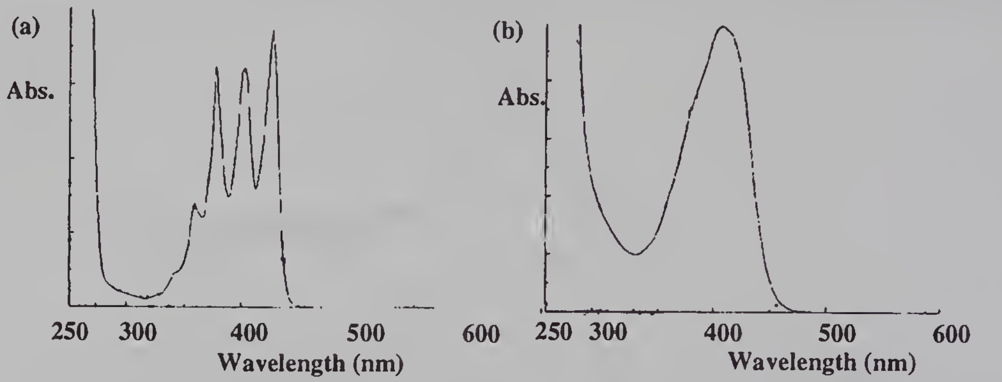


Figure 6. UV-vis Absorption Spectra of (a) DCA and (b) DCA polymer in $CHCl_3$ at r.t.

REFERENCES

1. For example, (a) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (b) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930. (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.
2. (a) Brown, H. C.; Dodson, V.H. *J. Am. Chem. Soc.* **1957**, *79*, 2302. (b) Ramsey, B. G.; Isabelle, L. M. *J. Org. Chem.* **1981**, *46*, 179.
3. Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112.
4. For example, (a) Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.*, **1962**, *84*, 1162. (b) Good, C. D.; Ritter, D. M. *J. Chem. Eng. Data, 1.* **1962**, 416. (c) Zweifel, G.; Clark, G. M.; Leung, T.; Whitney, C. C. *J. Organomet. Chem.* **1976**, *117*, 303.
5. Matsumi, N.; Miyata, M.; Chujo, Y. *Macromolecules*, **1999**, in press.
6. For example, (a) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119. (b) Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.*, **1994**, 991. (c) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791. (d) Kanbara, T.; Miyazaki, Y.; Yamamoto, T. *J. Polym. Sci. part A: Polymer Chemistry*, **1995**, *33*, 999. (e) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389. (f) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.
7. Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776.
8. Matsumi, N.; Kotera, K.; Naka, K.; Chujo, Y. *Macromolecules*, **1998**, *31*, 3155.
9. Niedenzu, K.; Dawson, J. W. *Boron-Nitrogen Compounds*; Springer-Verlag: New York, 1965.
10. (a) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123. b) Paezold, P. von Bennigsen-Mackiewick, *Chem. Ber.* **1981**, *114*, 298.
11. Matsumi, N.; Naka, K.; Chujo, Y. *Macromolecules*, **1998**, *31*, 8047.

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Catalytic Syntheses of Linear Polycarboranes

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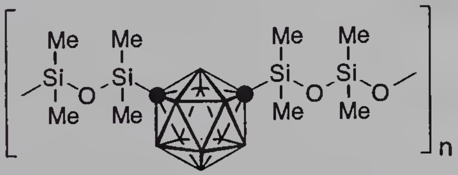
1 INTRODUCTION

The extreme thermal stability of icosahedral carboranes has long attracted the interest of polymer chemists seeking to develop new materials for high-temperature applications.[1] Nevertheless, only the elastomeric poly(carborane-siloxane)s, for example **1**, have ever been manufactured on an industrial scale.[2] This situation reflects not only the very high cost of carborane-based starting materials, but also a failure to develop linkages *between* carborane cages which can match the stability of the carborane unit itself.



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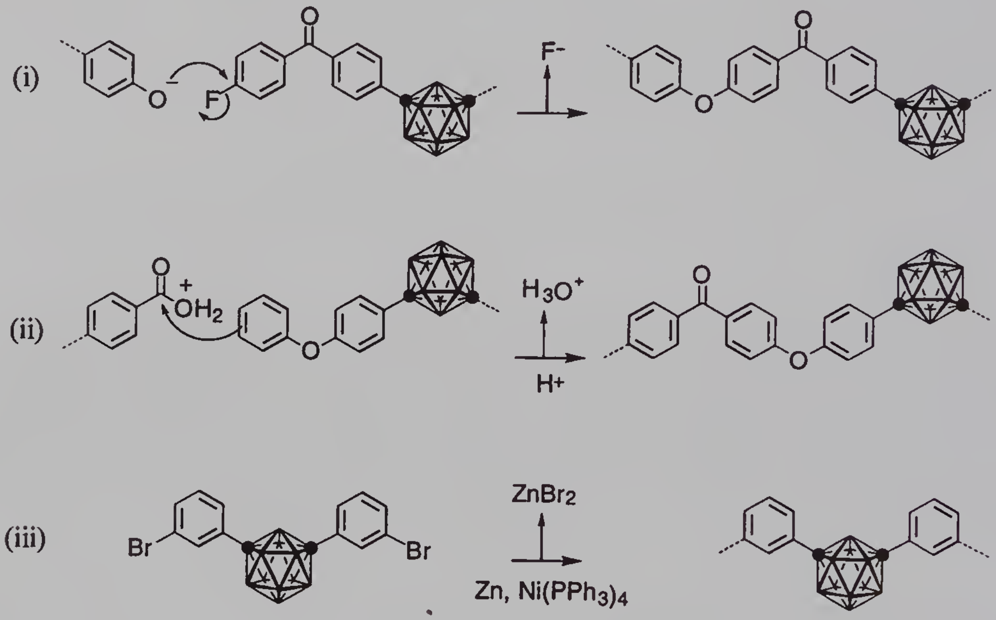
However, in view of the high-temperature capabilities of thermoplastic materials based on aromatic rings linked by thermally and oxidatively stable units such as ether, ketone, sulfone, or direct bonds,[3] we have attempted to develop linear, carborane-copolymers of this same general type. We here describe synthetic and crystallographic studies of such materials, and report on their potential applications in membrane separation and in ceramic-precursor chemistry.

2 RESULTS AND DISCUSSION

Several different approaches to the construction of poly(arylene-carborane)s were initially considered (Scheme 1). These included; (i) nucleophilic polycondensation between a bis-phenol and an activated, carborane-based dihalide in the presence of base, a reaction used for the synthesis of commercial polyetherketones and polyethersulfones,[4] (ii) electrophilic polycondensation between an aromatic diacid and a carborane-based diarylether in the presence of a strong-acid catalyst,[5] and (iii) direct, homogeneously-catalysed coupling of a carborane-based dihalide.[6] However, exploratory reactions between halogenoaryl derivatives of *ortho*-carborane and phenoxide ion gave evidence for deboronation of the icosahedral skeleton with formation of *nido*-C_2B_9 derivatives, and this approach has not been pursed further. (It should be noted however that the greatly enhanced stability of *para*-carborane towards nucleophilic attack suggests that nucleophilic polycondensations with derivatives of this carborane might yet be possible.)



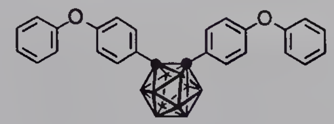
Scheme 1 *Potential routes to poly(arylene-carboranes)*

We therefore turned our attention to reaction (ii) (Scheme 1), the acid-promoted acylation of an aromatic-ether-carborane unit. Model reactions using the superacid trifluoromethanesulfonic acid as both solvent and catalyst were immediately encouraging and this approach in fact proved extremely successful for polymer synthesis, allowing the production of a wide range of new film- and fibre-forming polycarboranes. Molecular weights (M_W) up to ca. 250,000 are readily achieved, and the method is general for derivatives of all three (*o*-, *m*-, and *p*-) icosahedral carboranes.[7,8] Characterisation of these materials by ^{13}C NMR confirms that the polymers are linear and unbranched, and that the selectivity for *para*- over *ortho*-substitution in superacid-catalysed polyacylation reactions is greater than 200:1. Table 1 shows some of the monomers successfully exploited in this type of polymerisation reaction, together with characterisation data for a number of the polymers produced.

Most of the poly(etherketone-carborane)s so far prepared are non-crystalline and thus readily soluble in organic solvents such as chloroform or NMP, from which tough, coherent films and coatings can be obtained by solvent evaporation. However, we have found two polymers of this type, both derivatives of *p*-carborane, which display significant levels of crystallinity.[8] Thus, the semi-aliphatic polymer derived from bis(4-phenoxyphenyl)-*p*-carborane (**3**) and hexadecanedioic acid (**6**) undergoes solvent-induced crystallisation on contact with NMP, and then shows a crystal melting point of 122 °C.

Table 1. Monomers for polyetherketone-carboranes and polymer characterisation data

1



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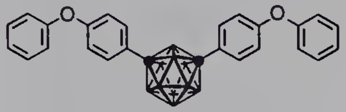

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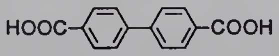

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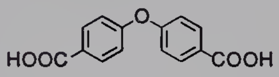

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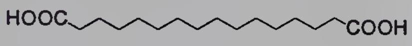

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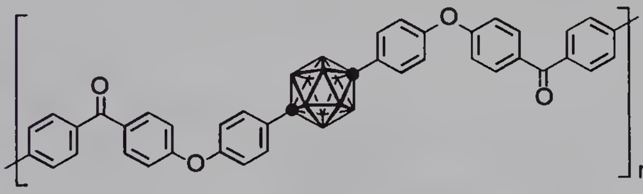
Monomers	M_n / M_w by GPC	Inherent viscosity (dl g^{-1})	T_g / T_m (°C)
1 + 4	37,100 / 61,500	0.58	212 / -
2 + 4	45,900 / 90,400	0.66	210 / -
3 + 4	155,000 / 254,200	1.21	267 / 386
3 + 5	53,800 / 111,400	1.09	236 / -
3 + 6	20,100 / 66,900	0.85	91 / 122

More interestingly perhaps, the polyketone 7, derived from bis(4-phenoxyphenyl)-*p*-carborane (**3**) and biphenyl-4,4'-dicarboxylic acid (**4**), is essentially amorphous on isolation from trifluoromethanesulfonic acid, but crystallises on heating above its glass transition temperature (267 °C) before finally melting at around 390 °C.



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Fibres of polycarborane **7**, wet-spun from trifluoromethanesulfonic acid, can be oriented and crystallised by drawing to five times their original length at ca. 300 °C, and the X-ray diffraction pattern from such a fibre is shown schematically in Figure 1. The two meridional arcs, with *d*-spacings of 5.3 and 4.6 Å, appear to correspond to sixth- and seventh-order reflections from a *d*-spacing of ca. 32 Å, approximately the distance calculated for a fully-extended chemical repeat of polymer **7**. In an effort to interpret the fibre-diffraction data in more detail, an oligomer-analogue (**8**) was synthesised by condensation of 4-bromobenzoic acid with monomer **3**, and its structure was determined by single crystal X-ray diffraction (Figure 2).†

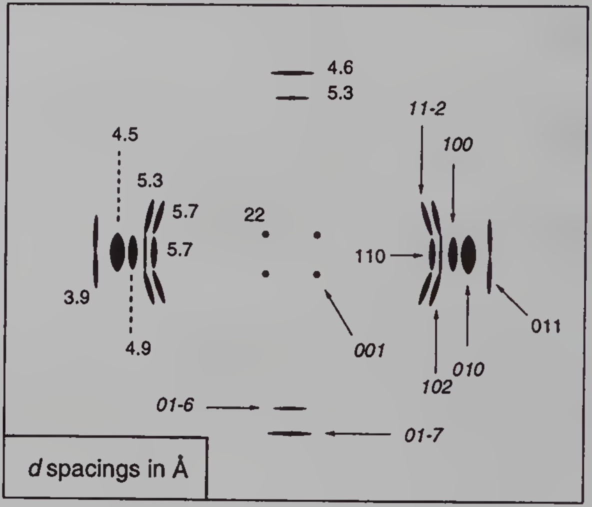


Figure 1 *X-ray fibre diffraction pattern (schematic) for polymer* 7

Geometrical and conformational data from this oligomer were then used to model possible crystal structures for polymer 7 using the molecular simulation and diffraction-modelling program *Cerius2* (MSI, San Diego, CA). The fibre pattern can provisionally be indexed, as shown in Figure 1, on the basis of a triclinic unit cell (one chain per cell) with dimensions $a = 6.50$, $b = 7.00$, $c = 32.8$ Å; $\alpha = 120$, $\beta = 87$, $\gamma = 58°$. A preliminary polymer structure based on this unit cell is shown in Figure 3.

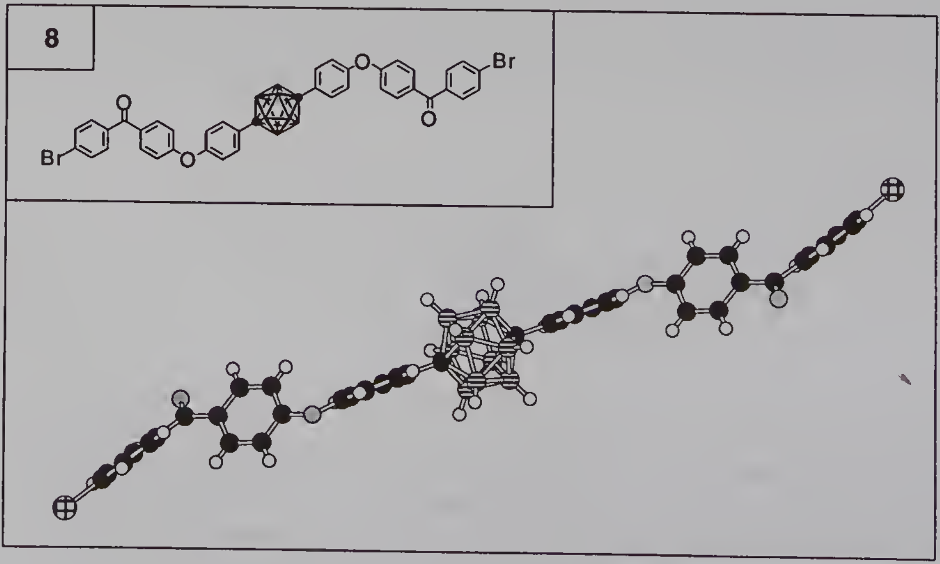


Figure 2 *Single crystal X-ray structure of an oligomer-model for polymer* 7

It is evident that efficient packing of polymer chains containing aromatic rings and carborane units requires significant longitudinal displacement of adjacent chains, unlike the situation for all-aromatic systems where little or no such displacement is observed.[9]

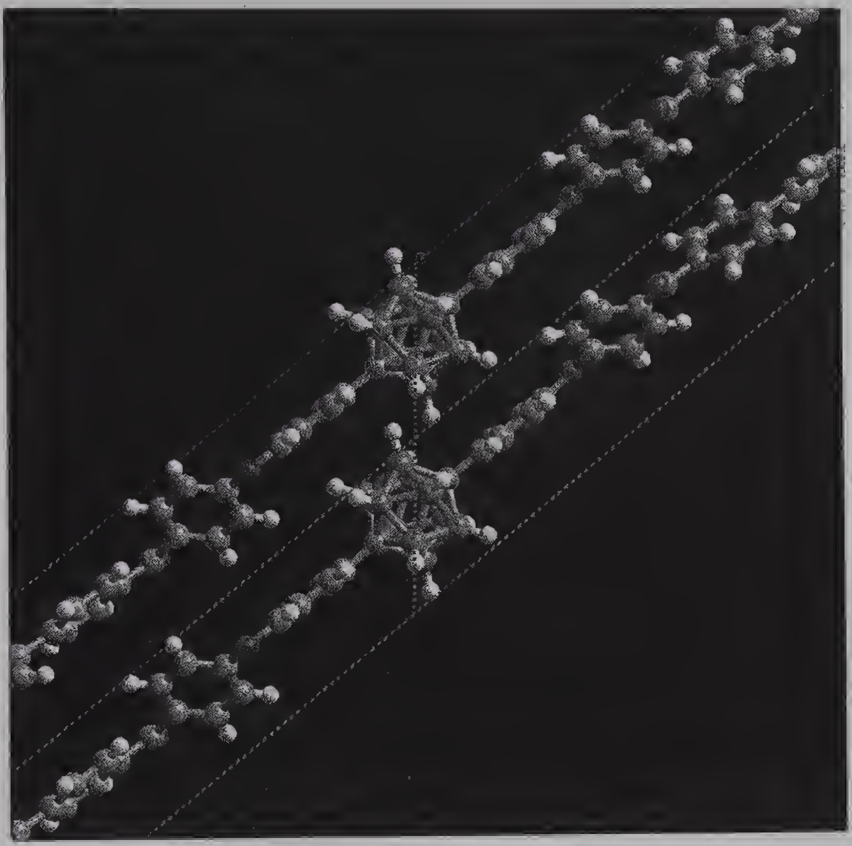
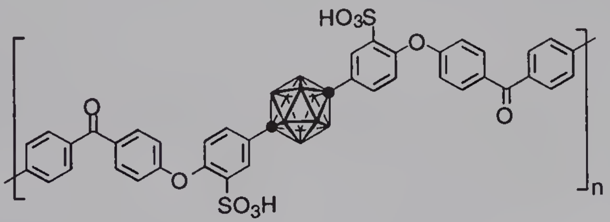


Figure 3 *Provisional crystal structure for polymer* 7*, viewed along the* a*-axis*

A potentially valuable characteristic of poly(ether-ketone-carborane)s is that they display enormously enhanced char-yields (up to 95% on pyrolysis in air), compared to the yields obtained from analogous all-aromatic polymers.[7] This behaviour suggests that carborane-based polyketones such as 7 could eventually find application as fire-retardants and as precursor polymers for carbon-ceramic materials.



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Polymer **2** dissolves slowly in 98% sulfuric acid without degradation of molecular weight, and is sulfonated regiospecifically and quantitatively to give ionomer **9**. This material, unlike the parent polymer 7, is strongly hydrophilic and dissolves readily in solvents such as methanol or ethanol, from which it can be coated onto a microporous polysulfone support-membrane to give a composite *nano*-filtration membrane (Figure 4). The surface film of polycarborane sulfonic acid is extremely thin, no more than 1000 Å in thickness, and shows high permeability to water (ca. 50 l m^{-2} h^{-1} at 5 bar pressure) and up to 96% rejection for ionic species, especially those containing divalent anions.[8] Such membranes are thus potentially applicable to processes such as the demineralisation and softening of drinking water.

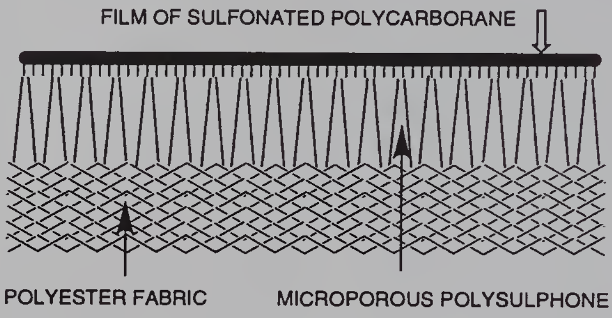
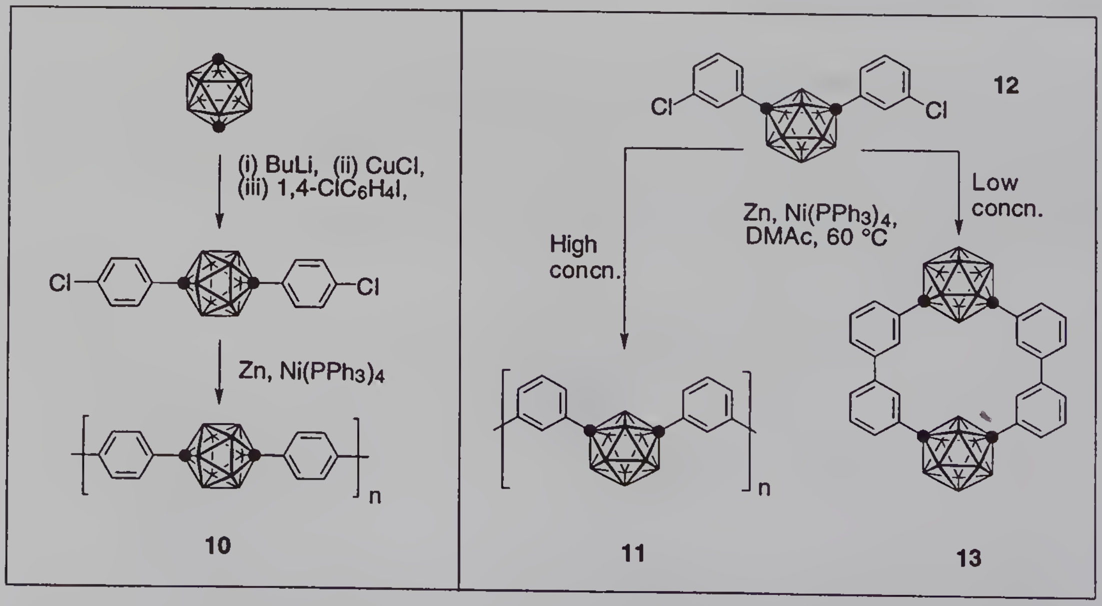


Figure 4 *Schematic cross section of a thin-film-composite nanofiltration membrane*

An alternative approach to the synthesis of arene-based polycarboranes involves the homogeneous, nickel-catalysed coupling reaction of bis(halogeno-aryl)carboranes with metallic zinc. We have used this reaction to synthesise the novel polymers **10** and **11**, carborane-based analogues of poly(*para*-phenylene) and poly(*meta*-phenylene) respectively (Scheme 2). Polymer **10**, like poly(*para*-phenylene) itself, is highly crystalline, extremely insoluble and does not melt below its decomposition temperature. However, it gives a very well-resolved X-ray powder pattern from which its crystal structure has been determined,[10] using the molecular simulation/diffraction modelling approach outlined above.



Scheme 2 *Polycondensation and macrocyclisation of bis(chlorophenyl)carboranes*

In contrast, the corresponding all-*meta* polymer **11** is much more tractable, being soluble in hot N-methylpyrrolidone (NMP), and softening above 250 °C to give a viscous melt from which fibres can be drawn. Analysis by DSC shows that polymer **11**, as isolated, is crystalline with a melting point of 248 °C, but that cooling fom the melt leads to vitrification rather than crystallisation, giving an amorphous polymer with a glass transition temperature of 169 °C. The inherent viscosity of polymer **11** (0.1% in NMP) was 0.42 dL g^{-1}, indicating that the polymer does not crystallise from solution until relatively high molecular weight is achieved. As shown in Scheme 2, catalytic coupling of 1,7-bis(3-chlorophenyl)-1,7-dicarbadodecaborane (**12**) at *low* concentration (< 1%) leads to macrocyclisation rather than polycondensation, affording the cyclodimer **13**. The structure of **13** has been confirmed by X-ray diffraction (Figure 5) which shows the molecule to be centrosymmetric, with non-planar 3,3'-biphenylene units.§

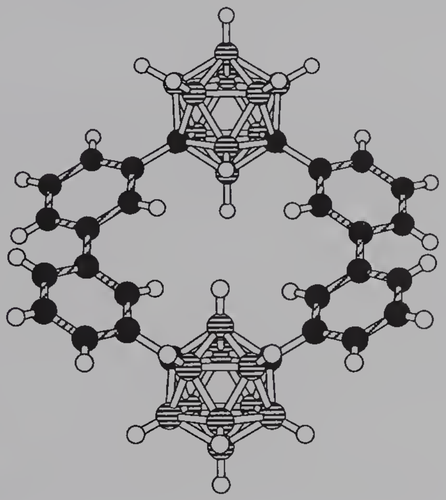


Figure 5 *Single crystal X-ray structure of macrocycle* **13**

3 CONCLUSIONS

High molecular weight poly(arylene-carborane)s may be synthesised by both acid-catalysed electrophilic aromatic substitution and by metal-catalysed dehalogenative coupling reactions. Structural analysis by X-ray powder- and fibre-diffraction, interfaced to molecular modelling and difraction-simulation, indicates that the crystal structures of poly(arylene-carborane)s are dominated by a requirement for non-adjacent packing of the bulky carborane units. Such polymers, many of which may be spun as fibres or fabricated into films and coatings, display unusually high char-yields. Poly(etherketone-carborane)s are cleanly sulfonated on dissolution in concentrated sulfuric acid, to give ionomers with excellent properties as nanofiltration membranes.

4 ACKNOWLEDGEMENTS

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Footnotes and References

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[†] ***Crystal data for* 8.** $C_{40}H_{34}B_{10}Br_2O_4$, $M = 846.59$, monoclinic, $P2_1/n$, $a = 7.307(1)$, $b = 22.040(1)$, $c = 11.712(1)$ Å, $\beta = 93.29(1)$, $V = 1882.9(2)$ Å^3, $T = 293$ K, $Z = 2$, $D_c = 1.493$ g cm^{-3}, μ(Cu-Kα) = 30.64 cm^{-1}, $F(000) = 852$. $R_1 = 0.0412$, $wR_2 = 0.1123$ for 2694 independent observed reflections [$2\theta \leq 120°$, $F_o > 4\sigma(F_o)$].

[§] ***Crystal data for* 13.** $C_{28}H_{36}B_{20}$, $M = 846.59$, monoclinic, $P2_1/n$, $a = 7.161(1)$, $b = 11.809(1)$, $c = 19.028(2)$ Å, $\beta = 94.99(1)$, $V = 1602.9(3)$ Å^3, $T = 173$ K, $Z = 2$, $D_c = 1.220$ g cm^{-3}, μ(Cu-Kα) = 4.21 cm^{-1}, $F(000) = 608$. $R_1 = 0.0507$, $wR_2 = 0.1322$ for 2374 independent observed reflections [$2\theta \leq 120°$, $F_o > 4\sigma(F_o)$].

Full crystallographic details for **8** (CCDC-130232) and **13** (CCDC-130233) have been deposited at the Cambridge Crystallographic Data Centre. Copies can be obtained by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ. Email: deposit@ccdc.cam.ac.uk.

1. R.E. Williams, *Pure Appl. Chem.*, 1972, **29**, 569.
2. E.N. Peters, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1979, **C17**, 173.
3. R.B. Seymour and G.S. Kirshenbaum (Eds.), “High Performance Polymers: Their Origin and Development”, Elsevier, New York, 1986.
4. R.N. Johnson, A.G. Farnham, R.A. Clendinning, W.F. Hale, and C.N. Merriam, *J. Polym. Sci. A-1*, 1967, **5**, 2375.
5. H.M. Colquhoun and D.F. Lewis, *Polymer*, 1988, **29**, 1902.
6. M. Ueda, Y. Seino, and J. Sugiyama, *Polym. J.*, 1993, **25**, 1319.
7. H.M. Colquhoun, D.F. Lewis, J.A. Daniels, P.L. Herbertson, J.A.H. MacBride, I.R. Stephenson and K. Wade, *Polymer*, 1997, **38**, 2447.
8. H.M. Colquhoun, D.F. Lewis, P.L. Herbertson and K. Wade, *Polymer*, 1997, **38**, 4539.
9. D.J. Blundell and A.B. Newton, *Polymer*, 1991, **32**, 308.
10. H.M. Colquhoun, P.L. Herbertson, K. Wade, I. Baxter and D.J. Williams, *Macromolecules*, 1998, **31**, 1694.

Thermal, Photochemical, and Redox Reactions of Borane and Metallaborane Clusters with Applications to Molecular Electronics

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1. INTRODUCTION

Photochemical transformations are widely employed in both organic and organometallic chemistry and have been extensively used as synthetic strategies for the formation of a variety of new compounds.[1] Part of our recent research has focused upon an exploration of the photochemical reactions of borane and metallaborane clusters. As a contextual setting for these photochemical studies, we have also explored several aspects of the thermal and redox chemistry of these clusters. In this paper, we present a summary of our recent work on the thermal, photochemical, and redox reactions of borane and metallaborane clusters. In addition, recent work directed toward the application of these clusters to several aspects of molecular electronics will be presented.

2. PHOTOCHEMICAL AND RELATED REACTIONS OF CLUSTERS

2.1. Background

Prior to our work reported here, several examples of photochemical reactions of clusters had been reported. For main group organometallic clusters specifically, the photochemistry of four metal complexes had been reported.[2l,m,3] In the first example, it was observed that the irradiation of $[(Fe(\eta^5\text{-}C_5H_5)(CO)_2B_{10}H_{13}]$ in ether yielded $[Fe(\eta^5\text{-}C_5H_5)B_{10}H_{10}C(L)]$ (where L = OEt_2 or THF) in 1 to 3 % yield.[2l] This unexpected product presumably resulted from the net loss of a CO ligand and the insertion of both an $[Fe(\eta^5\text{-}C_5H_5)]$ fragment and a carbon atom, possibly from a former CO ligand, into the cage. Another example involved the irradiation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\mu\text{-}4,5\text{-}C_2B_4H_7)]$, resulting in the formation of $[Fe(\eta^5\text{-}C_5H_5)(H)C_2B_4H_6]$ and $[Fe(\eta^5\text{-}C_5H_5)C_2B_4H_6]$ in equal quantities.[2k,m] The third report involved the photo-insertion of alkynes into $B_4H_8Fe(CO)_3$ to yield new higher carboranes.[2g] In the final prior case, we investigated the photochemistry of a phosphino substituted σ-metallated pentaborane complex, $[(\mu\text{-}2,3\text{-}(P(C_6H_5)_3)\text{-}4\text{-}(Fe(\eta^5\text{-}C_5H_5)(CO)_2)B_5H_8]$.[4b] In that work, irradiation of the complex produced a new metallaborane compound in which a carbonyl ligand and a cage boron had been lost, followed by a structural rearrangement to yield a substituted *arachno*-pentaborane(11)-based cluster, $[Fe(\eta^5-C_5H_5)(CO)B_4H_6(P(C_6H_5)_2)]$.[5b]

Relatively few studies have been directed toward the photochemistry of the boranes themselves.[6] Early work on the high energy photochemistry of gaseous *nido*-pentaborane(9) found that a variety of species were generated upon irradiation including H_2, BH_3, B_2H_6, B_4H_5, $B_{10}H_{14}$, and $B_{10}H_{16}$, depending upon the conditions employed.[6-8] Several key mechanistic steps in this photoprocess were suggested but a clear picture of this complex mechanism is far from certain. The gas-phase mercury-photosensitized reactions of a variety of small boranes and carboranes have also been investigated by Sneddon.[9a] The products of these photoreactions were typically coupled boranes, such as tetraborane(10) from diborane(6) and $2,2'-(1-CH_3B_5H_7)_2$ from $1-CH_3B_5H_8$. In addition, small *closo*-carboranes were found to react with photo-generated atomic sulfur (^1D) to provide a convenient method for preparing the corresponding B-mercaptocarboranes.[9b] Finally, the cophotolysis of different carboranes was found to result in the formation of mixed cage coupled species.

2.2. Photochemical Pathways

We have found that borane and metallaborane compounds clearly display at least five different photochemical reaction modes depending upon the compound, conditions (i.e., temperature, solvent, etc.), and wavelength of irradiation. These photoreactions include; (1) ligand dissociation and cage insertion reactions, (2) cage isomerization reactions, (3) hydrogen (H_2) loss reactions, (4) homolytic bond cleavage reactions, and (5) cage substitution reactions. The products of these reactions have typically been characterized by multinuclear and multidimensional NMR, X-ray crystallography (simple line drawings rather than ORTEP plots are used in this paper for clarity of view), FTIR and other spectroscopic techniques. Work has been primarily focused on three polyhedral cages; pentaborane, nonaborane, and octadecaborane cages.

2.2.1 Ligand Dissociation and Cage Insertion Reactions. We have investigated the photochemistry of several borane derivatives of the well known $[Fe(\eta^5-C_5H_5)(CO)_2]$ organometallic fragment (Figure 1).[4] Detailed photochemical

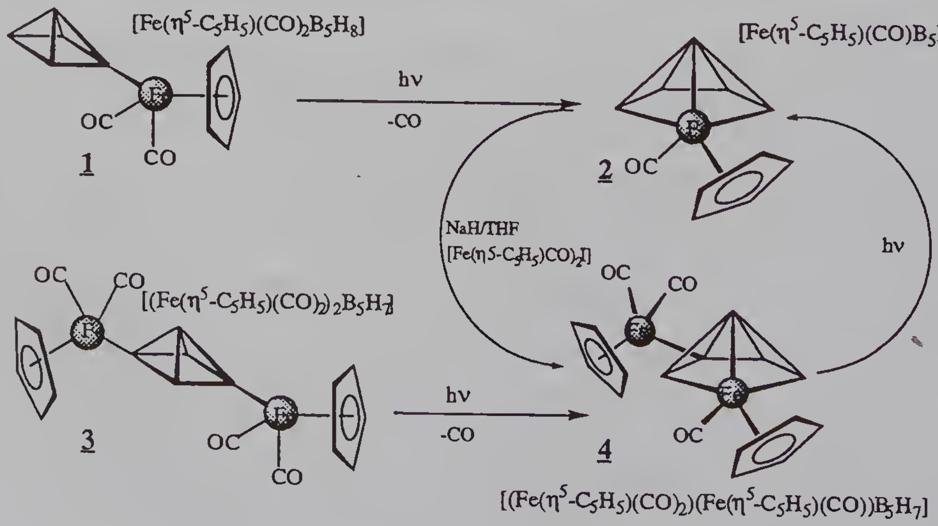

Figure 1. Photochemical reactions of iron-substituted pentaborane clusters.[10]

investigations of the related $[Fe(\eta^5\text{-}C_5H_5)(CO)_2R]$ (where R = alkyl or aryl) organometallic compounds have been previously reported in the literature.[11] From this earlier work, it appears that the primary photochemical step for these organic complexes involves either the photo-induced dissociation of a carbonyl ligand or, much less efficiently, the homolytic bond cleavage of a M-R linkage.

The synthesis of the σ-metallated pentaborane cluster, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2B_5H_8]$, 1, had been previously reported[12] and we were able to confirm the structural geometry of this starting species crystallographically.[4] The irradiation of complex 1 in THF showed its quantitative conversion into a new complex, $[Fe(\eta^5\text{-}C_5H_5)(CO)B_5H_8]$, 2, in which the organometallic iron fragment had lost a carbonyl group and was inserted into the base of the pentaborane cage forming a new *nido*-pentagonal pyramidal cluster.[4] The quantitative formation of 2 is in sharp contrast to the very low yield observed for the insertion reaction of the related decaborane(14) $[(Fe(\eta^5\text{-}C_5H_5)(CO)_2B_{10}H_{13}]$ complex reported earlier.[2m] In a fashion similar to complex 1, the bis-σ-metallated $[(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ complex 3[12] was also prepared and upon irradiation was observed to cleanly lose a single carbonyl ligand from one iron center to yield one inserted and one terminally B_5-cage bound iron unit leading to the formation of complex 4.

2.2.2 Cage Isomerization Reactions. Thermal cage isomerization reactions are known for both borane and metallaborane cages.[13] To our knowledge, however, none had been reported to occur photochemically. Group 12 organometallic species are known from the literature to undergo a variety of photoreactions and, therefore, it became of interest to explore the borane analogues of these photoactive species. In particular, the group 12 metallaborane compounds were investigated in which two borane cages were bonded to a single metal, thereby completely filling the coordination sphere of the metal center (Figure 2).[14] Thus, the $[M(B_9H_{13})_2][NMe_4]_2$ complexes (where M = Zn and Cd) were prepared in 80-90% yield from the metathesis reaction of $K_2[B_9H_{13}]$ with MCl_2.[15] The molecular structure of the cadmaborane species showed that two *nido*-6-cadmadecaborane clusters were conjoined at a common cadmium atom in an overall "S" shape with both of the $B_9H_{13}Cd^-$ subclusters essentially identical. When irradiated at 254 nm in CD_3CN, the zinc complex, 6a, is believed to undergo a transformation leading to a new complex, 7, which is an isomer of the starting complex (not yet crystallographically characterized).[15] In complex 6a, the zinc is presumed coordinated to the "end"

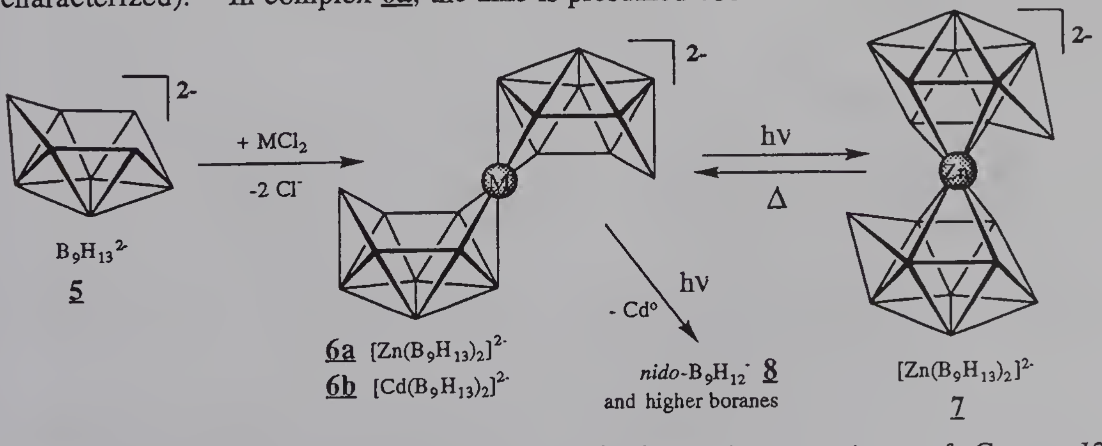

Figure 2. Photochemical isomerization and elimination reactions of Group 12 metalla-bis-nonaboranes.[5]

triborane subunit of the $[B_9H_{14}]^-$ cage both "directly" (through Zn-B bonds) and "indirectly" (through B-H-Zn bonds) as crystallographically observed for the cadmium analog.[16] In the proposed structure of the new isomer, 7, the metal is thought to be coordinated to the "interior" four boron atoms of the cage. After complex 7 was photochemically generated, it was found to undergo a slow thermal transformation back to the starting complex 6a. The total conversion to the starting isomeric form takes approximately one week at room temperature. This transformation, however, can be accelerated by refluxing the photoproduct (total conversion in refluxing CD_3CN in 10 hours). It appears that this process of the photochemical generation of isomer 7 followed by the thermal regeneration of the starting complex 6a is a completely reversible process and appears to be a rare example in metallaborane chemistry of such an entirely intramolecular "cyclic" isomerization pattern. In contrast to complex 6a, the analogous cadmaborane complex 6b was found to undergo a redox process upon irradiation to yield cadmium metal, the *nido*-$B_9H_{12}^-$ cage and higher boranes.[16]

We have also studied the photochemistry of the nonaborane organometallic derivatives of manganese, rhodium, and rhenium in detail. First, the isoelectronic and isostructural $[Mn(CO)_3B_9H_{13}]^-$ (10)[17] and $[Rh(\eta^5\text{-}C_5Me_5)B_9H_{13}]$ (13)[18] complexes were prepared by literature methods. We found that all of these complexes yielded new metallaborane products upon UV irradiation, as summarized in Figure 3.[19,20] Upon irradiation, it was found that the $[Mn(CO)_3B_9H_{13}]^-$ complex was converted in high yield into a *hypercloso*-$[Mn(CO)_3B_9H_9]^-$ complex (9) through the loss of two equivalents of hydrogen.[19] The synthesis of a similar *hypercloso*-iridium complex by a different

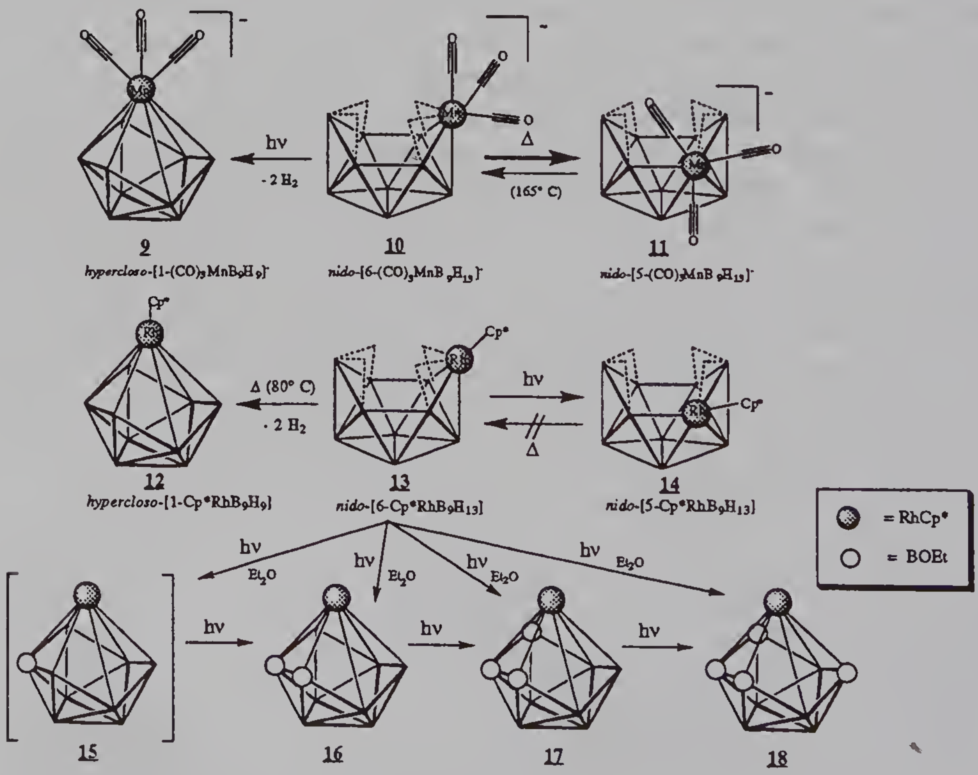

Figure 3. Photochemical isomerization, hydrogen loss/insertion and substitution reactions of metallanonaboranes.[5]

pathway has been reported previously.[21] It was somewhat surprising that no carbonyl loss was observed in the photolysis of 10. Upon heating (without irradiation), complex 10 was observed to cleanly undergo an isomerization reaction from the *nido*-[6-$Mn(CO)_3B_9H_{13}]^-$ isomer (10) to the *nido*-[5-$Mn(CO)_3B_9H_{13}]^-$ isomer (11).[20] Very similar products were observed from the analogous rhodium complex except that the photogenerated manganese *hypercloso*-complex (9) corresponded to the structure of the thermally generated rhodium *hypercloso*-complex (12) and the thermally generated manganese complex (11) corresponded to the photogenerated rhodium species (14). The reasons for this reversal of photo and thermal products between the manganese and rhodium systems are currently being explored.[22] In contrast, the photochemical irradiation of the starting complex 13 in Et_2O was found to yield B-substituted *hypercloso*-structures with one to four ethoxy units replacing terminal hydrogens of the borons attached to the metal center (Fig. 3).

Compounds such as *hypercloso*-9 and 12 have provided an entry into the long debated question of the relationship between the structures shown in Fig. 3 and the bicapped square antiprismatic structure for 10-vertex clusters.[23] Extended Hückel MO calculations on a model system showed that the bicapped square antiprismatic structure is preferred for the 2n+2 skeletal electron system (*closo*) while the C_{3v} structure was preferred for 2n electron systems (*hypercloso*).[23-25] Thus, the discussion has revolved around the description of compounds 9 and 12 as either *hypercloso* 2n electron systems[23] or as isomers of *closo* (*isocloso*) 2n+2 electron systems which apparently violate Wade's rules.[24b] While simple redox processes would be thought to interconvert these structures, this has not been experimentally shown for underivatized species. As shown in Figure 4, we have now observed, however, the reversible and

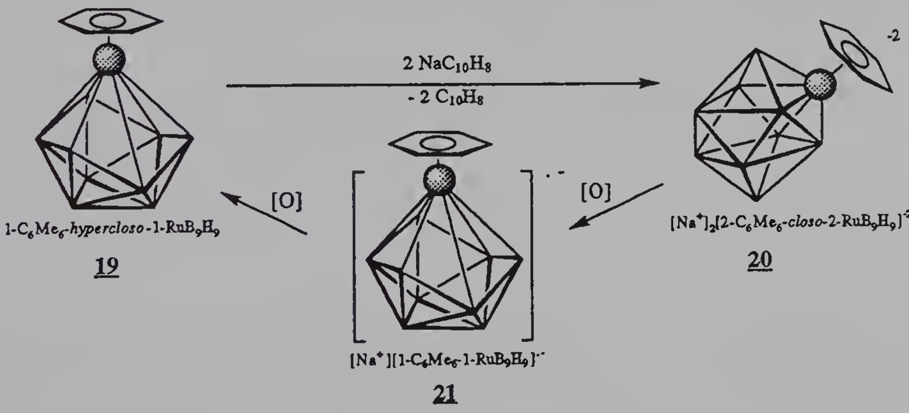

Figure 4. *Conversion of the* hypercloso-*MB_9 cluster to the* closo-*MB_9 species and the intermediate radical anion species.*

quantitative reductive conversion of the *hypercloso*-$[Ru(C_6Me_6)B_9H_9]$ C_{3v} species (19) to the predicted bicapped square antiprismatic *closo*-structure (20).[26] The dianion (20) is one of the very few crystallorgraphically characterized metalladecaborane clusters and the only cage unsubstituted species. Interestingly, a relatively stable radical anion intermediate (21) was also observed through the one electron oxidation of the dianion.[26]

2.2.3 Hydrogen Loss Reactions. Several hydrogen loss reactions have already been presented above.[24,27] For example, the photolysis of complex 10 (Figure 3) shows the clean elimination of two equivalents of hydrogen to generate the corresponding *hypercloso*-complex 9. These elimination reactions occur preferentially to carbonyl loss. The observed conversion of complex 10 into complex 9 is somewhat reminiscent of the few organometallic hydride complexes that have been photochemically investigated in which, however thermally resistant the complex is to hydrogen loss, photogeneration of hydrogen can be very easily accomplished.[28] It appears that the Mn-H-B bridging hydrogen atoms in complex **10** behave similarly to organometallic hydride ligands and thus preferentially eliminate hydrogen over other photoreactions.

2.2.4 Homolytic Bond Cleavage Reactions. Several examples of photochemical homolytic bond cleavage processes have already been presented. In the photolysis of the bis-σ-metallated $[(Fe(\eta^5\text{-}C_5H_5)(CO)_2)_2B_5H_7]$ complex (**3**, Figure 1), for example, the ultimate photoproducts upon continued irradiation were the previously identified mono-iron inserted complex, **2**, and the coupled organometallic fragment $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$.[4] Presumably, these products arise from the homolysis of the Fe-B linkage of the terminally bound fragment to generate two radical species. Once generated, these species would participate in radical reactions leading to the observed formation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and **2**. The other potential coupling product, $[Fe(\eta^5\text{-}C_5H_5)(CO)B_5H_7]_2$, was not observed. Instead, the monoiron complex, **2**, was formed, presumably arising through the abstraction of hydrogen from the solvent.

2.2.5 Cage Substitution Reactions. We have also explored the photo-substitution reactions of the *arachno*-octahydrotriborate(1-) anionic compound, $[B_3H_8]^-$ (Figure 5).[5c] This small borane shows exceptional oxidative and hydrolytic stability, in marked contrast to the extremely facile thermal hydrolysis and alcoholysis reactions of diborane(6) and pentaborane(9). We have found, however, that the chemically "inert" $B_3H_8^-$ species undergoes rapid and exceptionally clean photoinduced reactions.[5c,28] We have further expanded the scope of these photoreactions significantly and have found that the triborane anion also photoreacts with compounds which contain a halogen, a site of unsaturation, or an acidic proton. In the photo-reaction of $B_3H_8^-$ with ethanol, for example, the sequentially observed products were $HB(OC_2H_5)_2$ and $B(OC_2H_5)_3$.[28a] The irradiation of $B_3H_8^-$ in the presence of chlorohydrocarbons was found to sequentially produce halogenated products which could be readily isolated.[28b,c] In some of these reactions, the $B_3H_8^-$ cage system itself is believed to be the initially photoexcited species. In others, in which the solvent/reactant can be photoexcited at 254 nm (such as acetone and benzophenone), the solvent is presumably the primary chromaphore, leading to the observed substitution products.

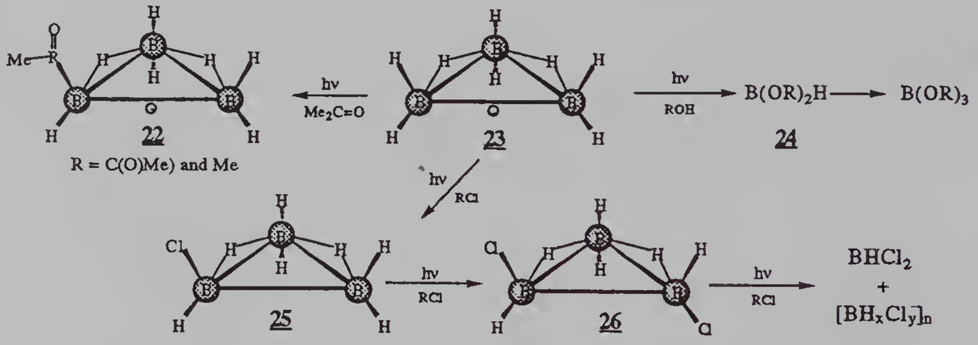

Figure 5. Photochemical reactions of the triborane anion.

3. MOLECULAR ELECTRONICS APPLICATIONS OF CLUSTERS

An emerging technologically important field is that of nonlinear optics (NLO). NLO materials typically respond to applied electromagnetic fields by generating new electromagnetic fields with altered properties, particularly in frequency and phase.[29] Many types of molecular NLO compounds have thus far been investigated, especially the organic and organometallic-based systems.[30] Most molecular second-order NLO materials employ electron donors and acceptors which are connected through an organic π-delocalized framework,[31] although several organometallic systems have also been explored.[32] Thus far, however, relatively little has been reported involving molecular polyhedral-based compounds with charged aromatic donor/acceptor moieties for NLO applications. Previous work has reported the synthesis and NLO second-order responses for a series of substituted 1,2-dicarba-*closo*-dodecaboranes.[33] First hyperpolarizabilities (β) for these compounds were reported between 2.7 and 13 x 10^{-30} cm^5 esu^{-1} at 1064 nm (1.17 eV). Recently, the synthesis and experimental NLO response of a 12-tropyl substituted 1-carba-*closo*-dodecaborate anion has also appeared.[34] In our recent work, we have investigated the nonlinear responses of main group polyhedral compounds with both charged aromatic donor and acceptor moieties, specifically cyclopropenyl, tropyl and cyclopentadienyl substituted boranes, which show exceptionally high calculated second-order nonlinear responses.

We have explored the calculated structures and second-order responses for a series of model cluster-based compounds using *semiempirical* methods.[35] These polyhedra were substituted with charged aromatic moieties, particularly cyclopropenyl, tropyl and cyclopentadienyl groups, and fully SCF optimized at the MNDO-AM1 level without symmetry restrictions. The molecular and electronic structures and the non-resonant β values for these compounds were calculated at 0.5 eV using the methods previously reported.[36] Examples of the species investigated and their calculated non-resonant first hyperpolarizabilities are given in Table 1. These compounds were found to typically display exceptionally large calculated hyperpolarizabilities. The magnitude of β is known to be very sensitive to excitation wavelength and increases significantly with increases in energy.[38] Therefore, the NLO responses for the new compounds reported here are even more remarkable when compared to other known NLO compounds at similar excitations. For example, the β values for some of these borane-based species are several orders of magnitude larger than that of the commonly use *p*-nitroaniline NLO benchmark (compared at the same excitation wavelength).[31]

Work is currently in progress on the synthesis of these and similar polyhedral-based NLO compounds with charged aromatic donor and acceptor groups in order to experimentally determine their molecular structures and measure their nonlinear responses.

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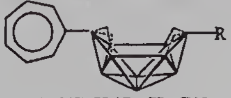
Table 1. Calculated second-order responses (β) **at 0.5 eV** for selected NLO clusters.[a,b]

	R	μβ[a]	β[a]
 *nido*-[$(C_7H_6)B_{10}H_{12}(R)$]	R = C_5H_4 R = C_5Me_4	22463.7 29155.6	1029.8 1371.7
 *conjuncto*-[$(C_7H_6)B_{18}H_{20}(R)$]	R = C_5H_4 R = C_5Me_4	92138.3 129963.9	2914.7 4145.7
 *closo*-[$(C_7H_6)B_{10}H_8(R)]^{2-}$	R = C_5H_4 *1,2-isomer* *1,10-isomer* R = C_5Me_4 *1,10-isomer*	 162.0 3379.0 606.5	 20.8 260.4 296.1
 *nido*-[$(C_7H_6)B_9H_{11}(R)]^{2-}$	R = C_5H_4 *Tp and Cp co-parallel* *Tp and Cp perpendicular*	 111.7 84.0	 25.5 12.0
		43.5	5.3 (6.2[c])

a. Calculated second-order responses (β) were completed using *semi-empirical* (MOPAC AM1) calculations at 0.5 eV using the E4 method. The values of β are given in units of -1 x 10^{-30} cm^5 esu^{-1} and μβ in x 10^{-48} esu.

b. Shown for representative molecules is a schematic line drawing. The terminal cage, tropyl, and cyclopentadienyl hydrogens have been omitted from the drawings and the cage borons are shown as unlabeled vertices.

c. Literature $\beta_{(\omega)}$ value (ref 37) was reported using *ab initio* methods at 6-31G** of 6.2 x 10^{-30} cm^5 esu^{-1}.

REFERENCES

1. N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, 1978.
2. (a) R. V. Schultz, F. Sato, and L. J. Todd, *J. Organometal. Chem.*, 1977, **125**, 115. (b) P. D. Grebenik, M. L. H. Green, M. A. Kelland, J. B. Leach, and P. Mountford, *J. Chem. Soc., Chem. Commun.*, 1989, 1397. (c) N. N. Greenwood and R. Greatrex, *Pure Appl. Chem.*, 1987, **59**, 857. (d) R. J. Astheimer and L. G. Sneddon, *Inorg. Chem.*, 1984, **23**, 3207. (e) J. S. Plotkin, R. J. Astheimer, and L. G. Sneddon, *J. Am. Chem. Soc.*, 1979, **101**, 4155. (f) T. P. Fehlner, *J. Am. Chem. Soc.*, 1978, **100**, 3250. (g) T. P. Fehlner, *J. Am. Chem. Soc.*, 1977, **99**, 8355. (h) G. Zweifel, G. M. Clark, and K. G. Hancock, *J. Am. Chem. Soc.*, 1971, **93**, 1308. (i) G. A. Kline and R. F. Porter, *Inorg. Chem.*, 1980, **19**, 447. (j) M. P. Irion, M. Seitz, K. L. Kompa, *J. Mol. Spectrosc.*, 1986, **118**, 64. (k) L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, 1973, **95**, 6623. (l) R. V. Schultz, F. Sato, and L. J. Todd, *J. Organometal. Chem.*, 1977, **125**, 115. (m) J. T. Spencer, M. R. Pourian, R. J. Butcher, E. Sinn, and R. N. Grimes, *Organometallics*, 1987, **6**, 335. (n) J. S. Plotkin and L. G. Sneddon, *J. Chem. Soc., Chem. Commun.*, 1976, 95.
3. J. E. Taylor and J. T Spencer, in preparation.
4. (a) B. H. Goodreau, L. R. Orlando, and J. T. Spencer, *J. Am. Chem. Soc.*, 1992, **114**, 3827. (b) B. H. Goodreau, L. R. Orlando, and J. T. Spencer, *J. Am. Chem. Soc.*, 1995, **117**, 11754.
5. (a) B. H. Goodreau, R. L. Ostrander, and J. T. Spencer, *Inorg. Chem.*, 1991, **30**, 2066. (b) B. H. Goodreau, L. R. Orlando, and J. T. Spencer, *Inorg. Chem.*, 1992, **31**, 1731.

(c) C. M. Davis, B. H. Goodreau, R. A. Nardone, L. R. Orlando, and J. T. Spencer, *Cur. Top. Chem. Boron,* 1994, 322.

6. R. F. Porter and L. J. Turbini, *Top. Curr. Chem.*, 1981, **96**, 1.
7. M. P. Irion and K. L. Kompa, *J. Photochem.*, 1987, **37**, 233.
8. (a) S. Trofimenko, *J. Am. Chem. Soc.*, 1966, **88**, 1899. (b) W. C. Kreye and R. A. Marcus, *J. Chem. Phys.,* 1962, **37**, 419.
9. (a) J. S. Plotkin, R. J. Astheimer, and L. G. Sneddon, *J. Am. Chem. Soc.*, 1979, **101**, 4155. (b) J. S. Plotkin and L. G. Sneddon, *J. Am. Chem. Soc.*, 1977, **99**, 4155.
10. Cage hydrogens have been omitted from this figure.
11. (a) J. P. Blaha and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 2694. (b) R. J. Kazlauskas and M. S. Wrighton, *Organometallics,* 1982, **1**, 602. (c) C. L. Randolph and M. S. Wrighton, *Organometallics,* 1987, **6**, 365.
12. (a) N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, and K. R. Trigwell, *J. Chem. Soc., Dalton,* 1978, 237. (b) M. B. Fischer, D. F. Gaines, and J. A. Ulman, *J. Organometal. Chem.*, 1982, **231**, 55.
13. (a) T. Onak, In “Comprehensive Organometallic Chemistry”, G. Wilkinson, F. G. A. Stone, and E. Abel, Eds., Pergamon, Oxford, 1982, Vol. 1, Chapter 5.4, p 411. (b) R. N. Grimes, In “Comprehensive Organometallic Chemistry”, G. Wilkinson, F. G. A. Stone, and E. Abel, Eds., Pergamon, Oxford, 1982, Vol. 1, Chapter 5.5, p 485. (c) P. D. Grebenik, J. B. Leach, M. L. H. Green, N. M. Walker, *J. Organomet. Chem.*, 1988, **345**, C31.
14. (a) R. N. Grimes, Ed., “Metal Interactions with Boron Clusters”, Plenum Press, New York, 1982. (b) R. N. Grimes, In “Comprehensive Organometallic Chemistry”, Pergamon Press, New York, 1982, Chapter 5.4. (c) L. Barton, and D. K. Srivastava, In “Comprehensive Organometallic Chemistry”, Pergamon, New York, 1995, Chapter 8. (d) L. -L. Ng, B. K. Ng, K. Shelly, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1991, **30**, 4278. (e) N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc. (A),* 1971, 809. (f) N. N. Greenwood and N. F. Travers, *J. Chem. Soc. (A),* 1968, 15. (g) N. N. Greenwood and N. F. Travers, *J. Chem. Soc. (A),* 1971, 3257. (h) N. N. Greenwood and N. F. Travers, *J. Chem. Soc. (A),* 1967, 880. (i) N. N. Greenwood and D. N. Sharrocks *J. Chem. Soc. (A),* 1969, 2334. (j) L. J. Guggenberger, *J. Am. Chem. Soc.*, 1972, **94**, 114. (k) F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 2072. (l) A. J. Wynd and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1987, 1174. (m) D. L. Denton, W. R. Clayton, M. Mangion, S. G. Shore, and E. A. Meyers, *Inorg. Chem.*, 1976, **15**, 541. (n) J. P. Brennan, R. Schaeffer, A. Davison, and S. S. Wreford, *J. Chem. Soc., Chem. Commun.*, 1973, 354. (o) D. F. Gaines, J. L. Walsh, and J. C. Calabrese, *Inorg. Chem.*, 1978, **17**, 1242. (p) J. C. Calabrese, D. F. Gaines, S. J. Hildebrandt, and J. H. Morris, *J. Am. Chem. Soc.*, 1976, **98**, 5489.
15. R. Littger, U. Englich, and J. T. Spencer, *Inorg. Chem.*, 1997, **36**, 6434.
16. R. Littger and J. T. Spencer, in preparation.
17. J. W. Lott and D. F. Gaines, *Inorg. Chem.*, 1974, **13**, 2261.
18. X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.
19. R. Littger and J. T. Spencer, submitted.
20. R. Littger and J. T. Spencer, in preparation. [Our data for compound <u>**17**</u> matches with literature values; M. Bown, H. Fowkes, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and K. Nestor, *J. Chem. Soc., Dalton Trans.*, 1988, 2597]
21. (a) E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1262. (b) J. Bould, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1982, 465. (c) J. E. Crook, M. Elrington, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1985, 2407.
22. (a) M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, 1977, **99**, 5231. (b) M. J. S. Dewar and W. Theil, *J. Am. Chem. Soc.*, 1977, **99**, 4907. (c) M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 3607. (d) M. J. S. Dewar, J.

Friedheim, G. Grady, E. F. Healy, J. J. P. Stewart, *Organometallics*, 1986, **5**, 375. (e) M. J. S. Dewar and H. S. Rzepa, *J. Comp. Chem.*, 1983, **4**, 158.

23. (a) R. L. Johnson and D. P. M. Mingos, *Inorg. Chem.*, 1986, **25**, 3321. (b) R. L. Johnson and D. P. M. Mingos, *New J. Chem.*, 1991, **15**, 831. (c) R. T. Baker, *Inorg. Chem.*, 1986, **25**, 109.
24. (a) R. S. Coldicott, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1996, 3619. (b) J. D. Kennedy, *Inorg. Chem.*, 1986, **25**, 111.
25. C. W. Jung, R. T. Baker, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1981, ***103***, 810.
26. R. Littger, U. Englich, K. Ruhlandt-Senge, and J. T. Spencer, submitted.
27. J. S. Ward and R. Pettit, *J. Am. Chem. Soc.*, 1971, **93**, 262.
28. Photosubstitution products of $B_3H_8^-$ (i.e., $B(OR)_2H$, $B(OR)_3$, $B_3H_7Cl^-$, $B_3H_6Cl_2^-$, etc...) have been previously prepared and characterized by chemical routes. Our data matches those previously reported for these compounds; (a) M. G. Hu and R. A. Geangel, *Inorg. Chem.*, 1979, **18**, 3297. (b) G. B. Jacobsen and J. H. Morris, *Inorg. Chim. Acta,* 1982, **59**, 207. (c) M. Arunchaiya, J. H. Morris, S. J. Andrews, D. A. Welch, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1984, 2525.
29. (a) P. R. Prasad and D. J. Williams, In "Introduction to Nonlinear Optical Effects in Molecules and Polymers; Introduction to Nonlinear Optical Effects in Molecules and Polymers", John Wiley and Sons, New York, 1991. (b) D. S. Chemla and J. Zyss, "Nonlinear Optical Properties of Organic Molecules and Crystals", Academic, Orlando, Florida, 1987. (c) R. A. Hann and D. Bloor, "Organic Materials for Nonlinear Optics ", Royal Society of Chemistry, London, 1989.
30. W. Blau, *Phys. Technol.*, 1987, **18**, 250.
31. D. R. Kanis, M. A. Ratner, and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.
32. S. D. Cummings, L. -T. Cheng, R. Eisenberg, *Chem. Mater.*, 1997, **9**, 440.
33. (a) D. M. Murphy, D. M. P. Mingos, and J. M. Forward, *J. Mater. Chem.*, 1993, **3**, 67. (b) D. M. Murphy, D. M. P. Mingos, J. L. Haggitt, H. R. Powell, S. A. Westcott, T. B. Marder, N. J. Taylor, and D. R. Kanis, *J. Mater. Chem.*, 1993, **3**, 139.
34. B. Grüner, Z. Janousek, B. T. King, J. N. Woodford, C. H. Wang, V. Vsetecka, and J. Michl, *J. Am. Chem. Soc.*, 1999, **121**, 3122.

35 (a) D. Li, M. A. Ratner, T. J. Marks, *J. Phys. Chem.*, 1992, **96**, 4325. (b) D. R. Kanis, M. A. Ratner, and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.

36 This method has been used extensively in the literature for the calculation of molecular hyperpolarizabilities. The calculations employed here utilized the MOPAC and ZINDO methods within the 4.0.1 CAChe Worksystem (Oxford Molecular) software package. MNDO-AM1 method and parameterization M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, 1977, **99**, 5231. Oscillator strengths were calculated using the ZINDO method.

37. I. D. L. Albert, T. J. Marks, and M. A. Ratner, *J. Am. Chem. Soc.*, 1998, **120**, 11174.

38 L. -T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, and S. R. Marder, *J. Phys. Chem.*, 1991, **95**, 10631.

Engineered Fullerenes–Carborane Conjugated Rods: New Hybrid Materials for NLO Devices

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1 INTRODUCTION

The design, synthesis, characterization and understanding of new molecular and macromolecular assemblies with large macroscopic optical nonlinearities represents a great challenge in modern chemistry, physics, and materials science. Tasks in this active field of photonic materials typify an important theme in contemporary chemistry.

Quadratic nonlinear optical (NLO) materials have increasingly attracted attention due to their direct application in the development of efficient optical telecommunication networks lacking electrical-to-optical and vice versa signal conversion. The primary objective is to optimize the first hyperpolarizability (β) by the right combination of Donor-π-Acceptor (D-π-A) species,[1-7] pragmatically called a push/pull system (using more potent donating or accepting moieties) or increasing the conjugation between the substituents with a precise conjugated bridge of a given length. Because of the high delocalization of electrons on the shell of fullerenes, C_{60} based materials are expected to exhibit large nonlinear optical effects comparable to those for π-conjugated polymers.[8] In addition, fullerenes (A) containing electron donor (D) moieties have been widely reported (A-D).[9] Yet, few studies have been conducted on fullerenes bearing an electron-poor fragment (A-A).[9] Furthermore no example of C_{60}-π conjugated spacer-D or A has yet been reported. It occurred to us that the electronic structure of closo carborane electron defficient three-dimensional cluster and its highly polarizable σ-aromatic moiety[10] would make it a potential attractor center if we can covalently link it by a conjugated spacer to a C_{60} core, and thus, the first diad A-π-A system would be produced. We report here the first successful synthesis and electrochemical studies of a C_{60}-π-carborane rigid-rod hybrid which exhibits a large[11] second-harmonic generation (SHG; frequency doubling of light).

1.1 Instruments

Fluorescence spectra and UV-vis absorption spectra were measured with a Hitachi F-4500 spectrofluorophotometer and Hitachi U-3000 UV-vis spectrometer, respectively. The HRS measurements were carried out by using a q-switched Nd:YAG laser (spectron LS-412, fwhm: 6 ns) as an incident light beam. The fundamental light intensity (λ = 1064 nm, I (ω)) was varied by rotating a half-wave plate positioned between two polarizers. The HRS signal, I (2ω) was detected by a photomultiplier (Philips, model XP 2020Q) as a function of I (ω). Both incident fundamental light and

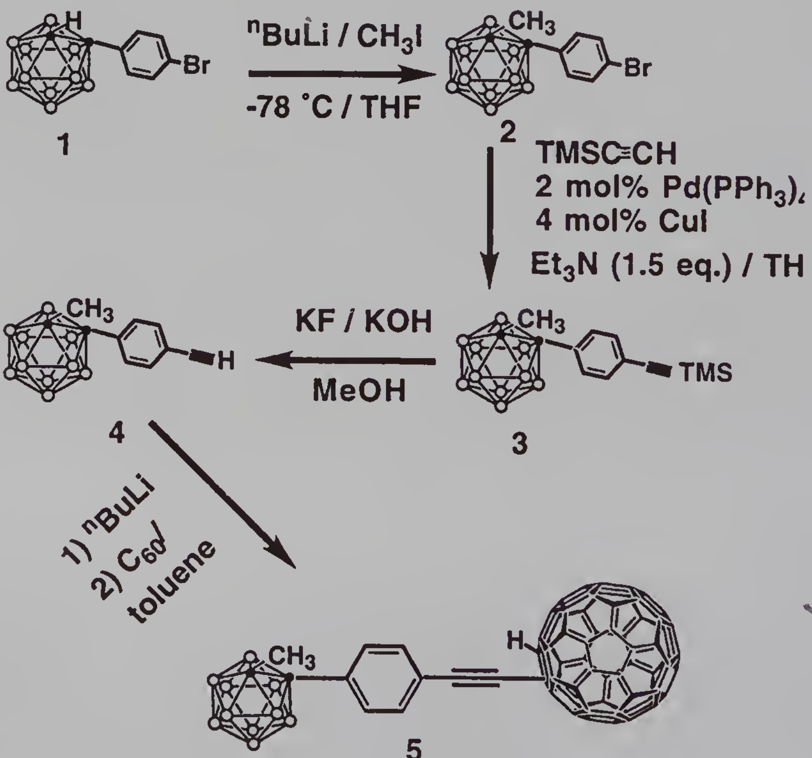
HRS light signals were fed into two gated integrators (Stanford Research System, model SR250) and out-put signals from the gated integrators were A-D converted and analysed on a personal computer.

2 SYNTHESIS OF THE HYBRID ROD C_{60}-π SPACER-CARBORANE

The synthesis of hybrid rod **5** is shown in Scheme 1.

2.1 Synthesis of 1-(4'-Br-C_6H_4)-1,2-$C_2B_{10}H_{11}$, 1

Potassium t-butoxide (5.61 g, 50 mmol) was stirred under nitrogen with dry glyme (80ml) and CuI (8.57, 45 mmol) at room temperature for 5 h and pyridine (10 ml) was added followed by *o*-carborane (4.26 g, 30 mmol). The mixture was stirred at 40 °C for 2 h. 4-Bromoiodobenzene (8.48 g, 30 mmol) was added in one portion to the copper (I) carborane solution. The mixture was heated and stirred under nitrogen at 100 °C for 5 days until GC-MS showed that the carborane was largely consumed. The solvent was evaporated and the crude oil was extracted with H_2O / Et_2O (40 ml / 120 ml). The organic layer was dried over $MgSO_4$. Concentration of the Et_2O solution gave a yellowish solid, which was crystallised from ethanol to give white fine crystals in 63 % yield. ^1H NMR (300 MHz, CD_3COCD_3): δ 3.84 (s, 1H), 7.19-7.42 (2d, 4H); ^{13}C NMR (75.45 MHz, CD_3COCD_3): δ 60.10, 129.17, 131.98; MS *m/z*: 299 (M^+); HRMS : calcd. for $C_8H_{15}B_{10}Br$, 300.1288; found 300.1330.



Scheme1

2.2 Synthesis of compound 2

To a THF solution of a mixture of 1-(4-bromophenyl)-1,2-carborane **1** (2.99 g, 10 mmol) and CH_3I (0.75 ml, 12 mmol) was added dropwise a hexane solution of ^{n}BuLi (1.57 M, 6.7 ml, 10.5 mmol) at -78°C under dry Ar. The solution was left overnight and the reaction progress was monitored by GC-MS. When the starting materials were consumed, the solvent was evaporated and the crude oil was extracted with H_2O / Et_2O (20 ml / 60 ml). The organic layer was dried over $MgSO_4$. Concentration of the Et_2O solution gave a yellowish solid. Silica gel PTLC chromatography of the crude solid (Hexane/CH_2Cl_2, 9/1) yielded **2** (Ref = 0.7) in 87% (2.72 g) as a white solid. IR (KBr): 2601, 2585, 2509, 1489, 829, 503 cm^{-1}; ^{1}H NMR (300 MHz, CD_3COCD_3): δ 1.80 (s, 3H), 7.70 (s, 4H); ^{13}C NMR (75.45 MHz, CD_3COCD_3): δ 24.26, 134.00, 134.77; MS *m/z*: 313 (M^+); HRMS : calcd. for $C_9H_{17}B_{10}Br$, 314.1445; found 314.1483.

2.3 Synthesis of compound 4

To a mixture of **2** (3.13 g, 10 mmol), catalytic amount of $Pd(PPh_3)_4$ (231 mg, 0.2 mmol), CuI (38 mg, 0.4 mmol), and triethylamine (2.1 ml, 15 mmol) in dry THF (50 ml) was added trimethylsilylacethylene (2.1 ml, 15 mmol) at 0 °C under dry Ar. The mixture was stirred at 100°C for 24 h under reflux. After the solvent was evaporated, KF (2.32 g, 40 mmol) and KOH (0.17 g, 3 mol) in methanol (100 ml) were added to the crude oil. The solution was stirred for 2 h at room temperature. After evaporation of methanol the residue was washed with brine / Et_2O(20 ml / 20 ml), and extracted with Et_2O (3 times of 20 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to give a yellowish solid, which was filtered over silica gel using hexane as eluent to yield **4** (2.06 g, 80%) as white solid. IR(KBr) 3288, 2584, 2563, 1508, 844, 664 cm^{-1}; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 1.79 (s, 3H), 3.76 (s, 1H), 7.43 (d, 2H, J = 8.7 Hz) , 7.57 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75.45 MHz, CD_3COCD_3) δ 80.49, 82.97, 122.31, 123.39, 132.57, 134.46. MS *m/z*: 258 (M^+); HRMS : calcd. for $C_{11}H_{18}B_{10}$, 260.2339; found 260.2324.

2.4 Synthesis of hybrid rod 5

The addition of 1equiv. ^{n}BuLi to a THF solution (**A**) of **4** (51.6 mg, 0.2 mmol) at 0°C gave arise to a purple colour. The solution was left to room temperature for 1h. A toluene solution (**B**) of C_{60} (72 mg, 0.1 mmol) was heated at 35°C under a very dry N_2 atmosphere. **A** was added slowly to **B**. The mixture turned amber-brown and the reaction was left overnight. After addition of CF_3COOH (2ml), the solvent was evaporated. The crude brown-black solid was dissolved in $CHCl_3$ then filtered (paper) to obtain a brown-amber solution and a fine unknown solid which is not soluble in any solvent other than CS_2. The chloroform was evaporated and the remaining brown solid was washed with hexane to eliminate excess of **4** (43%). The residual brown solid was submitted to flash chromatography (hexane eluent, silica gel) to recover the non reacted C_{60} (13%). **5** was obtained in 67% yield. IR(KBr) 2583, 1685, 1508, 1458, 1429, 1209, 1182, 1144, 844, 526 cm^{-1}; CS_2/CD_2Cl_2) δ 1.82 (s, 3H), 7.152 (s, 1H), (m, 4H); ^{13}C NMR (75 MHz, CD_3Cl/CS_2) δ 151.292, 151.135, 147.410, 147.146, 146.479, 146.231, 146.207, 146.050, 146.033, 145.638, 145.564, 145.490, 145.300, 145.259, 145.176, 144.509, 144.336, 143.042, 142.869, 142.440, 142.407, 141.904, 141.880, 141.847, 141.674, 141.509, 141.451, 140.174, 135.905, 134.948, 107. 487, 88.152, 61.919,55.318, 22.788.

Mass Electrospray Ionisation in CH_2Cl_2 (ESI$^-$), data for **5** in CH_2Cl_2 : 977.4 (M^- -H);

817.0 (M^- - (1-Me-1,2-$C_2B_{10}H_{11}$); 744.64 (M^- -(1-Me,2-Ph-1,2-$C_2B_{10}H_{10}$); 257.3 (1-(CC-Ph), 2-Me-1,2-($C_2B_{10}H_{10}$)); 234.12 (1-Me,2-Ph,1,2-$C_2B_{10}H_{10}$); 158,14 (1-Me-1,2-$C_2B_{10}H_{10}$).

3 RESULTS AND DISCUSSION

The cyclic voltammetry of the hybrid **5** in *o*-dichlorobenzene (**Figure 1**) showed three quasireversible reduction waves (E_{red}:E_{ox} mV; -1186:-549, -1657:-990, -2334:-1550) similar to those found for the parent C_{60} (E_{red}:E_{ox} mV; -1102:-549, -1535:-1599, -2002:-1599) under the same experimental conditions. The presence of an irreversible oxidation wave at -165 mV may correspond to the conjugated spacer fragment. The observation of four well resolved redox waves for **5** is consistent with the expected electrochemical process of the two covalently linked frameworks. The three reduction potentials of **5** are remarkably shifted to more negative values in comparison with those of the parent C_{60}, due to the saturation of a double bond.[15-17]Additionally, the electrochemical behaviour of **5** is dictated by the strongly attractive effect of the C_{60} cluster, indicating that the carborane-spacer framework charge withdrawing character was ineffective in the presence of the C_{60} moiety.

Absorption spectra of **5**/CH_3Cl in the UV-visible range showed a very weak absorption band between 430 and 620 nm (**Figure 2**), probably due to a forbidden transition, and two large absorption bands at 257 and 330 nm. In CH_3Cl, compound **4** is transparent in the UV-visible range; no absorption was observed. The fluorescence (**Figure 3**) spectra of **5** in $CHCl_3$ following excitation at 257 and 330 nm showed broad band emission in the range of 350-390 nm, which is attributed to Raman scattering of the $CHCl_3$ (fluorescence emissions were also absent in THF or CH_3CN). No spectroscopic absorption or/and emission was observed in the range of the double frequency value 532 nm, allowing us to have the concomitant measurement and deduction of the β coefficient of **5**. In **Figure 4**, the quadratic dependence of the second-harmonic signal intensity to the harmonic intensity is demonstrated for **5**.[18] The large [11] β was found to be 346 x 10^{-30} esu, while the second order polarizability, under the same experimental conditions, is $\beta = 23 \times 10^{-30}$ esu for *para*-nitroaniline and zero for C_{60} due to its centrosymmetric structure.

The NLO properties of the hybrid rod **5**, which constitutes the first example of its kind, are quite fascinating since it has often been surmised[19] that , by forming charge-transfer complexes with appropriate donors, the center of symmetry of C_{60} is broken inducing a significant second-order optical non-linearity. In our case the rod hybrid **5** did not form any charged complex but presented an important β value.

4 CONCLUSION

The straightforward availability of the hybrid rod **5** may make similar classes of compounds accessible for further investigations, such as substitution of *o*-carborane by the corresponding *meta* and *para* clusters. Further possibilities are to connect the C_{60} and carborane by various conjugated bridging aromatic groups (thiophene, aniline) and in particular their metallacarborane anion complexes forming a triad. We are currently investigating these possibilities along with the third-order optical non-linearities of fullerene-carborane (or -metallacarborane) hybrid rods.

Acknowledgement. We are grateful to the Japanese Society for Promotion of Science for support of this work (P97087).

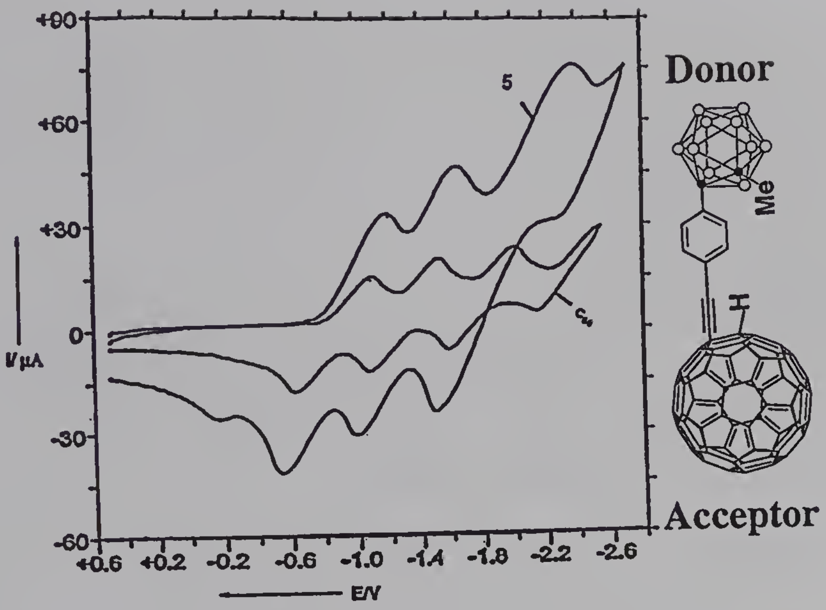


Figure 1. *C. V. of 5 ($5x10^{-3}$ M) and C_{60} ($2.5x10^{-3}$ M) in o-dichlorobenzene; suporting electrolyte : 0.1 M $^nBu_4NClO_4$; working electrode : glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01N $AgNO_3$ in acetonitrile with 0.1 M $^nBu_4ClO_4$ ($E_{1/2}$ (ferrocene/ferrocenium) = 180V); scan rate : 100 mVs-1.*

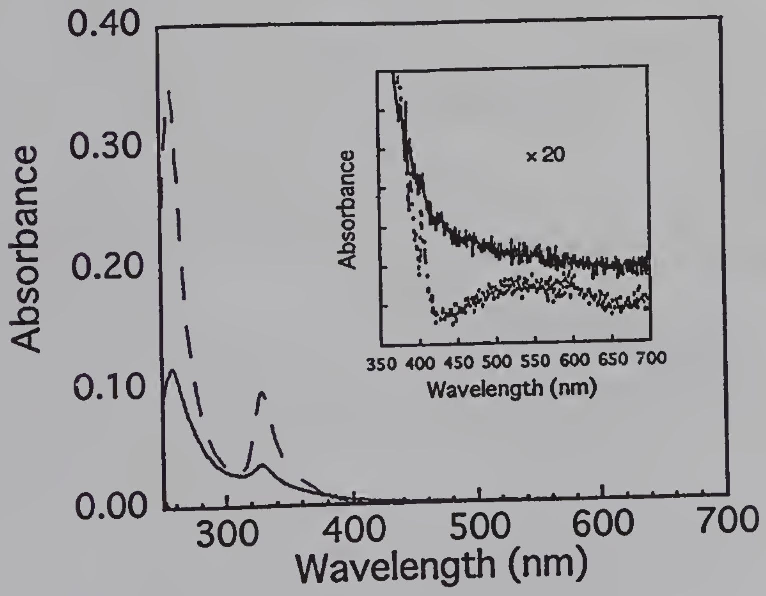


Figure 2. *Absorption spectra for 5 (–, 10^{-6} M) and C_{60} (---, 5 $x10^{-6}$ M) in chloroform*

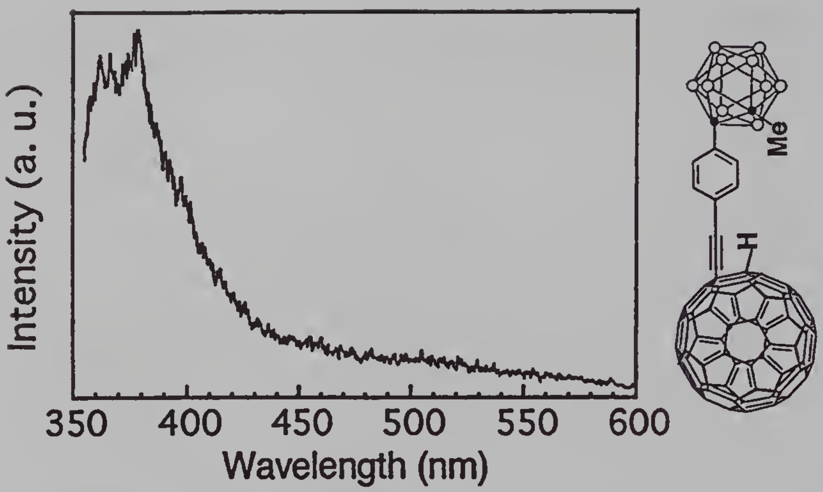


Figure 3. *Fluorescence spectrum of 5 in chloroform excited at 257 nm. The peak observed at around 370 nm is attributed to Raman scattering from the solvent.*

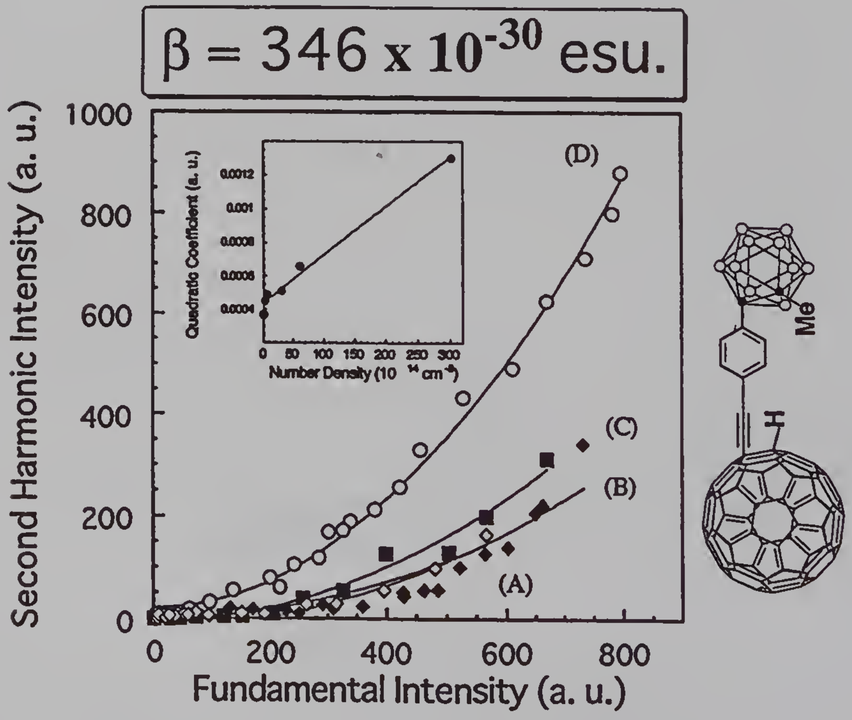


Figure 4. *Hyper-Rayleigh scattering signal for 5 in chloroform at different number densities in unit of* $10^{14}cm^{-3}$*: (A) 3.0, (B) 6.0, (C) 30, and (D) 301. (Inset) Quadratic coefficient* $I(2\omega)\ I^2(\omega)$ *vs. number density of 5.*

References

1. P. N. Prasad, D. J. Williams, 'Nonlinear Optical Effects in Molecules and Polymers', Wiley, New York, 1991.
2. L.-T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, *J. Phys. Chem.* 1991, **95**, 10643.
3. S. R. Marder, C. B. Gorman, B. G. Tiemann, L.-T. Cheng, *J. Am. Chem. Soc.* 1993, **115**, 3006.
4. For example; a) S.R. Marder, L.-T. Cheng, B. G. Tiemann, *J. Chem. Soc. Chem. Comm.* 1992, 672. b) A.E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, J. W. Perry, L.-T. Cheng, *J. Am. Chem. Soc.* 1991, **113**, 7568. c) V. P. Rao, A. K.-y. Jen, K.Y. Wong, K. J. Drost, *J. Chem. Soc. Chem. Comm.* 1993, 1119, and references cited therein.
5. S. R. Marder, D. N.Beratan, L-T.Cheng, *Science* 1991, **252**, 103.
6. M. Stahelin, D. M. Burland, J. E. Rice, *Chem. Phys. Lett.* 1992, **191**, 245.
7. S. Ramasesha, P. K. Dass, *Chem. Phys.* **1990**, *145*, 343.
8. P. Prasad, 'Nonlinear Optical Properties of Organic Materials' Plenum, New York, 1991.
9. N. Martin, L. Sanchez, B. Illescas, I. Perez, *Chem. Rev.* 1998, **98**, 2527
10. a) D. M. Murphy, D.M.P. Mingos, J. L. Haggitt, ; H. R. Powell, ; S. A. Westcott, T. B. Marder, N. J. Taylor, and D. R. Kanis, *J. Mater. Chem.* 1993, *3(2)*, 139. b) D. M. Murphy, J. M. Forward and D. M. P.Mingos, *J. Mater. Chem.* 1993, **3**, 67.
11. D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* 1994, **94**, 195.
12. Compound **1** was obtained following the slightly modified preparative route reported by Wade *et al.* R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *J. Organomet. Chem.* 1993, 19.
13. When ^{n}BuLi was first added to a THF solution of **1** and then MeI was added, the yield of **2** was very low. Accordingly, ^{n}BuLi should be added to the mixture of **1** and MeI.
14. a) T. P. Immerman, H. L. Anderson, R. Faust, J-F. Nierengarten, T. Habicher, P Seiler, F. Diederich, *Tetrahedron Lett.* 1996, 52, 4925. b) K. Komatsu, Y. Murata, N. Takimoto, S. Mori, N. Sugita, T. S. M. Wan, *J. Org. Chem.* 1994, **59**, 6101.
15. C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* 1995, **78**, 1334.
16. J. Chlistunoff, D. Cliffel, A. J. Bard, 'In Handbook of Organic Conductive Molecules and Polymers', H. S. Nalwa , John Wiley & Sons, New York, 1997, **1.1**, Chapter 7.
17. T. Suzuki, Y. Maruyama, T. Akasaka, W. Ando, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.* 1994, **116**, 1359.
18. For the calculation of β of the NLO-chromophore **5**, β (CH_3Cl) = -0.49 x 10^{-30}esu was used as an internal reference. See for example, F. Kajzar, I. Ledoux and Zyss, *J. Phys. Rev.* 1987, **A36**, 2210.
19. Y. Wang and L.-T. Cheng *J. Phys. Chem.* 1992, **96**, 530.

Aminoboranes as Versatile Precursors of Boron Nitride: Preparation of BN Matrices, Coatings and Fibres

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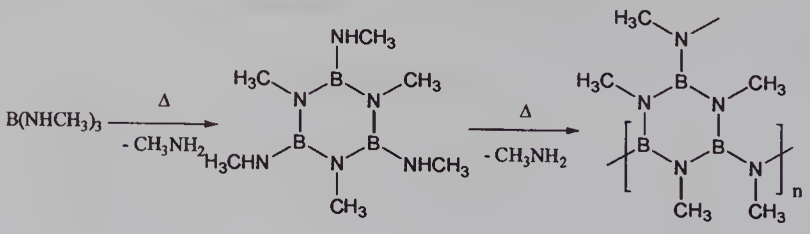
1 INTRODUCTION

Due to its unique properties, boron nitride has potential for use in the preparation of advanced composite materials, especially in complex shapes.[1] The difficult step of fabrication is obtaining precursors which can be processed. Polyborazinic precursors have been used to achieve the formation of such complex forms, but polymers with enhanced processing properties are clearly needed.[2] For this purpose, we have focused our interest on alkylaminoboranes $B(NHR)_3$ since they can lead to various polyborazines[3] and subsequently to boron nitride under selected conditions. Moreover, varying the polymerisation conditions and the nature of the substituent group on these molecular precursors may result in the formation of polymers with good processing properties. In this paper, we present some examples of the preparation of polymers obtained from $B(NHCH_3)_3$, $B(NHPr^i)_3$ and boryl-borazines derived therefrom. Subsequent processes and pyrolyses of these polymers demonstrate the importance of controlling hydrocarbon chains ratio if one is to generate boron nitride as coatings, matrices and fibres.

2 RESULTS AND DISCUSSION

2.1 Alkylaminoborane derived polymeric precursors of BN fibres

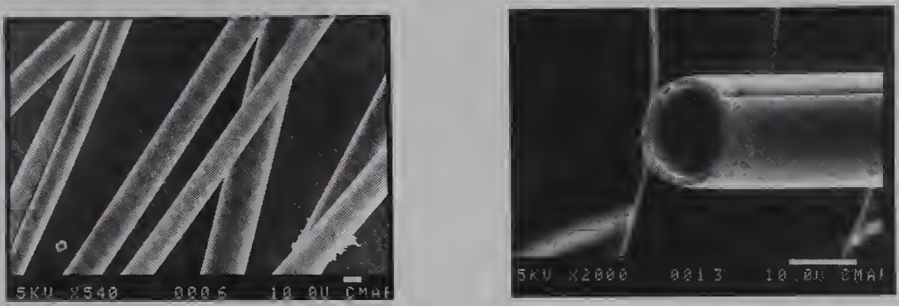
2.1.1. Processable polyborazines obtained from $B(NHCH_3)_3$. The conversion of tris(methylamino)borane into boron nitride has been previously reported.[4] $B(NHCH_3)_3$ undergoes easily classical cyclisation and polycondensation reactions, but reacts slowly with ammonia. The polyborazine obtained displays NH and NCH_3 bridges and could not be processed. On the other hand, the polymer (1) obtained by heating $B(NHCH_3)_3$ under argon displayed borazine rings linked through NCH_3 bridges[5] (Scheme 1).



(1)

Scheme 1

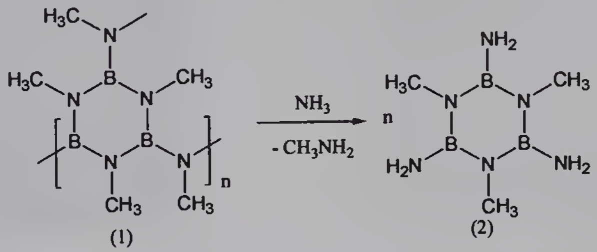
Polymer (1) showed good processing properties and has been spun at 150°C into crude fibres, uniform in diameter without apparent defects (Fig. 1-a). After thermal treatment for conversion into BN (NH_3 up to 650°C and N_2 up to 1200°C), the recovered BN fibres show an unexpected appearance since most of them were split whereas the others were tubular (Fig. 1-b).[5]



(a) **(b)**

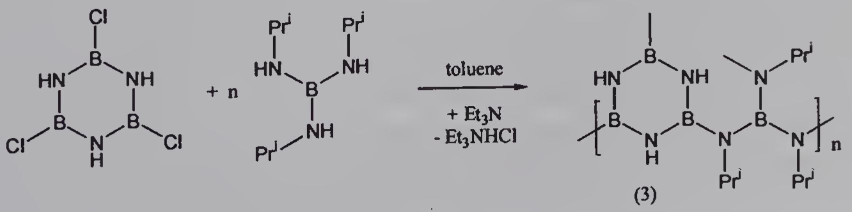
Figure 1 *SEM images of (a) crude fibres of polymer (1) and (b) tubular BN forms obtained after pyrolysis under ammonia*

According to TGA performed under NH_3/N_2, this behaviour is related to the effect of the ammonia during the pyrolysis. We observed that the formation of BN with a low carbon content was accompanied by a weight loss greater than the theoretical value involving the elimination of boron species. Actually, (1) is decomposed by ammonia yielding methylamine and 1,3,5-trimethyl-2,4,6-triamino-borazine (2) which sublimed partly (Scheme 2). Moreover, the tubular BN forms obtained after pyrolysis show a different behaviour between the surface and the core of the crude fibres. Therefore, the sublimation of (2) is limited at low temperature, and allows the surface of the crude fibres to undergo polymerisation reactions yielding a solid skin of reticulated polyborazine. At higher temperature, the core of the fibres reacts subsequently with ammonia leading to (2), whose sublimation prevails.



Scheme 2

2.1.2 Processable boryl-borazine based polymers. An alternative approach was undertaken in order to prepare polyborazines with multi-atom bridges between the rings. The reaction of 2,4,6-trichloroborazine with B(NHPr^i)$_3$ yields a polymer (3) in which the borazine rings are connected through N-B-N bridges (Scheme 3).



Scheme 3

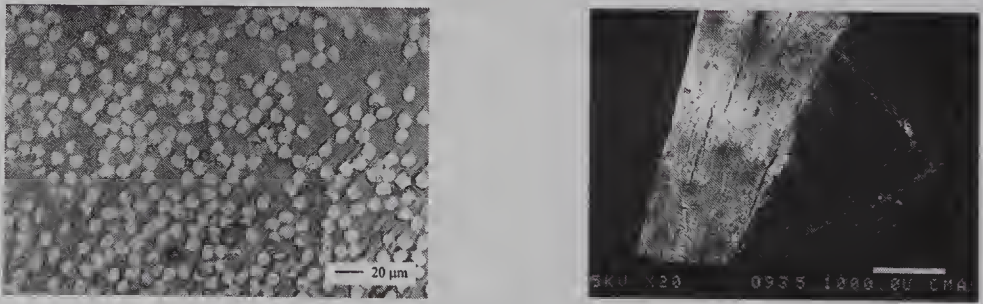
This polyborazine (3) could be melt spun but it was impossible to draw and wind the crude filaments on a spool. This behaviour is related to the high glass transition temperature of this polymer (T_g = 180°C) which probably reflects a high degree of polymerisation and/or reticulation. The irregular crude fibres were pyrolysed into BN filaments (Fig. 2) under similar conditions to those described for polymer (1) pyrolysis.

Figure 2 *SEM image of boron nitride fibres obtained from (3)*

2.2 Polymeric precursors of BN coatings and matrices

Expanding upon these results, we have investigated the potential of borylborazines for BN coatings and matrices. 2,4,6-$[(NHPr^i)_2\text{-}B\text{-}(NPr^i)]_3\text{-}B_3N_3H_3$ (4), prepared by reaction between TCB and $B(NHPr^i)_3$ (1:3) was heated in *vacuo* yielding an oligomer (5) (M_w = 1100g mol^{-1}) in which borazine rings are mainly connected through N-B-N bridges.[6] Bulk pyrolysis of (5) up to 1400°C was performed under NH_3/N_2 giving boron nitride with a low carbon content (<0.7%). XRPD analysis showed sharp lines including the (004) and (103) reflections and indicated a spacing of 3.38 Å for the (002) line, corresponding with the reported value for hexagonal boron nitride (3.33 Å).[1]

Carbon fibre/BN matrix composites were prepared by dipping the fibre bundles into a solution of (5) followed by pyrolysis under NH_3/N_2 up to 1200°C. Fig. 3-a shows that oligomer (5) has thoroughly wetted each carbon filament and has not been stripped during pyrolysis. The carbon fibres are distributed in a dense BN matrix, which follows exactly the shape of the bundle (Fig. 3-b).



(a) (b)

Figure 3 *Optical micrographs of (a) a cross section of a BN coated carbon fibres and (b) SEM image of the C/BN microcomposite. BN was obtained from (5)*

The matrices obtained are adherent and comparable to those prepared from $B(NHCH_3)_3$.[7] However, since (4) can be considered to be a derivative of $B(NHPr^i)_3$, their interest as BN films precursors may be compared. Thus, after the impregnation of carbon fibres by crude $B(NHPr^i)_3$, an ammonia treatment was required in order to reduce the volatility of the precursor before pyrolysis. $B(NHPr^i)_3$, which is stable with respect to auto-polymerisation, reacts spontaneously with NH_3 leading to a polyborazine with a low carbon content. The BN matrices obtained are not dense and the fibres are not totally embedded, indicating a lack of adherence of the BN matrix onto the fibres. This result could be related to the low hydrocarbon chain ratio of the polyborazine derived from $B(NHPr^i)_3$, which shorten drastically its carbon wetting properties.

The oxidation resistance properties of carbon cubes coated with BN obtained from (5) and $B(NHPr^i)_3$ were measured by isothermal TGA at 750°C under air.[6] The results confirmed the efficiency of the coatings against air-oxidation, both precursors providing good properties. However, the BN coating derived from $B(NHPr^i)_3$ become less effective when the oxidation time increases, probably due to the quality of the coatings. As shown on Fig. 4 and Fig. 5, the results are consistent with those described for matrices. The precursor (5) led to an homogeneous and adherent BN coating on the entire surface of the graphite cube, whist the coating prepared with $B(NHPr^i)_3$ is split and does not adhere to the substrate. The cracks between the plates make the oxygen attack at the carbon easier, and this limits the efficiency of this protection.

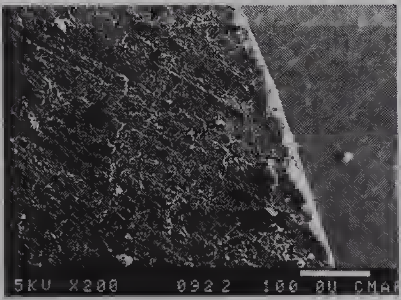


Figure 4 *SEM image of a cross section of (5)-derived BN coated graphite sample*

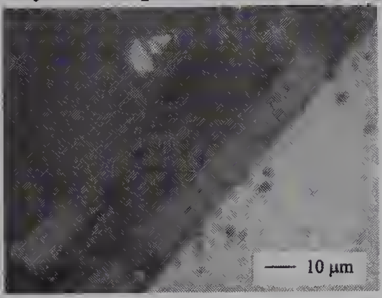


Figure 5 *Optical micrograph of a cross section of* $B(NHPr^i)_3$*-derived BN coated graphite sample*

3 CONCLUSIONS

In agreement with Sneddon's conclusions,[8] we have shown that the presence of alkyl groups in a pre-ceramic polymer improves its processing properties. The adherence of BN on graphite depends on the hydrocarbon chain ratio of the pre-ceramic polymer. In the case of $B(NHCH_3)_3$ derived fibres, the N-CH_3 bridges containing polyborazine displays good melt-spinning properties whereas the presence of CH_3 groups bound to the borazinic nitrogen atoms appears to be a serious drawback for the retention of the fibre's shape. Therefore, even if the ceramic yield of a precursor has to be considered, the control of its alkyl chain content is also of crucial importance for the preparation of BN in complex forms.

References

1. R. T. Paine and C. K. Narula, *Chem. Rev.,* 1990, **90**, 73 and refs therein.
2. R. T. Paine and L. G. Sneddon, *Chemtech,* 1994, **7**, 29.
3. D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.,* 1959, 2927.
4. B. Bonnetot, B. Frange, F. Guilhon, and H. Mongeot, *Main Group Met. Chem.,* 1994, **17**, 583.
5. D. Cornu, P. Miele, R. Faure, B. Bonnetot, H. Mongeot and J. Bouix, *J. Mater. Chem.,* 1999, **9**, 757.
6. D. Cornu, P. Miele, B. Toury, B. Bonnetot, H. Mongeot and J. Bouix, *J. Mater. Chem.,* submitted.
7. B. Bonnetot, F. Guilhon, J. C. Viala and H. Mongeot, *Chem. Mater.,* 1995, **7**, 299
8. T. Wideman, P. J. Fazen, K. Su, E. E. Remsen, G. A. Zank and L. G. Sneddon, *Appl. Organometal. Chem.,* 1998, **12,** 681.

Boron-containing, Non-oxide Ceramics from Organometallic Polymers: Synthesis, Thermolysis and the Influence of Boron on Materials Thermal Stability

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1 INTRODUCTION

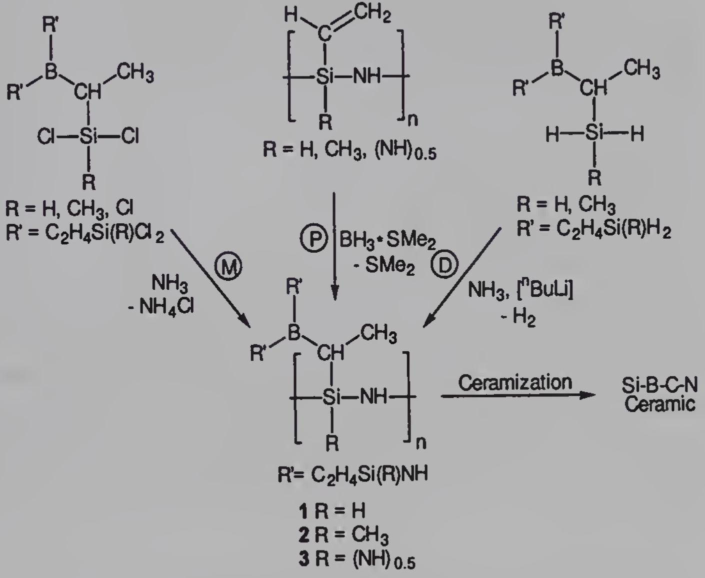
Thermolysis of organometallic networks is a suitable method for the synthesis of a wide variety of high performance ceramic materials. In particular, non-oxide silicon-based polymers, such as polysilanes, [1] polycarbosilanes, [2] polysilazanes, [3] and the materials obtained therefrom have been intensively investigated and reviewed. [4] Within this decade, boron-modified silicon-based ceramics became of considerable interest because of their exceptional high temperature and oxidation stability even to temperatures as high as 2000°C. [5-11] In this context, we now report the synthesis of boron-modified polysilazanes of type $\{B[C_2H_4Si(R)NH]_3\}_n$. These compounds are accessible by different methods *e.g.* metathesis reactions of tris(chlorosilylethyl)boranes with ammonia, hydroboration of vinylated polysilazanes, or dehydrogenative coupling of ammonia and hydridosilylethylboranes. Besides synthetic procedures, the polymer-to-ceramic conversion (ceramization) of the Si-B-C-N polymers, monitored by thermogavimetric analysis (TGA), is reported. High temperature investigations of the as-obtained amorphous ceramics carried out in inert gas atmosphere up to 2200°C, occasionally reflect a thermal stability towards decomposition up to 2000°C. XRD analyses of annealed samples indicate microstructural evolution in the 1550°C - 1750°C range to form α- and β-SiC and β-Si_3N_4 crystalline phases. Finally, the influence of boron nitride containing non-crystalline phases on the thermal stability of SiC/Si_3N_4 composites is discussed using a model that is based on thermodynamic calculations and that is additionally supported by HR-TEM investigations.

2 SYNTHESIS

Initial studies on polymers of the general type $\{B[C_2H_4Si(R)NH]_3\}_n$ were published in 1994 by Riedel et al. who synthesized $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ (**2***M*, also T21) by ammonolysis of $B[C_2H_4Si(CH_3)Cl_2]_3$. [10] Ceramic materials which are obtained from this precursor, reveal an outstanding thermal stability. Remarkable disadvantages include low ceramic yields during the polymer-to-ceramic conversion due to depolymerization and time intensive processing (separation of by-product ammonium chloride). In order to increase the ceramic yields and to simplify the work-up, we modified both the molecular structure and the reaction pathways.

Substitution of the methyl group in **2***M* (*M*onomer route) with a hydrogen atom or a NH-unit by using $B[C_2H_4Si(R)Cl_2]_3$ (R = H, Cl) as starting compounds, delivers the expected polymers $\{B[C_2H_4Si(R)NH]_3\}_n$ (R = H, **1***M*; R = $(NH)_{0.5}$, **3***M*) as colorless solids. Due to the decreased solubility of **1***M* as compared to **2***M*, it is obtained in only 70% yield. The high crosslinking in **3***M* causes it to be insoluble in all common solvents. It could thus be obtained in only 5% yield.

A modified procedure for the synthesis of compounds **1-3** is the hydroboration of vinyl-substituted polysilazanes with borane dimethylsulfide. Both reactants are soluble in organic solvents and are drop-wise mixed. In contrast to the synthesis by ammonolysis of the respective tris(chlorosilylethyl)boranes, no solid by-products form; the only by-product is dimethylsulfide which can be easily removed, together with the solvent by vacuum distillation. Moreover, **1-3***P* (*P*olymer route) are obtained in quantitative yield using this reaction pathway.



A further method for the synthesis of the title compounds with only hydrogen as by-product is the base-catalyzed dehydrogenative coupling (index *D*) of ammonia and tris(hydridosilylethyl)boranes, $B[C_2H_4Si(R)H_2]_3$ (R = H, CH_3). Initially, the strong base, *e.g.* n-butyl lithium, deprotonates ammonia. The highly nucleophilic amide replaces a silicon-bonded hydride to form a silylamine and lithium hydride, which then deprotonates ammonia, resuming the catalytic cycle. Under the conditions used, silylamines are not stable and by elimination of ammonia, polysilazane frameworks form. In addition, compounds $B[C_2H_4Si(R)H_2]_3$ can be obtained from vinylsilanes, $H_2C{=}CHSi(R)H_2$ (R = H, CH_3), and borane dimethylsulfide.

3 THERMOLYSIS

The thermally induced polymer-to-ceramic conversion is accompanied by formation of gaseous by-products. A suitable method for determining the amount of these species that form and the temperature range where they form, is given by thermogravimetric analysis (TGA). Figure 1 shows a comparison of the thermogravimetric behavior of compounds **1-3** during thermolysis. The replacement of the methyl-group in T21 with cross-linking $(NH)_{0.5}$ units results in increased ceramic yields of 83% (**3***D*) and 84% (**3***P*) compared to 51% (T21). The substitution of the methyl group in T21 with hydrogen produces precursors with even higher ceramic yields of 86.5% (**1***P*) and 88% (**1***M*). These findings and a comparison of the TGA of T21 with that of the isostructural polymer **2***P* (56%) which was obtained by hydroborating $[(H_2C{=}CH)(CH_3)SiNH]_n$ indicate that the ceramic yield of

$\{B[C_2H_4Si(R)NH]_3\}_n$ is mainly a function of the silicon-bonded moiety R, whereas the reaction pathway applied does not significantly influence the polymer-to-ceramic conversion.

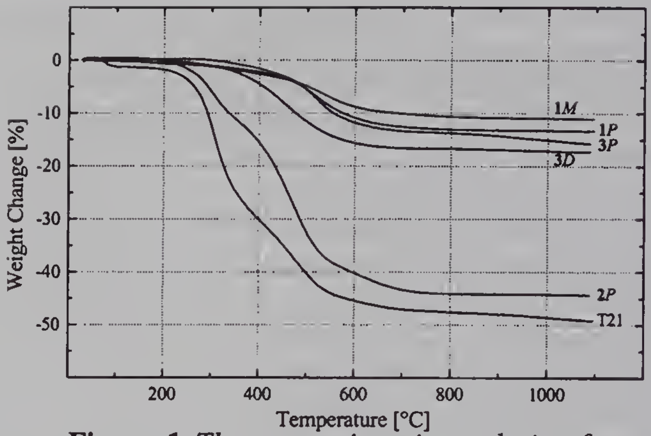


Figure 1 *Thermogravimetric analysis of compounds 1-3 in argon; heating rate 2°C/min.*

The single reaction steps that occur during thermolysis were in detail investigated by solid state NMR spectroscopy. In the ^1H NMR spectra it is observed that in between 300° and 500°C the hydrogen resonance signals disappear. Consequently, in the ^{13}C NMR spectra aliphatic *C*H resonance signals also disappear in this temperature range. At 1050°C carbon is observed in the sp^2 and sp^3 hybridized state. The ^{29}Si NMR spectra are more complex. Depending on the chemical composition of the polymers either SiN_4, $SiCN_3$, or SiC_2N_2 sites are seen. Interestingly, boron is four-fold coordinated in the polymers, possibly due to C_3B-N interactions in the solid state. Usually, at ~ 400°C the boron sites change dramatically because of B-C bond cleavage and simultaneous B-N bond formation (trigonal planar BN_3-sites).[12]

4 HIGH TEMPERATURE BEHAVIOR

High temperature investigations of as-obtained ceramic materials were performed using TGA up to 2300°C (Figure 2) and XRD up to 2000°C (Figure 3). A comparison of the TGA of **1***M*, **1***P*, **3***P*, and T21-derived materials demonstrates a significant difference in their thermal stability. While the **1***M*, **1***P*, and T21 ceramics decompose around 2000°C, the more nitrogen-rich **3***P*-derived material decomposes at approx. 1450°C. In addition, the mass loss of the first decomposition step at 24% corresponds to the amount of nitrogen, calculated thermodynamically to be bond as silicon nitride.

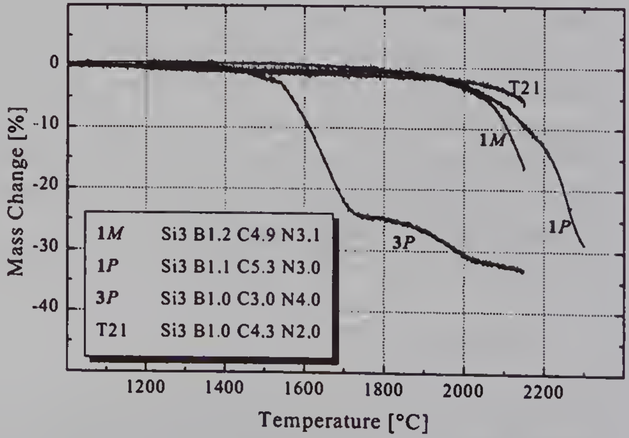


Figure 2 *High temperature TGA in argon of selected ceramic materials. Heating rate T < 1400°C: 5°C/min, T > 1400°C:2°C/min.*

The findings of the XRD experiments which were carried out with annealed samples (1400 - 2000°C, 1 bar nitrogen, dwell time 3h, carbon crucibles) reflect the TGA observations. While **3***P* ceramic crystallizes between 1500° and 1550°C to form α-SiC, the **1***M* and **1***P* (Figure 3) materials do not crystallize below 1700°C. Aside from α-SiC reflexes, the latter materials shows typical β-Si_3N_4 peaks that do not disappear even at 2000°C.

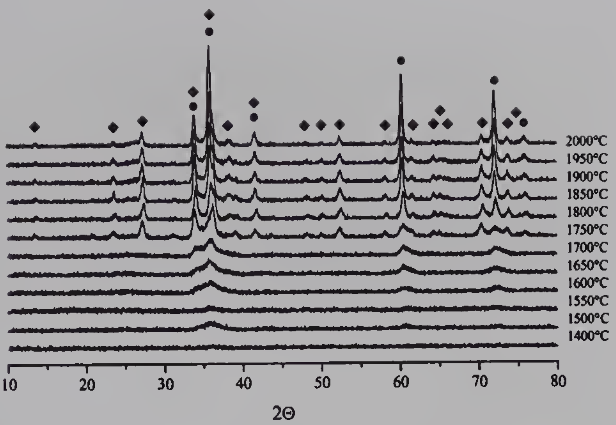


Figure 3 *X-Ray diffraction patterns at variable temperature of annealed 1P-material; 1 bar nitrogen;* ● = *α-SiC*, ◆ = *β*-Si_3N_4.

Initial explanations of the extraordinary high-temperature stability of precursor-derived Si-B-C-N ceramics were presented previously by Jalowiecki et al. [13] The authors investigated the microstructure of boron-doped silicon carbonitride composites by HR-TEM and found turbostratic BN(C) segregation occuring along grain boundaries of nano-sized silicon carbide and silicon nitride crystals. We suppose that the BN(C) phase binds free carbon, and thus decreases the carbon activity. Consequently, the reaction of silicon nitride with free carbon, $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$ (free carbon is present in all investigated materials), which limits the thermal stability of ternary Si-C-N ceramics, is shifted to higher temperatures (at 1 bar N_2, this reaction takes place at 1484°C). Additionally, the BN(C) grain boundary possibly serves as a diffusion barrier and retards grain growth. Due to encapsulation of the silicon nitride grains by the turbostratic BN(C) phase, the nitrogen pressure within the "shell" is sustained to some extent. The decomposition temperature for the reaction of silicon nitride into silicon and nitrogen is thus raised to higher values. [14] Besides the surprising high-temperature stability observed by TGA, the encapsulation also sufficiently explains the presence of crystalline silicon nitride in the XRD patterns of **1***M*- and **1***P*-derived ceramics - even at temperatures as high as 2000°C. [15]

REFERENCES

1. S. Yajima, J. Hayashi and M. Omori, *Chem. Lett.*, 1975, 931.
2. C. L. Shilling, J. P. Wesson, T. C. Williams, *Amer. Ceram. Soc. Bull.*, 1983, **62**, 912.
3. D. Seyferth, G. H. Wiseman, C. Prud`homme, *J. Amer. Ceram. Soc.*, 1983, **66**, C-13.
4. M. Birot, J.-P. Pillot and J. Dunogués, *Chem. Rev.*, 1995, **95**, 1443.
5. M. Takamizawa, T. Kobayashi and A. Hayashida, Y. Takeda, US 4,604,367, 1986.
6. D. Seyferth and H. Plenio, *J. Am. Ceram. Soc.*, 1990, **73**, 2131.
7. M. Jansen and H.-P. Baldus, DE 410 71 08 A1, 1992.
8. K. Su, E. E. Remsen, G. A. Zank and L. G. Sneddon, *Chem. Mater.*, 1993, **5**, 547.
9. R. L. Matsumoto and J. M. Schwark, US 5,206,327, 1993.
10. R. Riedel, A. Kienzle, G. Petzow, M. Brück and T. Vaahs, DE 432 07 83 A1, 1994.
11. M. Weinmann, R. Haug, J. Bill, F. Aldinger, J. Schuhmacher and K. Müller, *J. Organomet. Chem.* 1997, **541**, 345.
12. J. Schuhmacher, M. Weinmann, J. Bill, F. Aldinger and K. Müller, to be submitted.
13. A. Jalowiecki, J. Bill, F. Aldinger and J. Mayer, *Composites*, 1996, **27A**, 717.
14. H. J. Seifert, H.-L. Lukas and F. Aldinger, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 1309.
15. M. Weinmann, J. Schuhmacher, H. Kummer, S. Prinz, J. Peng, H. J. Seifert, M. Christ, K. Müller, J. Bill and F. Aldinger, *Chem. Mater.*, submitted.

Borosilicate Cage Chemistry

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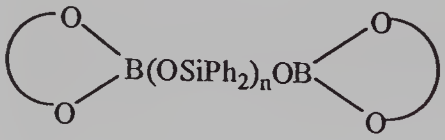
1 INTRODUCTION

Until relatively recently,[1,2,3] the chemistry of *molecular* borosilicates was mainly concerned with organosiloxyborates such as $B(OSiR_3)_3$ species,[4] one-dimensional chain compounds e.g. **1**, and two-dimensional cyclic species, e.g. **2**. Ill characterised and intractable polymers are also known.[4]



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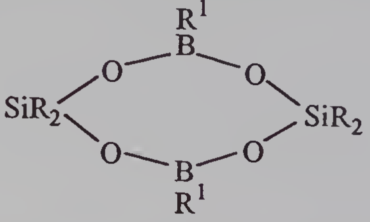
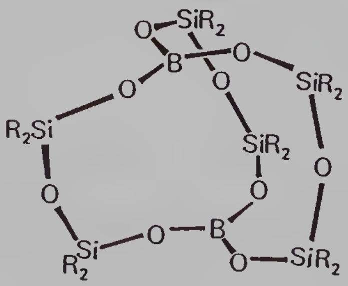


(2)

Since 1992, three types of three-dimensional borosilicate "cage" compounds have been characterised. These may be described as columnar, **3**,[2] spherical, **4**,[3] and cuboid, **5**.[1] Our recent attempts to better understand the reactions which give rise to cage compounds and to extend their chemistry are the basis of this report.



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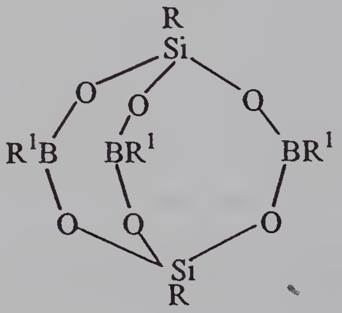

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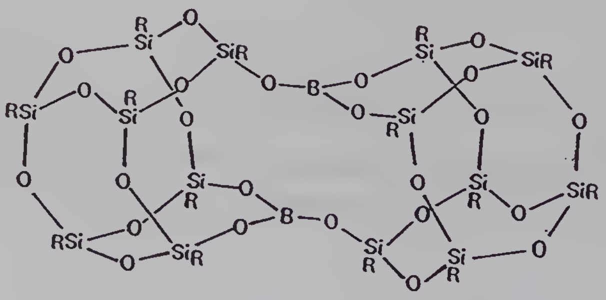
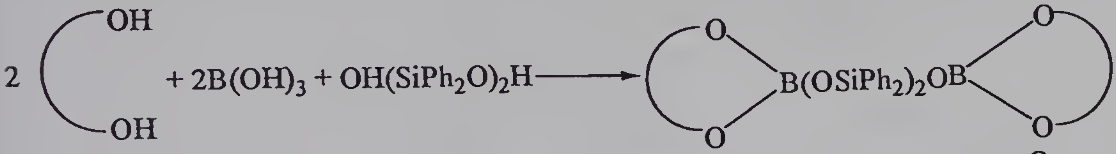


(5)

2 RESULTS AND DISCUSSION

Compounds of type **1**, where n = 2, are formed in high yield (typically 80-90%) from the reaction between *either* an organic diol, boric acid and 1,1,3,3-tetraphenyldisiloxane-1,3-diol in 2:2:1 molar ratio (Eq. 1) *or*, the diol, boric acid and diphenylsilanediol in unit molar ratio



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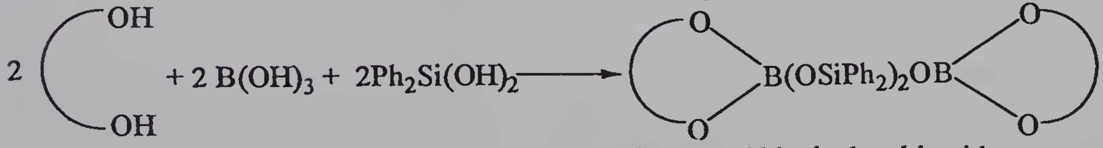
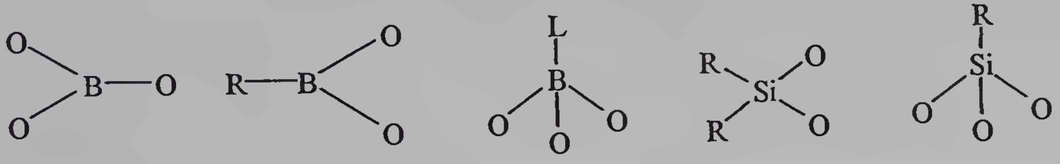


[2]

(Eq. 2), and no cyclic siloxane or boroxine products could be isolated in either case. This suggested that the formation of B-O-Si bonds is favoured over Si-O-Si or B-O-B bonds when B-OH and Si-OH species react and led us to consider the possibility of systematic syntheses of three-dimensional borosilicate cages with the connector units shown below. Clearly, at least two, three-connector units are required for the formation of three-dimensional cages such as **3**, **4**, and **5** above.



The columnar cage, **3**, was obtained in essentially the same yield (45%) from either the reaction between boric acid and diphenylsilanediol in 1:3 molar ratio or boric acid and 1,1,3,3-tetraphenyldisiloxane-1,3-diol in 2:3 molar ratio.[2]

Spherical cages, **4**, were synthesised in high yield (80-90%) when the R group attached to silicon was either Bu^t or *cyclo*-hexyl and R' at boron was Ph, ferrocenyl, C_6H_4X {X = 4-Br, 4-Bu^t, 4-Ph, 3-NO_2, 4-CHO, 4-C(O)Me}, or 2,4-$F_2C_6H_3$, but in lower yield (*ca.* 70%) when $\mathrm{Bu}^n\mathrm{B(OH)}_2$ was the boronic acid used, (Eq. 3).

$$2\,\mathrm{RSi(OH)_3} + 3\,\mathrm{R^1B(OH)_2} \longrightarrow [\mathrm{RSi(OBR^1O)_3SiR}] + 6\mathrm{H_2O} \qquad [3]$$

These compounds were characterised with microanalysis, IR and NMR spectroscopy and, for R = Bu^t and R' = ferrocenyl, C_6H_4X {X = Br, Bu^t, Ph, NO_2}, and 2,4-$F_2C_6H_3$, single crystal X-ray diffraction methods. Figure 1 depicts the structure of the 4-C_6H_4Br derivative. Notable structural features in all the compounds were (a) planarity of the borosilicate Si-O-B(C)-O-Si fragments, (b) coplanarity of the borosilicate fragments and aromatic rings directly attached to the boron atoms, (c) variation in values of B-O-Si bond angles. The last feature is common to many molecular borosilicate structures and is due to the shallow B-O-Si angle deformation energy profile.[5] We are presently exploring the possibility of joining these spherical cages at X and the reactions of the boron atoms in the cages with amines. In the latter case, products have been characterised with either one or two boron atoms bonded to an amine *e.g.* pyridine or 1,1-dimethylethylenediamine respectively.

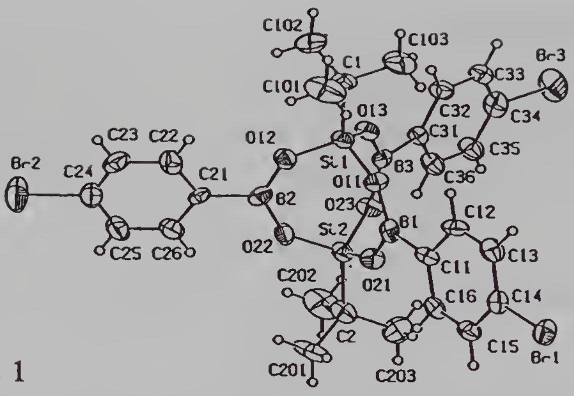
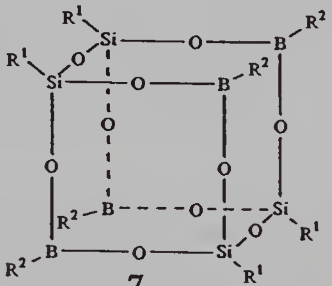


Figure 1

The reaction between *t*-butyltrichlorosilane, 4-vinylphenylboronic acid, aniline and water in a 2:2:4:1 molar ratio in refluxing toluene solution afforded compound, **6**, in 17% yield. Compound **6** had the central cuboid cage shown in **7**. An X-ray crystallographic study showed that there was an equal number of B and Si atoms present arranged as two B-O-Si-O-B-O-Si-O-faces of the cuboid joined *via* two Si-O-Si bonds. This arrangement was unprecedented. Previously reported Main Group cuboid compounds had contained Si/Al, Si/Ga, Si/In, and B/P combinations arranged as shown in **8**.[6] Figure 2 shows an ORTEP diagram of the structure of **6**. Individual B-O-Si angles varied from 137.5(2) to 154.4(2)° and the Si-O-Si angle was 154.14(14)°.



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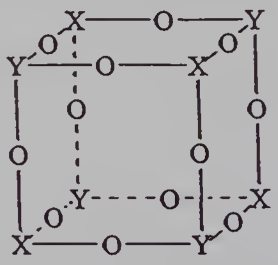

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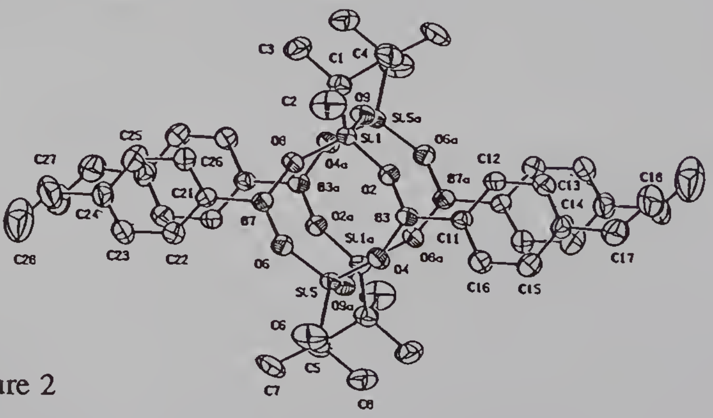
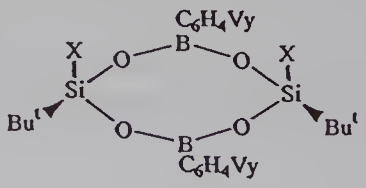


Figure 2

A possible mode of formation of **6** could be *via* the condensation of two cyclic intermediates with *cisoid* arrangements of Si-X groups (X = Cl or OH), *e.g.* **9**.



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A second cuboid cage, $(Bu^tSi)_4(\{Me_2NC_2H_4NH_2\}PhB)_4O_{10}$, **10**, was produced from the reaction between a spherical cage, (**4** with R = Bu^t and R' = Ph) and 1,1-dimethylethylenediamine in the presence of a trace amount of water. An ORTEP diagram of the central borosilicate cage of **10** is illustrated in Figure 3. We are currently studying the general applicability of degradation reactions of spherical cages and the further chemistry of cages like **4**, **6**, and **10**.

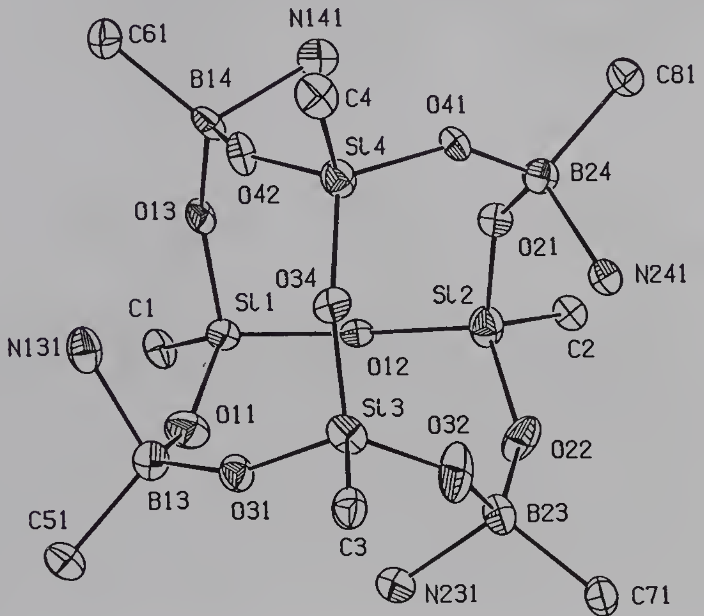

Figure 3

Acknowledgements

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References

1. F.J. Feher, T.A. Budzichowski and J.W. Ziller, *Inorg. Chem.*, 1992, **31**, 5100.
2. A.T. O'Dowd, T.R. Spalding, G. Ferguson, J.F. Gallagher and D. Reed, *J. Chem. Soc., Chem. Commun.*, 1993, 1816.
3. B. O'Leary, D.M. Murphy, T.R. Spalding and G. Ferguson, *J. Organometal. Chem.*, 1996, **526**, 195.
4. H. Steinberg (ed.), 'Organoboron Chemistry', Interscience, New York, **Vol.1**, 1964, (and references therein).
5. D. Murphy, J.P. Sheehan, T.R. Spalding, G. Ferguson, A.J. Lough and J.F. Gallagher, *J. Mater. Chem.*, 1993, **3**, 1275.
6. a) R. Murugavel, V. Chandrasekhar and H.W. Roesky, *Acc. Chem. Res.*, 1996, **29**, 183; b) R. Murugavel, A. Voigt, M.G. Walawalkar and H.W. Roesky, *Chem. Rev.*, 1996, **96**, 2205; c) A. Voigt, M.G. Walawalkar, R. Murugavel, H.W. Roesky, E. Parisini and P. Lubini, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2203; d) M.G. Walawalkar, R. Murugavel, H.W. Roesky and H.-G. Schmidt, *Organometallics*, 1997, **16**, 516; e) K. Diemert, U. Englert, W. Kuchen and F. Sandt, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 241.

Acid–Base Properties of Anhydrous Borate Systems

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1 INTRODUCTION

Investigation of the phase diagrams of borate systems has resulted in the synthesis of about 600 anhydrous borates, borosilicates and their structural derivatives, since the boron atom is capable of coordination in either three-fold or four-fold mode[1]. Most of them are incongruently melting. It is also well known that borate melts have a high viscosity due to their tendency to form various complex polyanions of different composition and configuration. The author of present paper has tried to find a correlation between the polymerization of anions in the structures of anhydrous borates and their acid-base properties with respect to the understanding of the capability of these inorganic polymers to crystallise.

2 BASIC STRUCTURAL UNITS IN ANHYDROUS BORATES

Generally, the structural chemistry of anhydrous borates is characterized by a variety of discrete and condensed BO_3 and BO_4 anions. Predominant among these structures, especially binary and more complex borates, are isolated BO_3 triangles (about 65%). Of the rest almost one-half is represented by framework structures containing three-dimensional B_nO_m polyanions. In this case, BO_3 and BO_4 groups join by sharing common O atoms. Then, it is followed by insular (pyroborates and ring metaborates), network and chain-forming structures.

There are more than 50 types of boron-oxygen anions and polyanions in anhydrous borate, borosilicate, boroaluminate and boroberylate structures.[1] However, all of them consist exclusively of three basic types of structural units of different composition (Fig.1). The first set of these basic types identify with BO_3 triangles (Δ) and BO_4 tetrahedra (□) as fundamental (elementary) structural units (FSU) which are shown in Fig. 1, I. They are isolated in orthoborate structures and can be merged in pyro-, meta-, and polyborates.

The second basic type of structural units is usually built up of several FSU (from 2 to 5) joined by sharing common O atoms. There is a rather limited number of these anionic groups. They are shown in Fig. 1, II.1 and II.2 and designated below as combined basic structural units (CSU). Only two of them, 2Δ and 3Δ, can be isolated in the structures of anhydrous pyroborates and some metaborates, respectively. The rest of the structural units of this type are as components of various one-, two- and three-dimensional B_nO_m polyanions by sharing their "free" O atoms.

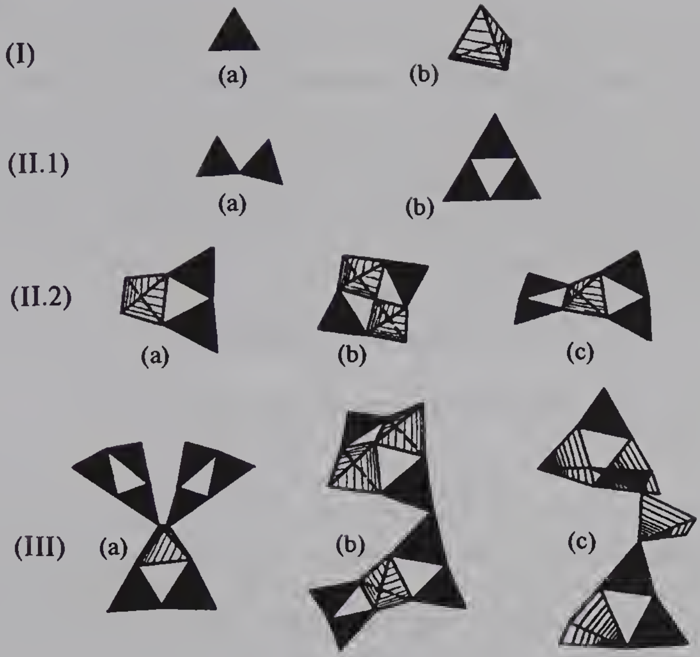

Figure 1 *Configurations of some basic B-O structural units in anhydrous borates:*

(I) Fundamental structural units (Δ and □ isolated forms occur in orthoborate structures only);
(II.1) Combined basic structural units as insular anions in pyro- (a) and metaborate (b) structures: (a) 2Δ and (b) 3Δ;
(II.2) Combined basic structural units forming network and framework polyanions: (a) 2Δ+1□, (b) 2Δ+1□, (c) 4Δ+1□;
(III) Complete radicals of polyanions in network and framework polyborate structures: (a) (2Δ+1□)+2(3Δ), (b) (4Δ+1□)+(2Δ+2□), (c) (2Δ+1□)+(2Δ+2□)+1□.

Finally, in polyanions of anhydrous borates it is expedient to distinguish one more type of structural unit. Structural elements of this category are, as a rule, more complex and characterize the borate structures on the whole. It is appropriate to designate these anionic groups as complete radicals of polyanions (CRP). Some of the typical CRP are demonstrated in Fig. 1, III. The CRP may be visualized as one or more of the CSU and additional FSU (BO_3 triangles and/or BO_4 tetrahedra) joined by sharing common O atoms. It thus represents a full repeating fragment of a polyanion (made up of 1-9 FSU), corresponding to the B-O-anion part in the structural formula of the borate. It is useful to note that the CRP identify themselves with the CSU in the anhydrous orthoborate structures, and with the CSU - in the pyroborates, metaborates, and in some more complex borate compounds.

Thus, there are numerous structural types of anhydrous borates. However, it is possible to reduce some of these complex structures to various combinations of the three types of the basic structural units mentioned above: FSU, CSU, and CRP.

3 CRYSTALLOCHEMICAL CRITERIA OF ACID-BASE RELATIONSHIPS

A major problem which awaits clarification concerns the detailed nature of the borate crystal growth processes from the melts and fluxed melts. From this point of view, it would be useful to develop a correlation between the polymerization of anions in the structures of anhydrous borates and their acid-base properties with respect to the understanding of the capability of these inorganic polymers to crystallize.

There were some attempts to estimate acid-base properties for oxide compounds, both solids and melts. The most popular of them is Lux-Flood's acid-base theory.[2,3] This concept seems to be more effective for estimating the acid-base characteristics of anhydrous borates and of some promising solvents for the flux growth of borate crystals. According to Lewis-Lux's equation,

$$\text{Acid} + O^{2-} \leftrightarrow \text{Base},$$

the acid-base parameters of melts depend on oxygen activity. Thus,

$$B_2O_3 + O^{2-} = B_2O_5^{4-},$$

which means that the pyroborate anion (2Δ) has more base properties than boron trioxide.

Taking into consideration the above concept, it is intuitively obvious that the simplest way to assess quantitatively acid-base properties of the anhydrous borates is to estimate the dependence of polymerization of anions in the borate structures on the sizes and valences of cations, and also on the ratio (N) of the total number of BO_3 triangles and BO_4 tetrahedra (N_B) to the total amount of cations (N_M) contained in the borate structural formula: $N = N_B/N_M$. From the crystallochemical point of view it is clear that the increase of the N-ratio increases the anion polymerization and the ratio N_B^{3+}/N_O^{2}. It leads to a decrease in the oxygen activity coefficient and simultaneously, to more acid properties of these compounds. Also, the value of $n = n_\Delta/n_\square$ (n_Δ - number of triangles, $n_\square$ - number of tetrahedra) increases (for $N \leq 1$), i.e. the ratio of the number of BO_3 triangles to BO_4 tetrahedra in the structures of compounds increases.

Tendency to polymerization and, therefore, to more acidic properties is also intensified with the decreasing cation valence. The polymerization of anions is accompanied by delocalization and decrease of their formal charges. This promotes the stability of a wide variety of polyborate structures with single and large double valence cations. Cations of higher valence can form rather rigid coordination polyhedra with oxygen atoms. These high-valence cations usually establish the basic framework of the structures and, therefore, in this case anionic stability is of secondary importance. Thus, due to the tendency of weakening of polymerization, these borate often have structures with isolated BO_3 triangles and isolated BO_4 tetrahedra having even higher charges (-3 and -5 respectively).

The regular variation of structural characteristics in borate series makes it possible to forecast new phase systems for the synthesis of predicted borate structures. For example, the $Li_2O{\cdot}4B_2O_3$ borate seems to contain a BO-framework. The ratio of $n = n_\Delta/n_\square$ is most likely equal to 2. The polyanions in the $Na_2O{\cdot}5B_2O_3$ and $Na_2O{\cdot}9B_2O_3$ borates are most probably three-dimensional with n equal to 4 and 8 respectively. The compounds $K_2O{\cdot}3B_2O_3$ and $Rb_2O{\cdot}3B_2O_3$ possibly also contain three-dimensional networks with $n = 2$. The structure of polyanions in these borates seems to be rather close to that in the corresponding potassium compound which consists of triborate groups as the CSU and CRP simultaneously. The polyanions of $Cs_2O{\cdot}4B_2O_3$ and $Cs_2O{\cdot}5B_2O_3$ borates are evidently also three-dimensional with $n = 3$ and 4 respectively. This analysis can be easily made for other anhydrous borates.

3 CONCLUSION

Numerous anhydrous borate structures can be reduced to various combinations of three types of basic structural units: 1) fundamental structural units, 2) combined basic structural units, and 3) full radicals of polyanions. The stability of the FSU, CSU and CRP units in solid and liquid borates is one of the most important issues, and will provide a better understanding of, and control of, phase formation in complex borate systems.

Crystallochemical examination of acid-base characteristics of the borates indicates ways to search for new compounds with desirable composition, structure and properties and facilitates evaluation of preferable flux systems for their crystallization.

References

1. N. I. Leonyuk and L. I. Leonyuk, Crystal Chemistry of Anhydrous Borates. Moscow, MSU, 1983 (in Russian).
2. H. Lux, *Z. Elektrochem.*, 1939, **45**, 303.
3. H. Flood and T. Forland, *Acta Chem. Scand.*, 1947, **1**, 592.

Synthesis and Lewis Acidity of Organo B–O–Si and B–O–Sn Derivatives

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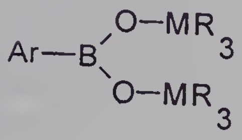
1 INTRODUCTION

Trivalent boron compounds, with a sextet of σ-electrons around the boron centre, are well-documented for their Lewis acidic properties.[1] Factors which affect this acidity are of interest to both academics and industrialists since this class of compound plays an important role in many stoichiometric and catalytic reactions; thus, for example, epoxy-resins may be 'cured' by addition of a suitable Lewis acid.[2] Incorporation of borate into the epoxy-resin by curing with $(MeO)_3B_3O_3$ has led to a transparent polymeric material with fire-retardant properties.[3] We were interested in attempting to improve the fire-retardant nature of these polymers by inclusion of organosilicates/stannates into the formulation as 'curing' agents, and this has led to the synthesis and characterisation of a number of new and previously reported compounds containing one or more B-O-Si/Sn linkages. Lewis acidity can be measured in a number of ways[4] but we have found that an NMR method, as developed by Gutmann,[5] is convenient and reliable. The Lewis acidities of the B-O-Si/Sn derivatives have been estimated and the effects of Si and Sn are described.

2 SYNTHESIS AND REACTIVITY

Molecular species containing the B-O-Si/Sn link are documented in the literature as the triorganosilyl/stannyl esters of boronic (**1**), orthoboric (**2**), and metaboric acids (**3**),[6] the *cyclo*-borasiloxane ring derivatives,[7] and over the last decade, by the borosilicate cages.[8] A convenient method of preparation of silyl/stannyl esters of boron acids is the azeotropic removal of water from mixtures of the appropriate boron acid and the triorganylsilanol or triorganylstannyl derivatives and the previously reported compounds $(R_3MO)_3B$ {M = Si with R = Et, ^{n}Pr, ^{n}Bu, Ph; M = Sn with R = Me, ^{n}Bu, Ph}, $(Et_3SiO)_3B_3O_3$, $(^nBu_3SnO)_3B_3O_3$, and $(Ph_3SiO)_2BPh$ were prepared by this method.[6] New triorganosilyl esters of orthoboric acid {$(R_3SiO)_3B$: R_3 = $BuMe_2$, $PhMe_2$, [2-(3-cyclohexenyl)ethyl]Me_2, (^{n}Octadecyl)Me_2, ^{n}Hex_3}, metaboric acid {$(R_3SiO)_3B_3O_3$: R_3 = ^{n}Pr_3, ^{n}Bu_3, ^{n}Hex_3, $EtMe_2$, ^{n}$BuMe_2$, [2-(3-cyclohexenyl)ethyl]Me_2, (thexyl)Me_2, (^{n}Octadecyl)Me_2, $PhMe_2$, Ph_2Me, Ph_3} and arylboronic acids {$ArB(OSiR_3)_2$: Ar = Ph with R_3 = ^{n}Pr_3, ^{n}Bu_3, Ph_2Me; Ar = *p*-BrC_6H_4 with R = Ph, ^{n}Pr; Ar = *o*-MeC_6H_4 with R = Ph, ^{n}Pr} were synthesised similarly from the triorganosilanol. Triorganostannyl esters of metaboric acid {$(R_3SnO)_3B_3O_3$: R = Ph, Me} and arylboronic



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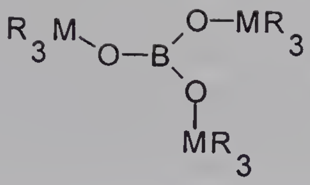

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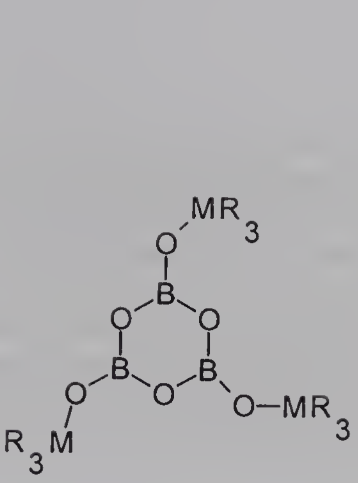
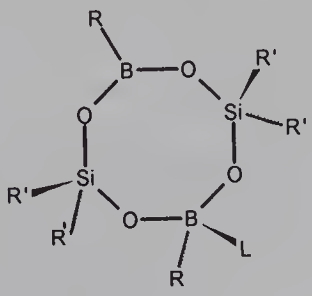


(3)

acids $\{(R_3SnO)_2BAr$: R = Ph with Ar = Ph, *p*-BrC_6H_4, *o*-MeC_6H_4; R = ^nBu with Ar = Ph, *p*-$BrC_6H_4\}$ were synthesised from R_3SnOH or $(^nBu_3Sn)_2O$.

Preparative routes to *cyclo*-borasiloxanes have involved cyclocondensation reactions[7] from either (i) $PhB(OH)_2$ and a dihydroxysilane or α,ω-dihydroxysiloxane, (ii) $PhB(OH)_2$ and a α,ω-dichlorosiloxane in the presence of NEt_3 or, (iii) $PhBCl_2$ and a dihydroxysilane. The *cyclo*-boratrisiloxanes $\{(RBO)(R'_2SiO)_2$: $R'_2 = Me_2$ with R = Ph, *p*-BrC_6H_4, *m*-$NH_2C_6H_4$; R'_2 = Me/Ph with R = Ph, *p*-BrC_6H_4, *m*-$NH_2C_6H_4\}$ and *cyclo*-diboratetrasiloxanes $\{(RBO)_2(R'_2SiO)_2$: $R'_2 = Ph_2$ with R = Ph, *p*-BrC_6H_4, *o*-MeC_6H_4, *m*-$NH_2C_6H_4$, *m*-$NO_2C_6H_4$, ^nBu; $R'_2 = {}^nOct/Me$ with R = Ph, *p*-BrC_6H_4, *m*-$NO_2C_6H_4\}$ derivatives were prepared by cyclocondensation of appropriate stoichiometric mixtures of organoboronic acid and organosilanols in toluene using a Dean-Stark apparatus. $(PhBO)_2(Ph_2SiO)_2$ has been previously reported by this method and the compounds $(PhBO)(Me_2SiO)_2$ and $(PhBO)(MePhSiO)_2$ have been previously prepared by the second route described above. The solid-state structure of (*p*-$BrC_6H_4BO)_2(Ph_2SiO)_2$ was determined by a single-crystal X-ray diffraction study which revealed that the ring parameters differ only slightly from that of the $(PhBO)_2(Ph_2SiO)_2$;[7] the borasiloxane ring of the brominated derivative is non-planar and centrosymmetric with bond lengths and angles about B and Si as expected but with Si-O-B angles of 144.7(3) and 150.7(3)°.

An investigation into the reactions of amines with these *cyclo*-borasiloxanes was initiated on the basis that trialkyl- and triarylboroxines react with amines[9] to form 1:1 adducts. *cyclo*-Boratrisiloxanes were found to be unreactive towards amines, but 1:1 adducts (**4**) were readily formed for corresponding reactions with the *cyclo*-diboratetrasiloxanes $(PhBO)_2(Ph_2SiO)_2$ (L = cyclohexylamine, Et_3N, pip, $^tBuNH_2$) and (*o*-$MeC_6H_4BO)_2(Ph_2SiO)_2$ (L = morpholine) in Et_2O solution at room temperature. The solid-state ^{11}B MAS NMR spectra of these adducts showed two equal intensity signals at



(4)

chemical shifts appropriate for 3- and 4-coordinate boron environments, whilst in solution at room temperature the adducts were characterised by a single ^{11}B resonance at a chemical shift similar to that calculated from averaging values obtained in the solid state; ligand dissociation-recombination is a likely mechanism for the equilibration of the solution ^{11}B environments.

All new compounds were characterised by ^{11}B, ^{1}H, and ^{13}C NMR and IR spectroscopy and experimental data (yields, b.pts/m.pts, elemental analyses, AN values) for the new compounds, and details of solid-state ^{11}B MAS NMR spectra and the single-crystal X-ray diffraction study of $(p\text{-}BrC_6H_4BO)_2(Ph_2SiO)_2$ are available elsewhere.[10]

3 LEWIS ACIDITY

Gutmann and co-workers have described a quantitative parameter (Acceptor Number, AN), derived from the ^{31}P NMR shifts produced in Et_3PO by electrophilic solvent interactions as a measure of solvent Lewis acidity;[5] the AN scale has reference points of hexane (0) and $SbCl_5$ (100). For comparison, the trigonal boron compounds BF_3 and $B(NMe_2)_3$ have AN values of 89 and 9, respectively.[4] The triorganosilyl/stannyl arylboronic acid esters and orthoborate esters were poor Lewis acids (AN values 23-31, and 23-36, respectively) whilst the esters of metaboric acid were stronger Lewis acids (AN = 44-81). The AN values of esters with B-O-Si/Sn linkages were in the same general ranges as those observed for organic esters *eg.* $(MeO)_3B$ (AN=23) and $(MeO)_3B_3O_3$ (AN =79).[4] The most highly acidic of those derivatives measured was $(PhMe_2SiO)_3B_3O_3$ (AN = 81) whose Lewis acidity was greater than that of $(MeO)_3B_3O_3$ and approached that of BF_3. As was found for the organic esters,[4] increasing the steric bulk of the R_3M moiety significantly reduced the AN value, *eg.* triorganosilylorthoborates: Et_3 (AN = 34) > $^nPr_3$ (28) > $^nBu_3$ (23), triorganosilylmetaborates: $EtMe_2$ (74) > Et_3 (72)> $^nPr_3$ (63) > $^nBu_3$ (56)> $^nHex_3$ (44), and there also appeared to be little differentiation between corresponding $^nBu_3Si$ and $^nBu_3Sn$ derivatives. The AN data demonstrate that there is a strong electron-withdrawing effect, associated with incorporating Si (or Sn) atoms into the ester linkage, which resulted in increased Lewis acidity at B. The AN data for the orthoborate esters also showed that the Si/Sn derivatives should be stronger Lewis acids than the isomeric C analogues *ie* $(Et_3SiO)_3B$ would be expected to be less acidic than $(H_3CO)_3B$ from steric considerations alone and yet $(Et_3SiO)_3B$ has an AN value 10 units higher. This effect is presumably due to a O(2p)-$MR_3(\sigma^*)$ π-bonding interaction reducing O(2p)-B(2p) π-bonding. The effect is moderated in the metaborate esters where the M:B ratio is reduced to 1:1; however it is still observable and $(EtMe_2SiO)_3B_3O_3$ and $(^nPr_3SiO)_3B_3O_3$ with bulky substituents at Si have similar Lewis acidities to $(MeO)_3B_3O_3$ and $(^nBuO)_3B_3O_3$ (65).[4]

The relative reactivities of the *cyclo*-boratrisiloxanes and *cyclo*-diboratetrasiloxanes towards amines was in agreement with AN values for these derivatives. *cyclo*-Diboratetrasiloxanes had AN values in the range 47-62, and comparable in strength to triorganoboroxines (~50) which formed isolatable amine adducts. *cyclo*-Boratrisiloxanes had AN values considerably lower (22-28) and were comparable in Lewis acid strength to orthoborate esters. The relatively low Lewis acidity of the *cyclo*-boratrisiloxanes when compared to boroxines (*cyclo*-triboratrisiloxanes) requires consideration. The 6-membered *cyclo*-boratrisiloxane rings contain a unique ring O atom *trans*-annular to B as part of a Si-O-Si linkage. The Si atoms, whose π-acceptor requirements are effectively satisfied by this unique π-donor O atom, become less electron-withdrawing with respect to the remainder of the ring. This results in more π-electron density from the O atom in the adjacent B-O-Si linkages residing on the B atom. AN measurements indicated that the electronic effects of {$-SiR_2OSiR_2-$} towards {RBO_2} was similar to that found for 2{$-SiR_3$} groups in bis(triorganosilyl)boronate esters (**1**). The *cyclo*-diboratetrasiloxanes contain the {RB} and {R_2Si} ring π-acceptor fragments sandwiched by an equal number of O π-donor atoms and arranged without any such Si-O-Si linkages. Thus the {R_2Si} ring fragments remain more strongly π-accepting with increased Lewis acidity at B as a consequence of greater competition for the available π-electron density from the O atoms of the B-O-Si links.

Acknowledgements

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References

1. W.W. Porterfield, '*Inorganic Chemistry: a Unified Approach*', 2nd Ed., 1993, Ch.6, 313, Academic Press, London.
2. C.S. Chen, B.J. Bulkin, and E.M. Pearce, *J. Appl. Polym. Sci.*, 1982, **27**, 1177.
3. K.S. Varma and D.P. Parkes, *GB Patent*, 1992, GB2255560A.
4. M.A. Beckett, G.C. Strickland, J.R. Holland, and K.S. Varma, *Polymer*, 1996, **37**, 4629, and refs therein.
5. U. Mayer, V. Gutmann, and W. Gerger, *Monatshefte fur Chemie*, 1975, **106**, 1235.
6. S.K. Mehrotra, G. Srivastava, and R.C. Mehrotra, *J. Organomet. Chem.*, 1974, **73**, 277, and refs therein; D. Murphy, J.P. Sheehan, T.R. Spalding, G. Ferguson, A.J. Lough, and J.F. Gallagher, *J. Material Chem.*, 1993, **3**, 1275.
7. S.K. Mehrotra, G. Srivastava, and R.C. Mehrotra, *J. Organomet. Chem.*, 1974, **73**, 277, and refs therein; U. Wannagat and G. Eisele, *Z. Naturforch*, 1978, **33B**, 475; D.A. Foucher, A.J. Lough, and I. Manners, *Inorg. Chem.*, 1992, **31**, 3034; D.A. Foucher, A.J. Lough, and I. Manners, *J. Organomet. Chem.*, 1991, **414**, C1; B.J. Brisdon, M.F. Mahon, K.C. Molloy, and P.J. Schofield, *J. Organomet. Chem.*, 1992, **436**, 11; A. Mazzah, A. Haoudi-Mazzah, M. Noltemeyer, and H.W. Roesky, *Z. Anorg. Allg. Chem.*, 1991, **604**, 93.
8. G. Ferguson, B.J. O'Leary, D.M. Murphy, and T.R. Spalding, *J. Organomet. Chem.*, 1996, **526**, 195; A.T. O'Dowd, T.R. Spalding, G. Ferguson, and J.F. Gallagher, *J. Chem. Soc., Chem. Commun.*, 1993, 1816; F.J. Feher, T.A. Budzichowski, and J.W. Ziller, *Inorg. Chem.*, 1992, **31**, 5100.
9. M.A. Beckett, D.E. Hibbs, M.B. Hursthouse, P. Owen, K.M.A. Malik, and K.S. Varma, *Main Group Chem.*, 1998, **2**, 251.
10. M.A. Beckett, P. Owen, and K.S. Varma, *J. Organomet. Chem*, 1999, **588**, 107; M.A. Beckett, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, P. Owen, and K.S. Varma, manuscript in preparation.

Synthesis and Properties of Vanadoborate Cluster Materials

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1 BACKGROUND

We are interested in vanadoborate cluster materials[1-7] both as precursors to porous solids and as a new class of molecular magnets. We have synthesized a variety of vanadoborate cluster compounds **1 - 7**, primarily by use of two different synthetic routes. The first involves hydrothermal synthesis, using sodium tetraborate ('borax') as the boron source and the second uses molten boric acid as the reaction medium. In general anionic clusters are found. Herein we report that these have novel electronic and bonding arangements which affect their magnetic behaviour and also that they may be cross-linked together by metal centers such as Cd to form stable microporous phases.

2 CLUSTER ARCHITECTURE

Four main cluster skeletons have been found as shown in Figure 1 (a-d). All clusters found to-date are anionic and may be broken down into segregated vanadate and borate components which are linked through either V_2OB or VOB_2 triply bridging oxygen atoms. It is a key feature of both components that they are each highly extended so that isolated borate or vanadate polyhedra are not found. This contrasts the general case in metal phosphate chemistry, where P-O-P and M-O-M linkages are strongly disfavavoured compared to M-O-P. Solution speciation is probably the most important factor for the breaking of this 'Lowenstein' type rule although the more electropositive nature of boron (2.04) than phosphorus (2.19) may also play a role.

The vanadate moieties are made up of 5-coordinate vanadyl centres which link together via $[V_2O_2]$ rings. In general the oxidation state of vanadium is 4+, although some mixed 4+/5+ clusters have been found. Since V4+ is a d^1 centre the arrangement of the cluster d - electrons is of interest both from the point of view of cluster bonding and also for the molecular magnetism found in these compounds.

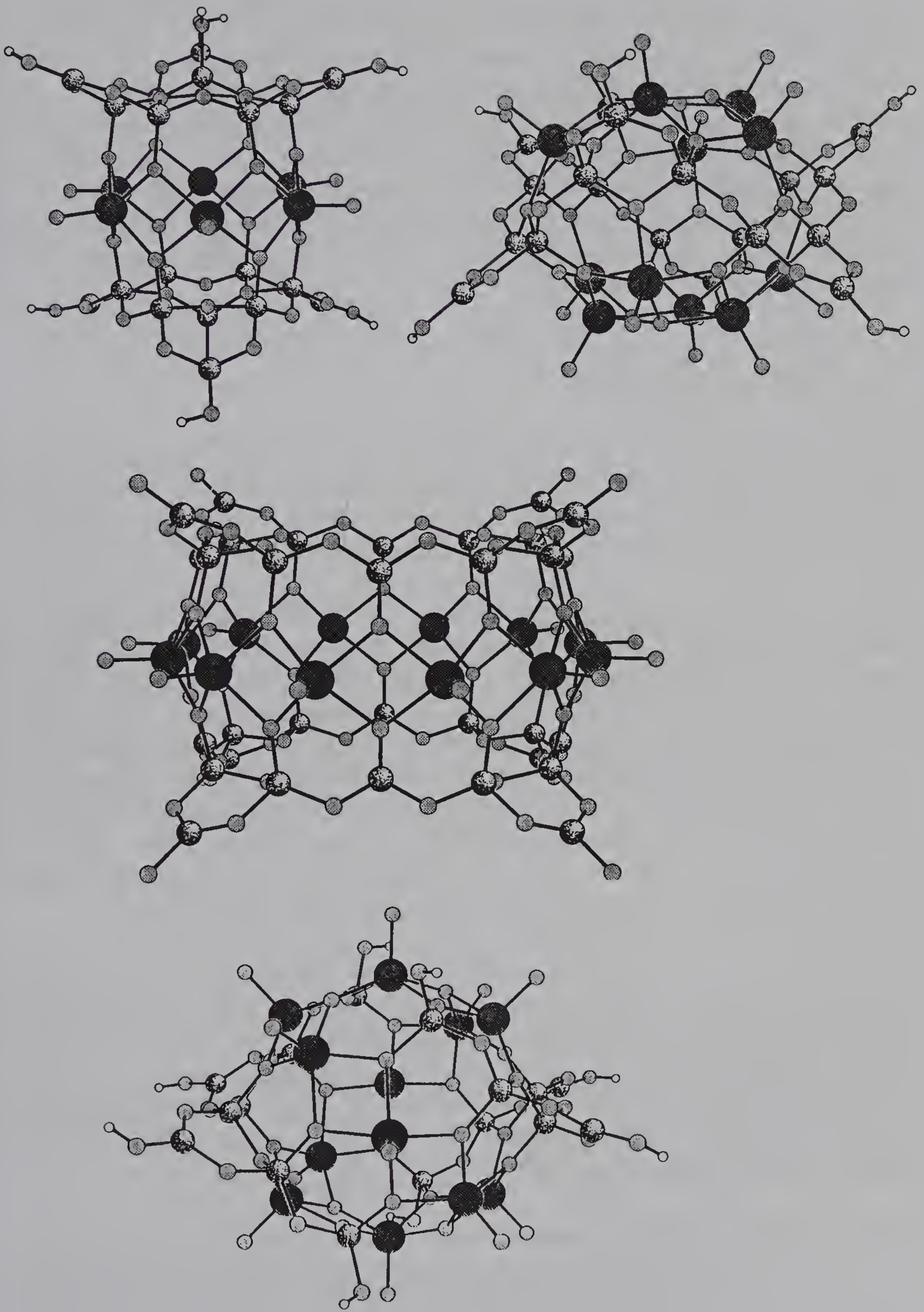

Figure 1. *Vanadoborate Cluster Types.*

a) $[V_6B_{20}O_{50}H_8]^{8-}$ b) $[V_{12}B_{18}O_{60}H_6]^{12-}$ c) $[V_{12}B_{32}O_{84}H_8]^{16-}$ d) $[V_{12}B_{16}O_{58}H_8]^{12-}$

The borate components which are shown in isolation in Figure 2 are made up of both trigonal and tetrahedral BO_3 and BO_4 centres. These can be involved in triborate rings or as exocyclic moieties, just as found for natural borate minerals. Depending on the synthetic conditions and the metals available these building blocks can be combined to give a wide range of 'ligand' types. Whilst rationalization of these is difficult, it should be noted that the unusual 'condensed' decaborate $[B_{10}O_{22}H_4]$ is favoured by the 'flux' rather than hydrothermal conditions of synthesis. One factor assisting diversity is the apparent 'fit' of the (V-O-V-O) toroidal rings with (O-B-O-B) rings. These can match each other in size and angular disposition. Compounds with $[V_6]$, $[V_{10}]$ and $[V_{12}]$ rings have been found to date and others no doubt await discovery.

3 CLUSTER SYNTHESIS

Hydrothermal synthesis at 180°C using borax, V_2O_5, and en, as starting reagents can result in phase-pure formation of the water soluble cluster compound **2** $Na_{10}[V_{12}B_{18}O_{60}H_8]$. The Na ions can then be exchanged with M^{2+} at lower temperatures to form insoluble materials. Some of these have since been shown to be microporous phases.

Addition of other metal dications M, such as Zn, Co, Mn and Cd directly to the hydrothermal reaction mixture can also be used to extend the product range to other heterometallic borate compounds, including expanded neutral clusters $[\{M(en)_2\}_6V_{12}B_{18}O_{60}H_6]$ **6** or novel open-framework materials in which the clusters are cross-linked by the M^{2+} ions. For example cadmium can form stable cubic phases such as **7** with 3-D interpenetrating channels, with the Cd atoms linking $[V_{12}B_{18}]$ clusters through ligation of the borate oxygens. By contrast use of Zn^{2+} results in an open 2-D polymer **5** containing $[Zn_{10}V_{10}B_{28}]$ formula units. Four Zn atoms lie *within* the cluster skeleton and assist formation of a 10-membered vanadyl toroidal ring. The clusters are connected through $Zn(en)_2$ bridges, which ligate adjacent clusters via the V=O groups.

Our second strategy involves *molten boric acid flux synthesis*.[1] Unlike most parallel hydrothermal reactions with $[H_3BO_3]$ the method gives typically higher yield and purity of products, though product type is sensitive to reaction conditions. Thus at 180°C the 1-D polymer $2[enH_2]4[enH][V_6B_{22}O_{53}H_8]$ is formed in excellent yield from V_2O_5, ethylene diamine (en) and boric acid. At 200°C the salt $4[enH_2][V_6B_{20}O_{50}H_6]$ **1** containing discrete $[V_6B_{20}]$ cluster anions is formed instead. The compounds are notable for containing triangular raft like $[B_{10}]$ decaborate ligands.

Characterization of all cluster compounds has been carried out primarily by single crystal x-ray structure determination. In some cases the exact structural details are ambiguous, for example cluster charge can be difficult to determine due to i) possible mixed valence of the vanadium centres, ii) difficulty in location of hydroxy protons and iii) the possibility that waters of crystallization may infact be hydroxonium ions. In some structures boron hydroxy protons are well located and imply that all trigonal B-O termini around these clusters are protonated, since the reaction pH (7-9) is similar in most cases.

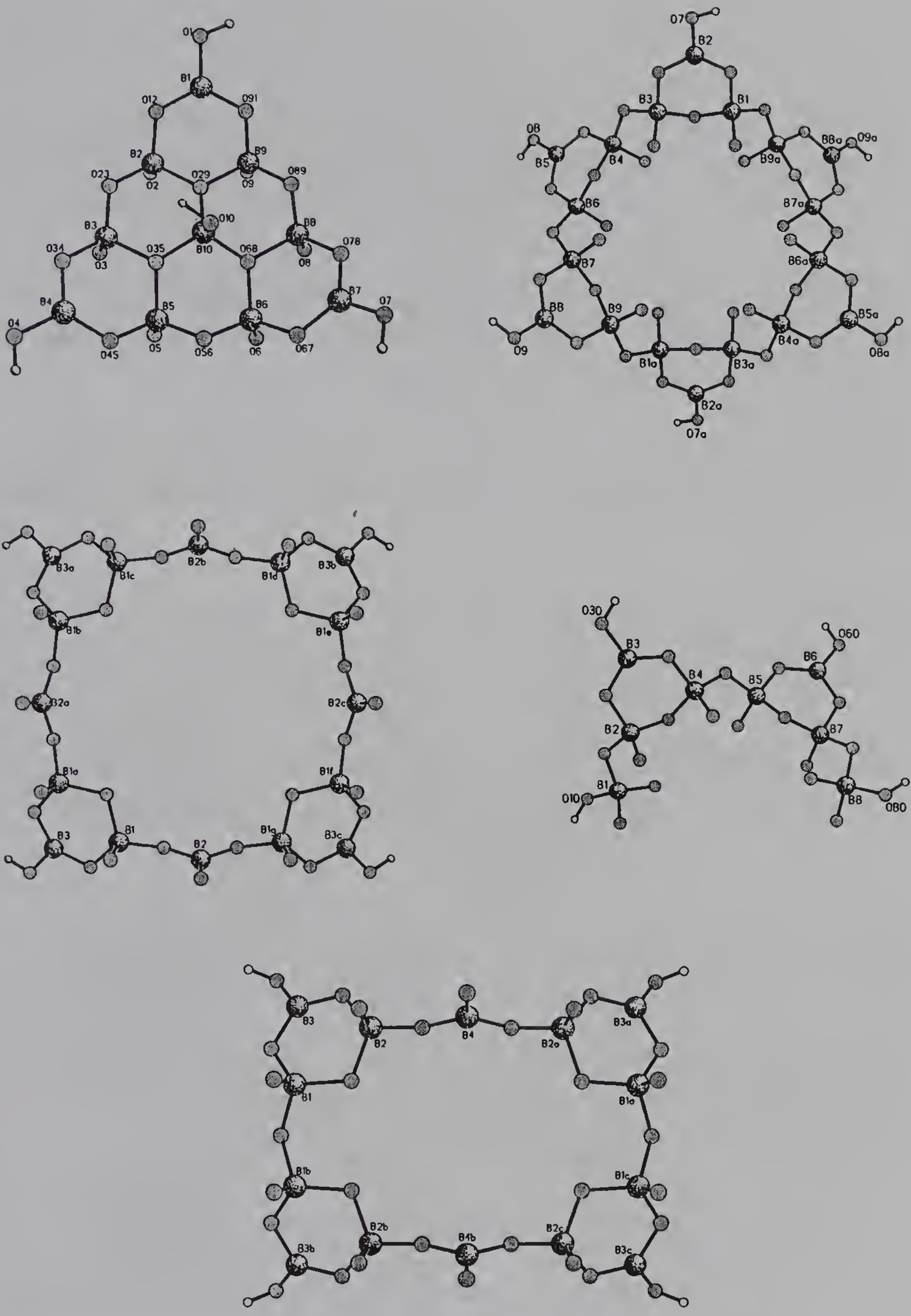

Figure 2. *Borate Components of Vanadoborate Clusters.*

a) $[B_{10}O_{22}H_4]$ **(1)**

b) $[B_{18}O_{42}H_6]$ **(2, 6, 7)**

c) $[B_{16}O_{36}H_4]$ **(3)**

d) $[B_8O_{21}H_4]$ **(4)**

e) $[B_{14}O_{32}H_4]$ **(5)**

Table 1. *Synthetic and Crystallographic Details for Vanadoborate Cluster Compounds* ***1-7***

1 $[enH_2]_4[V_6B_{20}O_{50}H_8]$ (ref 1) $1V_2O_5 : 25H_3BO_3 : 6en$, 200°C, 3days. Pale green prisms, 90% yield. Triclinic P-1, $a = 11.426(2)$, $b = 11.919(2)$, $c = 12.030(2)Å$, $\alpha = 86.00(2)$, $\beta = 62.39(2)$, $\gamma = 77.09(2)°$, $V = 1413Å^3$.

2 $Na_{10}[V_{12}B_{18}O_{60}H_8]$ (ref 3) $1V_2O_5 : 10Na_2B_4O_7 : 6en : 55H_2O$. 180°C, 7 days Dark red blocks, 70% yield. Monoclinic, $P2_1/n$ $a = 13.591(4)$, $b = 16.990(4)$, $c = 14.382(3)Å$, $\beta = 97.53(2)$, $V = 3292Å^3$.

3 $[enH_2]_4[V_{12}B_{32}O_{84}H_8]^{n-}$ (this work) $1V_2O_5 : 8H_3BO_3 : 8en : 8HF : 55H_2O$. 180°C, 7 days. Green pyramids, 30% yield. Tetragonal, I4/mmm, $a = 19.104(4)$, $c = 19.709(3)Å$, $V = 7193Å^3$.(c.f. ref 5)

4 $[enH_2]_4[Mn_2V_{12}B_{16}O_{58}H_8(H_2O)_4]$ (this work) $1V_2O_5 : 10Na_2B_4O_7 : 6en : 2Mn(OAc)_2 : 100H_2O$. 180°C, 4 days. Olive plates, 40% yield. Monoclinic, C2/c, $a = 13.347(2)$, $b = 19.557(2)$, $c = 23.971(4)Å$, $\beta = 98.14(2)$, $V = 6194Å^3$.

5 $[Zn_{10}(en)_{12}V_{10}B_{28}O_{76}H_8]$ (this work) $1V_2O_5 : 4H_3BO_3 : 3en : 1.5Zn(OAc)_2 : 50H_2O$. 180°C, 8days. Blue-green prisms, 40% yield. Tetragonal, $P4_2/mnm$, $a = 17.147(4)$, $c = 20.329(6)Å$, $V = 5977Å^3$.

6 $[M_6(en)_{12}V_{12}B_{18}O_{60}H_6]$ M = Ni, Co, Zn (ref 4) $1V_2O_5 : 8H_3BO_3 : 6en : 2M(OAc)_2 : 100H_2O$, 180°C, 10 days. Orange-brown prisms, 70% yield. Rhombohedral, R-3c, M = Ni: $a = 20.904(3)$, $c = 21.301(3)Å$, $V = 8061Å^3$.

7 $[Cd_3(en)_3V_{12}B_{18}O_{60}H_6]^{n-}$ (this work) $1V_2O_5 : 10H_3BO_3 : 6en : 2Cd(OAc)_2 : 100H_2O$. Dark red swords, 90% yield. 180°C, 10days. Cubic, Ia-3d, $a = 31.972(2)Å$, $V = 32{,}682Å^3$.

Typical degree of hydration 10-20 non-coordinated H_2O per cluster unit for **1-7**.

Such B-OH are frequently involved in strong B-OH--O-B hydrogen bonds to neighbouring clusters, and short O---O contacts are seen even in the absence of direct location of hydrogen atoms.The possibility of hydroxonium ions is harder to rule out definitively, especially as aquation in these crystals is often highly disordered. The bond valence sums for the vanadium metals are usually between 4.0-4.1.

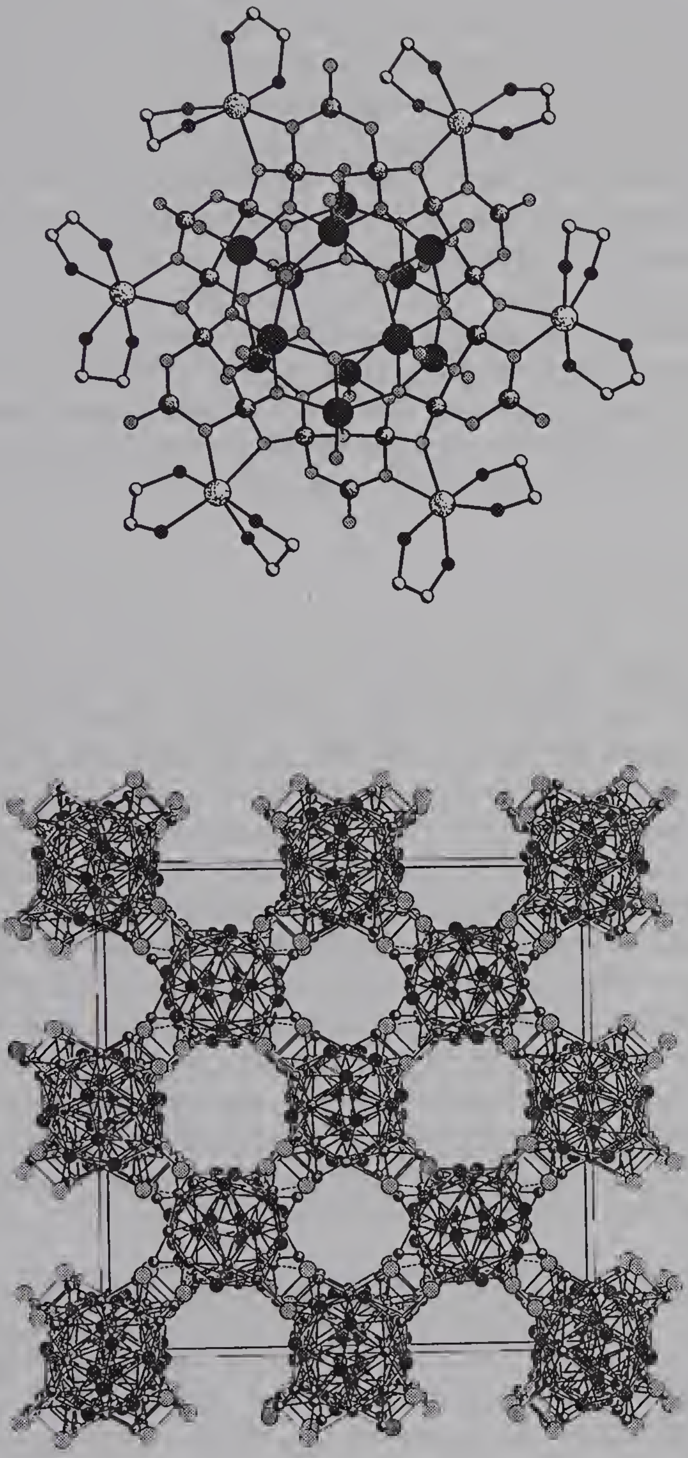

Figure 3. *Metallo-coordinated Vanadoborate Cluster Materials.*

a) A new Class of Molecular Magnet - $[M_6(en)_{12}V_{12}B_{18}O_{60}H_6]$ **6**

b) A Cluster-based Microporous Solid - Cubic $[Cd_3(en)_3V_{12}B_{18}O_{60}H_6]^{n-}$ **7**

On the basis of this evidence compound **2** is formulated as having ten sodium and two hydroxonium counterions for a 12- cluster anion. This contrasts the work of Haushalter and Zubieta who claim a 10- anion for the [pnH_2] salt which necessitates mixed $V^{(IV)}/V^{(V)}$ oxidation states.[2] The colours of the crystals range from pale green (V_6B_{20}) to dark red-brown ($V_{12}B_{18}$). The involvement of cluster frontier orbitals renders assignment of valence state based on colour invalid. Supporting evidence is provided by thermal gravimetric analysis which usually shows a 2-stage weight loss 50-150°C due to loss of water and 250-500°C due to pyrolysis of organic counterions.

The temperature of reaction plays an important role in hydrothermal synthesis. At 180°C the [$Mn_2V_{12}B_{16}$] cross-linked polymer **4** is formed. Attempts to introduce Mn_3O units into the cluster through use of lower temperatures and [$Mn_3O(OAc)_6py_3$] as Mn source instead resulted in formation of new class of organically templated mixed metal oxide, [enH_2] [$Mn_3V_4O_{14}(H_2O)_2$] with no incorporation of borate whatsoever.[8]

4 MATERIAL PROPERTIES

Over the last few years there has been growing interest in magnetism of cluster compounds.[9] The molecular magnetism of both the [V_6B_{20}] and the [$V_{12}B_{18}$] based materials has been investigated and appears to involve partial spin-pairing of the V^{4+} d^1 centres. Both compounds **1** and **2** are paramagnetic down to 4K and have molecular magnetic moments of 4.1 and 4.0 BM respectively. The bonding in both cluster types have been examined theoretical calculations at both extended Hückel and the ab initio levels and the frontier orbitals are V d(xy) in character.[10,11] Due to the diffuse nature of the vanadium 3 d orbitals there is significant overlap of these. In the [V_6B_{20}] case this gives rise to six d(xy) orbital combinations around the V_6 ring which bear analogy to the π-orbitals of benzene. The in-phase bonding combination (a_{1g}) is doubly occupied and there are four unpaired electrons, an arrangement we have termed high spin aromaticity.[11] The bonding pattern in **2** is different but 4 unpaired electrons are also found for the cluster.[10] Within such materials the possibility exists for high spin-low spin transitions, analogous to that seen for isolated metal centers. The application of spin transition polymers to information storage in magnetic 'Smart cards' has been reported recently by Kahn.[12]

Another area for potential applications lies in the area of microporous solids, either for separation or catalysis. New generation microporous solids are being sought with properties complementary to zeolites. Recently we reported the formation of a stable coordination polymer [$Cu_3(TMA)_2$] which has 40% porosity, is stable to 240°C and can be chemically functionalized. One key is that its SBU is made up of an octahedral cluster-like building block containing twelve Cu ions.[12] By analogy vanadoborate clusters may offer useful building blocks if they can be connected together. As mentioned above we have succeeded in this respect with the Cd cross-linked material **7**. This has been found by to have structural stability up to 300°C and to reversibly desorb and resorb water of 11% by weight, (20% by volume). Furthermore it can also absorb simple organic molecules and undergo partial ion exchange, since the framework has a negative charge.

5 FUTURE PROSPECTS

Further work on the use of organic bases other than ethylene diamine is underway. Initial findings indicate that similar clusters may be formed but as salts with different solubilities than the [enH_2] type. This should allow organic solubilization of certain clusters. With respect to heterometallic clusters the potential for new cluster types such as [$Zn_4V_{10}B_{28}$] clearly exists. The super-clusters of the [$Ni_6V_{12}B_{18}$] type are under further study for their magnetic properties, and electrochemical measurements will be made on soluble analogues. The metal cross-linked cluster solids offer much scope for further design and possible application as microporous sorbents or catalysts. Use of larger clusters such as the [$V_{12}B_{32}$] system may allow larger pore sizes to be achieved and incorporation of potentially catalytic metal centers, such as platinum, should also be possible. As has been demonstrated by the examples above, these metals may serve either as direct bridges between clusters, or as entities coordinated to individual cluster surfaces.

Acknowledgements

We are grateful to the Research Grants Council of Hong Kong (grants 681/96P, 6081/98P and 6188/99P) and the Industry Department, HKSAR (Industrial Support Fund AF 155/99) for financial support, Mr. Alvin Siu and Mr. Jiaqi Zheng for their technical assistance and Dr. Lin Zhenyang (HKUST) and Prof. R.B. King (U. Georgia) for helpful discussions.

References

1. I.D.Williams, H.H-Y.Sung, M.Wu, X.X.Zhang and J.Yu, *Chem. Commun.*, 1998, 2253.
2. J.T. Rijssenbeek, D.J. Rose, R.C. Haushalter and J. Zubieta, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1008.
3. M. Wu, H.H-Y. Sung and I.D. Williams, *J. Solid State Chem*, in prep
4. M. Wu, H.H-Y. Sung and I.D. Williams *Inorg. Chem. Commun.*, submitted.
5. C.J. Warren, D.J. Rose, R.C. Haushalter and J. Zubieta, *Inorg. Chem.*, 1998, **37**, 1140.
6. T. Yamase, M. Suzuki and K. Ohtaka, *J. Chem. Soc., Dalton Trans.*, 1997, 2463.
7. C.J. Warren, J.T. Rijssenbeek, D.J. Rose, R. C. Haushalter and J. Zubieta, *Polyhedron.*, 1998, **17**, 2599.
8. I.D. Williams, T.S-C. Law and H.H-Y. Sung, *Solid State Sciences*, 2000, **1**, 000.
9. D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science*, 1994, **265**, 1054.
10. I.D.Williams, M.Wu, H.H-Y.Sung, T.S-C. Law, Z. Lin and X.X.Zhang, *Adv. Mater., Opt. Elec.*, 2000, 000.
11. I.D. Williams, Z. Xu, Z. Lin and R.B. King, *J. Amer. Chem. Soc.*, submitted.
12. O. Kahn and C.J. Martinez, *Science*, 1998, **279**, 44.
13. S.S-Y. Chui, S.M-F.Lo, J.P.H. Charmant, A.G. Orpen and I.D. Williams, *Science*, 1999, **283**, 1148.

Medicinal Applications

Synthesis of Boron-rich Building Blocks for Phosphodiester Oligomers in Boron Neutron Capture Therapy

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INTRODUCTION

Successful treatment of tumors by radiation therapy demands that the dose ratio between tumor tissue and surrounding healthy tissue is greater than unity, and that the radiation dose to the healthy tissue approaches the tolerance dose. This requirement is generally achieved in conventional radiotherapy when applied successfully. It must also be fulfilled in boron neutron capture therapy (BNCT).

In BNCT, the first demand is largely determined by the compound chosen. The way of administration, time point of administration in relation to therapy, and the amount administered are important factors. Additionally, the treatment planning plays a role in maximizing the dose ratio. The second demand is determined by the dose prescribed and the treatment plan. Only this aspect is similar to conventional radiotherapy.

In general, compounds for BNCT are more suited for therapy if they can be administered in high doses without concomitant toxicity. The more of a given compound can be given, the lower can the differential accumulation in tumor tissue be for a given dose ratio (1).

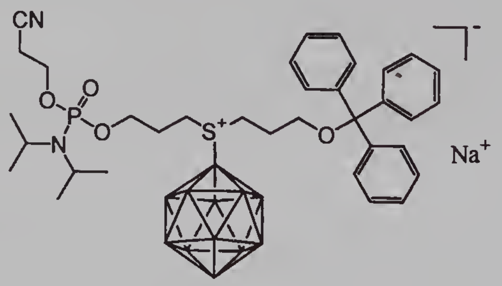
A number of new compounds have been suggested for BNCT. These include porphyrins (6, 2), sugars (7) and a great number of other drugs. One porphyrin, VCDP (3, 4, 5) has been investigated concerning its toxicity and biodistribution in mice. It is taken here as an example to illustrate the procedure to be taken for a new compound in BNCT.

VCDP shows marked toxicity in mice. the LD50 value of the drug is around 30 µg VCDP per gram body weight as a single dose, the LD10 is around 20 µg/g. Repeated administration at this dose level is tolerated. Thrombocytopenia, granulocytosis and altered liver enzyme levels were measured in the blood. With repeated administration of VCDP (three injections of 20 µg VCDP each per day over four days), tumor concentrations of 30 ppm boron are reached, with blood concentrations of around 10 ppm. Boron uptake in the tumor is highly heterogeneous, as observed for a number of other porphyrins (6, 1). Therapy could be carried out successfully even without optimization of the irradiation procedure and maximization of the radiation dose (5).

For any compound to be useful in patient trials, its availability must be adequate. For VCDP, at an injected dose of a total of 250 µg porphyrin per gram body weight, around 20 g porphyrin would be required per patient. The preparation of these large amounts of the porphyrin would require methods different from those originally proposed (3) and represent a major industrial effort.

The amount of boron to be given depends thus not only on toxicity, availability, and other factors, but also on the relative amount of boron present. It is therefore desirable to explore the attachment of boron-rich polymers to tumor-targeting compounds (8). Starting the preparation with $B_{12}H_{11}SH^{2-}$ leads to building blocks with twelve boron atoms. For BNCT high concentrations of ^{10}B in the tumor are required. Therefore boron containing building blocks are synthesized for polymerization, so that up to one thousand boron atoms can be attached through a single bond. Such a macromolecule could be bound to a tumor seeking antibody or other tumor seekers. In order to achieve this, building blocks are required which contain ^{10}B and two alcohol functions, which can be differentiated chemically.

We have synthesized two building blocks (1 + 2) for polymerization, which contain $B_{12}H_{11}SH^{2-}$, which is used as a boron component for this application. The polymerization can be achieved by using monomers, which contain two functionalized hydroxyl groups, one protected by a trityl or dimethoxytrityl group and one bound to the coupling reagent β-cyanoethyl-N,N-diisopropylamino phosphoramidite (CDP). Polymers can be prepared in an automated solid-phase technique, normally used for the synthesis of DNA and RNA. A good method for this synthesis is the phosphoramidite approach. Monomers are polymerized in a stepwise manner on controlled pore glass (CPG) by alternation of coupling and deprotection for the next coupling. The elongation of an oligomer contains at least three steps. In the first step the terminal hydroxyl group of the oligomer on the solid support is to be deprotected. The deprotected alcohol can be coupled to the next building block by cleavage of the reactive P-N-bond in the incoming monomer. Each elongation step is followed by a subsequent step, in which the phosphoramidite is oxidized to the stable phosphate analogues.



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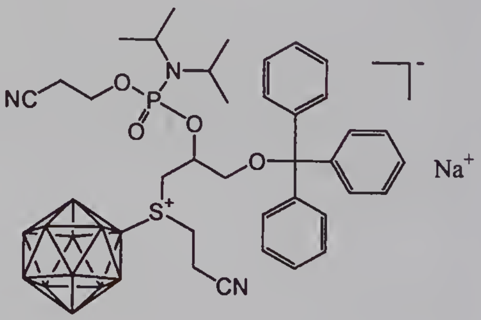

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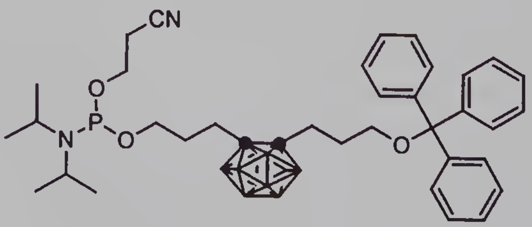
RESULTS AND DISCUSSION

Two known carboranes (3 + 4) are used as patterns for the preparation of the borane derivatives, synthesized by Drechsel (9) and Kane (10).



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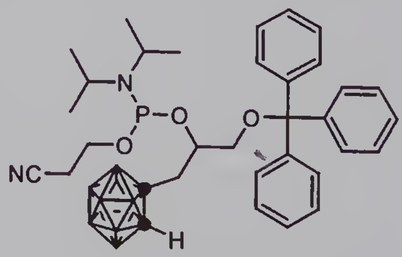

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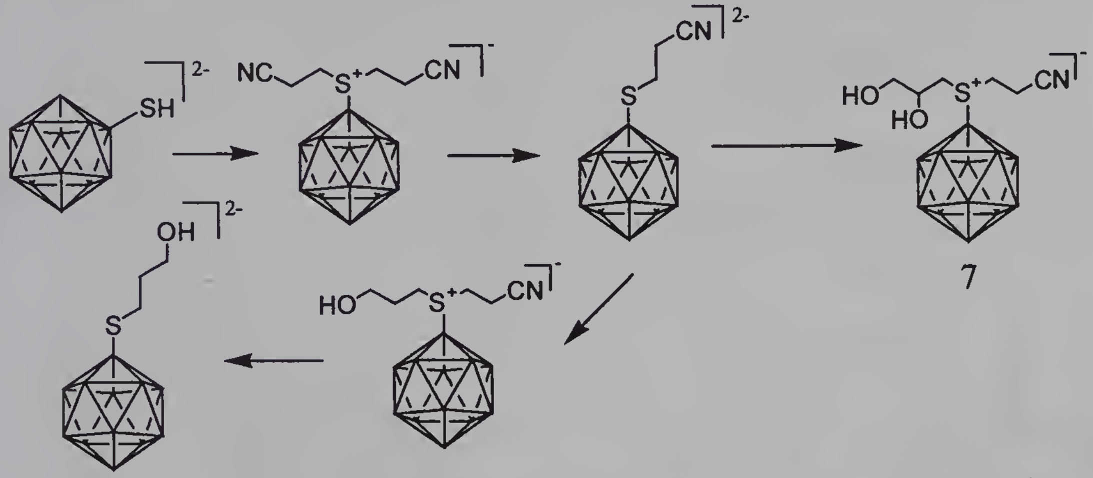
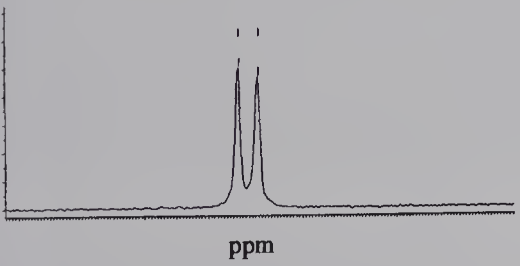
The nucleophilic property of the sulphur in $B_{12}H_{11}SH^{2-}$ is used for the preparation of the borane derivatives. After selective exchange of alkyl groups at this position the synthesis of the building blocks ends up with the tritylation and the phosphorylation. The exchange of alkyl groups can be achieved by basicly induced beta-elimination. Reaction of trityl bromide and boranes leads unfortunately to tritylation at the cage of the boranes. The trityl group can be introduced indirectly with a trityloxy containing alkyl bromide at the sulphur. After this reaction one cannot eliminate the cyanoethyl group in 6, because this would deprotect the alcohol again.

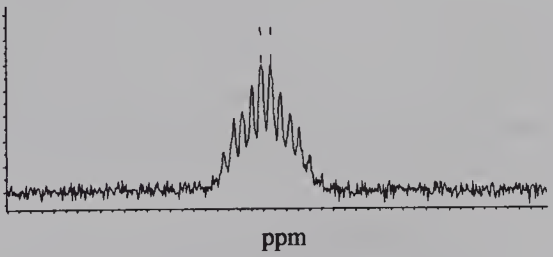


All compounds with more than one chiral centre yield diastereomeric mixtures. All heteroalkylated species have a chiral centre at the sulphur. In the compounds 6 and 2 the carbon 5 is chiral, too. After phosphorylation there is one more centre at the phosphorus. So the appearance of two diastereomeres in 1 and 6 and four in 2 respectively is expected. This expectation is verified by NMR-results. In ^{13}C-NMR as well as ^{31}P-NMR spectra one can see multiple resonances corresponding to almost all nuclei of the compounds. The ^{31}P-spectrum of 1 and the ^{13}C-spectrum of 6 are the most significant for this phenomenon.

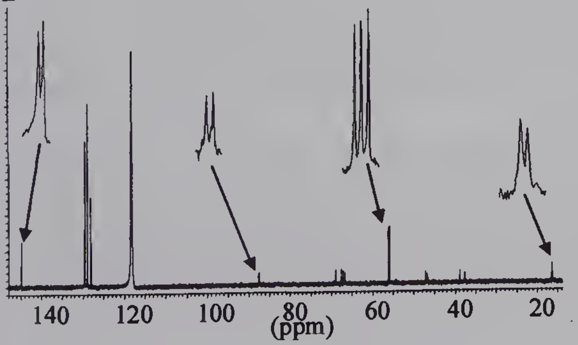
1: ^{31}P{^{1}H} in CD_3CN 21.4.99

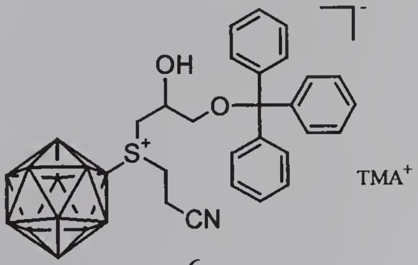


1: ^{31}P in CD_3CN 21.4.99



6: ^{13}C in CD_3CN 1.5.99





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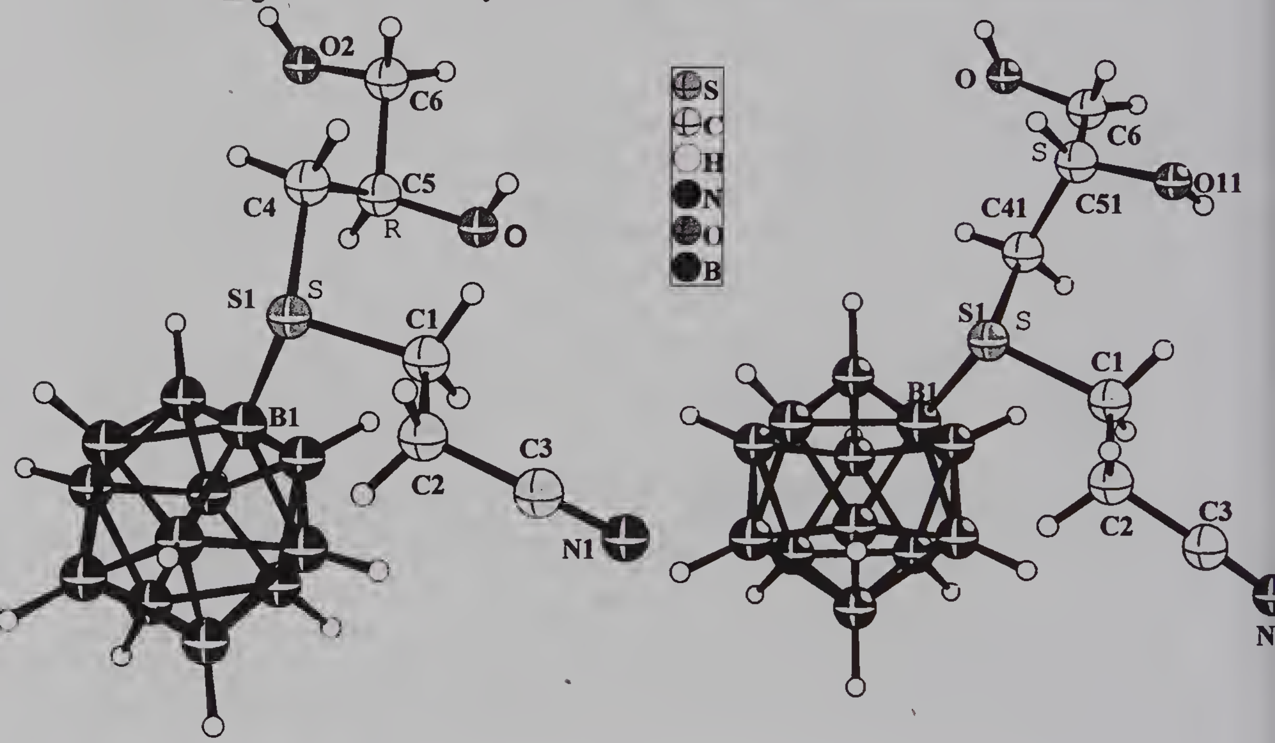
After tritylation it is very hard to crystallize the species because of their hydrophobic protecting group. Therefore successful crystallization was done with 7, which does not contain the trityl group but has two chiral centres. The separation of the two diastereomers by crystallization should be expected after x-ray structure analysis. The detected crystal contains S-configurated sulphur only, whereas the chiral carbon appears in both configurations. Other crystals should contain the RS- and RR-isomers.



CONCLUSION

New compounds, while in principle more promising, pose a considerable problem in all aspects of the clinical trial. The example of VCDP shows the problems of acute toxicity (which is considerable), of late phototoxicity of the skin (which has not been analyzed), the administration of the compound (which needs to be optimized) and the availability of the compound (which is difficult to prepare in large quantities). Whereas these problems are not insurmountable for any new compound, ethical and practical questions must be answered satisfactorily before a clinical trial protocol can be prepared.

REFERENCES

1 Gabel, D. Radiobiological considerations concerning the development of compounds for boron neutron capture therapy. Strahlenther. Onkol. *169*, 65-70, **1993**.

2 Kahl, S.B.; Koo, M.-S. Synthesis of tetrakis-carborane-carboxylate esters of 2,4-bis-(α,ß-dihydroxyethyl)-deuteroporphyrin IX. J. Chem. Soc. Chem. Commun. 1769-71, **1990**.

3 Miura, M.; Gabel, D.; Oenbrink, G.; Fairchild, R.G. Preparation of carboranyl porphyrins for boron neutron capture therapy. Tetrahedron. Lett. *31*, 2247-50, **1990**.

4 Miura, M.; Micca, P.L.; Heinrichs, J.C.; Gabel, D.; Fairchild, R.G.; Slatkin, D.N. Biodistribution and toxicity of 2,4-divinyl-nido-o-carboranyldeuteroporphyrin IX in mice. Biochem. Pharmacol. *43*, 467-76, **1992**.

5 Miura, M.; Micca, P.; Gabel, D.; Fairchild, R. G.; Slatkin, D. Biodistribution, toxicity and efficacy of a boronated porphyrin for boron neutron capture therapy. Allen, B.J.; Moore, D.E.; Harrington, B.V. Progress in neutron capture therapy for cancer. New York: Plenum Press; **1992**. pp. 455-8.

6 Oenbrink, G.; Gabel, D. Accumulation of porphyrins in cells and tissue: synthesis of boronated porphyrins. Strahlenther. Onkol. *165*, 130, **1989**.

7 Peymann, T.; Preusse, D.; Gabel, D. Synthesis of S-glycosides of mercaptoundecahydro-closo-dodecaborate(2-). Larson, B.; Crawford, J.; Weinreich, R. Advances in neutron capture therapy Vol II. Amsterdam: Elsevier; **1997**. pp. 35-37.

8 Gabel, D. Boron neutron capture therapy of tumors: Principles, problems and perspectives. Adv. Tech. Radiother. 85-115, **1992**.

9 Drechsel, K.; Lee, C.S.; Leung, E.W.; Kane, R.R.; Hawthorne, M.F. Synthesis of new building blocks for boron-rich oligomers in boron neutron capture therapy (BNCT). l. Tetrahedron Lett., *35*, 6217-6220, **1994**.

10 Kane, R.R.; Drechsel, K.; Hawthorne, M.F. Automated synthesis of carborane-derived homogeneous oligophosphates: Reagents for use in the immunoprotein-mediated boron neutron capture therapy (BNCT) of cancer. J. Am. Chem. Soc., *115*, 8853-8854, **1993**.

The Development of Boron Neutron Capture Agents Utilizing Positron Emission Tomography

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1 INTRODUCTION

Boron neutron capture therapy (BNCT) is a binary therapy which is dependent on the selective deposition of boron-10 in the tumor prior to irradiation by slow (thermal) neutrons.[1] The interaction of a boron-10 atom with a thermal neutron produces an α-particle and a high energy lithium-7 ion. The linear energy transfer (LET) of these heavy charged particles (^{4}He and ^{7}Li) has a range of approximately one cell diameter and thus they are lethal to the cells in which they are generated. To minimize damage to normal tissues, the quantity of boron in the tumor (≈30 mg ^{10}B/g of tumor) must exceed that in the surrounding normal tissues by a factor exceeding 3.[1,2] Various carrier molecules are being developed but *p*-boronophenylalanine, **1**, is the agent currently being used in clinical trials in the U.S. for the treatment of brain tumors and metastatic malignant melanoma in human patients.[3]

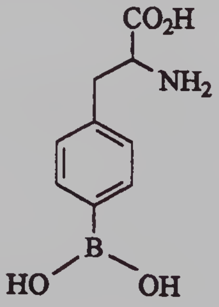

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Figure 1 *p-Boronophenylalanine, BPA*

One of the major difficulties facing successful BNCT is the paucity of in-vivo pharmacokinetics data. Standard analytical techniques are simply not applicable to the *in vivo* detection of boron. To solve this problem, PET [4] and MRI[5] procedures have been developed in our laboratories and the PET technique is now being used in BNCT treatment planning. In fact, a fluorine-18 analogue of BPA, **2**, has been used in eight patients at University of Tennessee Medical Center to study the pre- and post-BNCT status of cancer patients.[4] These patients underwent BNCT treatment of their brain tumors at Brookhaven National Laboratory and at the Massachusetts Institute of Technology (in collaboration with Harvard Medical School).

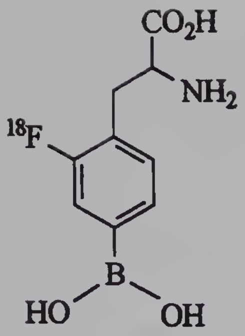

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Figure 2 *Fluorine-18 Labeled para-Boronophenylalanine.*

2 BACKGROUND

Our BNCT research has focused on radiolabeling BPA and on the creation of boron analogues of an unnatural cyclic α-amino acid, 1-aminocyclobutanecarboxylic acid (ACBC), as a carrier molecule, Figure 3. This unnatural amino acid is known to be preferentially retained in intracerebral tumors. In fact, carbon-11 labeled ACBC, **3**, is used for imaging brain tumors at the University of Tennessee Medical Center.[6] Recently, we reported the syntheses of a *m*-carboranyl containing ACBC derivatives which were lipophilic in nature.[7]

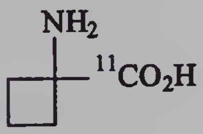

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Figure 3 *1-Aminocyclobutanecarboxylic acid*

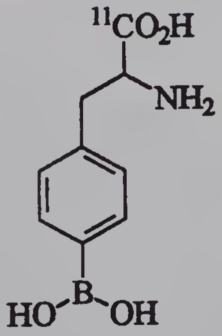

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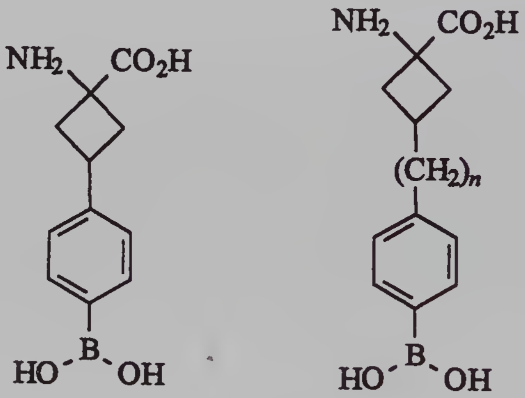
Figure 4 *Carbon-11 Labeled para-Boronophenylalanine*

3 RESULTS AND DISCUSSION

We now report the syntheses of the carbon-11 labeled BPA, **4**, as well as the preparation of a new series of boron-containing ACBC molecules **5** - **8**, Figure 5. The preparation of **4** was undertaken so that more accurate pharmacokinetics could be obtained for use in pre-treatment planning of patients who are scheduled to undergo BNCT. The novel boronated unnatural amino acids, **5** - **8**, contain a 4-boronophenyl moiety as the boron source and were prepared in the hope that they would supply boron to tumor sites more effectively than BPA. The syntheses of these molecules were undertaken because of the tumor selectivity we have observed for carbon-11 labeled ACBC, **3**. We postulated that these boronated ACBC derivatives would more effectively deposit boron into tumor tissues than BPA. We introduced varying numbers of carbon spacers (as methylene units) between the boronophenyl moiety and the ACBC group to introduce different degrees of lipophilicities into molecules. It is known that lipophilicity plays an important role in the transport of biologically active molecules.



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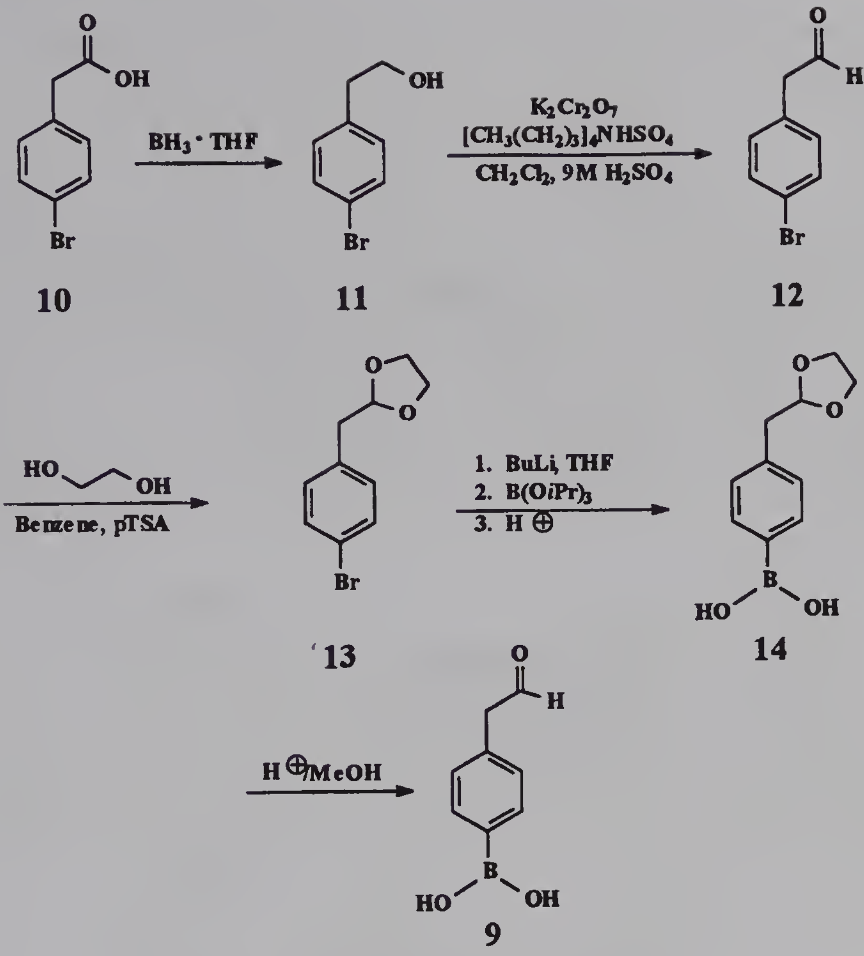
6, ***n*** = **2**
7, ***n*** = **3**
8, ***n*** = **7**

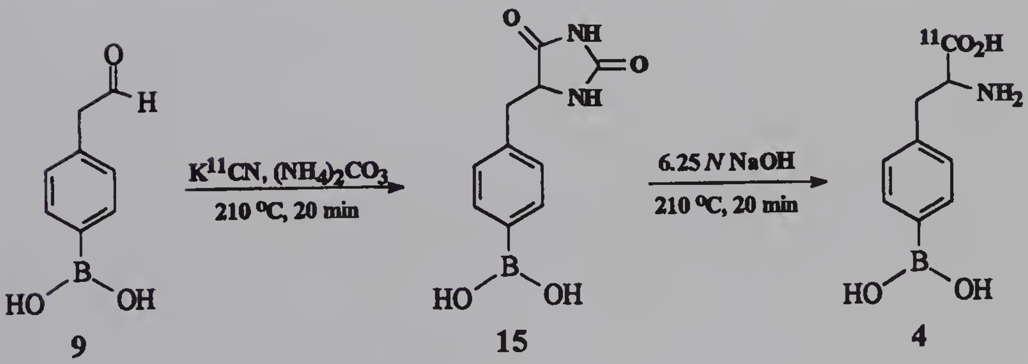
Figure 5 *p-Boronophenyl-Containing Amino Acids*

4 SYNTHESES

Carbon-11 labeled BPA, **4**, was synthesized from the corresponding aldehyde, 4-boronophenylacetaldehyde, **9**. This boronated aldehyde was prepared from commercially available 4-bromophenylacetic acid, **10**, in five synthetic steps (Scheme1). The synthesis was initiated by the borane reduction[8] of acid **10** to the 2-(4-boronophenyl)ethyl alcohol, **11**. Alcohol **11** was then carefully oxidized[9] to aldehyde **12**. In the next step, 4-bromophenylacetaldehyde ,**12**, was refluxed with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid to obtain the corresponding acetal **13**.[10] The boronic acid moiety was introduced at the *para* position of the phenyl ring by the reaction with butyllithium followed by triisopropyl borate[11] to obtain the 4-bronophenylacetaldehyde ethylene acetal, **14**. In the final step of the synthesis, acetal **14** was treated with concentrated hydrochloric acid in methanol as solvent to obtain the desired precursor, 4-boronophenylacetaldehyde, **9**, for the synthesis of carbon-11 labeled BPA, **4**, Scheme 2.

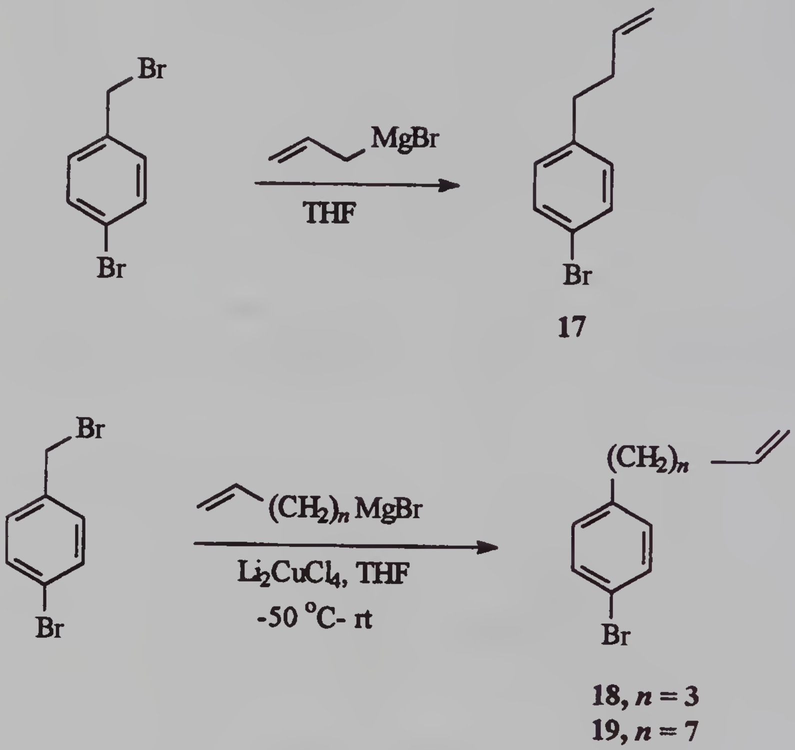


Scheme 1 *Synthesis of 4-Boronophenylacetaldehyde*



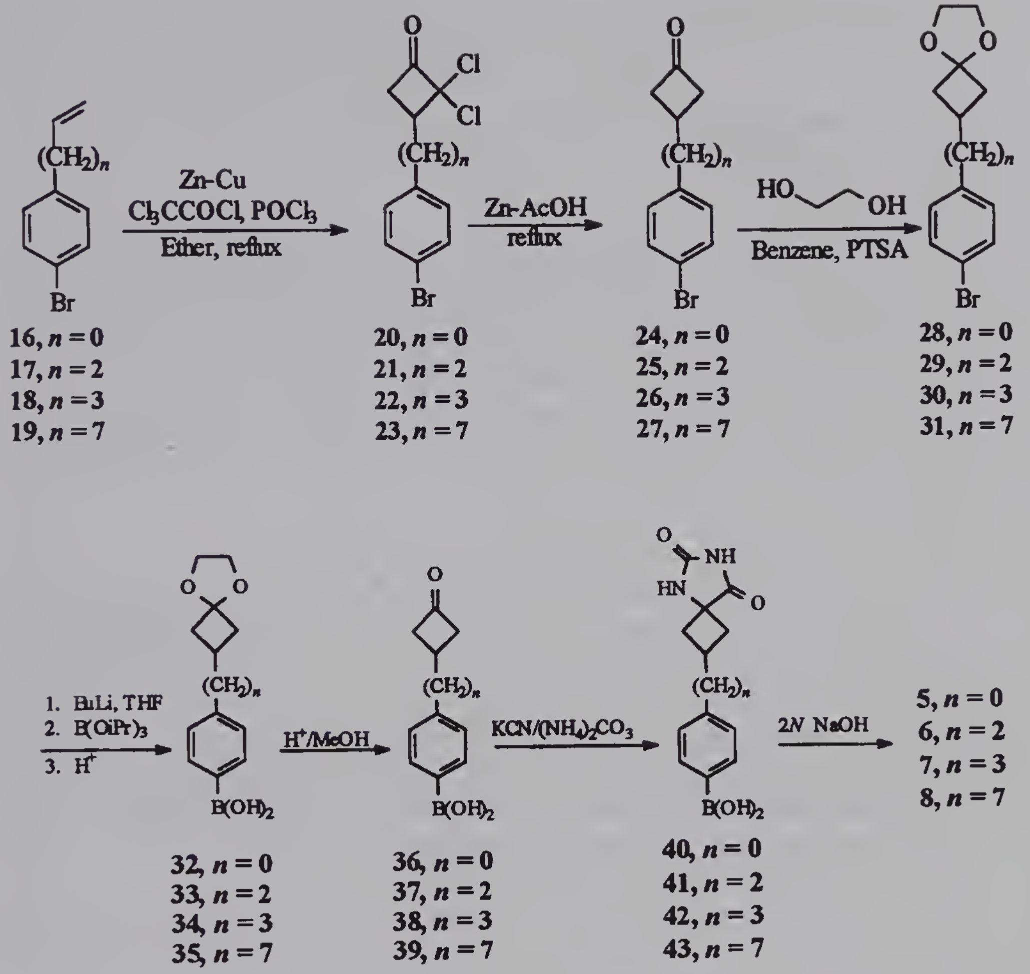
Scheme 2 *Synthesis of ^{11}C-4-Boronophenylalanine*

The key synthetic steps in the formation of the desired unnatural amino acids, **5** - **8**, involved the preparation of appropriately substituted cyclobutanones followed by a Bücherer-Strecker amino acid synthesis.[12] The syntheses of the boron-containing amino acids were initiated utlizing alkenes **16** -**19**. Alkene **17** was prepared by a S_N2 displacement of bromide from 4-bromobenzyl bromide (Scheme 3). In the syntheses of alkenes **18** and **19**, a catalytic amount of lithium tetrachlorocuprate was necessary for the successful production of the desired products.[13]



Scheme 3 *Synthesis of Alkenes*

(Alkene **16** is commerically available.) The cyclobutanones were then prepared (Scheme 4) via a 2 + 2 cycloaddition of the alkenes with dichloroketene[14] which was generated *in-situ* via the reaction of trichloroacetyl chloride and phosphorous oxychloride in the presence of a Zn-Cu couple. The individual ketones (dichlorocyclobutanones **20** - **23**) from the ketene addition were subjected to a reductive dechlorination using zinc and acetic acid. The resultant *p*-bromophenyl-substituted cyclobutanones **24** -**27** were then protected as ethylene ketals, **28** - **31**, by reaction with ethylene glycol (Scheme 4).[10] The ethylene ketals were then reacted with butyllithium followed by triisopropyl borate,[11] the reactions were quenched with dilute sulfuric acid to obtain the ethylene ketal boronic acids, **32** - **35**. The ketal groups were eventually removed by dilute hydrochloric acid in methanol to regenerate the ketone fuctionality in compounds **36** - **39**. The resultant ketones were allowed to react with ammonium carbonate and potassium cyanide in a pressure tube. The hydantoins **40** - **43** were formed in excellent yields. In the final step of the syntheses, the hydantoins were heated in the presence of sodium hydroxide to generate the desired amino acids **5** - **8** in good yields.



Scheme 4 *Synthesis of Boronated ACBC Derivatives*

5 CONCLUSION

We report the synthesis of carbon-11 labeled BPA for use in pre-treatment planning for BNCT. We also synthesized novel boronic acid-containing analogues of a tumor seeking, unnatural, cyclic α-amino acid, 1-aminocyclobutanecarboxylic acid. Boronic acid-containing analogues of ACBC with varying degree of lipophilicities were synthesized and the agents are being evaluated as potential BNCT agents.

6 ACKNOWLEDGEMENT

This research was supported by the US Department of Energy and the Robert H. Cole Foundation.

7 REFERENCES

1. R. F. Barth, A. H. Soloway, and R. M. Brugger, *Cancer Investigation* 1996, 14, No. 6, 534.
2. (a) R. G. Fairchild and V. P. Bond *Int. J. Radiat. Oncol. Biol. Phys.* 1985, 11, 831. (b) R. G. Zamenhof, A. M. Kalend and W. D. Bloomer *J. Natl. Cancer Inst.* 1992, 84, 1290.
3. (a) H. Hatanaka and Y. Nakagawa *Int. J. Radiat. Oncol. Biol. Phys.* 1994, 28, No. 5, 1061. (b) J. Coderre, P. Rubin, A. Freedman, J. Hansen, T. S. Wooding, D. D. Joel, D. V. M. and D. Gash, D. *Int. J. Rad. Onco. Biol. Phys.* 1994, 28, No. 5, 1067.
4. G. W. Kabalka, G. T. Smith, W. S. Reid, C. P. D. Longford, T. G Roberts, N. K. Reddy, E. Buonocore and K. F. Hubner *J. Nucl. Med.* 1997, 38, 1762.
5. G. W. Kabalka, C. Tang and P. Bendel *J. Neuro-Oncology* 1997, 33, 153.
6. (a) L. C. Washburn, T. T. Sun, B. L. Byrd, R. L. Hayes and T. A. Butler *J. Nucl. Med.* 1980, *20*, No. 10, 1055. (b) K. F. Hubner, G. T. Smith, J. A. Thie and E. Buonocore *J. Nucl. Med.* 1992, *33*(5), Suppl. 922.
7. (a) R. R. Srivastava, R. R. Singhous and G. W. Kabalka *J. Org. Chem.* 1997, *62*, 4476. (b) R. R. Srivastava and G. W. Kabalka *J. Org. Chem.* 1997, *62*, 8730. (c) G. W. Kabalka, R. R. Srivastava and G. Li Presented at the Eight International Symposium on Neutron Capture Therapy for Cancer, 13-18 September, La Jolla, California.
8. H. C. Brown, P. Heim and N. M. Yoon *J. Am. Chem. Soc.* 1979, *92*, 1637.
9. D. Pletcher and S.J.D. Tait *Tetrahedron Lett.* 1978, *18*, 1602.
10. M. T. Crimmins and J. A. Deloaza, *J. Am. Chem. Soc.* 1986, 108, 800.
11. H. C. Brown and T. E. Cole *Organometallics* 1983, 2, 1316.
12. H. R. Henz and R. J. Speer *J. Org. Chem.* 1942, 64, 522.
13. G. A. Tolstikov, V. N. Odinokov, R. I. Galeeva and R. S. Bakeeva *Tet. Lett.* 1978, *1*, 1857.
14. L. R. Krepski, A. Hassner *J. Org. Chem.* 1978, *43*, 2879.

Synthesis and Evaluation of DNA Tumor Targeting Agents for Neutron Capture Therapy

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1 INTRODUCTION

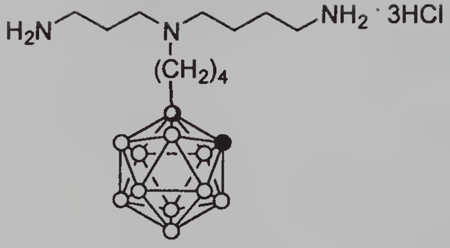
Developing non-radioactive compounds with the capacity for selectively targeting tumor cells offers the potential for discretely destroying such cells without compromising the viability of adjacent normal cells. This form of targeted radiotherapy (BNCT) is based on the fission reaction that generates high linear energy transfer (LET) particles that are confined to a radius of 5-9 μm, comparable to the dimensions of a single cell.[1]

$$
{}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow [{}^{11}_{5}\mathrm{B}] \begin{cases} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{7}_{3}\mathrm{Li} + 2.79\ \mathrm{MeV}\ (6\%) \\ \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{7}_{3}\mathrm{Li} + \gamma\, 0.48\ \mathrm{MeV} + 2.31\ \mathrm{MeV}\ (94\%) \end{cases}
$$

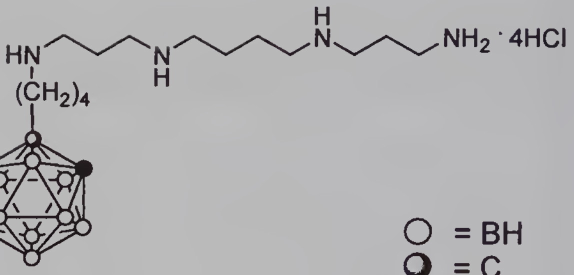
The ideal subcellular organelle for targeting is the tumor cell's nucleus by reason of its involvement in cellular replication. Among the chemical entities being developed are those with the potential for becoming incorporated into or binding to the tumor cell's DNA since such a locus would enhance the destructive activity of the capture reaction by a factor of 2-5[2,3] over what would be observed if the compounds were evenly distributed within the cell's cytoplasm. Among the boron compounds being developed are nucleic acid precursors,[1] alkylating agents,[2] intercalators,[3] groove binders,[4] polyamines,[5] and antisense agents.[6] Our own major focus has been on polyamines[4,5] and nucleosides.[6,7,8]

2 POLYAMINES

The polyamines were chosen since the native compounds, putrescine, spermidine and spermine, bind electrostatically to DNA, are essential both for cellular growth and differentiation, and their depletion inhibits the growth of tumors. Representative compounds that were initially synthesized are the o-carboranyl substituted analogs, SPD-5 and SPM-1, shown below:



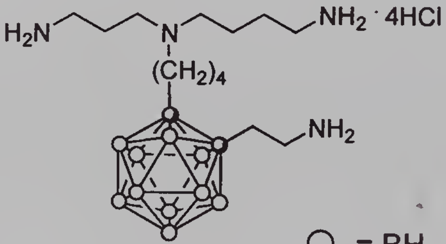
SPD-5



SPM-1

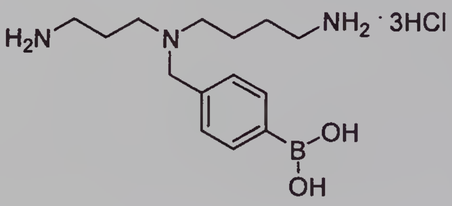
○ = BH
◑ = C
● = CH

Though such structures, using the polyamine scaffold to target malignant cells *in vitro*, appeared to have potential where the polyamine transport system was upregulated, the cellular and *in vivo* toxicity of these and related compounds precluded their consideration as BNCT agents. The development of less toxic boronated polyamines became an important objective if this class of DNA targeting agents were to have any clinical potential in BNCT. Two representative boronated polyamines with significantly lowered *in vitro* and *in vivo* toxicity are ASPD-5 and BBSPD-5 shown below:



ASPD-5

○ = BH
◑ = C



BBSPD-5

The latter was extremely nontoxic and, under *in vitro* conditions, both of these compounds were sequestered by tumor cells at a level comparable to the clinically-useful BSH and BPA but at a media concentration that is 10-100 fold less. Nevertheless, in biodistribution studies with tumor-bearing animals placed on a polyamine-deficient diet and simultaneously given an inhibitor of ornithine decarboxylase, conditions designed to maximize tumor uptake, the cellular concentrations obtained in tumor was one to two orders of magnitude lower than those observed for liver, spleen and kidney. In the case of BBSPD-5, tumor concentrations were not even measurable.[5]

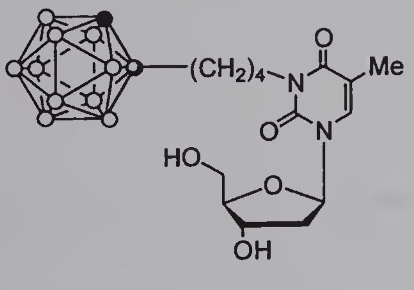
The apparent conclusion is as a "stand alone" agent these boronated polyamines are not useful (however, ASPD-5 in combination with other BNCT agents maybe useful). The obvious question is why are these boronated polyamines not useful and could such pitfalls be avoided in the design of future agents for BNCT?

In retrospect, before embarking upon the elaborate synthetic schemes that we undertook, it would have been highly desirable to have carried out biodistribution studies in tumor-bearing animals with spermidine and spermine, containing a measurable label and at a dosage necessary for any clinically-useful BNCT compound. If such naturally-occurring substrates, using polyamine inhibitors, do not achieve the needed levels in tumor, then it would be highly unlikely that any boronated analog would as well. In essence, if one is trying to use a boron analog to mimic the action of a naturally-occurring compound, it is very pertinent to use such a substrate, not in tracer amounts but at a dosage comparable to what a BNCT agent would be used clinically. In this way, one would be able to determine the desirability of embarking upon an extensive synthetic undertaking. This is a lesson that we have now learned but it is certainly applicable to other boron-containing analogs of other naturally-occurring biochemicals.

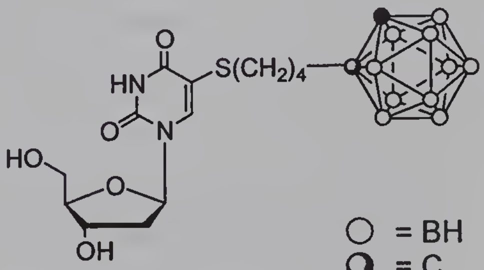
3 NUCLEOSIDES

Nucleoside kinases play a very important role in the use of nucleosides for cancer and antiviral therapy and they may be equally important targets for BNCT. Boronated derivatives of thymidine may enter malignant and benign cells via facilitated transport or passive diffusion. The key step for their intracellular entrapment is the phosphorylation by cytosolic thymidine kinase (TK1), a deoxynucleoside kinase of the salvage pathways, to the corresponding 5'-monophosphate. Cellular efflux of the latter structure should be retarded due the negatively charged phosphate group. This would occur primarily in proliferating tumor cells in which TK1 has elevated activity levels compared with quiescent cells. Further conversion of the monophosphate to the di- and triphosphate and the subsequent incorporation into tumor cell DNA could result in the relocation of boron in close proximity to DNA, the most critical target of the neutron capture reaction.

Thus, the minimum biochemical proviso for a selective tumor uptake of boronated thymidine analogs is that they are good substrates for TK1. It is very important to obtain information about the TK1 substrate characteristics of boronated thymidine analogs before embarking on time consuming and expensive *in vitro* and *in vivo* studies with such structures. Phosphoryl transfer assays with recombinant enzymes might provide an inexpensive and easy test system to accomplish such an objective. A second thymidine kinase of the salvage pathways, mitochondrial thymidine kinase (TK2), is predominantly localized in mitochondria and seems to be equally active in proliferating and non-proliferating cells, thus providing no basis for selective uptake of boronated thymidine analogs in tumor cells. The substrate specificities of TK1 and TK2 differ significantly and it is therefore important to obtain information about the substrate characteristics of boronated thymidine analogs for TK2 as well.



N-4



S-4

○ = BH
◐ = C
● = CH

Until now, we have carried out phosphoryl transfer assays with 24 carboranyl thymidine analogs using recombinant TK1 and TK2. Various carborane-containing substituents were attached either to the N-3- or the C-5 position of the nucleoside scaffold. Most of the tested N-3 substituted carboranyl structures proved to be good substrates for TK1 while they were not or very poorly phosphorylated by TK2. For example, the phosphorylation velocity observed for **N-4** with TK1 was 28% that of thymidine. None of the tested C-5 substituted carboranyl thymidine analogs were phosphorylated by TK1 and in only 50% of all compounds low to medium phosphorylation rates were shown with TK2. Of all tested compounds, **S-4** appeared to be best substrate for TK2 with a phophorylation rate of approximately 2% of that of thymidine.

The phosphoryl transfer assays conducted in our laboratories indicate that C-5 substituted carboranyl thymidine analogs are not phosphorylated by TK1, which, based on currently available information, may be the critical target enzyme for a clinical use of boronated thymidine analogs in BNCT rather than TK2. To the best of our knowledge, results from previous *in vitro* and *in vivo* evaluations did not permit this conclusion. Furthermore, the TK1 phosphoryl transfer test system was very sensitive to minor modifications in the structures of the N-3 substituted carboranyl thymidine analogs which makes it the ideal method for structure optimization. In summary, TK1 and TK2 phosphoryl transfer assays proved to highly effective and inexpensive high-capacity screening systems for a rational design of boronated nucleosides. More traditional *in vitro* and *in vivo* evaluation methods used in BNCT research cannot provide a comparable efficacy and it appears to be desirable to develop and apply more biological screening systems that operate on the level of the most fundamental biochemical mechanisms for a selective uptake of BNCT agents into tumor cells.

Acknowledgement

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References

1. Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Rolf F. Barth; Wyzlic, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 1515-1562.
2. Gabel, D.; Foster, F.; Fairchild, R. G. *Radiat. Res.* **1987**, *111*, 14-25.
3. Kobayashi, T.; Kanda, K. *Radiat. Res.* **1982**, *91*, 77-94.
4. Cai, J.; Soloway, A. H.; Barth, R. F.; Adams, D. M.; Hariharan, J. R.; Wyzlic, I. M.; Radcliffe, K. *J. Med. Chem.* **1997**, *40*, 3887-3896.
5. Zhuo, J.-C.; Cai, J.; Soloway, A. H.; Barth, R. F.; Adams, D. M.; Ji, W.; Tjarks, W. *J. Med. Chem.* **1999**, *42*, 1282-1292.
6. Rong, F.-G.; Soloway, A. H.; Ikeda, S.; Ives, D. H. *Nucleosides Nucleotides* **1997**, *16*, 379-401.
7. Soloway, A. H.; Zhuo, J.-C.; Rong, F.-G.; Lunato, A. J.; Ives, D. H.; Barth, R. F.; Anisuzzaman, A. K. M.; Barth, C. D.; Barnum, B. A. *J. Organomet. Chem.* **1999**, *581*, 150-155.
8. Lunato, A. J.; Wang, J.; Woollard, J. E.; Anisuzzaman, A. K. M.; Ji, W.; Rong, F.-G.; Ikeda, S.; Soloway, A. H.; Eriksson, E.; Ives, D. H.; Blue, T. E.; Tjarks, W. *J. Med. Chem.* **1999**, in press.

Stabilised Liposomes with Double Targeting for Use in BNCT

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INTRODUCTION

Liposomes are hollow fat particles composed of a closed lipid bilayer. Due to their unique structure, allowing transport of both water-soluble and fat-soluble compounds, and the fact that they may be easily prepared from completely biocompatible materials, liposomes have come into widespread use as vehicles for drug delivery.

By encapsulation of the drug in liposomes a favourable alteration of the pharmacokinetics, as well as a lowered toxicity, may be obtained. Even more important is the fact that liposomes collect spontaneously in areas of inflammation and in tumour tissue. This property, which is believed to be due to the inherently leaky vasculature in these areas, has led to the development of several liposomal anti-inflammatory and anticancer agents.

Liposomes have been suggested as promising candidates for the transport of boron-rich compounds in BNCT[1-7], and encouraging results have been reported for the liposomal delivery of both hydrophilic and lipophilic compounds to tumours. [1-7]

However, the degree of accumulation of liposomes in tumour tissue depends on their blood circulation time. In order to maximise the accumulation of liposomes, and thus boron, in the tumour, liposomes with long survival time in systemic circulation, should be employed. The liposomal circulation time may be dramatically increased by attachment of long flexible polyethylene glycol (PEG) chains to a proportion of the lipids in the liposomal membrane. Such sterically stabilised liposomes have been shown to circulate for several days, up to a week, without detection by the immune system.

For successful treatment of cancer by BNCT, it is, however, not enough that the liposomes collect in tumour tissue. For best effect the liposomes should specifically bind to, and be internalised by, the tumour cells. In addition, it is important that the boron-containing compound, after its release from the internalised liposome, is retained within the cell and preferably localises within the cell nucleus.

In order to fulfil the above requirements we have developed a concept that comprises sterically stabilised liposomes with double targeting (SLT-particles).[8] Specific targeting is achieved by providing the sterically stabilised liposomes with ligands directed towards receptors that are overexpressed on the surface of the tumour cells. Furthermore, by choosing ligands that are directed towards receptors that mediate endocytosis, internalisation of the liposomes and their cargo may be realised. The second step in the targeting process, the localisation of the boron-rich compounds in the cell nucleus, is accomplished by using compounds, recently developed by us, where the boron containing moiety is linked to a DNA interacting, or intercalating, species. The same concept is also applied for specific delivery of radionuclides such as ^{211}At, ^{125}I and ^{131}I bound to DNA intercalating or interacting compounds.

We have given the name nuclisomes to SLT particles which are loaded with DNA interacting compounds labelled with radionuclides or nuclides that become activated upon neutron irradiation. A schematic drawing of a boron containing nuclisome is given in Figure 1.

By employing nuclisomes we hope to achieve not only a modality for specific delivery of large amounts of boron-10 to the nucleus of cells in solid tumours, but also to provide a method for the treatment of spread cells.

In this paper we report some of our work with stabilized liposomes containing boronated DNA intercalating compounds.

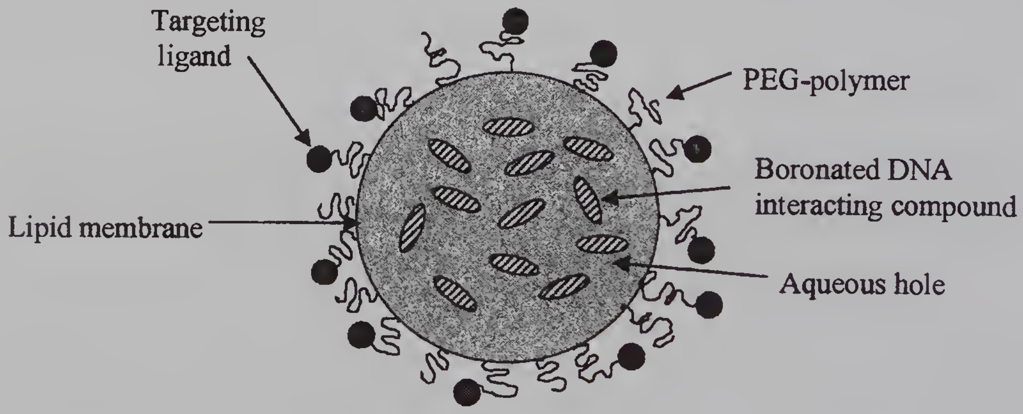

Figure 1 Schematic drawing of a nuclisome.

RESULT AND DISCUSSIONS

We have earlier reported details of the synthesis of a number of DNA intercalating compounds containing boron clusters.[9-13] Three of these boronated compounds (Figure 2) are specially promising for use in nuclisomes, namely the acridine derivative **1** (**WSA-1**; water soluble acridine 1)[11], the phenantridine derivative **2** (**WSP-1**) [10], and the naphtalimide derivative **3** (**WSN-1**)[12]. All three compounds contain chromophores that are known to intercalate with DNA, namely the acridine, the phenantridinium (also found in the well known DNA staining compound ethidium bromide; see Figure 2) and the nitronaftalimide chromophore for **WSA-1**, **WSP-1** and **WSN-1**, respectively. **WSA-1** and **WSN-1** also contain a spermidine residue, which fulfil the double purpose of increasing the water solubility of the compounds as well as enhancing the DNA binding properties. The aminopropyl residue in **WSP-1** is attached in order to increase the water solubility. The amino functions in **1-3** allow active looding of the drugs into the liposomes (see below).

The compounds **1-3** all intercalate with DNA as supported by the enhancement of the fluorescence intensity of the compounds on addition of DNA. This phenomenon is illustrated in Figure 3 for **WSP-1**[14]. The experimental method used for the measurements is described elsewhere.[15-16]

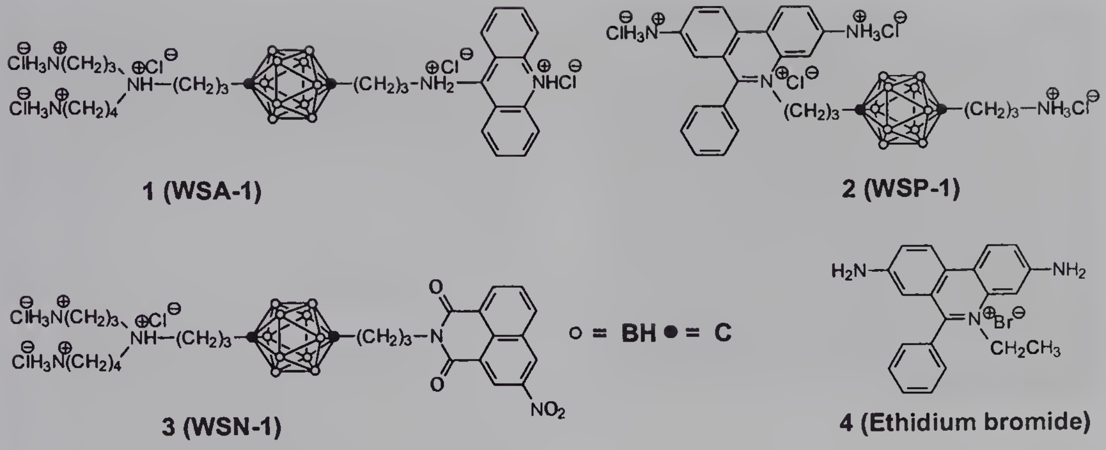

Figure 2 *The three boronated DNA intercalators* ***WSA-1, WSP-1, WSN-1*** *and the DNA staining compound ethidium bromide.*

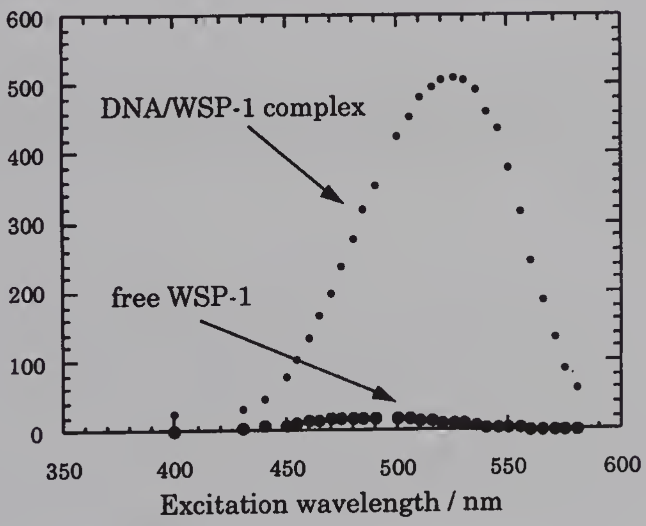

Figure 3 *Fluorescence scan of WSP1 with and without added DNA at the emission wavelength of 600 nm.*

Sterically stabiliszed liposomes were prepared from cholesterol **(Cho)**, the phospholipid 1,2-distearoyl-sn-glycero-3-phosphatidylcholine **(DSPC)**, and the PEG-lipid 1,2-distearoyl-sn-glycero-3-phosphatidylethanolamine-*N*-[poly(ethylen glycol)-2000] **(DSPE-PEG)**. The composition of these components were **DSPC:Cho:DSPE-PEG** 55:40:5 (mol%). The boronated compounds **1-3** were actively encapsulated with high drug/lipid ratios [up to 0.50:1 (mol:mol)] using a transmembrane pH gradients[7,14] and trapping efficiences ≥ 90% were obtained. The high concentration of the drugs within the liposomes resulted in drug precipitation as illustrated in Figure 4a for **WSP-1**.

The *in vitro* stability of the liposomes loaded with **1** and **2** were studied both in buffer and in 25% human serum.[7,14] The stability was excellent as examplified in Figure 4b by the leakage of **WSP-1** and for comparison ethidium from actively loaded liposomes.

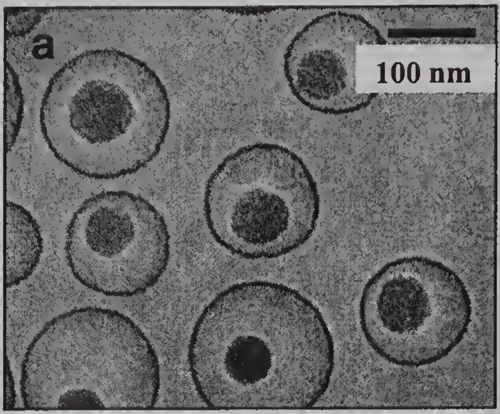

Figure 4a Cryo-electron micrograph of stabilized **DSPC/Cho/DSPE-PEG** (55/40/5) liposomes loaded with **WSP-1**. The dark spot inside each liposome is precipitated **WSP-1**.

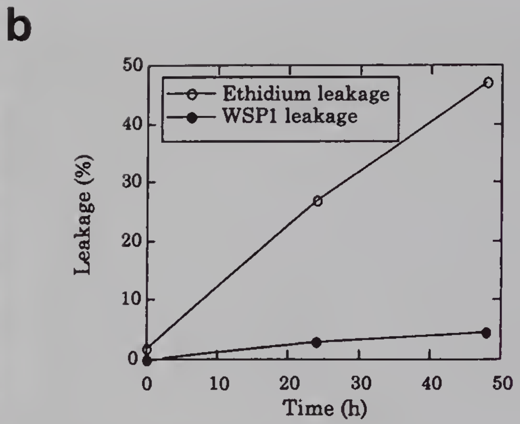

Figure 4b Leakage of **WSP-1** and ethidium from **DSPC/Cho/DSPE-PEG** (55/40/5) liposomes in Hepes buffert (20 mM Hepes, 150 mM NaCl, pH 7.4).

ACKNOWLEDGEMENT

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REFERENCES

1. K. Shelly, M.F. Hawthorne, and P.G. Schmidt, 1991, Proceeding of the 4th International Symposium on Neutron Capture Therapy for Cancer.
2. H. Yanagié, T. Tomita, H. Kobayashi, Y. Fujii, T. Takahashi, K. Hasumi, H. NariuChi, H., and M. Sekiguchi, *Br. J. Cancer* 1991, .**63**, 522.
3. K. Shelly, D.A. Feakes,M.F. Hawthorne, P.G. Schmidt, T.A. Krisch, W.F. Bauer, *Proc. Natl. Acad. Sci. USA*, 1992, **89**, 9030.
4. D.A. Feakes, K. Shelly, C.B. Knobler, and M.F. Hawthorne, *Proc. Natl. Acad. Sci. USA*, 1994, **91**, 3029.
5. S.C. Mehta, J.C.K. Lai, and D.R. Lu, *J Microencapsulation* 1996, **13**, 269.
6. M.F. Hawthorne, and K. Shelly, *J Neuro-Oncology* 1997, **33**, 53.
7. M. Johnsson, N. Bergstrand, and K. Edwards, *J. Liposome Res.* 1999, **9**, 53.
8. E. Bohl, J. Carlsson, K. Edwards, S. Sjöberg, and L. Gedda, "SLT-particles for two-step targeting in boron neutron capture therapy". Proceedings from the Eight International Symposium on Neutron Capture Thearpy. In press 1999.
9. W. Tjarks, H. Ghaneolhosseini, C. Henssen, J. Malmquist, and S. Sjöberg, *Tetrahedron Lett.* 1996, **37**, 6905.
10. H. Ghaneolhosseini, W. Tjarks, and S. Sjöberg, *Tetrahedron* 1997, **53**, 17519.
11. H. Ghaneolhosseini, W. Tjarks, S. Sjöberg, *Tetrahedron* 1998, **54**, 3877.
12. H. Ghaneolhosseini, and S. Sjöberg, *Acta Chem Scand.* 1998, **53**, 298.
13. L. Gedda, M. Silvander, S. Sjöberg, W. Tjarks, and J. Carlsson, *Anticancer Drug Design* 1997, **12**, 671.
14. M. Silvander, M. Johnsson, and K. Edwards. Unpublished observations.
15. M. Silvander, and K. Edwards, *Anal. Biochem.* 1996, **22**, 40.
16 M. Silvander, M. Johnsson, and K. Edwards, *Chem. Phys. Lipids* 1998, **97**, 15.

Synthesis of *O*-Bonded Derivatives of *closo*-Dodecaborate Anion. $[B_{12}]$–$[C_2B_{10}]$ Double Cage Boron Compounds – A New Approach to Synthesis of BNCT Agents

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Introduction

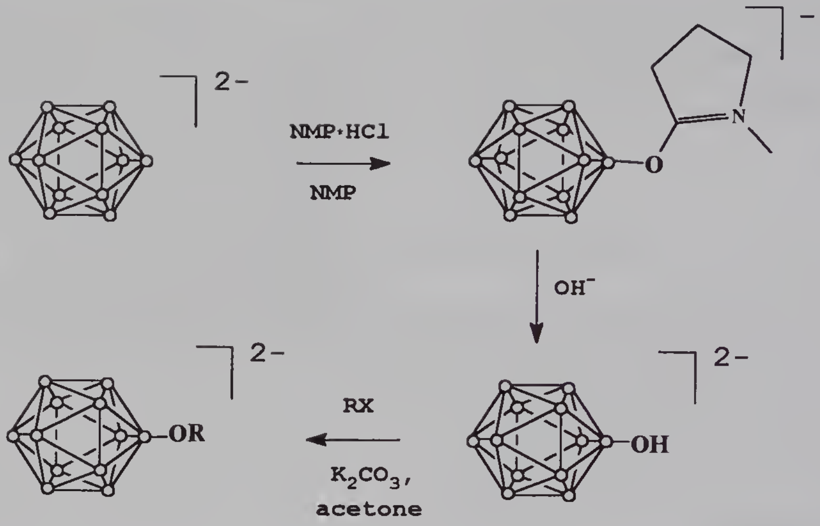
The increased current interest in chemistry of the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ is caused by the intense development of boron neutron capture therapy. The main features of the *closo*-dodecaborate anion are high, close to spherical, symmetry that produces lack of a clearly defined reaction center and high reactivity in respect to electrophiles which often results in mixtures of polysubstituted products. The traditional approach to the $[B_{12}H_{12}]^{2-}$ anion functionalization consists in an introduction of a primary substituent (reactive center) such as amino[1-3], mercapto[4-6], or hydroxy[7,8] group or iodine atom[9] into the boron cage followed by a reaction at this center to attach a side chain containing functional group. Besides, a few examples of direct attachment of different organic particles to the *closo*-dodecaborate cage are known[10-13], however their use for synthesis of BNCT agents seems to be problematic .

Here we describe two different approaches to the synthesis of *O*-bonded functional derivatives of the *closo*-dodecaborate anion as well as the synthesis of the first $[B_{12}]$-$[C_2B_{10}]$ double-cage boron compounds.

Results and Discussion

Alkylation of the $[B_{12}H_{11}OH]^{2-}$ Anion. The first approach to the synthesis of *O*-bonded functional derivatives of the *closo*-dodecaborate anion consists in the introduction of hydroxy group in the boron cage followed by alkylation of the hydroxy derivative obtained. This approach was first proposed by Gabel, however strong basic conditions used (5-fold excess of KOH in dimethylsulfoxide in combination with heating at 60°C during the work-up stage) limit synthetic utility of this method[7]. This prompted us to study milder conditions to alkylate $[B_{12}H_{11}OH]^{2-}$.

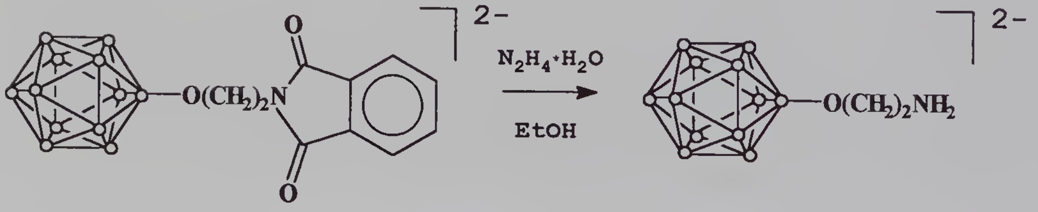
We found that heating of $(Bu_4N)_2[B_{12}H_{11}OH]$ with an equimolar amount of the appropriate alkylating agent in acetone at 40-45°C in the presence of potassium carbonate results in the corresponding alkoxy derivatives in moderate to high yields. Compounds containing allylic-, nitro-, cyano-, and protected amino functions were prepared[14] (Scheme1). The derivative with free amino function was obtained by removing the phthalimide protective group with hydrazine hydrate in refluxing ethanol (Scheme 2).



X = Br, I

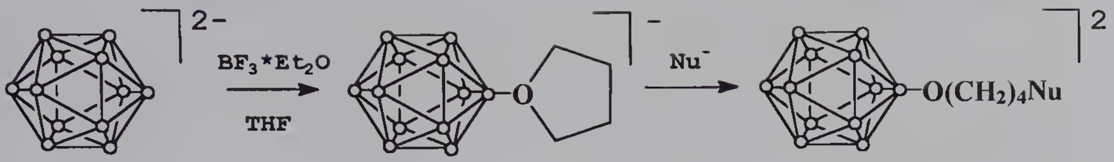
R = C_2H_5, $CH(CH_3)_2$, $(CH_2)_{15}CH_3$, $CH_2CH{=}CH_2$,
$CH_2C_6H_5$, p-$CH_2C_6H_4CN$, p-$CH_2C_6H_4NO_2$,
p-$CH_2CH_2C_6H_4NO_2$, $CH_2CH_2N(CO)_2C_6H_4$

Scheme 1



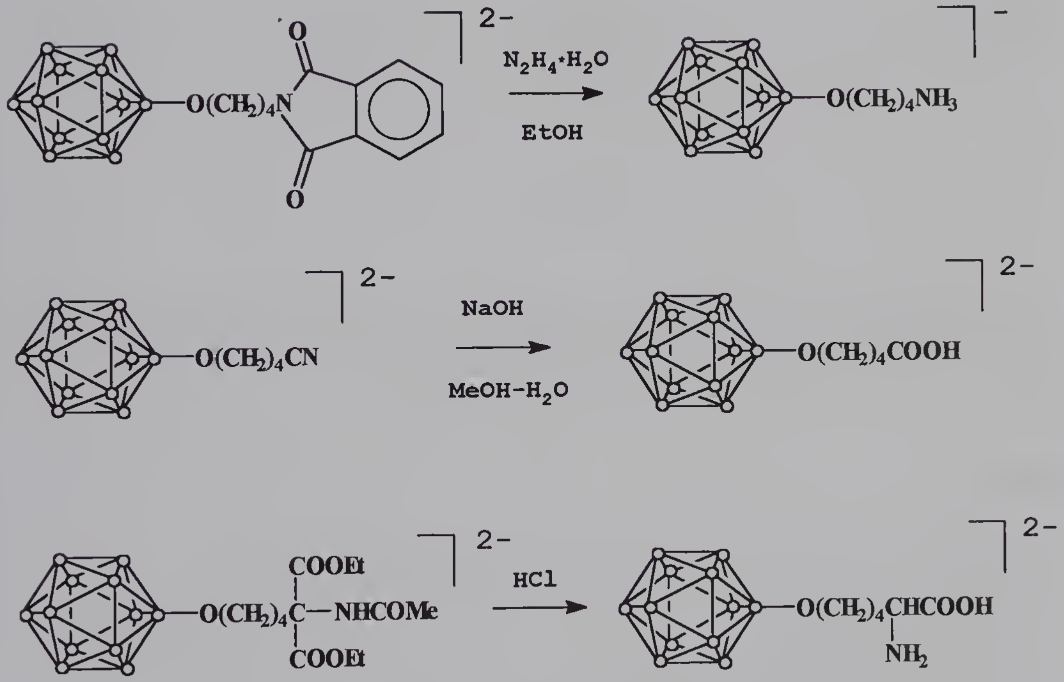
Scheme 2

Nucleophilic Ring-Opening in $[B_{12}H_{11}O(CH_2)_4]^-$. The second approach to the synthesis of *O*-bonded functional derivatives of the *closo*-dodecaborate anion consists in initial addition of organic substituent – tetrahydrofuran molecule - to the boron cage followed by its transformation into various derivatives under nucleophilic attack. Sodium methoxide, sodium hydroxide, potassium phthalimide, sodium cyanide (carboxylic group anion equivalent), 2-lithio-1,3-dithiane (aldehyde group anion equivalent), and sodium diethyl acetamidomalonate (glycine anion equivalent) were used as nucleophiles. The corresponding *closo*-dodecaborate derivatives were produced in high yield (Scheme 3). Using functional group interconversion reactions the corresponding amine, acid, and amino acid were prepared[15] (Scheme 4). The important advantage of this approach is the possibility to apply various types of nucleophilic reagents widely used in organic chemistry to synthesis of *closo*-dodecaborate derivatives.



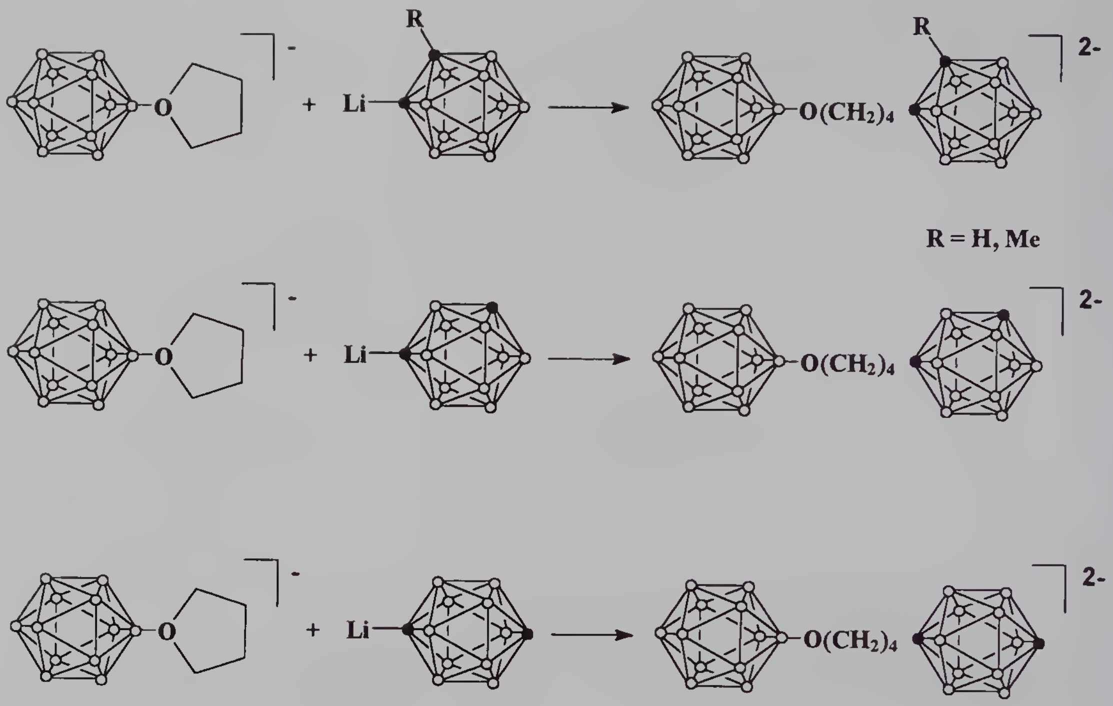
Nu = OH
$N(CO)_2C_6H_4$
CN
$CHS_2(CH_2)_3$
$CNHCOMe(COOEt)_2$

Scheme 3



Scheme 4

$[B_{12}]$-$[C_2B_{10}]$ Double Cage Boron Compounds. The ring-opening reaction in the tetramethylene oxonium derivative was used to prepare the first $[B_{12}]$-$[C_2B_{10}]$ double-cage boron compounds. In these compounds the *closo*-dodecaborate acts as hydrophilic substituent providing for water-solubility of the molecule, whereas the carborane cage can be used for attachment to biomolecules using earlier developed methods. Using this approach at least double boron contents in biomolecule can be obtained.



Scheme 5

Acknowledgments: The authors thank the Royal Swedish Academy of Sciences (1320), the Swedish Cancer Society (4092-B98-01XAA), and the Russian Foundation for Basic Researches (99-03-33073) for financial support.

References

1. T. Peymann, E. Lork, M. Schmidt, H. Nöth, D. Gabel, *Chem. Ber.*, 1997, **130**, 795.
2. B. Grüner, B. Bonnetot, H. Mongeot, *Collect. Czech. Chem. Soc.*, 1997, **62**, 1185.
3. I. B. Sivaev, A. B. Bruskin, V. V. Nesterov, M. Yu. Antipin, V. I. Bregadze, S. Sjöberg, *Inorg. Chem.*, 1999, accepted.
4. K. Nagasawa, M. Narisada, *Tetrahedron Lett.*, 1990, **31**, 4029.
5. D. Gabel, D. Moller, S. Harfst, J. Röesler, H. Ketz, *Inorg. Chem.*, 1993, **32**, 2276.
6. D. H. Swenson, B. H.Laster, R. L. Metzger, *J. Med. Chem.*, 1996, **35**, 1540.
7. T. Peymann, E. Lork, D. Gabel, *Inorg. Chem.*, 1996, **35**, 1355.
8. A. A. Semioshkin, P. V. Petrovskii, I. B. Sivaev, E. G. Balandina, V. I. Bregadze, *Russ. Chem. Bull.*, 1996, **45**, 683.
9. T. Peymann, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.*, 1998, **37**, 1544.
10. W. Preetz, R.Bismark, *J. Organomet. Chem.*, 1991, **441**, 25.
11. T. Koch, W. Preetz, *Z. Naturforsch.*, 1997, **52B**, 939.
12. U. Krause, W. Preetz, *Z. anorg. allg. Chem.*, 1995, **621**, 516.
13. A. A. Semioshkin, P. V. Petrovskii, D. Gabel, B. Brellochs, V. I. Bregadze, *Russ. Chem. Bull.*, 1998, **47**, 950.
14. I. B. Sivaev, S. Sjöberg , V. I. Bregadze, D.Gabel, *Tetrahedron Lett.*, 1999, **40**, 3451.
15. I. B. Sivaev, A. A. Semioshkin, B. Brellochs, S. Sjöberg, V. I. Bregadze, 1999, unpublished results.

A New Medicinal Application of Boron Clusters. Potent Nuclear Receptor Ligands Bearing Carborane as a Hydrophobic Pharmacophore

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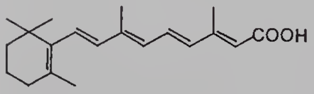
Introduction

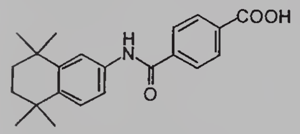
The icosahedral carboranes (dicarba-*closo*-dodecaboranes) exhibit remarkable thermal stability, are resistant to attack by most types of reagent, and are generally biologically inactive. Their icosahedral geometry and the delocalization of 26 skeletal electrons account for these unusual properties, which make such compounds uniquely suitable for several specialized applications, including some in the field of materials science. In the medicinal field, incorporation of large numbers of boron atoms into tumor cells for boron neutron capture therapy (BNCT) has attracted much interest in recent years.[1] Since the early application of carboranes for BNCT, various compounds have been synthesized by adding carborane units to nucleic acids, amino acids, porphyrins, DNA binders, etc. In contrast, little attention has been paid to the possible use of carboranes as components of biologically active molecules. From the standpoint of receptor-ligand complexation, the exceptionally hydrophobic character and spherical geometry of carboranes may allow their use as a hydrophobic pharmacophore in biologically active molecules. We have been engaged in the design and synthesis of new nuclear receptor ligands and have recognized the importance of hydrophobic interaction in receptor-ligand complexation. Differences of binding constants between a ligand having a suitable hydrophobic group and a ligand without such a group sometimes reach 100~1000 times. Here we describe the state of the art in the design, synthesis and biological evaluation of potent nuclear receptor ligands, focusing on retinoid and estrogen receptor ligands containing a carborane cage as a hydrophobic pharmacophore.

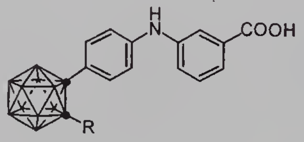
1 Application of Boron Clusters as a Hydrophobic Pharmacophore for Retinoids

Retinoids are of particular interest as chemopreventive and therapeutic agents in the fields of dermatology and oncology. Retinoids are able to induce differentiation of a wide spectrum of cell types, such as embryonal carcinoma cells, and promyelocytic leukemia cells.[2] The mechanism of these effects involves modulation of specific gene transcription through binding of retinoic acid to the retinoic acid receptors (RARs). The retinoidal actions are also modulated by retinoid X receptors (RXRs). RAR-RXR heterodimers bind to the RA-responsive element of DNA and regulate biological actions.[3] The first step of the regulation is binding of retinoid to the ligand binding domain of RAR. Recent work on the three-dimensional structures, such as X-ray crystallography of RARγ-all-*trans*-retinoic acid complex, have revealed the structural requirements for the appearance of retinoidal activity.[4] The endogenous ligand, all-*trans*-retinoic acid (**1**) and the synthetic retinoid: AM80 (**2**) are oriented in the ligand-binding pocket by two types of contact, i.e., hydrogen bonding at carboxylic acid and hydrophobic interaction with a suitable size of hydrocarbon skeleton.

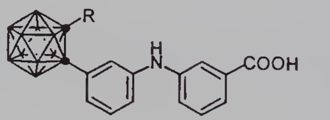
The design of carborane-containing retinoids is based on the skeletal structure of diphenylamine with 1,2-dicarba-*closo*-dodacaborane substituted on the *para*- or *meta*-position of one aromatic nucleus as a hydrophobic region (**3** and **4**).[5] The compounds bearing 1,2-carborane at the 4-position (**3**) exhibited potent differentiation-inducing activity toward HL-60 cells, as shown in Figure 1. The agonistic activity was increased by introduction of an *n*-propyl or *n*-butyl group on the carborane cage. For example, the EC50 value of **3d** is 1.5 X 10^{-9} M. This activity is comparable to that of all-*trans*-retinoic acid. Compounds bearing a 2-carborane at the 3-position (**4**) also exhibited potent retinoidal activity. The effect of the introduction of an alkyl group on the carborane cage of **4** was similar to that in the case of the *para*-isomer. On the other hand, the activity was completely abolished by the introduction of a methyl group on the nitrogen atom (**3g**). These effects may arise from changes in the twisting conformation at the phenyl-N-phenyl moiety caused by the alkyl group on the nitrogen.







3a R = H
3b R = CH_3
3c R = Et
3d R = *n*-Pr
3e R = *iso*- Pr
3f R = *n*-Bu



4a R = H
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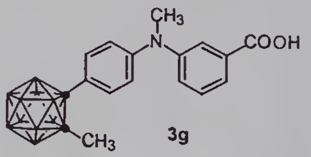

3g

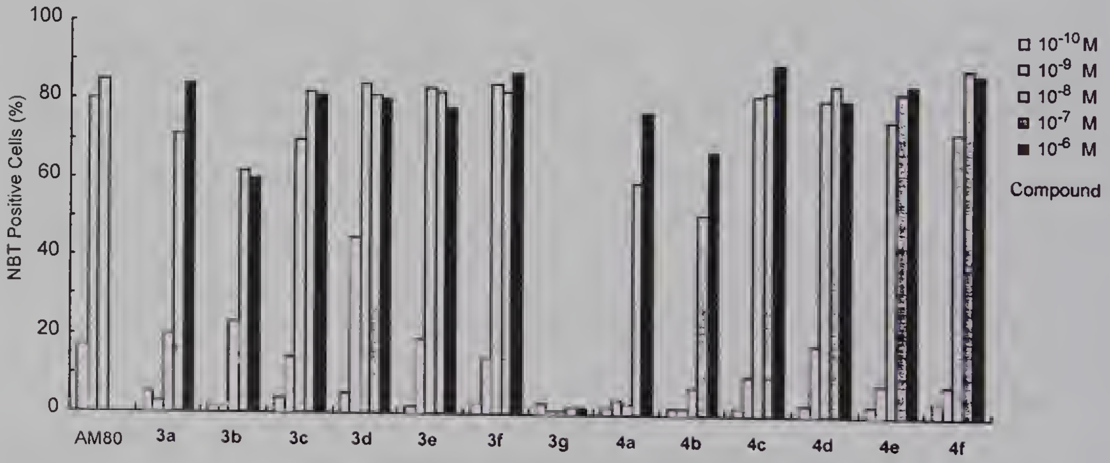

Figure 1 HL-60 Cell Differentiation-inducing Activity of Carborane-containing Compounds at 10^{-10}M to 10^{-6} M Concentration.

2 Application of Boron Clusters as a Hydrophobic Pharmacophore for Estrogens

Estrogen (*i.e.* 17β-estradiol, **5**) is an important hormone that mediates a wide variety of cellular responses through its binding to a specific nuclear estrogen receptor (ER).[6] The hormone-bound ER forms an active dimer, which functions as a transcription factor that mediates biological response by binding to specific promoter elements of DNA to regulate gene transcription.[7] Compounds that either induce or inhibit cellular estrogen responses have potential value as biochemical tools and candidates for drug development. High binding affinity for ER and the appearance of substantial estrogenic activity require a phenolic ring, an appropriate hydrophobic group adjacent to the phenolic ring, and another hydroxyl group located at a suitable position on the molecule.

Therefore, we designed a simple compound having a 4-phenolic residue and a hydroxymethyl group on the 1,12-carborane (**6b**). The structure of the designed compound seems to match very closely that of estradiol. (Figure 2) We have synthesized the designed compound and related phenolic compounds bearing a 1,12- or 1,7-carborane cage (**6** and **7**).[8]

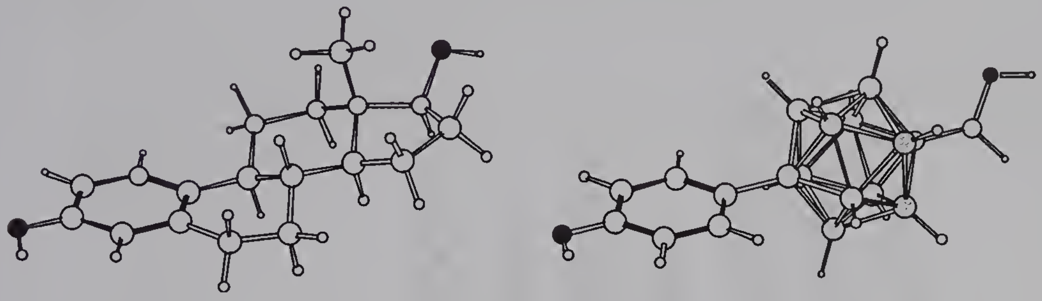

Figure 2 Structures of 17β-estradiol (5, left) and Estrogen Bearing Carborane (6b, right)

The estrogenic activities of the synthesized compounds were examined by luciferase reporter gene assay, in which a rat ERα-expression plasmid and a reporter plasmid, which contains 5 copies of the estrogen response element, are transiently transfected into COS-1 cells. Surprisingly, the simple compound 4-(1,12-carboranyl)phenol (**6a**) exhibited a potent transcriptional activity (Figure 3). Its potency is comparable to that of 17β-estradiol. The activity was increased by the introduction of a hydroxymethyl group or an amino group onto carbon of the carborane cage. The potency of the most potent compound, 1-(hydroxymethyl)-12-(4-hydroxyphenyl)-1,12-carborane (**6b**), was at least 10-fold greater than that of estradiol. The activity of the amine **6d** seemed to be somewhat stronger than that of estradiol, and the carboxylic acid **6c** exhibited moderate activity. The activity of the compounds bearing a *meta*-substituent on the carborane cage (**7**) was weaker than that of the *para*-substituted compounds. However, the potency of 1-(hydroxymethyl)-7-(4-hydroxyphenyl)-1,7-carborane (**7b**) is similar to that of 17β-estradiol.

In vitro ERα binding assays were performed on the three most active compounds (**6a**, **6b**, **6d**) and 17β-estradiol to confirm that the gene-regulatory activity correlated with the binding affinity for ERα. The assays were done by measurement of inhibition of [6,7-^{3}H]-17β-estradiol binding (K_d =0.4 nM) to human recombinant ERα. The ERα binding data for these compounds are consistent with the results of the luciferase reporter gene assay. Compounds **6a** and **6d** showed high affinity for the ER. The potency was almost the same as that of estradiol. The most active compound in the luciferase reporter gene assay, **6b**, also showed the highest affinity for the ER and its affinity (K_i =0.10 nM) was several times higher than that of estradiol.

Recent studies on the three-dimensional structure of the complex formed by estradiol and the human estrogen receptor-α ligand binding domain have revealed the structural requirements for the appearance of estrogenic activity.[9] 17β-Estradiol is oriented in the ERα ligand-binding pocket by two types of contacts: hydrogen bonding at both ends and hydrophobic contacts along the body of the skeleton. The phenolic hydroxyl group and hydroxymethyl group on the carborane cage of **6b** may play corresponding roles to the case of estradiol. The ligand-binding pocket seems to have some latitude around the C-ring and D-ring of estradiol. The high activity of **6b** suggests that the carborane cage works as a hydrophobic group for binding to the hydrophobic cavity of ER, and the contacts along the spherical carborane cage produce a stronger interaction than that in the case of estradiol.

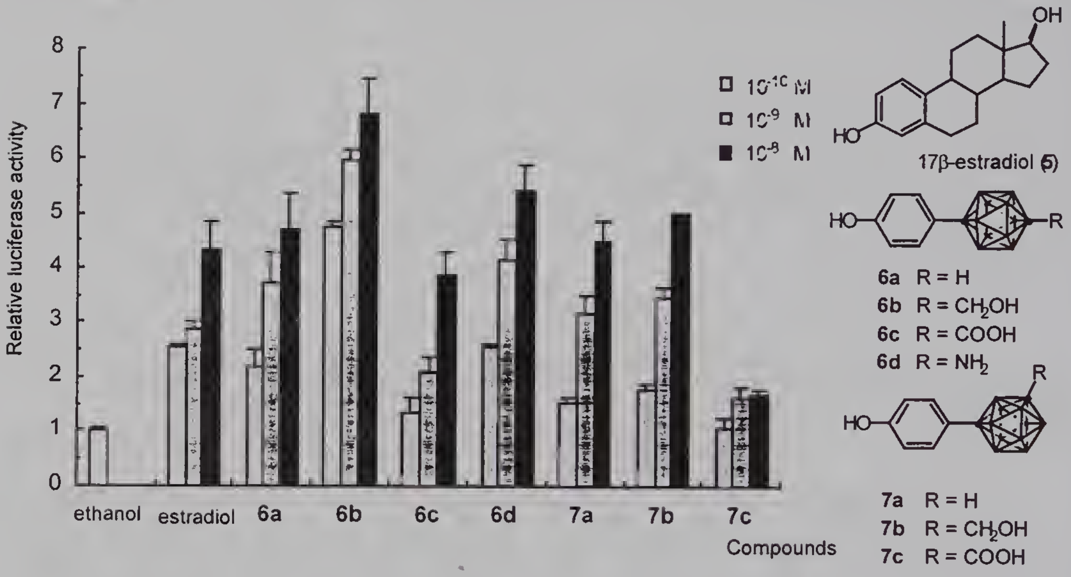

Figure 3 Luciferase Reporter Gene Assay of Estrogens Bearing Carboranes. COS-1 cells were transfected with EREx5-pGL-TKand pCI-rER□ and incubated with the compounds at the indicated concentrations (10^{-10}M to 10^{-8}M). Results are shown as means ± S.D. for triplica

Conclusion

In summary, we have developed novel carborane-containing molecules with potent retinoidal and estrogenic activities. The unique character of biologically active molecules containing a carborane skeleton may give rise to unusual membrane transportation properties and metabolism, compared with conventional active molecules. The superagonistic character of the carborane-containing compounds raises the possibility of the development of more selective agonists and antagonists, which could be useful as therapeutic agents.

References

1. M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 950-984; A. H. Soloway, W. Tjarks, B. A. Barnum, F.-G. Rong, R. F. Barth, I. M. Codogni, J. G. Wilson, *Chem. Rev.*, 1998, **98**, 1515-1562.
2. M. B. Sporn, A. B. Roberts, D. S. Goodman Eds., 'The Retinoids', 2nd ed., Raven

Press, New York, 1994.

3. M. Petcovich, N. J. Brand, A Krust, P. Chambon, *Nature*, 1987, **330**, 444-450; R. M. Evans R. M., *Science*, 1988, **240**, 889-895.
4. J.-P. Renaud, N. Rochel, M. Ruff, V. Vitat, P. Chambon, H. Gronemeyer, D. Moras, *Nature*, 1995, **375**, 681-689.
5. Y. Endo, T. Iijima, H. Kagechika, K. Ohta, E. Kawachi, K. Shudo, *Chem. Pharm. Bull.*, 1999, **47**, 585-587; T. Iijima, Y. Endo, M. Tsuji, E. Kawachi, H. Kagechika, K. Shudo, *Chem. Pharm. Bull.*, 1999, **47**, 398-404.
6. S. Ray, I. Dwivedy., ‘Advances in Drug Research’, Vol. 29, ; Edited by B. Testa, U. A. Meyer, Academic Press, San Diego, 1997, p. 171-270.
7. M. J. Tsai, B. W. O’Malley, *Annu. Rev. Biochem.*, 1994, **63**, 451-486.
8. Y. Endo, T. Iijima, Y. Yamakoshi, M. Yamaguchi, H. Fukasawa, K. Shudo, *J. Med. Chem.*, 1999, **42**, 1501-1504.
9. A. M. Brzozowski, A. C. W. Pike, Z. Dauter, R. E. Hubbard, T. Bonn, O. Engstrom, L. Ohman, G. L. Greene, J. Gustafsson, M. Carlquist, *Nature*, 1997, **389**, 753-758.

closo-Dodecaborate (2–) Anion as a Prosthetic Group for Labelling Proteins with Astatine

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INTRODUCTION

Astatine-211 is a promising radionuclide for systemic therapy[1-3] due to its decay properties with a half-life of 7.2 hours and an effective emission of one α-particle per decay. However, the weakness of the astatine-protein bond formed after direct astatination[1,4] has so far limited its clinical use. To overcome these problems indirect labelling methods have been tried such as the use of *N*-succinimidyl-(trialkylstannyl) benzoate as an intermediate for the astatination of antibodies using conjugation procedures.[5-8]

An attractive alternative would be to attach a prosthetic group to the targeting protein, which could then form a stable bond with astatine in a direct labelling procedure. Possible candidates are polyhedral boron compounds like *closo*-dodecaborate, *closo*-decaborate, and *closo*- and *nido*-carboranes. Basic knowledge regarding conjugation of these boron cage compounds was recently gained in connection with the development of compounds for boron neutron capture therapy (BNCT).[9] The polyhedral boron compounds are easily halogenated[10-12] and form thermodynamically very stable boron-halogen bonds. Some labelling attempts have already been made.[13,14]

Carboranes have so far attracted most attention because the cage carbon atoms can relatively easy be functionalised in order to allow attachment to tumour-seeking molecules. Here we suggest the use of derivatives of the *closo*-dodecaborate(2-) anion as a prosthetic group for astatination. The *closo*-dodecaborate cage does not contain carbon atoms and is therefore somewhat more difficult to attach to proteins. However, several methods have been reported for the synthesis of *closo*-dodecaborate derivatives containing organic side-chains[15-18]. These boron cages also differ from *closo*- and *nido*-carboranes in charge and lipophilicity properties. These differences may be utilised in the modification of the biochemical properties of the halogen-labelled compounds, including aspects of non-specific binding to normal cells, intracellular retention and excretion of the label after catabolism of the targeting compound.

The aim of this paper is to study the influence of different reaction parameters on the labelling yield in the astatination of and to evaluate the merits of this anion as a possible prosthetic group for astatination of protein.

RESULTS AND DISCUSSION

The four thin layer chromatograms in Figure 1 demonstrate typical results from the labelling experiments of *closo*-dodecaborate(2-) with At-211. Figure 1a represents the results of a blank experiment with no NaI added. A narrow peak is seen at the starting point of the TLC, most likely representing oxidised astatine, i.e. oxoanions, is followed by a broad radioactivity distribution, probably reflecting a continuous astatine oxidation during the TLC development. A blank experiment with NaI added as a carrier (Figure 1b) clearly shows the positive role of the iodide anion as a non-isotopic carrier for astatine analysis. Astatine is probably stabilised in the form of AtI or AtI_2^- compounds.[19] In a chromatogram obtained after the standard labelling procedure (Figure 1c), the central peak ($R_f = 0.5$-0.6) represents the astatinated dodecaborate anion, which is well resolved from both highly oxidised and reduced astatine. This peak has the same R_f value as monoiodinated dodecaborate anion in this system. Figure 1d shows the result of spontaneous labelling in the absence of oxidising agent.

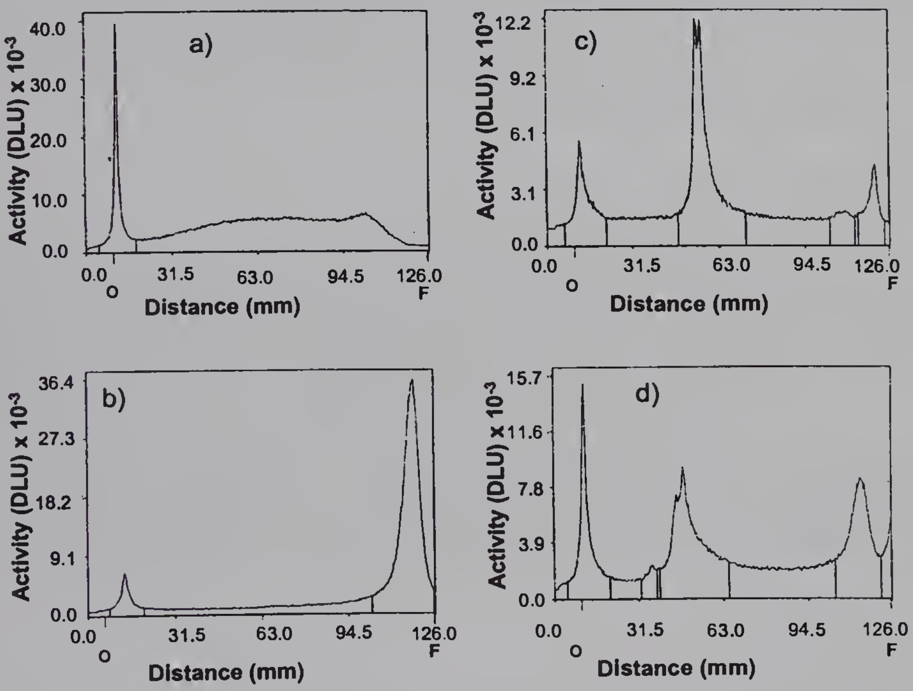

Figure 1. *Radiochromatograms obtained using TLC: a) ^{211}At distribution after oxidation and subsequent reduction of astatine in the absence of closo-dodecaborate and sodium iodide; b) ^{211}At distribution after oxidation and subsequent reduction of astatine in the absence of closo-dodecaborate; c) ^{211}At distribution after oxidation and subsequent reduction of astatine in the presence of closo-dodecaborate. d) Spontaneous labelling closo-dodecaborate in the absence of oxidising agent Sodium iodide carrier was added to the reaction mixture before analysis in samples b) c) and d). Merck silica gel 60F 254 TLC aluminium sheets were used and the eluent was acetone/0.1 M ammonia (9/1, v/v). The TLC strips (15×140 mm, elution path 120 mm) were measured on the Cyclone™ Storage Phosphor System and analysed on the OptiQuant™ Image Analysis Software.*

The labelling yield decreased when the time increased between the astatine separation and the labelling. For this reason, the labelling dependence on each parameter was always measured at the same time in relation to the production time in order to exclude the influence of this astatine ageing effect.

The reaction was essentially completed during 5 minutes incubation at room temperature. The astatination yield reached its maximum in the pH range of 7.0-8.0. Further increasing or decreasing of pH lead to a decrease of the yield. The astatination yield increased steadily as a function of the *closo*-dodecaborate concentration and reached a plateau at 25-30 nmol of dodecaborate. The labelling yield was reduced marginally when the amount of dodecaborate was halved. A marked change in labelling efficiency was found in different buffers (phosphate and phosphate buffered saline) and at low concentrations of *closo*-dodecaborate. The use of chloride-containing buffer (PBS) affected positively the labelling yield, thus enabling a more effective labelling of smaller substrate amounts.

The precursor was labelled efficiently even at very low amounts of Chloramine-T. Spontaneous labelling (no Chloramine-T present) gave a decreased, but still substantial, labelling of about 15%. If sodium metabisulfite was added before astatine in the solution, no labelling occurred.

The stability of boron-astatine bond was studied both at room temperature and at 37°C. Samples of the labelling reaction mixture were stored at both temperatures and analysed on TLC at 0, 3, 5 and 7 h post reaction termination. In both cases no significant change was seen in the reaction mixture composition.

LABELLING PROTOCOL

An aqueous solution of di(triethylamonium) dodecahydro-*closo*-dodecaborate(2-), $(Et_3NH)_2B_{12}H_{12}$, (10 µl, 1mg/ml) and an astatine solution in methanol (5 µl) were added to 30 µl of buffer solution (pH 7.5). Labelling was started by addition of 10 µl of solution of the sodium salt of *N*-chloro-*p*-toluenesulfonamide, Chloramine T, (5 mg/ml in water). The mixture was vortexed for a few seconds and left to react for 5 min. The reaction was quenched with 20 µl of solution of sodium metabisulfite, $Na_2S_2O_5$, (4 mg/ml in water). Sodium iodide, NaI, (5 µl, 20 mg/ml in water) was added as carrier before analysis.

Blank experiments were performed according the same protocol but without adding *closo*-dodecaborate. Some experiments were done without adding iodide carrier.

CONCLUSION

The closo-dodecaborate(2-) is proposed as a prosthetic group for direct labelling of proteins with ^{211}At for radionuclide therapy. An efficient TLC analytical procedure for resolving the labelled boron compound from other chemical forms of astatine is described. Astatination of *closo*-dodecaborate(2-) anion using Chloramine-T was studied, and the influence of pH, reaction time, amount of substrate and oxidant was determined. A maximum labelling yield of 55 - 75% was found in the pH range 7-8. A spontaneous astatination of *closo*-dodecaborate(2-) in the absence of Chloramine-T was also found, presumably due to generation of oxidising products from radiolysis of water. The B-At bond is stable *in vitro* for at least one half-life of ^{211}At. Derivatives based on dodecaborate(2-) anion are potential candidates as prosthetic groups in direct labelling of proteins.

ACKNOWLEDGEMENT

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REFERENCES

1. I. Brown, *Appl. Radiat. Isot.* 1986, **37**, 789.
2. R. Weinreich. In: Advances in Hadrontherapy, U.Amaldi, B. Larsson and Y. Lemoigne (Eds.). Elsevier Science, Amsterdam. 1997, p. 359.
3. G. Vaidyanathan, and M.R. Zalutsky, *Phys. Med. Biol.* 1996, **41**,1915.
4. G.W.M. Visser, E.L. Diemer, and F.M. Kaspersen, *Int. J. Appl. Radiat. Isot.* 1981, **32**, 905.
5. M.R. Zalutsky, and A.S. Narula, *Appl. Radiat. Isot.*, 1988, **39**, 227.
6. S.W. Hadley, D.S. Wilbur, M.A. Gray, and R.W. Atcher, *Bioconjugate Chem.* 1991, **2**, 171.
7. D.S. Wilbur, R.L. Vessella, J.E. Stray, D.K. Goffe, K.A. Blouke, and R.W. Atcher, *Nucl. Med. Biol.* 1993, **20**, 917.
8. U.P. Schwarz, P. Plascjak, M.P. Beitzel, O.A. Gansow, W.C. Eckelman, and T.A. Waldmann, *Nucl. Med. Biol.* 1998, **25**, 89.
9. M.F. Hawthorn, *Pure&Appl. Chem.*, 1991, **63**, 327.
10. W.H. Knoth, H.C. Miller, J.C. Sauer, J.H. Balthis, Y.T. Chia, E. Muetterties, *Inorg.Chem.* 1964, **3**, 159.
11. F.P. Olsen,. and M.F. Hawthorn, *Inorg. Chem.* 1965, **4**, 1839.
12. G.B. Dunks, and M.F. Hawthorn, *Inorg. Chem.* 1970, **9**, 893.
13. D.S. Wilbur, D.K. Hamlin, C.F. Foulon, M.R. Zalutsky, and P.M. Pathare. In: *Proceedings of XIIth International Symposium on Radiopharmaceutical Chemistry.* Uppsala, Sweden. June 15-19, 1997, p. 76.
14. A. Sjöström, V. Tolmachev, J. Koziorowski, O. Lebeda, L. Einarsson, S. Sjöberg, J. Carlsson, and H. Lundqvist. In: Koziorowski J. "Radiohalogenation of biomolecules" Acta universitatis Upsaliensis, Uppsala, 1998.
15. L. Gedda, P. Olsson, J. Ponten, and J. Carlsson, *Bioconjug Chem.,* 1996, **7**, 584.
16. A.B. Bruskin, A.M. Orlova, I.B. Sivaev, A.A. Semioshkin, V.I. Bregadze, and S. Sjöberg. In: Advances in Neutron Capture Therapy, B. Larsson, J.Crawford, R.Weinreich (Eds.). Elsevier, 1997, **2**, 46.
17. I.B. Sivaev, A.B. Bruskin, V.V. Nesterov, M.Y. Antipin, V.I. Bregadze, and S. Sjöberg, *Inorg. Chem.* In press 1999.
18. I.B. Sivaev, S. Sjöberg, V.I. Bregadze, and D. Gabel, *Tetrahedron Lett.* 1999, **40**, 3451.
19. G.W.M. Visser, *Radiochim. Acta* 1989, **47**, 97.

Effect of Ionising Radiation on the Labelling of *closo*-Dodecaborate (2^-) Anion with ^{125}I

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1 INTRODUCTION

The organic side-chain derivatives of dodecahydro-*closo*-dodecaborate (2^-) anion seem to provide suitable tool for the delivery of different nuclides to the place of destination in nuclear medicine. Potential of these derivatives in BNCT was already demonstrated.[1,2] Recently, *closo*-dodecaborate (2^-) anion has been suggested as prosthetic group for attachment of radiohalogens to bigger organic carrier molecules (peptides, proteins etc.), namely of different isotopes of iodine and astatine which are of interest both in diagnostics and therapy.[3,4] The rationale of this proposal is based on easy halogenation of this compound,[5] higher binding energy in pairs B-I and B-At compared to C-I and C-At,[6] simple and reliable conjugation of *closo*-dodecaborate(2^-) to biomolecules[7] and expected resistance of boron-halogen bond towards enzymatic systems.[3]

In the labelling of *closo*-dodecaborate derivatives with iodine isotopes Chloramine-T or other oxidants are used, for spontaneous labelling (i.e. the reaction between *closo*-dodecaborate and appropriate radionuclide in n.c.a. state in absence of oxidation agent) does not practically occur. However, the astatination of *closo*-dodeca-borate with ^{211}At (half-life 7.214 h) makes an exception.[4] It has been observed that even in absence of Chloramine-T there is still remarkable labelling yield around 15% left at pH = 7.2, whereas the labelling of *closo*-dodecaborate (2-) anion with ^{125}I (half-life 59.41 d) under the similar conditions does not result in any observable yield (*vide infra*). This fact could be simply explained by chemical stabilization of astatine in form of single charged cation At^+. On the other hand, there is still one important factor which may also significantly influence the labelling yield: intensive alpha radiation of ^{211}At itself, producing ions, radicals and new, often oxidizing compounds (e.g. peroxides) in the solution. These radiolytical products probably affect chemical state of the astatine atoms left in the solution, and thus also its reactivity.

The oxidant-free labelling of *closo*-dodecaborate(2^-) anion with ^{125}I may serve as a suitable model system for estimation of ionising radiation effect on the yield, for the effect of the weak X-rays of ^{125}I itself is negligible.

The aim of this study was, therefore, to trace the impact of directly and indirectly ionising radiation on the labelling of *closo*-dodecaborate with ^{125}I, and to determine the labelling yield dependence on the dose absorbed.

2 MATERIALS AND METHODS

2.1 Materials

Sodium iodide (NaI), methanole (MeOH), dichlormethane (CH_2Cl_2), acetone, citric acid and sodium mono- and dihydrogenphosphates were of p.a. grade (E. Merck, Darmstadt, Germany). Di(triethylammonium) dodecahydro-*closo*-dodecaborate (Et-B_{12}) and di(tetrabutylammonium) dodecahydro-*closo*-dodecaborate (Bu-B_{12}) were synthesized according to the published method[8] and used as 1 mg/ml solutions in water (Et-B_{12}) and in MeOH (Bu-B_{12}). N-chloro-p-toluene sulfonamide sodium salt (Chloramine-T, CAT), Sigma, St. Louis, MO, USA was used as 5 mg/ml solution in water, or in MeOH. Sodium metabisulphite ($Na_2S_2O_5$, NAT), Sigma, St. Louis, MO, USA was used either as 4 mg/ml solution in water, or 1 mg/ml solution in MeOH. Sodium iodide was used as 20 mg/ml solution in water. ^{125}I was prepared by dilution of 1 μl of commercial product (^{125}I n.c.a. in NaOH, 3.7 GBq/ml, Amersham) in 300 μl of water, or in MeOH. ^{211}At solution in MeOH was obtained as described elsewhere.[4] CAT, NAT, NaI, ^{125}I and ^{211}At solutions were prepared a few minutes before experiment and stored in Eppendorf's tubes, Et-B_{12}, Bu-B_{12} and buffer solutions were prepared several hours before experimental work and stored in plastic vessels. Aqueous solutions were prepared with use of high quality ELGA water (specific resistance > 18 MΩ/cm).

2.2 Methods

2.2.1. *Standard labelling.* 30 μl of buffer (citrate-phosphate, pH = 7.0) in Eppendorf's tube were mixed with 10 μl of Et-B_{12} and 5 μl of ^{125}I. Then 10 μl of CAT were added, the resulting mixture was vortexed for several seconds and left to react for 5 min. The reaction was quenched by 20 μl of NAT, and NaI (5 μl) was added as carrier. Standard labelling of Bu-B_{12} was analogous, only the buffer was replaced by the same volume of MeOH, all agents except NaI were used as methanolic solutions and the reaction was quenched by addition of 40 μl NAT. Blanks were performed in the same way, but in absence of 10 μl of the *closo*-dodecaborate salts. Experiments were performed in duplicates.

2.2.2. *Spontaneous labelling.* 30 μl of buffer (citrate-phosphate, pH = 7.0) in Eppendorf's tube were mixed with 10 μl of Et-B_{12} and 5 μl of ^{125}I, and the resulting mixture was left to react for 2 hours. The reaction was quenched by 20 μl of NAT, and NaI (5 μl) was added as carrier. Spontaneous labelling of Bu-B_{12} was analogous, only the buffer was replaced by the same volume of MeOH and all agents except NaI were used as methanolic solutions. Experiments were performed in duplicates.

2.2.3. *Spontaneous labelling affected by alpha radiation.* 30 μl of buffer (citrate-phosphate, pH = 7.0) in Eppendorf's tube were mixed with 10 μl of Et-B_{12}, 5 μl of ^{125}I and 5 μl of ^{211}At, and the resulting mixture was left to react for 30 minutes. The reaction was quenched by 20 μl of NAT, and NaI (5 μl) was added as carrier. There were employed three ^{211}At solutions of different concentration, so that the dose absorbed in reaction mixtures was 1.33, 21.1 and 284 Gy respectively. Reaction mixtures were analyzed after the decay of ^{211}At (> 80 h). Experiments were performed in duplicates.

2.2.4. *Spontaneous labelling affected by gamma radiation.* 30 μl of buffer (citrate-phosphate, pH = 7.0) in Eppendorf's tube were mixed with 10 μl of Et-B_{12} and 5 μl of ^{125}I. The resulting mixtures were exposed to gamma radiation on external ^{60}Co source at constant dose rate 13 mGy/s for 15, 30, 120 and 360 min respectively. The reaction was quenched by 20 μl of NAT, and NaI (5 μl) was added as carrier. The dose absorbed in reaction mixtures was 11.7, 23.4, 94 and 280 Gy respectively. Analogous experiments were performed with Bu-B_{12} in MeOH. Experiments were performed in duplicates.

2.2.5. *TLC system.* Silica Gel (0.2 mm thick layer on Aluminium, 20×20 cm plates, E. Merck, Germany) in strips (15×100 mm, elution path 80 mm) was pre-washed by acetone:CH_2Cl_2 (4:1) mixture, 1-2 μl of the reaction mixture were applied per TLC strip, left to dry on free air, developed by the same acetone:CH_2Cl_2 mixture and measured on the Cyclone™ Storage Phosphor System. The obtained radiochromatograms were analyzed via OptiQuant™ Image Analysis Software.

2.2.6. *Radioactivity measurements.* ^{211}At radioactivity in single reaction mixtures was determined using high purity germanium detector (EG&G Ortec, USA).

3 RESULTS AND DISCUSSION

3.1 Results

The TLC system provides good resolution of radiolabelled *closo*-dodecaborate salts ($R_f \approx 0.95$) from unreacted ^{125}I in form of iodide ($R_f \approx 0.30$) and iodate ($R_f \approx 0.00$). All peaks were well distinguished. Except peaks ascribed to above mentioned ^{125}I forms there were no other peaks observed on the radiochromatograms.

The TLC analysis of blanks did not reveal any peak in position of radiolabelled Et-B_{12} and Bu-B_{12}. Standard labelling gave the yield 94.4(1.7)% (Et-B_{12}) and 98.8(0.5)% (Bu-B_{12}). (The value in round brackets denotes the range.) Spontaneous labelling gave no yield in the case of Et-B_{12} and 2.0 (1.0)% in the case of Bu-B_{12}.

Results of spontaneous labelling of Et-B_{12} affected by alpha radiation are summarized in Table 1. Results of spontaneous labelling of Et-B_{12} and Bu-B_{12} affected by gamma radiation are summarized in Table 2.

Table 1 *Et-B_{12} labelling with ^{125}I - the yield dependence on the absorbed dose at spontaneous labelling affected by alpha radiation*

Dose [Gy]	Labelling yield [%]
0	0
1.33	0.8 (0.4)
21.1	7.7 (0.6)
284	15.6 (2.0)

Table 2 *Et-B_{12} and Bu-B_{12} labelling with ^{125}I - the yield dependence on the absorbed dose at spontaneous labelling affected by gamma radiation*

Dose [Gy]	Et-B_{12} labelling yield [%]	Bu-B_{12} labelling yield [%]
0	0	0
11.7	1.7 (0.8)	6.8 (1.5)
23.4	2.9 (0.5)	10.0 (6.8)
94.0	13.8 (0.6)	32.0 (17.6)
280	26.6 (1.3)	56.2(13.8)

3.2 Discussion

Ionising radiation influences significantly the yield of *closo*-dodecaborate(2^-) labelling with ^{125}I. Alpha radiation effect does show, probably due to rather localized character of interactions between alpha particles and solution, faster saturation compared to the effect of gamma radiation exhibiting more even distribution of radiolytical products (Figure 1).

In spite of bad statistics in Bu-B_{12} labelling results, they follow in general the pattern of Et-B_{12} labelling under the same conditions in aqueous medium. Surprisingly, the yield of radiolabelled Bu-B_{12} in MeOH is on average higher than the yield of radiolabelled Et-B_{12} in water, although methanole acts as efficient radical scavenger.

The radiation effect is very likely based on the oxidation of iodine by radiolytical products into the I^+ form, but it is very difficult to analyze in detail the processes underlying the complex mechanism of the effect. Higher sensitivity of astatine towards oxidation indicates that strong alpha radiation of ^{211}At could affect the labelling with this radionuclide even negatively (oxidation into higher oxidation states).

The described phenomenon represents an interesting aspect of labelling chemistry, which deserves more thorough study.

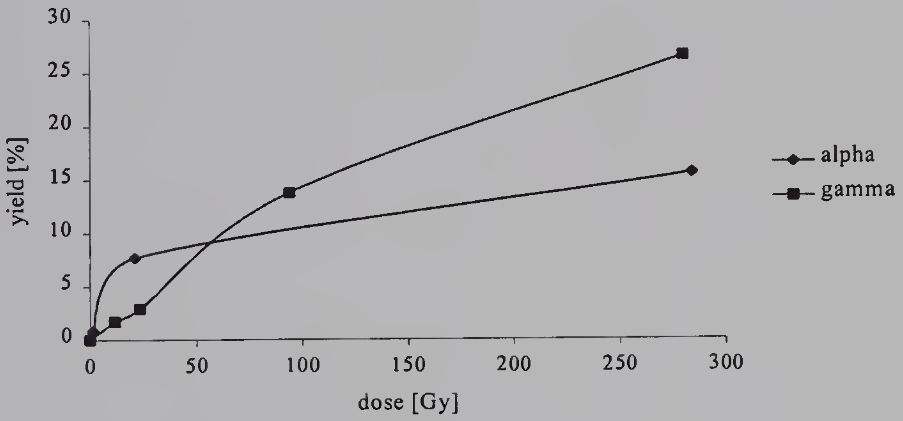

Figure 1 *Et-B_{12} labelling with ^{125}I - comparison of the yield dependence on the dose delivered via irradiation with alpha particles and with gamma rays*

References

1. A. H. Soloway, H. Hatanaka and M. A. Davis, *J. Med. Chem.*, 1967, **10**, 714.
2. H. Hatanaka and Y. Nakagana, *Int. J. Radiat. Oncol. Biol. Phys.*, 1994, **28**, 1061.
3. V. Tolmachev, J. Koziorowski, I. Sivaev, H. Lundqvist, J. Carlsson, A. Orlova, L. Gedda, P. Olsson, S. Sjoberg and A. Sundin, *Bioconjugate Chem.*, 1999, **10**, 338.
4. A. Orlova, O. Lebeda, V. Tolmachev, H. Lundqvist, J. Carlsson and S. Sjoberg, Astatination of *Closo*-Dodecaborate (2-) Anion - contribution to IMEBORON X
5. W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 159.
6. J. A. Kerr, Strengths of Chemical Bonds, in.: Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1992.
7. L. Gedda, P. Olsson, J. Ponten and J. Carlsson, *Bioconjugate Chem.*, 1996, **7**, 584.
8. R. M. Adams, A.R. Siedle and J. Grant, *Inorg. Chem.*, 1964, **3**, 461.

Cluster Synthesis

A Convincing Evidence of the S^+ Charge in $SB_{11}H_{11}$ and its Derivatives

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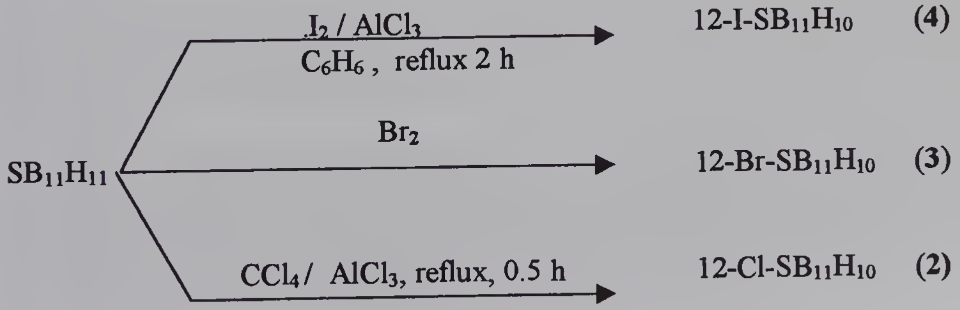
1 INTRODUCTION

While borane chemists consider the sulfur vertex to be positively charged in *closo-* and *nido*-thiaboranes[1] and the opposite boron atom the electron rich end of the molecule, a higher electronegativity of sulfur in relation to boron atom (S 2.58 > B 2.04)[2] could lead to the conclusion that the direction of dipole moments in the cage thiaboranes might be just opposite.[3] In this case, sulfur should be the negative and the opposite BH vertex the positive ends of the respective cluster. A crucial compound of this series is the icosahedral thia-*closo*-dodecaborane(12) $SB_{11}H_{11}$ (1) (Figure 1) with most delocalized electrons in the skeleton.

In contrast to closo-carboranes (e.g. $CB_{11}H_{12}^-$,[4] $1,2\text{-}C_2B_{10}H_{12}$,[3]) where electrophilic substitution occurs predominantly at the most electronegative boron atoms which are opposite to the carbon vertices, the $SB_{11}H_{11}$ molecule is sensitive to reaction conditions and affords either B(7)[5] or B(12) derivatives or their mixture.[5] Halogenation affords at lower temperatures first the 7-X-derivatives[6] whereas at reflux in low boiling medium (benzene, bromine, tetrachloromethane) the 12-X-compounds **2, 3** and **4** are the main products (see scheme). The absence of a direct electrophilic halogenation in the B(12) position under mild conditions seems to deny a high electron density at this end of the $SB_{11}H_{11}$ molecule.

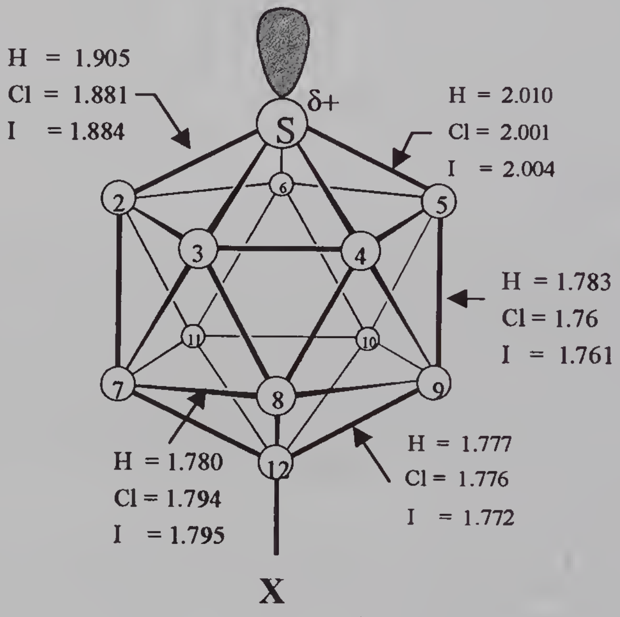
$$B_{10}H_{14} + 2\,S + NEt_3H \xrightarrow[CHCl_3]{Et_3N.BH_3} \text{“}Et_3NH\ SB_{10}H_{11}\text{”} \xrightarrow[\Delta]{} \underset{(1)}{SB_{11}H_{11}}$$



On the other hand, there are several facts which provide evidence for a low electron density of the sulfur vertex:

a) reluctance against the S-alkylation
b) high J(BH) coupling values of the neighbor B(2-6)H bonds
c) ESCA measurements

For the final evidence that sulfur vertex is the positive pole of the $SB_{11}H_{11}$ **(1)** molecule, the 12-Cl-$SB_{11}H_{10}$ **(2)**, 12-Br-$SB_{11}H_{10}$ **(3)** and 12-I-$SB_{11}H_{10}$ **(4)** derivatives were prepared and their dipole moments (D) measured.



1 X = H 1.190
2 = Cl 1.798
3 = Br*
4 = I 1.169

* For the Br derivative **3**, the respective distances were not determined yet.

Figure 1

2 EXPERIMENTAL

The starting thia-*closo*-dodecaborane $SB_{11}H_{11}$ **(1)** and its 12-Br-$SB_{11}H_{10}$ derivative **(3)** were prepared according to the paper[7]. The optimum conditions for the preparation of 12-halogen-$SB_{11}H_{10}$ derivatives are shown in the reaction schemes (see above).

The dipole moments were determined at 25 °C in benzene (five solutions, weight fraction 1.8×10^{-4} to 1.1×10^{-3}), showing the 3.84 D value for **(1)**, 5.47 D for **(2)**, 5.49 D for **(3)** and 5.34 D for **(4)**. Relative permitivities were measured at 6 MHz on a home-made DK-meter with direct frequency reading,[8] and refractive indices were measured on an Aerograph Refractive Index Detector (Varian). The dipole moments were obtained by extrapolation to infinite dilution according to Guggenheim[9] and Smith[10] methods.

The molecular structures of compounds **1**, **2** and **4** were determined by the X-ray diffraction analyses[11] and in the case of **1** also by *ab initio* calculations.[12] (Analogous calculations of **2**, **3** and **4** will be the subject of further investigation). The salient bond lengths of the individual types of bonds are depicted in Figure 1.

3 DISCUSSION

A comparison of the measured values of dipole moments for **1** (3.84 D) and its halogenated derivatives (5.47 D for **2**, 5.49 D for **3** and 5.34 D for **4**) shows that values of halogenated derivatives can be obtained by a simple addition of the dipole moment of **1** and group moments related to X substituents,[13] the latter amounting to 1.6 D for X = Cl, Br and to a bit lower value for iodine. Both moments lay on the $S\cdots B_{12}\cdots X$ axis and have the same direction.

The preliminary *ab initio* calculations of (**1**) and the respective halogenated derivatives[6] **2-4** indicate that in these derivatives the sulfur atom in **1** is positively charged (+0.33 with respect to the elementary charge, i.e. 0.534×10^{-19}C). This computing is in rough agreement with the results obtained by ESCA measurements (see below).

From the experimental value 3.84 D of the dipole moment for **1** can be deduced that the location of the negative pole of the dipole is separated from the sulfur atom by 240 pm and lies approx. at 2/3 distance of 365 pm[11] that represents the body diagonal S---B(12) (Figure 1). In addition, in halogenated derivatives the negative part of the B-X dipole is separated by approx. another 125 pm.[11]

The increase of dipole moments in the order $\mathbf{1} \ll \mathbf{4} < \mathbf{3} \leq \mathbf{2}$ gives evidence that in this series, the halogen atoms bound to the 12-boron vertices draw eletrons by their strong inductive effects from the positive center which is located on the main symmetry axis crossing the S(1) and B(12) vertices. A distinct increase of the dipole moments in the above series unambiguously confirms that the positive center must be the sulfur atom S(1).

The above results are in full agreement with the ESCA measurements of S(2p) electrons at the parent thia-*closo*-dodecaborane **1** [S(2p) 189.8 eV][1,15] which corresponds according to the Siegbahn's correlation diagram[14] to the charge value Q = + 0.72 e or, using the equation [$Q = (E_b - 163.8)/3.38$], can be calculated as + 0.68.[1] This result has clearly shown that the charge on the S-vertex is analogous to that on S^+ in $S(Me_3)^+ I^-$.[16] A relatively small differences among the values obtained with individual halogenoderivatives (see Table 1) and absence of any splitting of the ESCA B(1s) signal confirm the general knowledge of borane chemists that the decrease of electron density in the skeleton caused by individual substituents is spread over the surface of the molecule.

Further confirmation of the positive charge on S-vertices in compounds **1-4** follows from the fact that S (δ^+) strongly influence J(BH) coupling constants of individual BH vertices which decrease in the order B(2-6) >> B(7-11)H > B(12), i.e. in the order of decreasing influence of the charge on sulfur[17] (Table 1).

References

1. S. Heřmánek and J. Plešek, in *Current Topics in the Chemistry of Boron* (G.W. Kabalka, Ed.) 8th International Meeting on Boron Chemistry, Knoxwille, 11-15 July,1993, Royal Soc. of Chem., Cambridge, 1994.
2. A.L. Allred, *J. Inorg. Nucl. Chem.* 1961, **17**, 215.
3. R. Maruca, H. Schroeder, A.W. Laubengayer, *Inorg. Chem.* 1967, **6**, 572.4.
4. T. Jelínek, J. Plešek, S. Heřmánek and B. Štíbr, *Coll. Czech. Chem. Commun.* 1986, **51**, 819.
5. J. Plešek and S. Heřmánek, *J. Chem Soc., Chem. Commun.* **1975**, 127.
6. This paper.
7. W.L. Smith, B.J. Menegheli, D.A Thompson, P. Klymko, N. McClure, M. Bower and R.W. Rudolph, *Inorg. Chem.* 1977, **16**, 3008.
8. V. Všetečka, *Chem. Listy*, 1995, **89**, 256.
9. E.A. Guggenheim, *Trans Faraday Soc.* 1949, **45**, 714.
10. J.W. Smith, *Trans Faraday Soc.*, 1950, **46**, 256.
11. I. Císařová, personal communication.
12. D. Hnyk., E. Vajda, M. Bühl and P.v.R. Schleyer, *Inorg. Chem.*, 1992, **31**, 2464.
13. A.I Jecenstova, G.A. Anorova, V.I. Stanko, *Zhur. Struct. Khim.* 1975, **16**, 1075.
14. K. Siegbahn, C. Nordling, A. Fahman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S-E. Carlson, I. Linfgren and B. Lindberg, *in ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, p. 122, Almquist & Wiksells Boktryckeri AB, Uppsala, 1967.
15. Z. Bastl, personal communication.
16. B.J. Lindberg, K. Hamrin, G. Johansson, G. Gelius, V. Fahman, C. Nordling and K. Siegbahn, *Fys. Sci.* 1970, **1**, 286.
17. S. Heřmánek, J. Macháček, J. Fusek and V. Blechta, in *The Borane, Carborane Continuum*, 367 (J. Casanova, Ed.), J. Wiley & Sons, Inc.1998, New York.

Table 1 *The* ^{11}B *(*$\delta^{11}B$*) and (*$\delta^{1}H$*) NMR Chemical Shifts and ESCA Results (eV, Q in el.) of Individual Boron Atoms in* $SB_{11}H_{11}$ *(1) and its 12-Halogeno Derivatives 2-4*

	Compound (12-X)			
Characteristic	1 (H)	2 (Cl)	3 (Br)	4 (I)
δ ^{11}B(2-6)	-6.6 (178)	-7.9 (181)	-7.6 (177)	-6.8 (177)
(7-11)	-4.3 (153)	-4.8 (154)	-4.6 (156)	-3.7 (156)
(12)	18.3 (147)	22.4 ----	15.3 ----	-0.2 ---
δ ^{1}H(2-6)	2.5	2.5	2.5	2.6
(7-11)	2.7	2.8	2.9	3.1
(12)	3.5	---	---	---
EV *charge Q*	165.9 *+0.72*	166.3 *+0.79*	166.1 *+0.75*	166.1 *+0.75*

Reactions of the Undecaborate Anion $[B_{11}H_{11}]^{2-}$

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1 INTRODUCTION

In contrast to other members in the series of *closo*-anions $[B_nH_n]^{2-}$, little is known about the chemical properties and structure of $[B_{11}H_{11}]^{2-}$. Its octadecahedral C_{2v} structure was established by theoretical studies[1,2] and is in accord with the structures of *closo*-derivatives like $[B_{11}H_{10}(SMe_2)]^-$,[3] known from crystal structure analysis. A characteristic feature of the B_{11} *closo*-skeleton is the unusually high connectivity $c = 6$ of the B1 atom on the C_2 axis.

A dynamic skeletal rearrangement of $B_{11}H_{11}^{2-}$ with a low activation barrier is in accord with the NMR equivalence of all the eleven B atoms, even at low temperature.[1,4] A diamond-square-diamond (dsd) mechanism, as indicated in Fig. 1, was postulated for this rearrangement by theoretical arguments.[1,5] (Note that structures $\mathbf{A}^1$ and $\mathbf{A}^2$ are two out of a manifold of 11!/2 undistinguishable tautomers in that degenerate rearrangement.)

We describe here a method to obtain pure crystals of $[B_{11}H_{11}]^{2-}$ salts along with the crystal structure analysis. The reaction of the $[B_{11}H_{11}]^{2-}$ anion with the Brønsted acids, the expansion of $[B_{11}H_{11}]^{2-}$ to give $[B_{12}H_{12}]^{2-}$ by the action of BH_3, and an oxidative fusion of $[B_{11}H_{11}]^{2-}$ to give $[B_{22}H_{22}]^{2-}$ are also described.[6]

2 SYNTHESIS AND STRUCTURE OF *CLOSO*-UNDECABORATES

Starting from $NaBH_4$ and $BF_3(OEt_2)$, we synthesized $Na[B_{11}H_{14}]$ and transformed this salt into $B_{11}H_{13}(SMe_2)$ by the action of SMe_2 in the presence of sulfuric acid, according

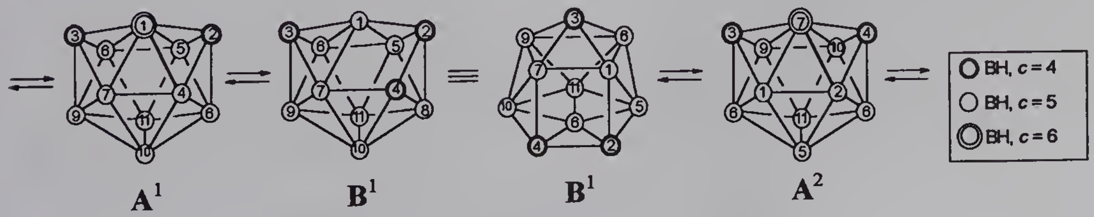


Figure 1 *dsd Mechanism for the $B_{11}H_{11}^{2-}$ skeletal rearrangement*

to a known route.[7,8] Dimethylsulfane-undecaborane can be deprotonated twice by bases like Li*t*Bu in tetrahydropyran (thp) or K[BHEt$_3$] in tetrahydrofuran (thf); under loss of SMe$_2$ it is transformed into the corresponding *closo*-undecaborates [Li(thp)$_3$]$_2$[B$_{11}$H$_{11}$] (83 %) and K$_2$[B$_{11}$H$_{11}$] (93 %). Undecaborates with non-metallic cations were crystallized from aqueous solutions of K$_2$[B$_{11}$H$_{11}$].

As judged from the ^{1}H, ^{11}B NMR and mass spectra, all the obtained *closo*-undecaborates were pure. Moreover, we characterized [Li(thp)$_3$]$_2$[B$_{11}$H$_{11}$] and [NBzlEt$_3$]$_2$[B$_{11}$H$_{11}$] by crystal structure analyses.

The solid state structure of [Li(thp)$_3$]$_2$[B$_{11}$H$_{11}$] is best described as ion triples built up from one undecaborate anion and two [Li(thp)$_3$]$^+$ cations. In contrast to these findings no remarkably short interionic contacts occur in [NBzlEt$_3$]$_2$[B$_{11}$H$_{11}$]. The structure of the anion is close to the idealized C_{2v} symmetry.

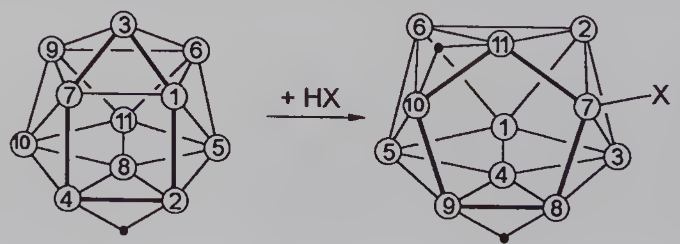
3 REACTIONS OF THE $[B_{11}H_{11}]^{2-}$ ANION WITH ACIDS

The *closo*-cluster anion $[B_{11}H_{11}]^{2-}$ reacts with trifluoroacetic acid CF$_3$COOH to give the *nido*-undecaborate $[B_{11}H_{13}(CF_3COO)]^-$, according to Eq. (1).

$$[B_{11}H_{11}]^{2-} \quad + \quad 2\ CF_3COOH \quad \longrightarrow \quad [B_{11}H_{13}(CF_3COO)]^- \quad + \quad CF_3COO^- \qquad (1)$$

Reaction (1) is certainly a multistep reaction. In order to get information about its mechanism, we followed the reaction by ^{11}B NMR. The one ^{11}B NMR signal of $[B_{11}H_{11}]^{2-}$ is transformed into a set of six doublets in the ratio 1:4:2:1:2:1 on the addition of CF$_3$COOH at −78 °C, indicating the formation of an eleven-vertex cluster with three vertices on a mirror plane and with two couples of vertices giving accidentally the same chemical shift. The observed 2D-^{11}B/^{11}B correlations reveal a skeletal arrangement that is in accord with structure **B**^{1} (Fig. 1). All the NMR spectroscopic evidence speaks for the presence of a $[B_{11}H_{12}]^-$ anion according to Fig. 2. This species is stable up to about −10 °C in the presence of excess CF$_3$COOH. Only the final product $[B_{11}H_{13}(CF_3COO)]^-$ is present at room temperature. During the second step of reaction (1), the acid molecule is added across the bond B1–B7 at the tetragonal open face of $[B_{11}H_{12}]^-$, this bond being opened; the proton thus fixed at B7 needs only to enter into a B3–B7 bridge for forming the final product (Fig. 2).

In the same way, the reaction of the $[B_{11}H_{11}]^{2-}$ anion with acetic or triflic acid gives corresponding *nido*-derivatives $[B_{11}H_{13}X]^-$, where X = CH$_3$COO or CF$_3$SO$_3$, whereas the



$[B_{11}H_{12}]^-$ **$[B_{11}H_{13}X]^-$**

Figure 2 *Protonation of $[B_{11}H_{11}]^{2-}$*

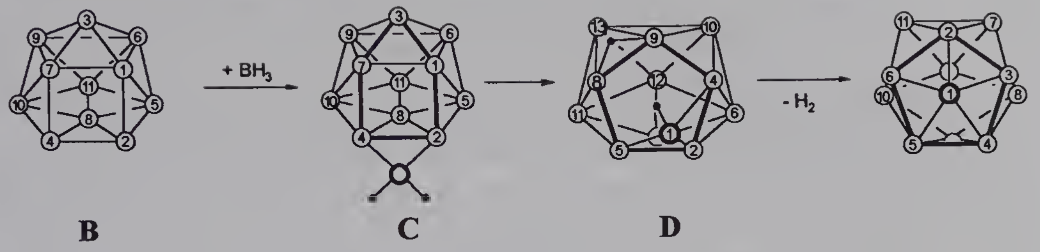


Figure 3 *Transformation of* $[B_{11}H_{11}]^{2-}$ *into* $[B_{12}H_{12}]^{2-}$ *upon addition of* BH_3

reaction with aqueous HCl results in the formation of *nido*-$[B_{11}H_{13}OH]^-$.

The small activation barrier of about 4-12 kcal/mol between type **A** and type **B** structures of $[B_{11}H_{11}]^{2-}$ (Fig. 1)[2] makes the lifetime of the intermediates **B** long enough to allow a rapid reaction like a protonation. The edge of structure **B** expected for the attack of a proton is the one that connects the low connectivity atoms B2 and B4, as actually observed. The same edge is also expected to invite Lewis acids like BH_3 for binding.

4 REACTION OF THE $[B_{11}H_{11}]^{2-}$ ANION WITH BH_3

The $[B_{11}H_{11}]^{2-}$ anion dissolved in $BH_3(NEt_3)$ is transformed into the $[B_{12}H_{12}]^{2-}$ anion under the evolution of H_2 at 130 °C, according to Eq. (2).

$$[B_{11}H_{11}]^{2-} + BH_3(NEt_3) \longrightarrow [B_{12}H_{12}]^{2-} + NEt_3 + H_2 \qquad (2)$$

We suppose that BH_3 adds to the low-connectivity edge B2-B4 of a type **B** structure (Fig. 1) comparable to the protonation of $[B_{11}H_{11}]^{2-}$. The adduct **C** (Fig. 3) rapidly rearranges at 130 °C: One of the B–H units of BH_3 adds to the B1–B7 bond of structure **C**, thus forming the B1–B4 bond and the hydrogen bridge B8–H–B9 of structure **D** (Fig. 3), in complete analogy to the addition of HX to $[B_{11}H_{12}]^-$. The bridging H atom and the one in *endo*-position at B1 are removed as molecular hydrogen at 130 °C, and the formation of the bonds B1–B8 and B1–B9 yields the anion $[B_{12}H_{12}]^{2-}$ as the final product.

5 OXIDATIVE FUSION OF TWO UNITS $[B_{11}H_{11}]^{2-}$

After earlier work[9] had indicated, that *nido*-undecaborate $[B_{11}H_{14}]^-$ could be fused to give a B_{22} cluster by the action of H_2O_2, Hosmane et al. repeated this oxidation and identified the cluster anion by means of X-ray analysis to be *conjuncto*-$[B_{22}H_{22}]^{2-}$.[10]

Not yet familiar with these results, we oxidized $[B_{11}H_{11}]^{2-}$ with $FeCl_3$ in an aqueous solution and precipitated $[NBzlEt_3]_2[B_{22}H_{22}]$ on addition of the corresponding ammonium chloride in a 62 % yield.

$$2\,[B_{11}H_{11}]^{2-} + 2\,Fe^{3+} \longrightarrow [B_{22}H_{22}]^{2-} + 2\,Fe^{2+} \qquad (3)$$

Single crystals of $[NBzEt_3][N(PPh_3)_2][B_{22}H_{22}]$ were analyzed by X-ray diffraction methods. It was showed that a $[B_{12}H_{10}]^{2-}$ unit, derived from icosahedral $[B_{12}H_{12}]^{2-}$ by formally removing two neighbouring H atoms, is bound to a $B_{10}H_{12}$ unit, derived from *nido*-$B_{10}H_{14}$ by removing the two bridging H atoms, in a way that the boron atoms of the B_{12} unit replace these bridging atoms, thus obtaining the unusual connectivity $c = 7$.

Remarkably long bonds are found for the four B–B connections between the *closo*-B_{12} and the *nido*-B_{10} unit (189 to 194 pm). With the exception of the bonds in the B_{12}–B_{10} linkage area, the bonds in the B_{12} and in the B_{10} unit are nicely comparable to those of *closo*-$[B_{12}H_{12}]^{2-}$,[11] and *nido*-$B_{10}H_{14}$,[12] respectively.

Thirteen ^{11}B NMR signals are resolved, one of which is a singlet. A unique assignment of all signals is possible on the basis of a 2D-$^{11}B/^{11}B$ COSY NMR spectrum. No indications for cage fluxionality were found, that had been postulated in the literature.[10] The ^{11}B chemical shifts of the B_{12} unit were located in the range –3.5 to –29.0 ppm. The average value is –13.4 ppm, as compared to –16.2 ppm for $[B_{12}H_{12}]^{2-}$.[13] The chemical shift values of the B_{10} unit are much closer to those of *nido*-$B_{10}H_{14}$[14] than to those of *arachno*-$B_{10}H_{12}(SMe_2)_2$.[15] The B_{10} unit of $[B_{22}H_{22}]^{2-}$ formally differs from $B_{10}H_{14}$ by the replacement of two BHB (3c2e) bonds by BBB (3c2e) bonds, a procedure that does not largely alter the *nido* character. Analogously, the B_{12} unit of $[B_{22}H_{22}]^{2-}$ differs from $[B_{12}H_{12}]^{2-}$ by the replacement of two BH (2c2e) bonds by two BBB (3c2e) bonds, which again should preserve *closo* character for the B_{12} unit. We conclude that the $[B_{22}H_{22}]^{2-}$ anion consists of a *closo*-B_{12} and a *nido*-B_{10} unit.

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References

1. E. I. Tolpin, W. N. Lipscomb, *J. Am. Chem. Soc.* **1973**, *95*, 2384.
2. D. A. Kleier, D. A. Dixon, W. N. Lipscomb, *Inorg. Chem.* **1978**, *17*, 166.
3. E. H. Wong, L. Prasad, E. J. Gabe, M. G. Gatter, *Inorg. Chem.* **1983**, *22*, 1143.
4. L. Muetterties. E. L. Hoel, C. G. Salentine, M. F. Hawthorne, *Inorg. Chem.* **1975**, *14*, 950.
5. R. B. King, *Inorg. Chim. Acta* **1981**, *49*, 237.
6. O. Volkov, W. Dirk, U. Englert, P. Paetzold, *Z. Anorg. Allg. Chem.*, in press.
7. L. J. Edwards, J. M. Makhlouf, *J. Am. Chem. Soc.* **1966**, *88*, 4728
8. D. L. Keller, J. G. Kester, J. C. Huffmann, L. J. Todd, *Inorg. Chem.* **1993**, *32*, 5067.
9. G. B. Dunks, K. Barker, E. Hedaya, C. Hefner, K. Palmer-Ordonez, P. Remec, *Inorg. Chem.* **1981**, *20*, 1692.
10. N. S. Hosmane, A. Franken, G. Zhang, R. R. Srivastava, R. Y. Smith, B. F. Spielvogel, *Main Group Met. Chem.* **1998**, *21*, 319.
11. J. A. Wunderlich, W. N. Lipscomb, *J. Am. Chem. Soc.* **1960**, *82*, 4427.
12. A. Tippe, W. C. Hamilton, *Inorg. Chem.* **1969**, *8*, 464.
13. N. N. Greenwood, J. H. Morris, *Proc. Chem. Soc.* **1963**, 338.
14. W. D. Phillips, H. C. Miller, E. L. Muetterties, *J. Am. Chem. Soc.* **1959**, *81*, 4496.
15. D. E. Hyatt, F. R. Scholer, L. J. Todd, *Inorg. Chem.* **1967**, **6**, 630.

Synthesis of Schiff Bases and Monoalkylamino Derivatives of *closo*-Dodecaborate(2–) Anion

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Introduction

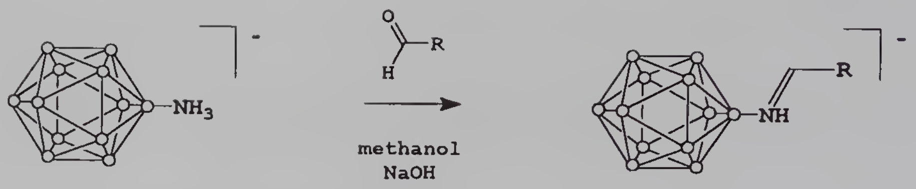
Dodecahydro-*closo*-dodecaborate(2-) anion $[B_{12}H_{12}]^{2-}$ as well as carboranes $C_2B_{10}H_{12}$ have been considered for a long time as promising boron moieties for boron neutron capture therapy[1]. The $[B_{12}H_{12}]^{2-}$ anion is especially attractive due to its simple synthesis from ^{10}B-enriched reagents and high water solubility of their derivatives as sodium salts. However, the absence of clearly defined reaction center in the $[B_{12}H_{12}]^{2-}$ anion due to its high, close to spherical, symmetry and its high reactivity in respect to electrophiles often result in mixtures of polysubstituted products. One way to solve this problem is an introduction of a primarily reaction center, such as hydroxy, mercapto, or amino group or iodine atom.

The $[B_{12}H_{11}OH]^{2-}$ anion is a very weak nucleophile and its alkylation requires strong basic conditions[2,3]. Alkylation of the $[B_{12}H_{11}SH]^{2-}$ anion generally results in disubstituted sulfonium derivatives $[B_{12}H_{11}SR_2]^-$ [4]. The possibility of the B-C bond formation by the palladium-catalyzed coupling of $[B_{12}H_{11}I]^{2-}$ with Grignard reagents was demonstrated recently[5]. Alkylation of the $[B_{12}H_{11}NH_3]^-$ anion gives, as a rule, mixture of alkylation products with different substitution degree - $[B_{12}H_{11}NH_2R]^-$, $[B_{12}H_{11}NHR_2]^-$, and $[B_{12}H_{11}NR_3]^-$ [6,7]

In this contribution we describe a synthesis of Schiff bases derived from aminoundecahydro-*closo*-dodecaborate anion $[B_{12}H_{11}NH{=}CHR]^-$ and their reduction into monosubstituted amines $[B_{12}H_{11}NH_2CH_2R]^-$.

Results and Discussion

Synthesis of Schiff Bases. The reaction of $(Bu_4N)[B_{12}H_{11}NH_3]$ with aldehydes in methanol in the presence of catalytic amounts of alkali gives in high yield *N*-protonated Schiff bases $[B_{12}H_{11}NH{=}CHR]^-$ (R = C_6H_5, 2-C_6H_4OMe, 4-C_6H_4OMe, 4-C_6H_4SMe, 4-$C_6H_4NMe_2$, 4-$C_6H_4NHCOMe$, 4-C_6H_4CN, 4-C_6H_4Br, 4-C_6H_4Cl, 1-$C_{10}H_7$, 2-$C_{10}H_7$, CH=CH-Me, CH=CH-Ph) (Scheme 1). Immediately after addition of a few drops of sodium hydroxide solution to solution of $(Bu_4N)[B_{12}H_{11}NH_3]$ and aldehyde in methanol, the color of the solution turned yellow and after stirring for 20-120 min at room temperature, the corresponding Schiff bases $(Bu_4N)[B_{12}H_{11}NH{=}CHR]^-$ precipitated.



o = BH(B)

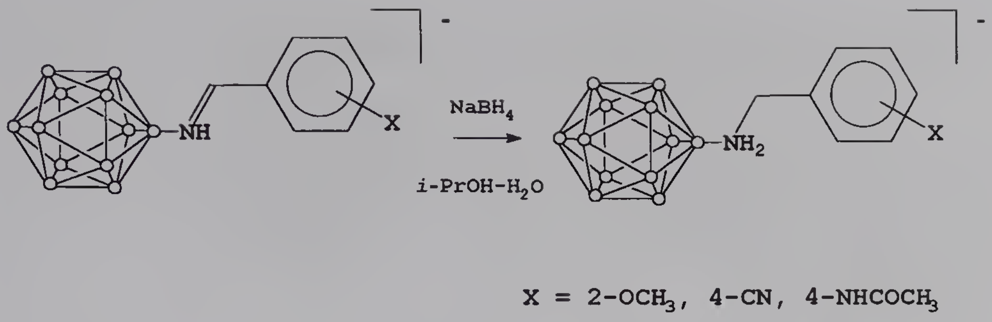
R = C_6H_5, 2-C_6H_4OMe, 4-C_6H_4OMe, 4-C_6H_4SMe, 4-$C_6H_4NMe_2$, 4-C_6H_4NHCOMe, 4-C_6H_4CN, 4-C_6H_4Br, 4-C_6H_4Cl, 1-$C_{10}H_7$, 2-$C_{10}H_7$, CH=CH-Me, CH=CH-Ph

Scheme 1

The ^1H NMR spectra of the Schiff bases in dimethylsulfoxide-d_6 contain signals of the N-H protons of the protonated imine group in the range of 10.7-12.6 ppm and of the C-H hydrogens of the imine group at 8.0-9.5 ppm. The signals normally appear as doublets (J ~ 19 Hz). The signal of the protonated imine N-H hydrogen rapidly disappears after addition of D_2O (the doublet of the imine C-H hydrogen transforms into the singlet) and is solvent-dependent (f.e., for $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}N(CH_3)_2]$, the N-H proton signal appears at 10.78 and 8.60 ppm in DMSO-d_6 and $CDCl_3$, respectively). The ^{13}C NMR spectra contain a signal of the imine carbon atom in the range of 164-170 ppm. The IR spectra of the Schiff bases contain a strong band of the C=N stretching at 1630-1650 cm^{-1} and bands of the N-H protons stretch vibrations which usually appear as two sharp bands approximately at 3250 and 3280 cm^{-1}.

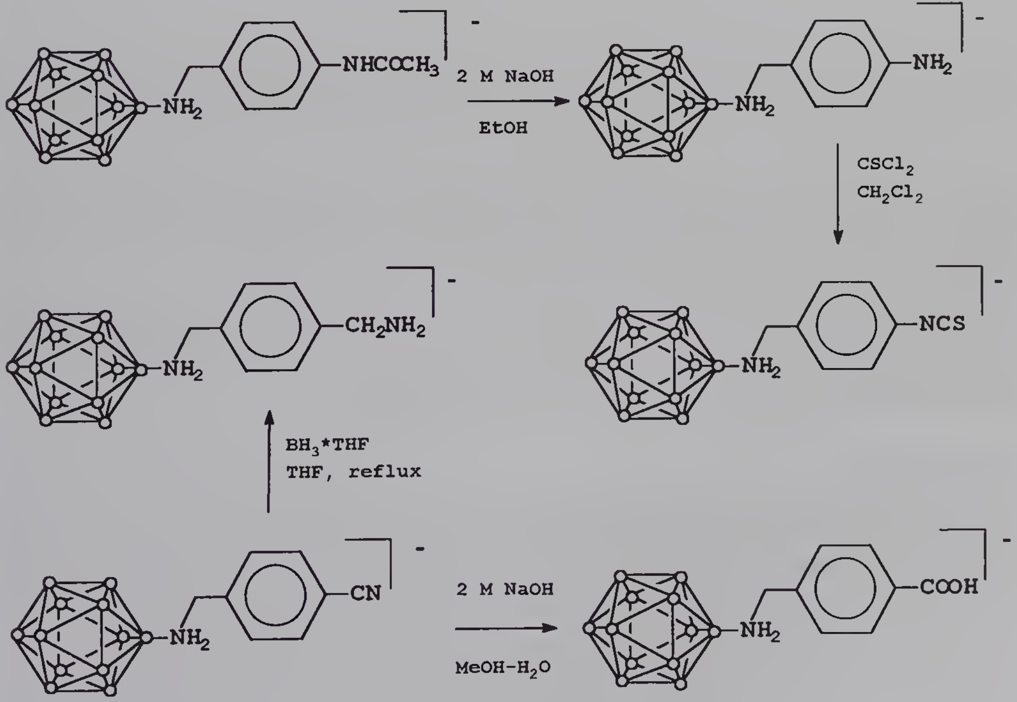
Structure of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]$ (I) and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$ (II). Molecular crystal structures of $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}4\text{-}NMe_2]{*}CHCl_3$ and $(Bu_4N)[B_{12}H_{11}NH{=}CHC_6H_4\text{-}2\text{-}OMe]$ were determined using the method of single crystal X-ray diffraction analysis. Compounds **I** and **II** crystallize in the monoclinic space group $P2_1/c$ with Z = 4. The unit cell parameters are a = 11.465(6) Å, b = 21.314(7) Å, c = 16.625(6) Å, β = 101.38(3)° for **I** and a = 10.282(2) Å, b = 20.272(5) Å, c = 17.052(3) Å, β = 105.31(2)° for **II**. Both anions have *trans*-configuration (Figure). The lengths of the B-N bond are 1.517(7) and 1.525(4) Å, respectively for **I** and **II.** The imine N=C bonds in **I** and **II** are 1.274(6) and 1.274(3) Å, respectively, which is typical for the C=N double bonds. The conformation of the substitutents in the both anions studied is close to planar. Strong intramolecular hydrogen bonding between the imine hydrogen atom and the methoxy oxygen atom at the *ortho*-position of the benzene ring (H(N1)...O(1) 1.98(2) Å) was found in the structure **II**.

Reduction of the Schiff Bases. Reduction of the Schiff bases $(Bu_4N)[B_{12}H_{11}NH{=}CHAr]$ (Ar = 2-$C_6H_4OCH_3$, 4-C_6H_4CN, 4-$C_6H_4NHCOCH_3$) with sodium borohydride in aqueous isopropanol (1 : 3) at room temperature results in the corresponding amines $(Bu_4N)[B_{12}H_{11}NH_2CH_2Ar]$ (Scheme 2).



Scheme 2

Functional Derivatives of the $[B_{12}H_{12}]^{2-}$ Anion. The described above mild method of synthesis of monoalkylamino derivatives of the *closo*-dodecaborate anion was used to prepare boron compounds containing functional groups on the aromatic ring (Scheme 3). Amine $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}NH_2]$ was prepared by deprotection of the acetamide $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}NHCOCH_3]$ in refluxing 2 M ethanolic sodium hydroxide. Alkaline hydrolysis of the nitrile $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}CN]$ in refluxing 2 M solution of sodium hydroxide in aqueous methanol (1:3) resulted in the corresponding acid $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}COOH]$ and reduction of the nitrile with BH_3*THF complex in refluxing tetrahydrofuran gave the corresponding amine $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}CH_2NH_2]$. The isothiocyanate $(Bu_4N)[B_{12}H_{11}NH_2CH_2C_6H_4\text{-}4\text{-}NCS]$ was prepared by the treatment of the corresponding amine with thiophosgene in dichloromethane.



Scheme 3

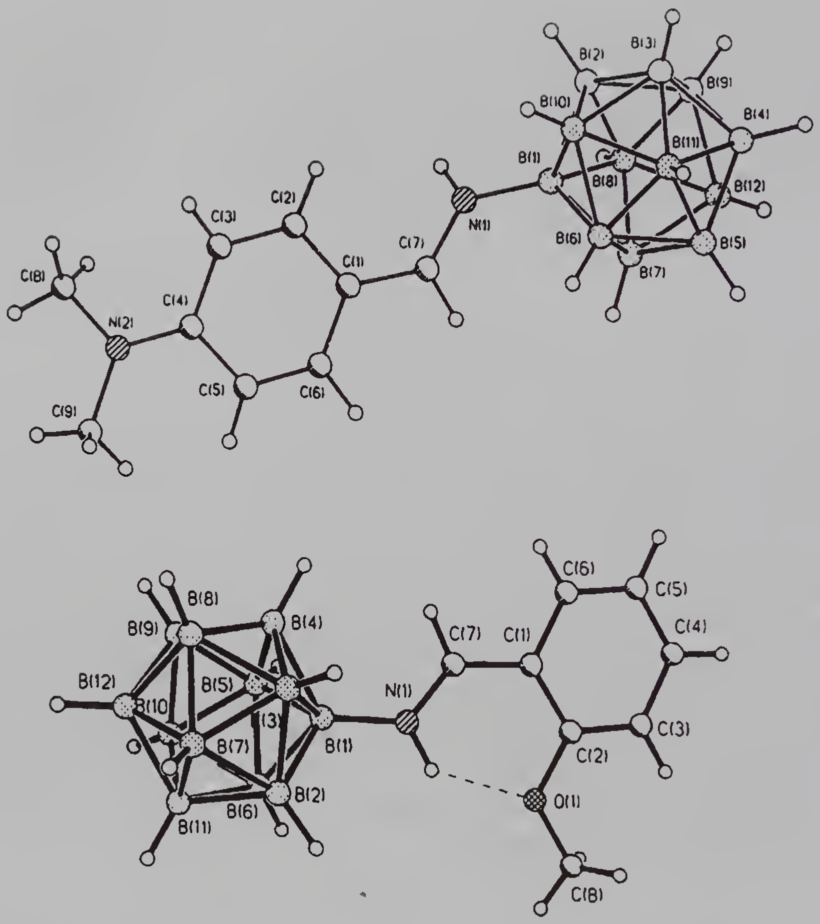


Figure *Structures of* $[B_{12}H_{11}NH{=}CHC_6H_4\text{-4-}NMe_2]^-$ *and* $[B_{12}H_{11}NH{=}CHC_6H_4\text{-2-}OMe]^-$

The functional derivatives prepared can be used not only for boron neutron capture therapy, but also as linkers for attachment of radioactive halogen labels to biomolecules for purposes of nuclear medicine[8].

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References

1. M.F. Hawthorne, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 950.
2. T. Peymann, E. Lork, and D. Gabel, *Inorg. Chem.*, 1996, **35**, 1355.
3. I.B. Sivaev, S. Sjöberg , V.I. Bregadze, D.Gabel, *Tetrahedron Lett.*, 1999, **40**, 3451.
4. D. Gabel, D. Moller, S. Harfst, J. Röesler, and H. Ketz, *Inorg. Chem.*, 1993, **32**, 2276.
5. T. Peymann, C.B. Knobler, and M.F. Hawthorne, *Inorg. Chem.*, 1998, **37**, 1544.
6. T. Peymann, E. Lork, M. Schmidt, H. Nöth, and D. Gabel, *Chem. Ber.*,1997, **130**, 795.
7. B. Grüner, B. Bonnetot, and H. Mongeot, *Collect. Czech. Chem. Soc.*, 1997, **62**, 1185.
8. V. Tolmachev, A. Bruskin, I. Sivaev, S. Sjöberg, Abstr. X Int. Conf. Boron Chem., Durham, 1999.

Chemistry of Inner Sulfonium Salts of Dodecaborane

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1. INTRODUCTION

Fully or partially charge-compensated complexes of general formulae $L_2B_{12}H_{10}$ or $[LB_{12}H_{11}]^-$ can be viewed as derived from $[B_{12}H_{12}]^{2-}$ by substitution of two or one H^- ligands for two or one neutral $2e^-$ donor molecules. When L is a sulfide, the above complexes may be considered as the inner sulfonium salts of the dodecaborane dianion:

sulfonium salt

Inner sulfonium salts of dodecaborane

$(Me_2S)B_{12}H_{11}^-$ **(1)** and $(Me_2S_2)B_{12}H_{10}$ **(2)** were obtained by Muetterties *et al.* [2] from the reaction of diborane with dimethylsulfide at 150°C and later from that of $[H_3O_2][B_{12}H_{12}]$ with dimethyldisulfide followed by transmethylation with Me_3SI[3]. Two isomers of **(2)** were detected by Kaczmarczyk *et al.*[4] after the reaction of $Na_2B_{12}H_{10}$ with DMSO in the presence of Ac_2O. Two isomers obtained after the reaction of $Li_2B_{12}H_{10}$ were identified as, 1, 12- and 1, 7-$(Me_2S)_2B_{12}H_{10}$ **(3,4)** from their ^{11}B NMR spectra. It was shown that the pyrolysis of the BH_3SMe_2 complex yielded **(1)**, **(3)** and **(4)** which were characterized by single-crystal X-ray diffraction analysis.[6] Here we report results obtained in the study of the chemistry of **(1)** and the isomers of **(2)**.

2. ISOLATION OF 1,2-$(Me_2S)_2B_{12}H_{10}$

Heating of BH_3 SMe_2 in a closed vessel at 130°C produces 1,2-$(Me_2S)_2B_{12}H_{10}$ **(5)** in 1.3% yield. The compound was characterized by its ^{11}B NMR spectrum and X-ray analysis (Fig. 1). The low yield and the ^{11}B NMR pattern similar to that of **(4)** are responsible for its not being detected earlier.

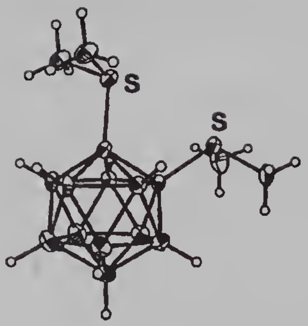


Figure 1 *The Molecular Structure of $1,2\text{-}(Me_2S)B_{12}H_{10}$*

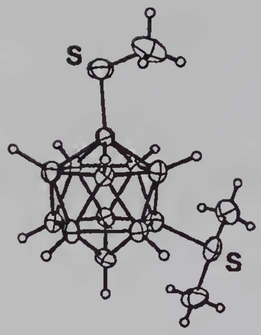
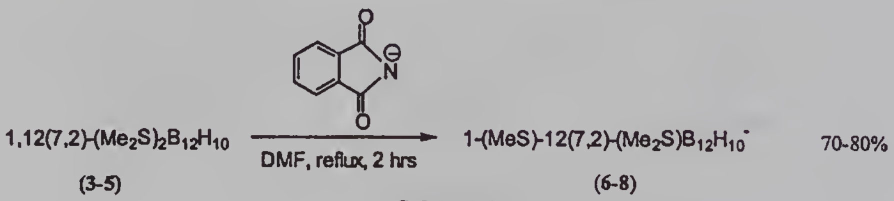


Figure 2 *The Molecular Structure of $1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}^-$*

3. SYNTHESIS OF DERIVATIVES OF $(Me_2S)B_{12}H_{11}^-$ (1) and $(Me_2S)_2B_{12}H_{10}$ (2)

3.1 Synthesis of Sulfide Anions by Reactions with Nucleophiles



Scheme 1

Muetterties *et al.*[7] showed that n-Bu_3P or potassium phtalimide are capable of removing a methyl group from a sulfur in $(Me_2S)_2B_{10}H_8$. Similarly, Soloway *et al.*[8] used phtalimide ion to prepare $[(MeS)(Me_2S)B_{12}H_{10}]^-$ from a mixture of isomers of **(2)**. We obtained and characterized the $[NMe_4]^+$ salts of the sulfide-sulfonium anions of **(3-5)**.

The $[MePPh_3]^+$ salt of **(4)** was characterized by X-ray analysis (Fig. 2). By a similar procedure $[(MeS)B_{12}H_{11}]^{2-}$ **(9)** was prepared from **(1)** and characterized as the $[MePPh_3]^+$ salt (Fig. 3). n-BuLi in THF can be used to obtain monoanions of **(3-5)** albeit in lower yield. If excess phtalimide is used and the reflux is carried out for a longer time, bissulfide dianions become major products of the reaction.

3.2 Synthesis of Dianions by Reduction with Alkali Metals

(3-5) react with excess of sodium or potassium in liquid ammonia producing exclusively dianions **(10-12)** in which one methyl group is removed from each sulfur.

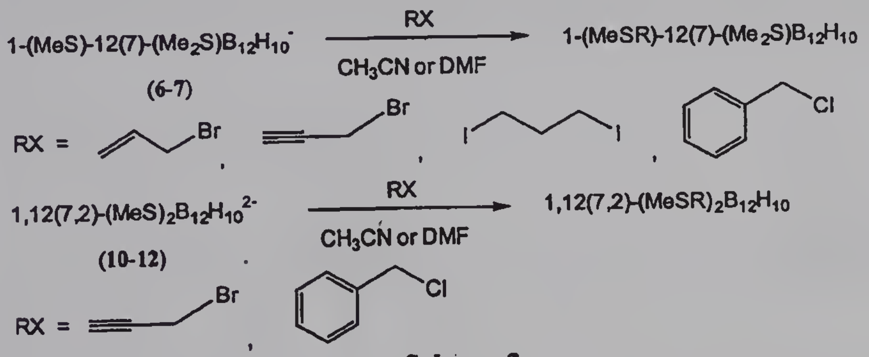
$$\underset{\textbf{(3-5)}}{1,12(7,2)\text{-}(Me_2S)_2B_{12}H_{10}} \xrightarrow[\substack{-40^{\circ}C \\ M = Na, K}]{M,\ NH_{3(l)}} \underset{\textbf{(10-12)}}{1,12(7,2)\text{-}(MeS)_2B_{12}H_{10}^{2-}} \quad 80\text{-}90\%$$

Scheme 2

Similarly, (9) can be obtained by reduction of (1). The reduction probably proceeds through formation of intermediate radical-anion(s) followed by C-S bond cleavage(s).

3.3 Alkylation of Anions

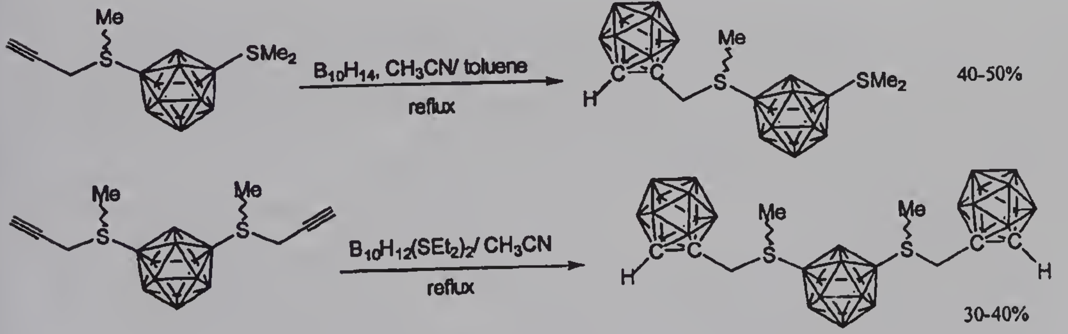
Mixtures of isomers of $(MeS)(Me_2S)B_{12}H_{10}^-$ were alkylated by Soloway *et al.* [8] using alkylhalides and tosylates. We obtained and characterized several products starting from isomerically pure anions **(6-7)** and **(10-12)**. Monoalkylation yields a racemic product. Since two chiral centers appear upon alkylation of **(10-12)**, a mixture of *meso-* and *(d,l)*-diastereomers is obtained. There is no evidence for diastereomers in the ^1H NMR spectra of 1,7- and 1,12-derivatives, but in the case of 1,2-$(HCCCH_2SMe)_2B_{12}H_{10}$ two diasteromers are detected probably, because of the proximity of the chiral centers.



Scheme 3

3.4 Synthesis of Dodecaborane-*ortho*-carborane Oligomers

Mono- and bispropargylsulfonium compounds obtained by alkylation of **(6,7)** and **(10-12)**, with propargyl bromide react with $L_2B_{10}H_{12}$ ($L = Et_2S$, CH_3CN) to yield two- and three-cage oligomers in moderate yields. These molecules contain a dodecaborane cage linked to one or two *ortho*-carborane molecules *via* an -$S(CH_3)$- CH_2- bridge(s).



Scheme 4

3.5 Oxidation of Anions

Sulfide, sulfide-sulfonium and bissulfide anions react with hydrogen peroxide in acetonitrile at room temperature yielding the corresponding sulfoxides. Excess of H_2O_2 leads to the formation of sulfones. 1, 12(7)-$(MeSO)_2B_{12}H_{10}^{2-}$ and 1-$(MeSO_2)$-12(7)-

$(MeSO)B_{12}H_{10}^{2-}$ were observed by ^1H and ^{11}B NMR spectroscopy as intermediates in the preparation of 1, 12(7)-$(MeSO_2)_2B_{12}H_{10}^{2-}$. No cage degradation was observed.

3.6 Bromination of $(Me_2S)_2B_{12}H_{10}$ Isomers

Considering the electron-withdrawing nature of the tertiary sulfonium substituents, one could expect that the charge distribution in the isomers of $(Me_2S)_2B_{12}H_{10}$ would be similar to that of the isomers of $C_2B_{10}H_{12}$. Not surprisingly, the behavior of the 1,7 and 1, 12 isomers of $(Me_2S)_2B_{12}H_{10}$ towards electrophilic brominations mimics that of *m*- and *p*- carborane.[9] Bromination of the 1,7 isomer occurs at positions 9, 10 (Fig. 4). A monohalogenated derivative can be isolated as a major product if one equivalent of reagent is used. When reacted with excess Me_2SBr_2 at room temperature, the 1, 12 isomer produced only the monohalogenated product. Under similar conditions the rate of bromination of the 1, 12 isomer was always considerably slower than that for the 1, 7 isomer.

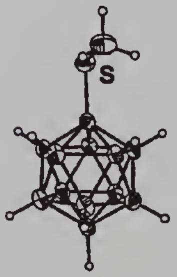


Figure 3 *The Molecular Structure of* $(MeS)B_{12}H_{11}^{2-}$

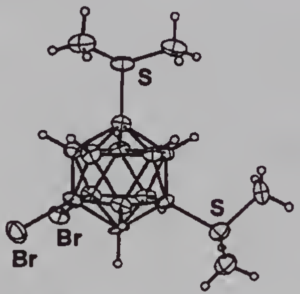


Figure 4 *The Molecular Structure of* 1,7-(Me_2S)-9,10-$Br_2B_{12}H_{10}$

ACKNOWLEDGMENT

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References

1. H. C. Miller, N. E. Miller, E. L. Muetterties, *J. Am. Chem. Soc.*, 1963, **85**, 3885.
2. H. C. Miller, N. E. Miller, E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 1456.
3. W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, E. L. Muetterties, *J. Am. Chem. Soc.*, 1964, **86**, 3973.
4. J. Wright, A. Kaczmarczyk, *Inorg. Chem.*, 1973, **12**, 1453.
5. S. A. Jasper, Jr., R. B. Jones, J. Mattern, J. C. Huffman, L. J. Todd, *Inorg. Chem.*, 1994, **33**, 5620.
6. E. J. M. Hamilton, G. T. Jordan IV, E. A. Meyers, S. G. Shore, *Inorg. Chem.*, 1996, **35**, 5335.
7. W. H. Knoth, W. R. Hertler, E. L. Muetterties, *Inorg. Chem.*, 1964, **4**, 280.
8. R. L. Sneath, Jr., A. H. Soloway, A. S. Dey, *J. Med. Chem.*, 1974, **17**, 796.
9. H. Beall and W. N. Lipscomb, *Inorg. Chem.* 1967, **6**, 874.

Macropolyhedral Boron-containing Cluster Chemistry. Further Progress Beyond the Icosahedron. July 1999

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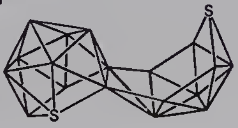
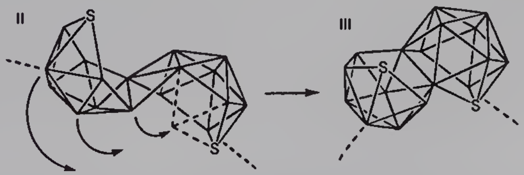
Boron-containing cluster chemistry has a natural single-cluster limit of about twelve vertices, as attained / approached by the very stable icosahedral cluster structures of $[B_{12}H_{12}]^{2-}$ and of the $C_2B_{10}H_{12}$ isomers. To liberate the full potential of polyhedral boron chemistry, a much bigger general matrix of behaviour is needed. Sigma-linking of the single clusters that conventionally typify borane chemistry, or their fusion at a common metal atom, can open up ways of doing this (see other articles in this volume). However, for fundamental development, the twelve-vertex barrier needs to be transcended, and another approach is needed here. One such approach is the more intimate fusion of single clusters to give very big clusters in which contiguous interboron multicentre bonding extends through the fused linkage. This 'macropolyhedral' area is potentially huge. Here we report new results from metallaborane work that attempts further to explore and develop this chemistry.

We reported to the previous IMEBORON meeting on a variety of macropolyhedral thiaboranes and their rearrangements (*e.g.* structures **I** to **V**).[1] This work is still on-going.[2,3] A new finding here is the isomerism of $S_2B_{16}H_{16}$, which exhibits both structures **V** and **VI**. Extensive isomerism will be a fascinating feature of future macropolyhedral chemistry.

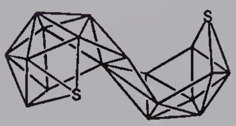
I



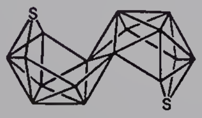
II
III



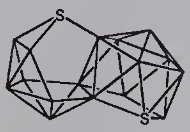
IV



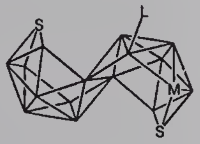
V



VI



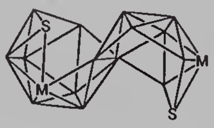
VII



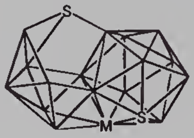
Addition of transition-element centres to these sulphur-containing macropolyhedrals generates an extensive variety of new architectures, *e.g.* **VII** - **IX**, and presages much further novelty, well exceeding that exhibited by the macropolyhedral thiaboranes themselves.[1,4]

In contrast to these macropolyhedral thiaborane results, however, transition-element Aufbau based on non-sulphur-containing species gives quite different diversities of behaviour. Basic structures from reactions of *syn*-$B_{18}H_{22}$ with metal reagents such as $[\{Ir(C_5Me_5)Cl_2\}_2]$ and $[\{(C_6H_6)RuCl_2\}_2]$ include $\{MB_{18}\}$'s of configuration **X** and, *via* B-vertex loss, $\{MB_{17}\}$'s of configuration **XI**. Double metal addition yields $\{M_2B_{18}\}$'s of configuration **XII** with a planar diamond *conjuncto* link, and triple addition gives the very condensed $\{M_3B_{18}\}$ species $[(C_5Me_5)Ir_3B_{18}H_{15}(OH)]$ of configuration **XIII A**.

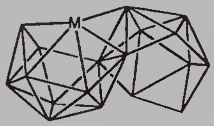
VIII



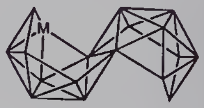
IX



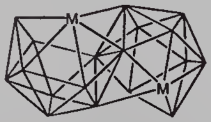
X



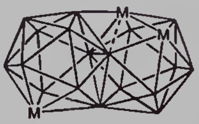
XI



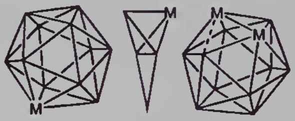
XII



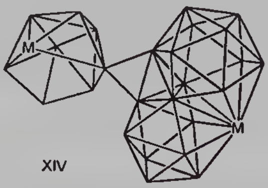
XIII A



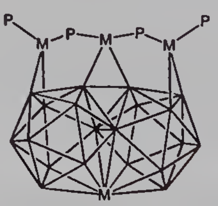
XIII B



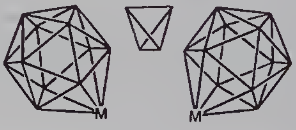
Consideration of this very condensed structure of $[(C_5Me_5)Ir_3B_{18}H_{15}(OH)]$ introduces an interesting structural concept with potentially important general connotations. Specifically, the central non-hydridic tetrahedral core (see **XIII B**) leads to a new 'megaloborane' concept for globular structures based on *central borons-only cores* surrounded by units based on boron hydrides which themselves may or may not be mutually fused.[1,5]



XIV



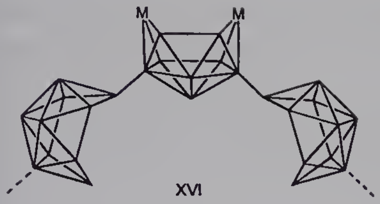
XVA



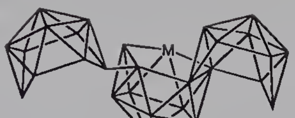
XVB

This $\{Ir_3B_{18}\}$ assembly is formed by multiple-atom Aufbau on *syn*-$B_{18}H_{22}$. In a second approach to this type of condensed compound, $[(PMe_3)_4(CO)Ir_2B_{26}H_{24}]$ (**XIV**) results from fusion of $[(PMe_3)_2(CO)HIrB_8H_{12}]$ with $B_{10}H_{14}$, using the concept of *molten boranes as solvents*.[6] A third type of approach, the conjunction of two anionic $[B_{10}H_{10}]^{2-}$ residues with $[PdCl_2(PPh_3)_2]$, results in $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$ (**XVA**).[5] These last two macropolyhedrals also have the globular boron-core cluster architecture (*e.g.* **XV B**), and have several other interesting features other than the $\{IrB_{18}H_{14}\}$ and $\{PdB_{20}H_{16}\}$ globules themselves.[5,6]

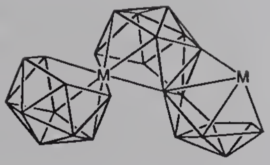
Use of the molten borane technique in another system, the fusion of $[(PMe_2Ph)_2PtB_8H_{12}]$ with $B_{10}H_{14}$, yields compounds that show an elegant progression of intimacy in intercluster fusion (**XVI** → **XVIII**),[7] and extension to the use of pre-formed macropolyhedrals themselves gives contiguous triple-cluster $[(PMe_2Ph)PtB_{26}H_{24}(PMe_2Ph)]$ **XIX** from *anti*-$B_{18}H_{22}$ and $[(PMe_2Ph)_2PtB_8H_{12}]$.[8] This may be the first molecular compound so intimately to fuse more than two clusters. Also, it very nicely links the **XVI** → **XVII** → **XVIII** progression of increasing intimacy of intercluster fusion to the culminating very condensed species such as **X**, **XIV** and **XV**.[7]



XVI

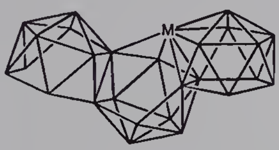


XVII

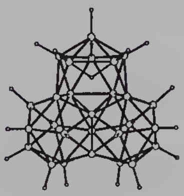


XVIII

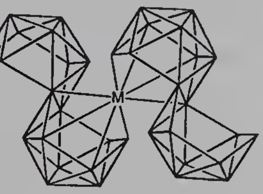
In contrast to large hollow-ball perceptions based on fullerene chemistry,[9] structures such as **X**, **XIV** and **XV** suggest an emerging new borane-based structural principle based on filled big balls, rather than hollow ones. Does this presage a new general globular 'megaloborane' chemistry, which will ultimately extend beyond a simple four-atom core unit? Ultimate viability here is supported by STO-3G *ab initio* calculations (at present a reasonably high level for preliminary surveys of such big molecules) on model systems based on domains of elemental boron matrices. These nicely stabilise in particular regions, *e.g.* neutral $B_{27}H_{21}$ (**XX**), based on a section of the solid-state matrix of β-rhombohedral boron.[5] This concept can be extended to other and bigger fragments to propose species such as $B_{84}H_{54}$,[5] although this is less likely to be synthetically viable on kinetic grounds, as it has a surface mostly of *endo* and bridging hydrogen atoms, expected to be reactive. In this regard $B_{27}H_{21}$ and $B_{84}H_{54}$ approach two extremes of surface character, because $B_{27}H_{21}$ has a surface of predominantly *exo* hydrogen atoms.



XIX



XX



XXI

These larger molecular assemblies often exhibit other interesting properties. These include a variety of surface and steric effects, for example as in *(a)* a waggling fluxionality of the $\{(Ph_3P)Pd(PPh_2)Pd(PPh_2)Pd(PPh_3)\}$ string over the surface of the $\{PdB_{20}H_{16}\}$ unit of **XV**,[6] *(b)* crevice behaviour resulting in restricted rotation of the PMe_3 groups of the $\{Ir(PMe_3)_2\}$ unit held in an eight-boron 'wedge' pocket in **XIV**,[7] and *(c)* extreme steric inter-subcluster interaction generating rigid slab-like species, as in the 77-atom $[Pt(B_{18}H_{20})_2]^{2-}$ anion **XXI** that also exhibits *(d)* an intimate interanionic stacking in the solid state.[10]

Conclusions

Studies in the macropolyhedral area continue to produce fascinating new chemistry, including new intercluster fusion modes, novel subcluster architectures not seen in single-cluster compounds, multiple fusions, and large slab-like molecules and other aggregates. Additionally, mutual proximity of the subclusters promotes unusual additional intercluster interactions ranging from weak 'agostic' to strong bridging bonds that can induce complete architectural changes. One fundamental significance is that, in macropolyhedrals that consist of fusions of clearly recognised single-cluster types, the chemistry generally takes a quite different course from that of the ostensible single-cluster models. This has many implications. Further, macropolyhedral heteroboranes appear to be much more malleable than the binary boron hydride macropolyhedrals for revealing the unpredictable new synthetic and structural phenomena in this hitherto poorly examined field. There are also potentialities for interesting supramolecular assemblies. Of possible ultimate high funda-mental significance is the principle of globular filled-cage 'megaloborane' structures, of which the synthesis will be a demanding challenge for future work.

We thank national funding agencies of our various countries for support. The presenting author (J. D. Kennedy) thanks in particular the UK EPSRC and the Royal Society.

References

1. J. D. Kennedy, in *Advances in Boron Chemistry,* Ed. W. Siebert, Royal Society of Chemistry, Cambridge, 1997, 451; T. D. McGrath, J. D. Kennedy, Y. M. McInnes and M. Thornton-Pett, *ibid.*, 480; T. Jelínek, B. Štíbr, J. D. Kennedy and M. Thornton-Pett, *ibid.*, 426.
2 T. Jelínek, J. D. Kennedy, B. Štíbr and M. Thornton-Pett, *Angew. Chem., Internat. Edn. Engl.*, 1994, **33**, 1599; T. Jelínek, J. D. Kennedy, B. Štíbr and M. Thornton-Pett, *Inorg. Chem. Commun.*, 1998, **1**, 179; T. Jelínek, I. Cisařová, B. Štíbr, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1998, 2965.
3 D. L. Ormsby, T. Jelínek, S. L. Shea, R. Greatrex, B.Štíbr and J. D. Kennedy, *Abstracts Tenth International Conference on Boron Chemistry (IMEBORON X), Durham, England, July 11-15 1999*, Abstract no. CA-8, p. 72; T. Jelínek, J. D. Kennedy, S. A. Barrett, M. Thornton-Pett and I. Cisařová, *ibid.*, Abstract no. CB-19, p.101; see also T. Jelínek, J. D. Kennedy, S. A. Barrett, M. Thornton-Pett and I. Cisařová, elsewhere in this volume.
4 P. Kaur, J. D. Kennedy, M. Thornton-Pett, T. Jelínek and B. Štíbr, *J. Chem. Soc., Dalton Trans.,* 1996, 1775; P. Kaur, M. Thornton-Pett, W. Clegg and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.,* 1996, 4155; P. Kaur, A. Brownless, S. D. Perera, P. A. Cooke, T. Jelínek, J. D. Kennedy, M. Thornton-Pett and B. Štíbr, *J. Organomet. Chem.,* 1998, **557**, 181.
5 H-J. Yao, C-H. Hu, J. Sun, R-S. Jin, P-J. Zheng, J. Bould, R. Greatrex, J. D. Kennedy, D. L. Ormsby and M. Thornton-Pett, *Collect. Czech. Chem. Commun.*, 1999, **64**, 927.
6 J. Bould, J. D. Kennedy, L. Barton and N. P. Rath, *J. Chem. Soc., Chem. Commun.*, 1997, 2405.
7 J. Bould, W. Clegg, S. J. Teat, L. Barton, N. P. Rath, M. Thornton-Pett and J. D. Kennedy, in *Boron Chemistry at the Millennium*, special edition of *Inorg. Chim. Acta*, 1999, **289**, 95.
8 Y-H. Kim, P. A. Cooke, N. P. Rath, L. Barton, R. Greatrex, J. D. Kennedy and M. Thornton-Pett, *Inorg. Chem. Commun.*, 1998, **1**, 375.
9 See, for example, A. Gindulyte, N. Krishnamachari, W. N. Lipscomb and L. Massa, *Inorg. Chem.*, 1998, **37**, 6546.
10 T. D. McGrath, T. Jelínek, B. Štíbr, M. Thornton-Pett and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1997, 2543.

Progress in the Chemistry of Fused-cage Boranes and Heteroboranes

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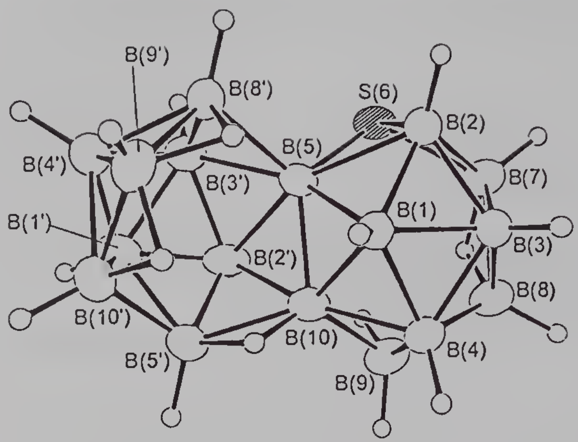
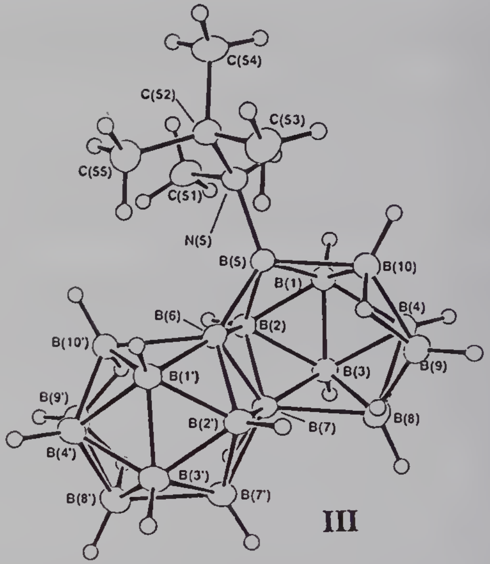
This presentation describes some recent extensions of studies concerned with the preparation, characterisation and chemistry of some larger boranes and heteroboranes of which the architecture consists of fused-cage skeletons that contain more than fifteen vertices. This extends work described in our previous IMEBORON IX[1] and deals with the following areas: *(a)* insertion of sulphur atoms into eighteen-vertex boranes and reactions of the resulting macropolyhedral thiaboranes; *(b)* reactions of eighteen-vertex boranes with isonitriles under various reaction conditions; *(c)* reactions of *anti*-$B_{18}H_{22}$ with pyridines. Other extensions, involving metallaborane work, are described elsewhere in this volume.

As we have previously described, the well-established and long-known *syn* and *anti* isomers of $B_{18}H_{22}$ easily react, in the form of their corresponding $[B_{18}H_{21}]^-$ monoanions, with elemental sulphur.[1,2,3] The two reactions give different macropolyhedral thiaboranes, and in each case the known eleven-vertex $[SB_{10}H_{11}]^-$ anion is a co-product. Whereas *anti*-$B_{18}H_{22}$ yields a nineteen-vertex monoanion,[2] $[S_2B_{17}H_{18}]^-$, the *syn* isomer gives a twenty-vertex monoanion,[3] $[S_2B_{18}H_{18}]^-$. Both anions are characterised by X-ray diffraction analyses and both have unusual and interesting structures. They are dithiaboranes: each contains two sulphur atoms, one in each of the two subclusters. We can now also describe the first macropolyhedral monothiaborane, also with interesting and so far unique structural features. This is a nineteen-vertex monoanion $[SB_{17}H_{20}]^-$ **I**, generated in 72 % yield by the reaction of *anti*-$B_{18}H_{22}$ with $K_2S_2O_5$ in aqueous THF solution; a small amount of the [*anti*-$B_{18}H_{21}]^-$ anion is also isolatable. X-ray diffraction analysis reveals that the structure of **I** consists of two ten-vertex subclusters: a *nido*-decaboranyl $\{B_{10}\}$ unit and an *arachno*-type $\{6\text{-}SB_9\}$unit, sharing two common boron vertices. The structure therefore nicely demonstrates a 10-vertex:10-vertex *arachno* : *nido* two-borons-in-common fusion, a significant but previously elusive target.

Both the dithiaboranes mentioned above undergo interesting rearrangement upon protonation. The twenty-vertex $[S_2B_{18}H_{19}]^-$ anion possesses a {BH} vertex that is extraordinary in that it is of cluster connectivity six, and forms the apex of an open hexagonal $\{B_6\}$ pyramid. Upon protonation, for example by using concentrated H_2SO_4, a neutral $S_2B_{18}H_{20}$ species is formed, in which this unusual {BH} vertex loses its cluster

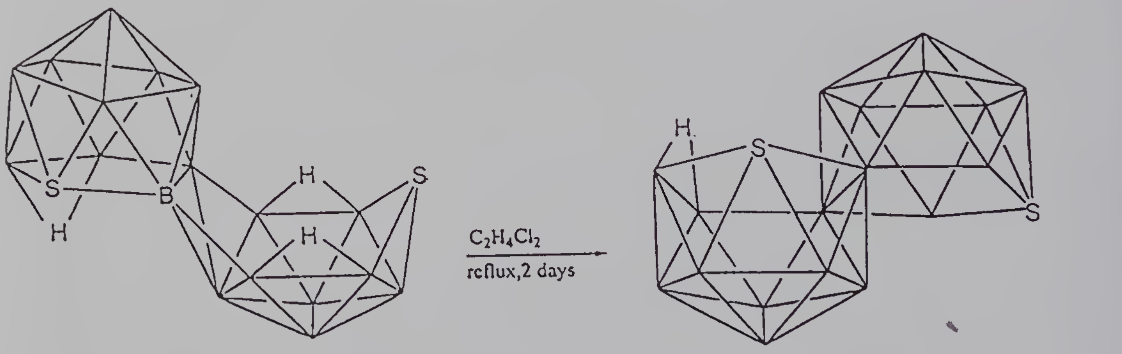


I



III

connectivity of six, probably reverting to a more usual cluster connectivity of five in mechanism involving a diamond-square-diamond rearrangement. Remarkably, upon deprotonation of neutral $S_2B_{18}H_{20}$ with tmnda (tetramethylnaphthalenediamine), the starting $[S_2B_{18}H_{19}]^-$ anion with its six-connectivity {BH} vertex is regenerated.[3] By contrast, a similar protonation of the nineteen-vertex *arachno* : *arachno* $[S_2B_{17}H_{18}]^-$ anion under comparable conditions results in a completely different process, yielding neutral *nido* : *nido* $S_2B_{17}H_{17}$,[4] entailing a dihydrogen loss and substantial swing in relative subculture orientation. A dehydrogenation of twenty-vertex $[S_2B_{18}H_{19}]^-$ can also be achieved, albeit thermally, for instance by prolonged heating in dichloromethane or toluene. The formulation of the resulting anion, $[S_2B_{18}H_{17}]^-$ **II**, is suggested by the results of NMR spectroscopy: its proposed structure involves two eleven-vertex *nido*-$\{SB_{10}\}$ subclusters joined *via* two common boron vertices. The sulphur atoms occupy the (10)-vertex in one subcluster and (9')-vertex in the other. The proposed generation of **II** is as follows:.

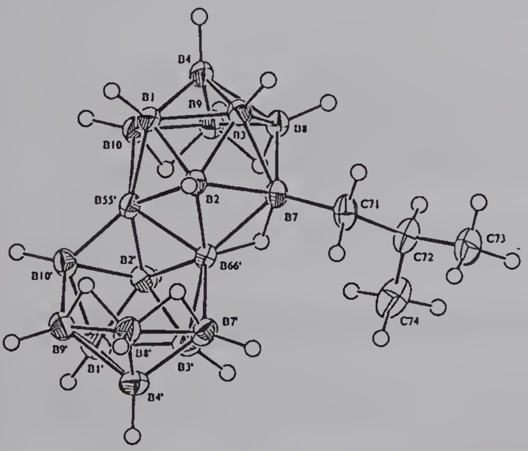


II

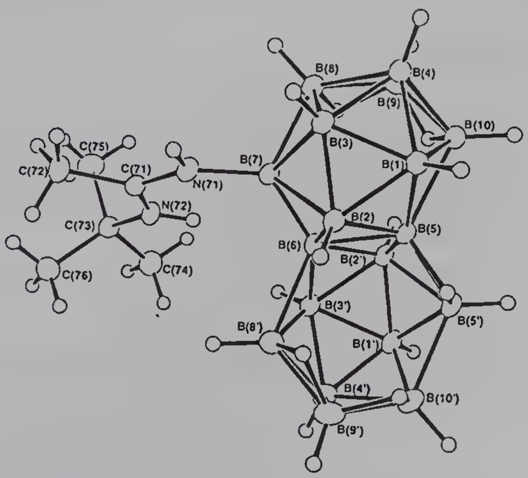
Our previous preliminary reports[5a,b] have indicated that reactions of $B_{18}H_{22}$ with isonitriles are most interesting, with many novel products, of which the nature depends upon the isonitrile and the solvent used. Thus, *anti*-$B_{18}H_{22}$ reacts with MeN≡C to give 7-

{MeNH)$C_2N_2HMe_2$}-*anti*-$B_{18}H_{22}$ that has an imidazole-ring-substituted vertex in the borane skeleton. On the other hand, ^{ter}BuN≡C performs quite differently, and the resulting products are strongly influenced by the solvent. In a non-polar solvent such as benzene there is a mixture of insertion compounds and ligand adducts of the 7-L-$B_{18}H_{20}$ type, in which L represents, for instance, ^{ter}BuMeNH (compound **III**). The insertion products so far identified are macropolyhedral carbaboranes, reported elsewhere.[5b]

By contrast, in polar solvents, such as chloroform and acetonitrile, ^{ter}BuN≡C reacts with *anti*-$B_{18}H_{22}$ to form several compounds that include mono- and disubstituted derivatives 7-L-*anti*-$B_{18}H_{21}$ **IV** and 7,7′-L_2-*anti*-$B_{18}H_{20}$ V, in which L, interestingly, is a simple ^{sec}Bu hydrocarbon substituent, *i.e.* CH_2CHMe_2. Here, ^{ter}BuN≡C behaves as an alkylating agent, with the elements of HCN being eliminated during the process. Both compounds **IV** and V exhibit marked fluorescence under UV radiation. For crystallographic confirmation, **IV** was converted to an anion **IVA** using tmnda, and it is of interest that the crystallography also revealed that it is the unsubstituted subcluster that loses a bridging proton to form the anion. Another product from the reaction of ^{ter}BuN≡C with *anti*-$B_{18}H_{22}$ in acetonitrile is 7-{(Me_3CNHMeC)NH}-*anti*-$B_{18}H_{20}$ **VI**, one of many mutually related ligand derivatives that may be isolated: in this set of compounds, the ligands derive from isonitrile oligomerisations.The solid-state structure of **VI** suggests zwitterionic character, with a formal positive charge on the carbon atom that is located between the two nitrogen atoms. Here the carbon-nitrogen interatomic distances of 131 pm and the planarity of the system support delocalised multiple-bond character for the N-C-N linkage, which would formally stabilise the positive charge on the carbon atom. Clearly, also, the constitution of this ligand shows an incorporation of the $CH_3C≡N$ solvent used in the reaction. By contrast, the reactions of the *syn*-$B_{18}H_{22}$ isomer with isonitriles under various conditions have so far only produced the [*syn*-$B_{18}H_{21}$]$^-$ anion as the only identifiable macropolyhedral product, although, as isolated, this may have oligomeric nitrogen-containing organic countercations; also, at elevated temperatures, isonitriles appear to polymerise in the presence of *syn*-$B_{18}H_{22}$. The variously coloured products can be separated on the basis of chromatography and their solubilities in polar solvents. They await characterisation.



IVA



VI

The reactions of *anti*-$B_{18}H_{22}$ with pyridines are interesting also. The basic reaction was reported long ago,[6] but the products were inconclusively investigated. With unsubstituted pyridine itself, we have now found that a bis(ligand)-substituted *arachno* : *nido* $py_2B_{18}H_{20}$ species **VII** is one of the many products. This compound involves one *nido*-decaboranyl $\{B_{10}\}$ subcluster, the second being of the *arachno* ten-vertex $\{6,9\text{-}L_2\text{-}B_{10}\}$cluster type. It can be seen that **VII** has a similar *arachno* : *nido* structural arrangement to that found for **I** discussed above. This reaction also results in $pyBH_3$, the $[anti\text{-}B_{18}H_{21}]^-$ anion, pyB_9H_{13} and an additional novel macropolyhedral compound **VIII**. X-ray diffraction analysis and NMR measurements characterise this last material as a $py_2B_{16}H_{18}$ species, *i.e.* a hexadecaborane bis(pyridine) complex. Its skeleton consists of two subclusters, *nido* ten-vertex $\{B_{10}\}$ and *arachno* eight-vertex $\{L_2B_8\}$, again with a two-borons-in-common fusion mode. This could perhaps be regarded as a Zwitterionic derivative of the so far unknown parent borane $B_{16}H_{22}$, although other rationalisations can be made. Mechanistically, this derivative **VIII** could originate from $py_2B_{18}H_{20}$ **VII**, in that two {pyBH} vertices are lost during attack of additional pyridine molecules at two other cluster boron positions. Because of the low solubility of **VIII** in common organic solvents and because of a partially disordered solid-state structure, the derivatives using 4-methylpyridine and 4-*iso*-propylpyridinewere also synthesised (**IX** and **X** respectively). X-ray diffraction work on **IX** required synchrotron radiation because of very small crystal size. A preliminary solution shows the heavier-atom structure illustrated. In contrast to this interesting *anti*-$B_{18}H_{22}$ behaviour, with *syn*-$B_{18}H_{22}$ and pyridine a dismantling of the macropolyhedral core has occured under all conditions attempted to date, and only $pyBH_3$ and pyB_9H_{13} have been isolated. On the other hand, it has been observed that *syn*-$B_{18}H_{22}$ reacts with $[(CH_3)_2N]_2SiH(CH_3)$ to produce a compound that, by NMR, has the same hexadecaboranyl $\{B_{16}\}$ cage as in the products **VIII**, **IX** and **X** from the pyridine reactions of *anti*-$B_{18}H_{22}$,[7] although the precise identity of the ligand system is at present uncertain.

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References

1 T. Jelínek, B. Štíbr, J. D. Kennedy and M. Thornton-Pett, *Advances in Boron Chemistry,* Ed. W. Siebert, Royal Society of Chemistry, Cambridge, 1997, 426.
2 T.Jelínek, J.D.Kennedy, B.Štíbr and M.Thornton-Pett, *Angew.Chem.Internat. Edn.Engl.*,1994, **33**, 1599-1601.
3 T. Jelínek, I. Cisařová, B. Štíbr, J. D. Kennedy and M. Thornton-Pett. *J. Chem. Soc., Dalton Trans.*, 1998, 2965-2967.
4 T. Jelínek, J. D. Kennedy, B. Štíbr and M. Thornton-Pett. *Inorg. Chem. Commun.*, 1998, **1**, 179-181.
5 a. T. Jelínek J. D. Kennedy, B. Štíbr and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1994, 1999-2000; b. 1995, 2404-2408.
6 R.L.Sneath and L.J.Todd, *Inorg.Chem.*, 1973, **12**, 44-48.
7 T. D. McGrath, unpublished observations in collaboration with the authors.

Synthesis and Structural Characterisation of the Anion *nido*-$[B_8H_{11}]^-$, and New Insights into the Structures of Other Octaborane Species

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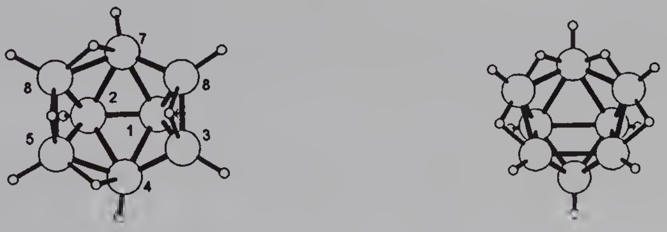
1 INTRODUCTION

The octaboranes remain one of the relatively unexplored areas of polyhedral borane chemistry. The known compounds are thermally fragile, and very little experimental work involving these species has been reported since the early 1970s. However, there has been continued interest in *nido*-octaborane(12) because of its unusual structure: B_8H_{12} crystallises with the *arachno*-8-vertex, six-membered open face geometry (ni-8<VI>) **1**,[1] rather than the five-membered open-face (ni-8<V>) geometry **2** that might have been predicted on the basis of Williams' early structural principles (Figure 1).[2] The (ni-8<V>) structure, generated by removing a high coordination vertex from a *closo*-9-vertex polyhedron (tricapped trigonal prism), has in fact been established for the compound *nido*-$S(\eta\text{-}C_5H_5Co)_2B_5H_7$,[3] which is isoelectronic with *nido*-B_8H_{12}. This sole borane exception to the early geometry rules has been explained (a) by using a different starting *closo*-polyhedron,[4] (b) by an alternative set of structural rules[5] and (c) by invoking steric crowding between *endo* and bridging hydrogen atoms.[6]



1

2

Figure 1 *The 8-vertex, six-membered open-face geometry (ni-8<VI>) 1 adopted by B_8H_{12}, and the five-membered open-face (ni-8<V>) geometry 2 that might have been predicted on the basis of Williams' early structural principles.*

More recently Tebben, Williams and Bausch have carried out ab initio calculations on a series of *nido*-8-vertex boranes comprising B_8H_{12}, $[B_8H_{11}]^-$, $[B_8H_{10}]^{2-}$, $[B_8H_9]^{3-}$, $[B_8H_8]^{4-}$ and $B_8H_{10}.L$, and have shown that geometry **1** is favoured energetically in all cases except for $[B_8H_9]^{3-}$, where geometry **2** is preferred.[7] Of this series only B_8H_{12} **1** and $B_8H_{10}{\cdot}NEt_3$[8] were known to exist. By use of the ab initio/IGLO/NMR method,[9,10] it was shown that the asymmetrically-bridged ("endo/bridging") hydrogen atoms at B4 and B7 in B_8H_{12} are involved in fluxional "windshield wiper" processes in solution, thereby accounting for the presence of three peaks in the boron NMR spectrum with intensities in the ratio 4:2:2. Similar fluxional behaviour was shown to occur in $B_8H_{10}.NEt_3$.

We now report definitive boron and proton NMR peak assignments, not only on B_8H_{12} but also on the structurally related *conjuncto* borane $B_{16}H_{20}$ **3** and the adduct $B_8H_{12}{\cdot}NCCD_3$ **4**.[11,12] The spectra of these latter two species were either unassigned or incorrectly assigned in earlier work.[12-14] We also report for the first time the synthesis of the unstable *nido*-8-vertex borane anion $[B_8H_{11}]^-$, its structural determination by the ab initio/IGLO/NMR method, and some preliminary results on the remarkably stable products of its decomposition. Finally, we present the results of a computational study on the structure and dynamic behaviour of the unstable octaborane B_8H_{14}, for which NMR data and proposed structures only are available in the early literature.[12,15] Standard ab initio methods were used at the levels indicated where appropriate in the text, using the Gaussian[16] and "direct IGLO"[17] packages. Theoretical ^{11}B chemical shifts have been referenced to B_2H_6 (16.6 ppm[18]) and converted to the usual $BF_3.OEt_2$ scale as described elsewhere.

2 RESULTS AND DISCUSSION

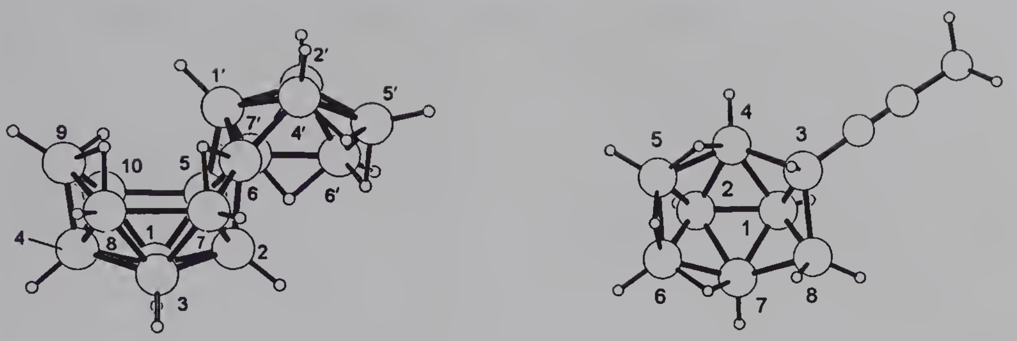
2.1 Experimental and Computational Studies on B_8H_{12}, $B_{16}H_{20}$ and $B_8H_{12}{\cdot}NCCD_3$

The original assignment of the boron NMR peaks for octaborane(12), B_8H_{12} **1**, at -19.4 and -22.0 ppm for B(4,7) and B(1,2) respectively,[13] was subsequently brought into question by an ab initio/IGLO/NMR study (see Table 1).[9] Our own IGLO computations on this system also cast doubt on this assignment, but we now find that GIAO calculations do not distinguish between the two sets of peaks. We have resolved this ambiguity by detailed boron (Table 1) and proton NMR spectroscopy. The line-narrowed ^{11}B spectrum reveals for the first time that the resonance assigned to B(4,7) is a doublet of doublets arising from couplings, J_{BHt} = 191 Hz and $J_{BH\mu}$ = 28 Hz, to *exo* and *endo*/bridging hydrogens respectively. Excellent agreement between computed and experimentally observed shifts is obtained if the computed shifts for B1 and B2 and for B3, B5, B6 and B8 are averaged, consistent with the proposed fluxionality.

Table 1 *Experimental and Computed (IGLO/GIAO)* ^{11}B *NMR Shifts for* B_8H_{12}

	B1	B2	*B1,2*†	B3,8	B5,6	*B3,5,6,8*†	B4,7
DZ/IGLO//MP2/6-31G*	7.9	-44.3	*-18.2*	10.3	6.0	*8.2*	-22.4
DFT-GIAO//B3LYP/6-31G*	4.9	-42.7	*-18.8*	7.5	2.9	*5.2*	-19.0
Exptl. (Schaeffer, 1972)			-22.0			7.5	-19.4
Exptl. (This work)			-18.9			8.0	-21.7

†*Averaged values (see text)*



3 **4**

Figure 2 *The conjuncto borane $B_{16}H_{20}$ **3** and the adduct $B_8H_{12}{\cdot}NCCH_3$ **4** whose spectra were either unassigned or incorrectly assigned in earlier work.*

The structure of hexadecaborane(20), $B_{16}H_{20}$, **3** has been determined by X-ray crystallography[19] and is viewed as a 'fusion' of B_8H_{12} and $B_{10}H_{14}$ (Figure 2). The boron and proton NMR spectra of this macropolyhedral borane, synthesised by decomposition of B_8H_{12}, have been fully assigned for the first time.[20] Calculated IGLO and GIAO NMR values, obtained from both the X-ray crystal structure[21] and ab initio-optimized geometry of $B_{16}H_{20}$, are in reasonable agreement with the observed values, indicating that the geometry of $B_{16}H_{20}$ remains non-fluxional in solution (Table 2). The agreement between the computed ^{11}B shifts for the static structure of B_8H_{12} and the experimentally observed values for the B_8 sub-cluster of $B_{16}H_{20}$ is also encouraging in this regard. The large differences between the IGLO and GIAO values for $B_{16}H_{20}$ suggest that the computed shifts for macropolyhedral boranes are quite sensitive to the level of theory used. Indeed, the DZ/IGLO computations would lead to an incorrect assignment for the two peaks at 3.2 and 7.7 pm, whereas the DFT-GIAO method correctly predicts the ordering of the shifts. Figure 3 shows that the agreement between the computed and experimental shifts is rather better for the DFT-GIAO computations than for the DZ/IGLO//MP2/6-31G* method for this particular compound.

Table 2 *Fully Assigned ^{11}B NMR Shifts and IGLO/GIAO Computations on $B_{16}H_{20}$*

	B1	B2	B3	B4	B5(8')	B6(3')	B7	B8
DZ/IGLO//MP2(fc)/6-31G*	13.6	-32.8	9.4	-42.0	5.0	13.4	-0.5	-0.7
DFT-GIAO//B3LYP/6-31G*	8.6	-27.2	9.4	-39.0	5.6	11.2	-1.6	-0.6
Exptl (This work)	8.7	-27.3	10.4	-39.1	6.0	13.0	-2.0	-1.1
	B9	**B10**	**B1'**	**B2'**	**B4'**	**B5'**	**B6'**	**B7'**
DZ/IGLO//MP2(fc)/6-31G*	8.1	-4.3	18.2	-43.4	-19.0	8.5	4.7	-20.9
DFT-GIAO//B3LYP/6-31G*	5.7	-2.3	16.4	-40.8	-18.6	1.4	5.5	-15.7
Exptl (This work)	7.7	-2.4	15.2	-39.1	-19.8	3.2	7.7	-17.9

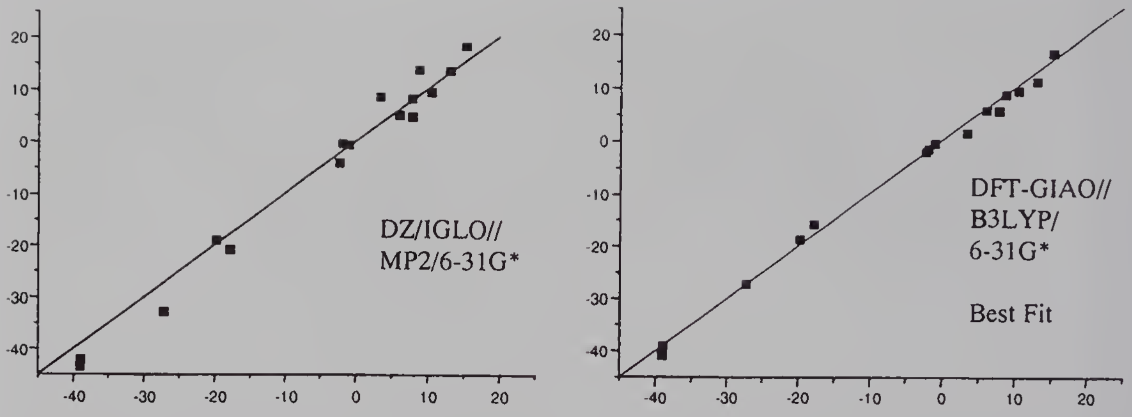


Figure 3 *Computed (vertical axis) versus experimental* ^{11}B *chemical shifts in ppm for the conjuncto borane* $B_{16}H_{20}$.

The only *arachno*-octaborane other than B_8H_{12} for which the structure has been determined by X-ray crystallography is $B_8H_{11}(\mu\text{-NHEt})NH_2Et$, and this has the expected *arachno*-8 vertex framework (ara-8<VI>) with a bridging NHEt group.[22] Several adducts are known to exist, including $B_8H_{12}{\cdot}NR_3$, $B_8H_{12}{\cdot}NCMe$ and $[B_8H_{12}{\cdot}NCS]^{-}$;[23] their structures have not been determined, but they are thought to adopt a structure similar to $B_8H_{11}(\mu\text{-NHEt})NH_2Et$ with the bridging NHEt replaced by a bridging hydrogen and the terminal NH_2Et group acting as a ligand.

We have now computed ^{11}B and ^{1}H NMR shifts from the *ab-initio* optimised structure of $B_8H_{12}{\cdot}NCMe$ **4**, and have found them to be in good agreement with experimental values obtained for $B_8H_{12}{\cdot}NCCD_3$ produced by dissolving B_8H_{12} in CD_3CN (Table 3).[12] The alternative structure for $B_8H_{12}.NCMe$, in which the MeCN ligand occupies the *endo* position, is ruled out on the basis of the computed energies of the two isomers, and from the poor agreement between the computed NMR shifts and the experimental data. The spectra of the adduct are now fully assigned. Interestingly, in contrast to $B_{16}H_{20}$, better agreement with the experimental data is obtained in this case from the DZ/IGLO computations (Figure 4).

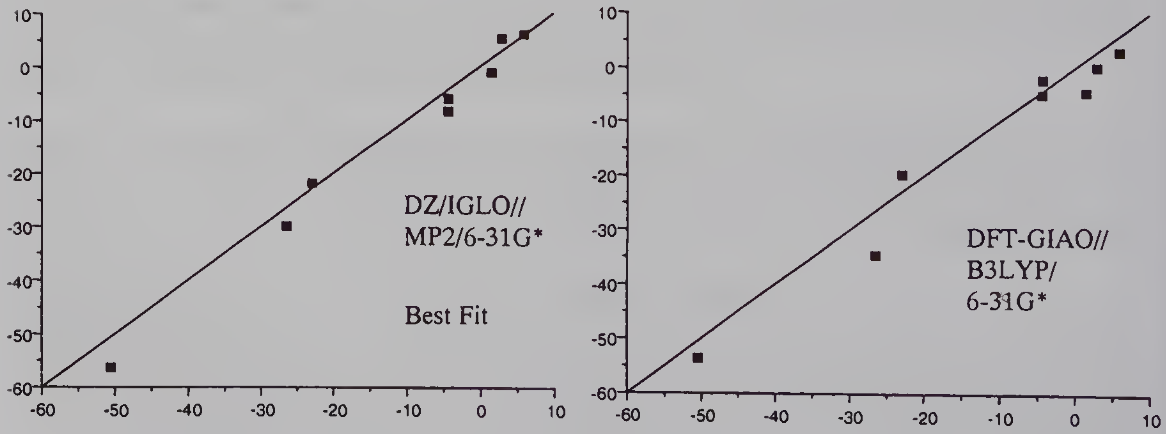


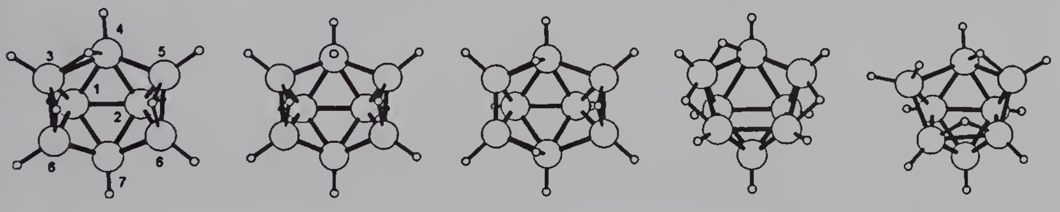
Figure 4 *Computed (vertical axis) versus experimental* ^{11}B *chemical shifts in ppm for the adduct* $B_8H_{12}{\cdot}NCCD_3$.

Table 3 *Experimental and Computed ^{11}B NMR Shifts for $B_8H_{12}{\cdot}NCCD_3$*

	B1	B2	B3	B4	B5	B6	B7	B8
DZ/IGLO//MP2/6-31G*	5.5	-56.2	-29.8	-8.2	-1.0	6.3	-5.9	-21.7
DFT-GIAO//B3LYP/6-31G*	0.4	-53.5	-34.4	-4.9	-4.3	3.1	-2.0	-19.6
Exptl. (This work))	3.0	-50.6	-26.5	-4.3	1.6	6.0	-4.3	-22.9

2.2 Synthesis, Structure and Decomposition Products of the New Anion $[B_8H_{11}]^-$

A solution from the reaction of *nido*-B_8H_{12} **1** with excess proton sponge (1,8-bis(dimethylamino)naphthalene) in dichloromethane at –35 °C gave five peaks with intensities in the ratio 2:2:2:1:1 in the low temperature $^{11}B\{^1H\}$ NMR spectrum. Peaks from a minor impurity product were also present at 5.6, -1.6, -32.2 ppm (intensities *ca.* 1:3.5:3.5). The most likely structure of $[B_8H_{11}]^-$ was deduced in a recent ab initio study to be a six-membered open-face geometry similar to that of B_8H_{12}, with an endo/bridging proton removed at B4 i.e. **5** (Figure 5).[7] Ab initio/IGLO-GIAO/NMR computations of the favoured structure **5** showed a good fit with experimental data (Table 4) when allowance was made for fluxional behaviour of the unique *endo*/bridging proton in solution similar to that found for $B_8H_{10}.NEt_3$.[7] Four other optimised $[B_8H_{11}]^-$ geometries **6-9** were located (including one previously reported in the recent ab initio study[7]), but all were of higher energy and none of their calculated NMR values were in agreement with experimental data. The minor peaks observed in the $[B_8H_{11}]^-$ NMR spectra are unlikely to arise from another isomer of $[B_8H_{11}]^-$ based on calculated NMR values of geometries **6-9**.



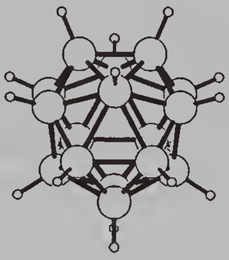
5 **6** **7** **8** **9**

Figure 5 *Optimised structures of $[B_8H_{11}]^-$. The relative energies of the five structures **5-9** are 0, 1.6, 11.7, 16.4 and 18.7 kcal mol^{-1} respectively.*

Table 4 *Experimental and Computed ^{11}B NMR Shifts for the New Anion $[B_8H_{11}]^-$*

	B1	B2	*B1,2*	B3	B5	*B3,5*	B4	B6	B8	*B6,8*	B7
IGLO-DZ// MP2/6-31G*	-36.3	-5.9	*-21.1*	-5.3	1.0	*-2.2*	-34.1	15.0	16.3	*15.7*	-21.8
DFT-GIAO// B3LYP/6-31G*	-35.0	-9.4	*-22.2*	-10.4	-3.0	*-6.7*	-31.1	11.9	13.2	*12.6*	-17.5
Exptl			-24.0			-2.4	-33.3			11.0	-17.6

Decomposition of the solution of $[B_8H_{11}]^-$ took place slowly at –35 °C and rapidly at ambient temperature to yield a complex mixture containing mainly $[B_9H_{14}]^-$ (47% based on boron consumed), $[B_6H_{11}]^-$ (10%), and two products that survived brief exposure to air.[20] The most abundant of these species (21%) gave three peaks in the $^{11}B\{^1H\}$ NMR spectrum, with intensities in the ratio 1:2:1 and chemical shifts of –9.9, -14.15 and -27.1 ppm respectively; the other gave five peaks of approximately equal intensity. Neither of these products could be identified from their shifts with any borane species reported in the literature. However, a structure that would yield the observed 1:2:1 ratio of peaks is the D_{2d} form of *closo*-$[B_{16}H_{16}]^{2-}$ **10**, first proposed by Lipscomb and co-workers in 1977/78 (Figure 6).[24] Recently, Schleyer and co-workers have shown that the lowest energy form of this anion at the B3LYP/6-31G* level of density functional theory is the D_{4d} structure **11** shown in Figure 7,[25] but this structure would be expected to give just two peaks of equal intensity in the $^{11}B\{^1H\}$ NMR spectrum. Our own computations at the same level agree with this conclusion, and indicate that the D_{2d} form is higher in energy than the D_{4d} form by 34.4 kcal mol^{-1}. However, the formation of the latter from two B_8 units in the decomposition of $[B_8H_{11}]^-$ may have a low kinetic barrier, and the GIAO predictions on this structure are consistent with the observed shifts. Attempts to obtain crystals of these compounds are underway.



10

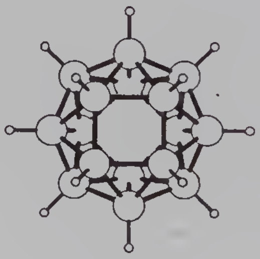


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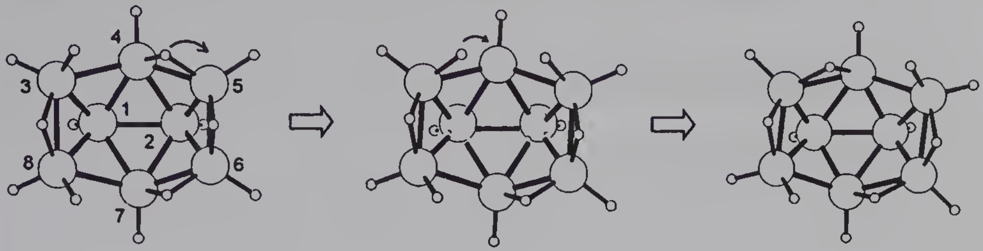
Figure 6 *Optimised structures of the D_{2d}* **10** *and D_{4d}* **11** *forms of $[B_{16}H_{16}]^{2-}$. The relative energies of the two forms are 34.4 and 0 kcal mol^{-1} respectively.*

2.3 Computational Studies on the Octaborane B_8H_{14}

We complete this article by mentioning briefly some very recent computational work on the highly unstable octaborane B_8H_{14}. A full report of this work will be published elsewhere. NMR data are available for this species, but its structure has not been definitively established by crystallographic methods Initially, on the basis of a low-field ^{11}B NMR study, a 6230 "resonance hybrid" structure featuring six bridging hydrogens was proposed for B_8H_{14},[12] but subsequent low-temperature ^1H and line-narrowed NMR studies were interpreted as favouring a static structure containing four "unique terminals" and two bridging hydrogens around the open face of the B_8 cage.[15] Various 4412 structures, such as the C_s structure **12** (Figure 7) were felt to be difficult to reconcile with the ^{11}B NMR data. Our computations on this system reveal that **12** is in fact the global minimum. A local minimum, **14**, with C_2 symmetry and an energy of +2.27 kcal mol^{-1} was located, together with a transition state, **13**, at +2.45 kcal mol^{-1}. The latter connects the two minima and permits an explanation of the observed ^{11}B spectra in terms of a fluxional process involving movement of the bridge and *endo* hydrogen atoms, one at a time, as shown in Figure 7. Excellent agreement between observed and computed shifts is obtained by averaging the shifts for B3, B5, B6 and B8 as indicated in Table 5.



12 **13** **14**

Figure 7 *Global minimum 12, transition state 13, and local minimum 14 for B_8H_{14}. The hydrogen atom movements indicated, combined with similar processes on the opposite side of the molecule, can account for the observed 1:2:1 intensity ratio in the ^{11}B spectrum.*

Table 5 *Comparison of Computed* ^{11}B NMR Shifts for B_8H_{14} (C_s global minimum), showing Good Agreement with the Experimental Values*

	B1	B2	*B(1,2)**	B(3,8)	B(5,6)	*B(3,5,6,8)**	B(4,7)
DZ/IGLO//MP2(fc)/6-31G*	-59.4	-16.0	*-37.7*	-1.8	-36.6	*-19.2*	27.7
DFT-GIAO//B3LYP/6-31G*	-57.7	-16.0	*-36.8*	-4.8	-36.1	*-20.5*	24.5
Expt. (Moody and Schaeffer)			*-38.2*			*-20.7*	24.9

*Values given in italics are the average values resulting from fluxionality of hydrogen atoms about the open face (see text)

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References

1. R. E. Enrione, F. P. Boer and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1964, **86**, 1451; *Inorg. Chem.*, 1964, **3**, 1659.
2. R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210.
3. G. J. Zimmerman and L. G. Sneddon, *J. Am. Chem. Soc.*, 1981, **103**, 1102;
4. R. E. Williams, *Adv. Organometal. Chem.* 1994, 36, 1.
5. R. E. Williams, "Advances in Boron Chemistry" Ed. W. Siebert, The Royal Society of Chemistry, Cambridge 1997 p15.
6. R. E Williams, Chapter 1 in "The Borane, Carborane, Carbocation Continuum", Ed. J. Casanova, Wiley-Interscience, New York 1998, p3.
7. A. J. Tebben, G. Ji, R.E. Williams and J. W. Bausch, *Inorg. Chem.* 1998, **37**, 2189.
8. J. J. Briguglio, P. J. Carroll, E. W. Corcoran Jr and L. G. Sneddon, *Inorg. Chem.*, 1986, **25**, 4618.

9. M. Bühl and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1992, **114**, 477.
10. For bibliography on application of the ab initio/IGLO/NMR method see reference 17 in M. Diaz, J. Jaballas, D. Tran, H. Lee, J. Arias and T. Onak, *Inorg. Chem.*, 1996, **35**, 4536.
11. J. Plesek, S. Hermanek and F. Hanousek, *Coll. Czech. Chem. Commun.*, 1968, **33**, 699.
12. J. Dobson and R. Schaeffer, *Inorg. Chem.*, 1968, 7, 402.
13. R. R. Rietz, R. Schaeffer and L. G. Sneddon, *Inorg. Chem.*, 1972, **11**, 1242.
14. L. J. Todd and A. R. Siedle, *Prog. NMR Spectroscopy*, 1979, **13**, 87-176.
15 D. C. Moody and R. Schaeffer, *Inorg. Chem.*, 1976, **15**, 233.
16. Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millman, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Peterson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malik, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
17. W. Kutzelnigg, *Isr. J. Chem.*, 1980, **19**, 193; M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, 1982 **76**, 1919; W. Kutzelnigg, U. Fleischer and M. Schindler, "NMR Basis Principles and Progress", Vol. 23, p. 165, Springer, Berlin Heidelberg, 1990 ; U. Meier, C. van Wüllen and M. Schindler, *J. Comput. Chem*. 1992, **13**, 551.
18. T. P. Onak, H. L. Landesman and R. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1533.
19. L. B. Friedman, R. E. Cook and M. D. Glick, *J. Am. Chem. Soc.*, 1968, **90**, 6862; *Inorg. Chem.*, 1970, **9**, 1452.
20. P. N. Condick, M. A. Fox, R. Greatrex and D. L. Ormsby, unpublished results. The NMR data on this and other compounds discussed in this paper will be reported in full elsewhere. 2D ^{11}B-$^{11}B\{^1H\}$ COSY, 2D ^1H-$^1H\{^{11}B\}$ COSY, $^1H\{^{11}B\}$-$^{11}B\{^1H\}$ correlation and subtracted $^1H\{^{11}B$ selective$\}$ spectra were carried out routinely.
21. Two terminal hydrogens missing in the X-ray structure of $B_{16}H_{20}$ **3** were optimised using MOPAC 7.0 prior to IGLO and GIAO calculations.
22. R. Lewin, P. G. Simpson and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1963, **85**, 478; *J. Chem. Phys.*, 1963, **39**, 1532.
23. G. B. Jacobsen, J. H. Morris and D. Reed, *J. Chem. Soc. Dalton Trans.*, **1984**, 415-421.
24. L. D. Brown and W. N. Lipscomb, *Inorg. Chem.*, 1977, **16**, 2989; J. Bicerano, D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, 1978, **17**, 3443; *ibid.* p. 2041.
25. P. von R. Schleyer, K. Najafian and A. M. Mebel, *Inorg. Chem.*, 1998, **37**, 6765.

Tetraboranes of the Type B_4R_4, $B_4H_2R_4$, $B_4H_4R_4$

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1 INTRODUCTION

Among the five parent tetraboranes B_4H_4, B_4H_6, B_4H_8, B_4H_{10} and B_4H_{12}, the *arachno*-species B_4H_{10} is the only one that is available as a storable substance, since A. Stock described it in 1912.[1] Numerous *arachno*-derivatives of B_4H_{10} have also been known, formed by replacing a H atom by X (e.g. B_4H_9X, $B_4H_8X_2$ etc.) or by replacing two H atoms by a Lewis base L (e.g. B_4H_8L, $B_4H_7L_2^+$) or by removing a proton ($B_4H_9^-$).[2] Some derivatives of *hypho*-B_4H_{12} of the type $B_4H_8L_2$, $B_4H_9L^-$, $B_4H_7L_3^+$ have also been described, though little is known about the structures.[3] The derivative B_4Cl_4 of what might be called *hypercloso*-B_4H_4 became a well characterized text-book molecule, and B_4Cl_4 opened a way to B_4Br_4 and B_4tBu_4 by exchange of the corresponding ligands.[4] The *nido*-anion $B_4H_7^-$ was claimed to be formed from the action of NH_3 on B_5H_9,[5] but its characterization has not been completed and is doubtful in the light of the results presented in this article.

We summarize here the formation and characterization of the tetraorganoboranes B_4R_4, $B_4H_2R_4$, $B_4H_4R_4$ and of the corresponding anions $B_4HR_4^-$ and $B_4H_3R_4^-$. The boranes $B_4H_2R_4$ are not only the first tetraboranes, which formally count as *closo*-species, they are also the first derivatives of a parent molecule in the homonuclear, neutral *closo*-borane series B_nH_{n+2}. Details of our results on tetraboranes will be found in the literature.[6-8]

2 SYNTHESES OF THE TETRAORGANOTETRABORANES

The boranes B_4R_4 and $B_4H_2R_4$, in general a mixture of both, are formed by the action of an alkali metal on either difluoroorganoborane [Eq. (1)] or dihaloorganoborane [Hal = Cl, Br; Eq. (2); $0 < x < 1$].

$$12\ RBF_2 + 8{+}2x\ K + 2x\ H^+ \longrightarrow 1{-}x\ B_4R_4 + x\ B_4H_2R_4 + 8\ K[RBF_3] + 2x\ K^+ \qquad (1)$$

$$4\ RBHal_2 + 8{+}2x\ K + 2x\ H^+ \longrightarrow 1{-}x\ B_4R_4 + x\ B_4H_2R_4 + 8\ KHal + 2x\ K^+ \qquad (2)$$

The protons come from the medium, more probably from groups R than from the solvent, since $B_4H_2R_4$ and not $B_4D_2R_4$ is formed in perdeuterotoluene as a solvent. Higher reaction temperature, longer reaction time, more polar solvent and heavier halogen favour the formation of $B_4H_2R_4$ over B_4R_4. Pure B_4tBu_4, e.g., is formed at 36 °C in 10 min in pentane from tBuBF$_2$, whereas $B_4H_2tBu_4$ is formed at 111 °C in 15 min in toluene from tBuBBr$_2$. Corresponding to these findings, the clusters B_4R_4 can be transformed into $B_4H_2R_4$ by the prolongated application of potassium in thf. The presence of [18]crown-6 [L in Eq. (3)] is necessary in order to achieve a two-electron reduction. Otherwise a radical anion $[B_4R_4]^{\cdot-}$ is formed, which had already been described in the literature in the case of R = tBu.[9] We observed, indeed, a reversible one-electron reduction of B_4tBu_4 at –1.77 V by cyclic voltammetry, but no further reduction up to –3.2 V. The reduction of B_4R_4 stops at the anion $B_4HR_4^-$, and a stronger acid than the medium, e.g. ethereal HCl, has to be applied in a separate reaction step in order to arrive at $B_4H_2R_4$ [Eq. (3)].

$$B_4R_4 + 2\,K + 2\,L + H^+ \longrightarrow [KL][B_4HR_4] + [KL]^+ \qquad (3a)$$

$$[KL][B_4HR_4] + HCl \longrightarrow B_4H_2R_4 + [KL]Cl \qquad (3b)$$

It is obvious that the reduction of RBHal$_2$ proceeds via a diborane(4) derivative Hal–BR–BR–Hal. Actually, we synthesized Cl–B(tBu)–B(CH$_2t$Bu)–Cl and reduced it to the corresponding tetraborane, according to Eq. (4). Two different ^{11}B NMR signals and even a 2D NMR cross-peak between them could be detected.

$$2\,Cl\text{–}B(tBu)\text{–}B(CH_2tBu)\text{–}Cl + 4\,Li \longrightarrow B_4tBu_2(CH_2tBu)_2 + 4\,LiCl \qquad (4)$$

The *hypercloso*- and *closo*-tetraboranes can easily be distinguished by their ^{11}B NMR signals, the one for B_4R_4 being found extremely low-field shifted. These signals and the mostly rather modest yields of the novel products are summarized in Table 1.

Table 1 *Mode of Synthesis (Eq.), Yields (%), ^{11}B NMR Shifts (ppm) of Tetraboranes B_4R_4 and $B_4H_2R_4$*

	Eq.	*Yield*	*^{11}B NMR*	*Lit.*
B_4tBu_4	(1)	79	135.4	6
$B_4(CH_2tBu)_4$	(1)	2	139.3	8
$B_4(CMe_2Et)_4$	(1)	<1	137.0	8
$B_4tBu_2(CH_2tBu)_2$	(4)	4	134.5/138.7	8
$B_4H_2tBu_4$	(2)/(3)	13/74	14.8	7
$B_4H_2(CH_2tBu)_4$	(2)	6	9.0	8
$B_4H_2(CMe_2tBu)_4$	(1)	1	14.3	8

The *closo*-anions $B_4HR_4^-$ are either formed by the reduction of B_4R_4, according to Eq. (3a), or by the reduction of a protic hydrogen bridge in $B_4H_2R_4$ with lithium [Eq. (5); R = tBu].[7]

$$B_4H_2R_4 + 2\,Li \longrightarrow Li\,[B_4HR_4] + LiH \qquad (5)$$

When potassium is reacted with $B_4H_2R_4$ (R = tBu) in tetrahydropyrane (thp) for 3 days, a 7:3 mixture of the anions $B_4HR_4^-$ and $B_4H_3R_4^-$ is obtained. The anion $B_4HR_4^-$ is obviously formed in analogy to Eq. (5) by proton reduction, whereas the formation of $B_4H_3R_4^-$ goes back to a two-electron cluster reduction to give $B_4H_2R_4^{2-}$ and to subsequent deprotonation of the medium. Actually, we found a cyclovoltammetric reduction of $B_4H_2R_4$ at –2,36 V (reversible) and –2.87 V (irreversible). In order to increase the yield of $B_4H_3R_4^-$ in the obtained mixture as much as possible, a Brønsted acid is needed strong enough to transform $B_4HR_4^-$ back to $B_4H_2R_4$ and to protonate the hypothetical intermediate $B_4H_2R_4^{2-}$ more effectively than the organic medium. This acid must also be metastable towards reduction by potassium. We found that the disilazane $HN(SiMe_3)_2$ meets all these preconditions. The product of Eq. (6) can be obtained in 85 % yield. The subsequent protonation by ethereal HCl makes a quantitative yield of $B_4H_4R_4$ from $B_4H_3R_4^-$ available [Eq. (7), R = *t*Bu].[8]

$$B_4H_2R_4 + 2\,K + HN(SiMe_3)_2 + 6\,thp \longrightarrow [K(thp)_6][B_4H_3R_4] + K\,[N(SiMe_3)_2] \qquad (6)$$

$$B_4H_3R_4^- + HCl \longrightarrow B_4H_4R_4 + Cl^- \qquad (7)$$

3 STRUCTURES OF THE TETRABORANES

The B_4 skeleton of B_4tBu_4 forms a tetrahedron with bond lengths of 170.4(4) pm in the gas phase (from electron diffraction data)[10] and in the range 169.9 - 171.4 pm in the yellow crystalline material (space group C_2/c, molecular C_2 symmetry).[6] These data are well comparable to those of B_4Cl_4.

A tetrahedral B_4 skeleton with two H atoms bridging opposite edges exhibits the lowest-energy species of B_4H_6 in a series of four minimum structures on the potential hyperface (D_{2d}). The bridged edges are shorter than the other four (162.3 vs. 174.6 pm). The edges are stretched, when going from B_4H_6 to $B_4H_2Me_4$ (164.8 and 179.0 pm, respectively; MP2(fc)/6-31G* level).[7] An ^{11}B NMR shift of δ 13.9 ppm was calculated for $B_4H_2Me_4$ by the IGLO/DZ method.

Experimentally, the four BR units of $B_4H_2R_4$ turn out to be equivalent, according to the NMR spectra. The ^{11}B NMR shifts (Table 1) are close to those calculated for $B_4H_2Me_4$. NMR signals of the bridging protons at characteristic shift values (δ 0.85, 1.4, 1.1 for varying R in the sequence of Table 1) were detected with the ^{1}H/^{11}B-hmqc technique. A structural model of the colourless crystalline $B_4H_2tBu_4$ could not be refined on the basis of X-ray diffraction data, but the data allowed to recognize 16 stretched tetrahedra in the orthorhombic unit cell.[7]

The reduction of $B_4H_2R_4$ (R = *t*Bu) with Li in thp yielded crystals that contain the molecule $B_4HR_4[Li(thp)_2]$ with the unit $Li(thp)_2$ replacing one bridging H atom. The crystal structure analysis (C_2 symmetry) and the *ab initio* calculations of B_4HMeLi (C_{2v}) give comparable BB distances; the Li-bridged edge is the shortest (obs. 158.2, calc. 155.2 pm) followed by the H-bridged edge (obs. 161.9, calc. 161.5 pm), whereas the other four edges are distinctly longer (obs. 178.7, 179.3, calc. 177.1 pm).[7] In ethereal solutions of the lithiotetraborane, however, all the four B*t*Bu units are equivalent at room temperature, according to the NMR spectra; a dissociation into ions was concluded with the bridging proton of $B_4HR_4^-$ fluctuating along all the tetrahedral edges. The situation changes on cooling the solution. At –80 °C, the NMR data speak for an equilibrium between an undissociated C_{2v} species like in the crystal and an ionized species with a pseudotetrahedral $B_4HR_4^-$ anion in the ratio 5:1.

Structural information about the *nido*-anion $B_4H_3R_4^-$ originates first from energy calculations for $B_4H_7^-$ (MP2(fc)/6-31G*).[8] Four minima could be localized on the potential hyperface (Fig. 1).

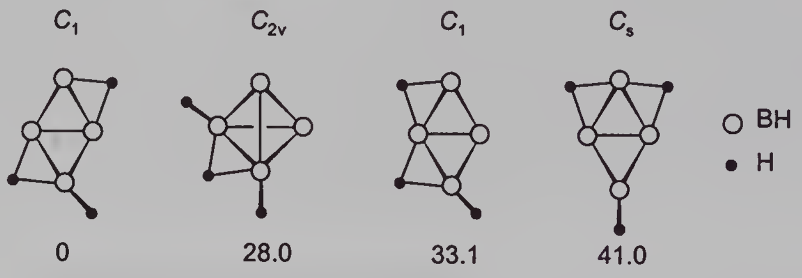

Figure 1 *Calculated minimum structures and relative energies* ($kJ\ mol^{-1}$) *of* $B_4H_7^-$ [8]

The NMR data observed for $B_4H_3tBu_4^-$ are in accord with the bicyclobutane-type structure at the calculated lowest minimum. This structure is expected for a B_4 *nido* species. The bridging protons are rigid at the NMR time scale at –30 °C, but fluctuate at 60 °C. An activation barrier of $\Delta G^{\neq} = 59\ kJ\ mol^{-1}$ was concluded from the coalescence temperature of 45 °C for the B2/B3 ^{11}B NMR signals. The high-temperature C_s structure (Fig. 2) represents the transition state for the enantiomerization of the C_1 ground-state structure, apparently. We assume the *t*Bu group at B5 in an *endo*-position, mostly from analogy to the structure of neutral $B_4H_4tBu_4$.[8]

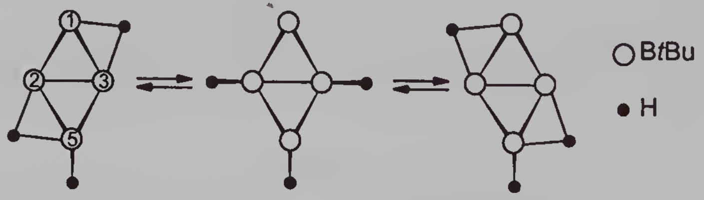

Figure 2 *Enantiomerization of the nido-anion* $B_4H_3tBu_4^-$

The observed NMR data of $B_4H_3tBu_4^-$ and the ^{11}B NMR data computed for $B_4H_3Me_4^-$ with Me in *endo*-position are summarized in Table 2. The assignments of the *t*Bu signals in the positions 1 and 5 are uncertain and might be interchanged, and the same is true for those in the positions 2 and 3. Signals for the two bridging protons are found at δ –1.32 and –1.39 at –30 °C and assigned to bridge B1-B3 and B2-B5, respectively, by the aid of 2D $^1H/^{11}B$ hmqc. (Actually, the cross-peak with B1 could not be detected because of the line width ($\omega_{1/2} = 620$ Hz) of the δ 59.1 signal.) 2D $^{11}B/^{11}B$ cross-peaks B1/B2 and B3/B5 confirm the assignment, with the fact in mind that cross-peaks between H-bridged B atoms are hardly recognized. The ^1H NMR shift of the terminally bound H atom at δ 1.63 (–30 °C) helps to assign the structure by couplings with B5 ($^1J = 100$ Hz) and μH(2-5) ($^2J = 6.5$ Hz), the coupling constant ^1J being more typical for *exo*- than for *endo*-bound hydrogen. The 60 °C spectra (Table 2) make the vertices 2 and 3 equivalent and also both of the bridging H atoms (δ –1.32), but not these H atoms and the *exo*-H (δ 1.96). The calculated and the observed ^{11}B NMR shifts are in satisfying agreement, considering the striking difference between the ligands Me and *t*Bu.

Table 2 *Observed ^1H and ^{11}B NMR Shifts δ (ppm) for the four BtBu Vertices of nido-$B_4H_3tBu_4^-$ in d_8-thf at −30 and +60 °C and IGLO/DZ-Calculated ^{11}B NMR Shifts of endo-$B_4H_3Me_4^-$ (Numbering of Vertices See Fig. 2)*

	1	2	3	5
δ(^{1}H), −30 °C	1.12	1.00	0.90	0.73
δ(^{1}H), +60 °C	1.16	0.92	0.92	0.73
δ(^{11}B), −30 °C	59.1	10.3	6.1	−9.7
δ(^{11}B), +60 °C	59.1	8.2	8.2	−9.3
δ(^{11}B), calc.	49.5	12.4	16.5	−10.6

Four minimum structures had also been calculated for the parent *nido*-B_4H_8, together with three transition states (MP2(fc)/6-31G*).[8] The two bicyclobutane-type structures are distinctly lower in energy than the two tetrahedral structures (Fig. 3).

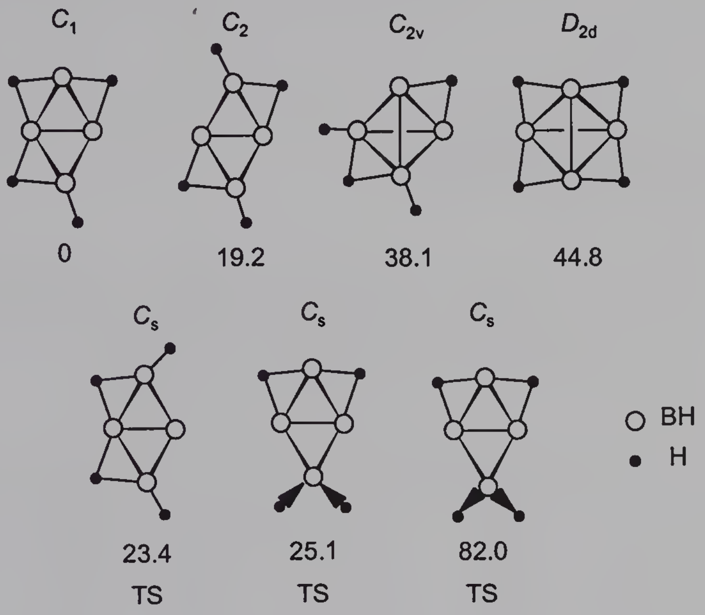

Figure 3 *Calculated minimum structures, transition states and relative energies (kJ mol^{-1}) of B_4H_8*[8]

The experimental NMR data fit again well the lowest minimum structure. There is again a dynamic process, which is recognized by the NMR spectra at 60 °C and at −80 °C. The activation barrier is $\Delta G^{\neq} = 50$ kJ mol^{-1} at a coalescence temperature of 10 °C (B2/B3). An enantiomerization of the C_1 ground-state structure via a C_s transition state is again involved (Fig. 4). This time, the B2–B5 bridging and the *exo*-terminal H atoms are exchanged, whereas the other two bridging H atoms presumably remain rigid, though they become equivalent during the dynamic process.

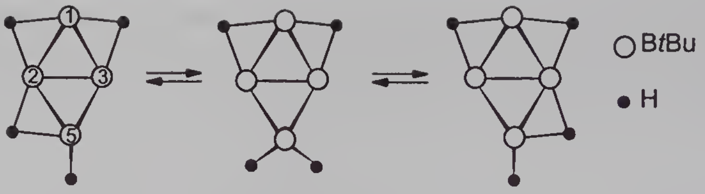

Figure 4 *Enantiomerization of nido-*$B_4H_4tBu_4$

The observed NMR data are shown in Table 3. ^{11}B NMR shifts were IGLO/DZ-calculated for *endo*-$B_4H_4Me_4$ on the basis of geometric data computed for B_4H_4tBu (RHF/6-31G*).[8] The assignment of the *t*Bu groups in the positions 2 and 3 are arbitrary and might be interchanged. An assignment of the ^{13}C NMR quartets to *t*Bu goes back to $^1H/^{13}C$ 2D correlations. The three bridging H atoms give signals at δ 3.70 (1-2), –0.62 (1-3), 0.01 (2-5) at –50 °C and can be assigned by all the six possible 2D $^{11}B/^1H$ correlations; a ^1H NMR shift of δ 2.14 for the *exo*-terminal H atom is related to δ –4.2 of B5. The vertices 2 and 3 become equivalent at 60 °C, according to *pseudo*-C_s symmetry, and the same is true for the two bridging H atoms 1-2 and 1-3, δ = 1.5. The exchange of μ-H(2-5) and *exo*-H(5) brings about a *pseudo*-triplet for the ^{11}B NMR shift δ –3.7 (^1J = 76 Hz), which is related to the ^1H NMR shift δ 1.2 (averaging the –50 °C shifts δ 0.01 and 2.14). The *pseudo*-C_s symmetry averages the corresponding low temperature shifts fairly well. The observed ^{11}B NMR shifts agree nicely to the calculated ones.

Table 3 *Observed* ^1H, ^{11}B *and* ^{13}C *NMR Shifts δ (ppm) for the four BtBu Vertices of nido-*$B_4H_4tBu_4$ *in* d_8*-thf at –50 °C and +60 °C and IGLO/DZ-Calculated* ^{11}B *NMR Shifts of endo-*$B_4H_4Me_4$ *(Based on the Calculated Geometry of endo-*$B_4H_4tBu_4$*)*

	1	2	3	5
δ(^1H), –50 °C	1.24	1.13	1.00	0.90
δ(^1H), +60 °C	1.24	1.07	1.07	0.90
δ(^{13}C), –50 °C	33.8	31.7	34.8	31.5
δ(^{11}B), –50 °C	37.2	16.0	10.7	–4.2
δ(^{11}B), +60 °C	36.9	13.7	13.7	–3.7
δ(^{11}B), calc.	34.8	10.3	8.5	–6.6

We deduce the *endo*-position of *t*Bu at B5 from NOE experiments. We find NOE correlations at 60 °C for the ^1H NMR signals at δ 1.24 and 1.07, as expected for neighbouring *exo*-*t*Bu groups, but also for those at δ 1.24 and 0.90, unexpected for two *exo*-*t*Bu groups in position 1 and 5, but reasonable for the interaction of an *exo*-1- and an *endo*-5-*t*Bu group. In agreement with these observations, a NOE correlation between the ^1H NMR shifts δ 0.90 and 1.07, which would relate the *exo*-2- and -3-*t*Bu groups to *endo*-5, is not found. The transition state with the *endo*-*t*Bu group in position 5 corresponds to the high energy transition state ($\Delta U^{\neq}$ = 82 kJ mol^{-1}) for B_4H_8 (Fig. 4). We expect a smaller activation barrier in the stericly overcrowded $B_4H_4tBu_4$ as compared to the parent borane B_4H_8, because of a more positive activation entropy. The experimental barrier of $\Delta G^{\neq} = 50$ kJ mol^{-1} looks reasonable, therefore.

Considering B_4H_8 or $B_4H_4R_4$ in terms of localized molecular orbitals (LMO), the 24 available atomic orbitals and the 20 available valence electrons must be organized in four (3c2e) and six (2c2e) molecular bonds. The only bicyclobutane-type structure in accord with these simple requirements is the one found by theory and by experiment (Fig. 5).

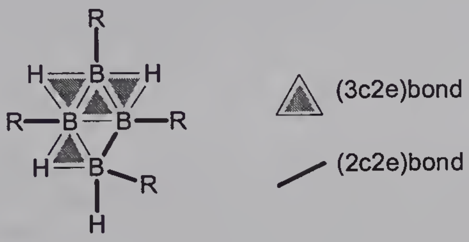

Figure 5 *The molecule $B_4H_4R_4$ in the LMO description*

4 REACTIONS OF TETRABORANES

The tetraborane $B_4H_2R_4$ (R = *t*Bu) was found to react with 2-butyne to give the 1,5-dicarba-*closo*-pentaborane $Me_2C_2B_3R_3$ in 63 % yield [Eq. (8)]. The hypothetic second product $(RBH_2)_2$ is certainly not stable under the reaction conditions (160 °C, 6 bar, excess of butyne).[8] The structural identification of the carbaborane by the NMR data followed well known data of analogous carbaboranes, e.g. $Me_2C_2B_3Et_3$.[11]

$$B_4H_2R_4 + MeC{\equiv}CMe \longrightarrow Me_2C_2B_3R_3 + \tfrac{1}{2}\,(RBH_2)_2 \tag{8}$$

A more interesting product is formed when iodomethane is reacted with the *nido*-anion $B_4H_3R_4^-$ (R = *t*Bu). The carba-*nido*-tetraborane $CB_3H_4R_3$ is formed in 90 % yield [Eq. (9)].[12] Haloalkynes with bigger alkyl groups oxidize nido-$B_4H_3R_4^-$ to give *closo*-$B_4H_2R_4$, according to Eq. (10) in the case of bromoethane.[12]

$$B_4H_3R_4^- + CH_3I + thf \longrightarrow CB_3H_4R_3 + RBH_2(thf) + I^- \tag{9}$$

$$B_4H_3R_4^- + C_2H_5Br \longrightarrow B_4H_2R_4 + C_2H_6 + Br^- \tag{10}$$

Considering the series B_4H_8, CB_3H_7, NB_3H_6 of isoelectronic tetraboranes, *tert*-butyl derivatives are now available of all three of them: $B_4H_4R_4$ as described above, $CB_3H_4R_3$ [Eq. (9)], and $NB_3H_2R_4$, two isomers of which had been reported earlier[13] (R = *t*Bu). A bicyclobutane-type skeleton is the structural basis of these *nido*-cluster molecules (Fig. 6). The $CB_3H_4R_3$ cluster can also be interpreted as a novel derivative of *nido*-B_3H_7; starting from a hypothetical $B_3H_4R_3$, two terminal H atoms are substituted by a methylene bridge to give $B_3H_2R_3(CH_2)$, which is another spelling of the formula $CB_3H_4R_3$.

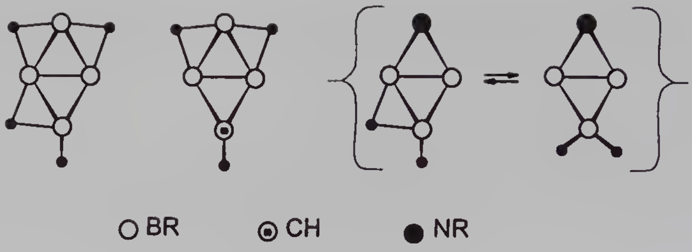

Figure 6 *Isoelectronic nido-clusters* $B_4H_4R_4$, $CB_3H_4R_3$, *and* $NB_3H_2R_4$ *(R = tBu)*

Acknowledgement

We gratefully acknowledge the stimulating theoretical help that we enjoyed during our collaboration with Paul von Ragué Schleyer and Matthias Hofmann.[7,8] The Deutsche Forschungsgemeinschaft generously supported this work.

References

1. A. Stock, C. Massenez, *Ber. Dtsch. Chem. Ges.*, 1912, **45**, 3539.
2. Gmelin Handbook of Inorganic Chemistry, 8th ed., Boron Compounds, vol. 52 and 3rd Supplement vol. 1, Springer, Berlin 1978 and 1987.
3. a) McShimoi, G. Kodama, *Inorg. Chem.*, 1983, **22**, 1542; b) M. Kameda, G. Kodama, *Inorg. Chem.*, 1984, **23**, 3705; M. Kameda, G. Komada, *Inorg. Chem.*, 1990, **29**, 4837; c) M. Kameda, G. Kodama, *Collect. Czech. Chem. Commun.*, 1997, **62**, 1279.
4. T. Davan, J. A. Morrison, *J. Chem. Soc., Chem. Commun.*, **1981**, 250.
5. G. Kodama, U. Engelhardt, C. Lafrenz, R. W. Parry, *J. Am. Chem. Soc.*, 1972, **94**, 407.
6. T. Mennekes, P. Paetzold, R. Boese, D. Bläser, *Angew. Chem.*, 1991. **103**, 199; *Angew. Chem. Int. Ed. Engl.*, 1991, **30** 173.
7. A. Neu, T. Mennekes, U. Englert, P. Paetzold, M. Hofmann, P. von R. Schleyer, *Angew. Chem.*, 1997, **109**, 2211; *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2117.
8. A. Neu, T. Mennekes, P. Paetzold, U. Englert, M. Hofmann, P. von R. Schleyer, *Inorg. Chim. Acta*, 1999, **289**, 58.
9. H. Klusik, A. Berndt, *J. Organomet. Chem.*, 1982, **234**, C17.
10. D. Hnyk, *Polyhedron* 1996, **16**, 603.
11. R. Kister, B. Wrackmeyer, *Z. Naturforsch.* 1981, **36b**, 704.
12. A. Neu, K. Radacki, P. Paetzold, *Angew. Chem.* 1999, **111**, 1358; *Angew. Chem. Inter. Ed. Engl.* 1999, **38**, 1281.
13. M. Müller, T. Wagner, U. Englert, P. Paetzold, *Chem. Ber.* 1995, **128**, 1.

Carboranes

Broadening the Conflux of Boron and Carbon Chemistries

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1 INTRODUCTION

Of all of the elements of the Periodic Table, only neighboring carbon and boron share the properties of self-bonding (catenation) and the support of electron-delocalized structures based upon these catenated frameworks. Carbon catenation, of course, leads to the immense field of organic chemistry. Boron catenation provides the *nido*-, *arachno*-, and *hypho*-boranes, which may be considered as the borane equivalents of aliphatic hydrocarbons, and the discrete families of *closo*-borane derivatives which bear a formal resemblance to the aromatic hydrocarbons, heterocycles, and metallocenes. Aside from these analogies, boron and carbon chemistries are also important to each other through their extravagant ability to mix in ways not available to other element-pairs. Thus, the conflux of boron and carbon chemistries effectively provides an element-pair for exploitation in a variety of novel ways.

In 1996, the author presented a plenary lecture to the Ninth Imeboron in Heidelberg, Germany. The title of the lecture and the resulting entry in the meeting proceedings[1] was "Carborane Chemistry at Work and at Play." That lecture described a number of applications of carborane chemistry to a variety of chemical problems and challenges that had been examined by us prior to the Ninth Imeboron. At the time of the Tenth Imeboron just held in Durham, England, the author again presented a lecture in which very recent advances in both icosahedral *closo*-carborane and *closo*-borane chemistries were described. This short paper memorializes the Durham lecture and conceptual interplay of carbon and boron chemistries from the element-pair viewpoint presented above. Consequently, the author intends this paper to be a report on new advances which are complementary to those presented in 1996.

2 CARBORANES IN MODULAR ARRAYS; CARBORODS, CARBORACYCLES, AND MERCURACARBORANDS

As previously reported,[1] the three isomers of the icosahedral $C_2B_{10}H_{12}$ carboranes are uniquely suited to play the role of building-blocks in the construction of molecular scaffolding and stereochemically rigid platforms. These versatile components often can be used for functionalization of the macrostructure or add other interesting chemical properties. Three classes of carborane derivatives which are a part of this category are carborods, carboracycles, and mercuracarborands as earlier defined.[1]

2.1 Carborods

The carborods originally described by us[2] were comprised of 1,12-$C_2B_{10}H_{10}$ carboranylene groups linked through their C-vertices to form dimeric and tetrameric structures with substituent groups attached to the termini of the rods. Removal of these substituents from the tetramer resulted in an insoluble and synthetically intractable solid. Hence, chemistry of this sort had reached its limit. Subsequent developments have resulted in the synthesis of very long carborods having reasonable solubility properties. Solubility was achieved by introducing methyl groups at all available BH vertices and by including –C≡C– and –C≡C–C≡C– linkages in the rod structure. To date, such species have been characterized by high resolution mass spectrometry and ^{13}C, ^{1}H and ^{11}B NMR studies. The rod lengths are calculated since X-ray diffraction studies are not yet available. Figure 1 displays representative carborods.[3] Work continues on the functionalization of terminal carbon atoms for attachment to other molecules or surfaces.

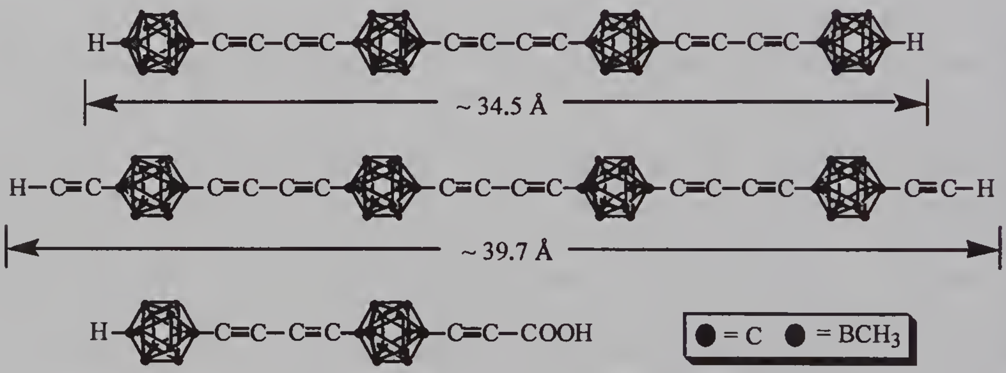

Figure 1 *Representative carborods obtained by a variety of synthetic routes*

2.2 Carboracycles

While the synthesis of a variety of simple macrocycles containing 1,2- and 1,7-$C_2B_{10}H_{10}$ carboranylene linkers has been described,[4] more recent work[5] has focused upon functionalization of the carborane cages from which these hydrophobic species are comprised and the discovery of methods by which such molecules could be made water-soluble. Water solubility would place a hydrophobic cavity bounded by carborane cages in aqueous media and provide a means to support the solubilization of hydrophobic hydrocarbon or carborane-rich structures. Derivatization of B-vertices of carboracycles derived from 1,2- or 1,7-$C_2B_{10}H_{10}$ carboranylene groups is easily accomplished by well established methods.[6]

Figure 2 illustrates the structure of a hydrophobic hexameric carboracycle derived from 9,12-$(C_6H_5)_2$-1,2-$C_2B_{10}H_{10}$ units joined by trimethylene linkers.[7] This species crystallizes from 1,3-dimethoxybenzene with two molecules of solvent enclosed in the resulting structure.

Figure 3 displays the synthesis of a hydrophilic carboracycle whose water-solubility is based upon the presence of eight sulfonate substituents and accompanying sodium cations. The properties of this system and other similar hydrophilic species are the subjects of ongoing research. Variables of interest are the size of the hydrophobic cavity, linker structure and the identity of the hydrophilic groups attached to the carborane cages.

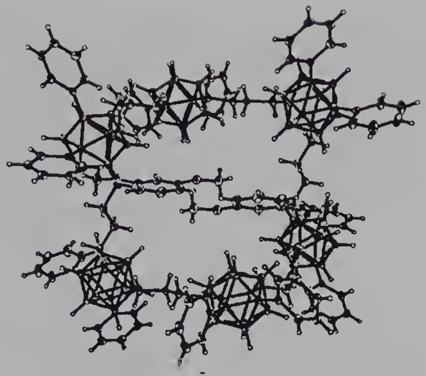

Figure 2 *Structure of a representative hexameric carboracycle with 9,12-diphenyl-substituted carboranylene units which contain two 1,3-dimethoxybenzene molecules of crystallization*

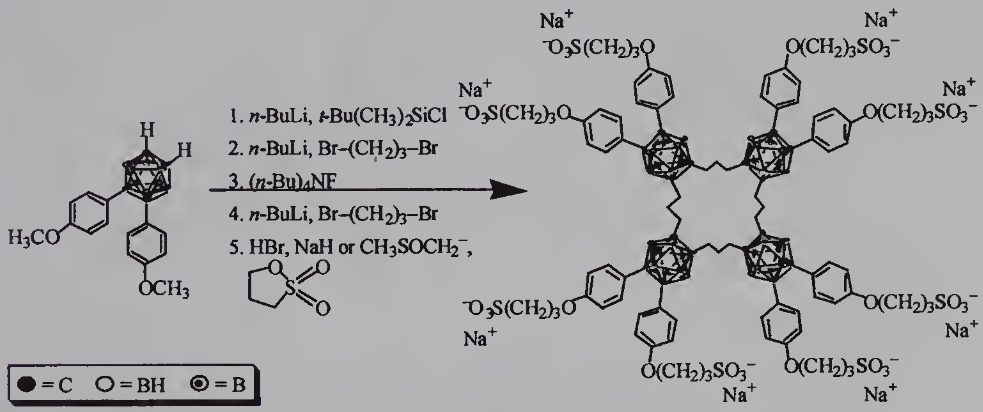

Figure 3 *Synthesis of a water-soluble carboracycle*

2.3 Mercuracarborands

Mercuracycles have been extensively studied[8] and a variety of new structures and applications developed. Of particular importance is the ability of mercuracycles of the tetrameric 12-mercuracarborand-4 and trimeric 9-mercuracarborand-3 types to selectively bind anions of diverse structures. The simple halide ions provide a variety of structurally distinct complexes with 12-mercuracarborand-4 exemplified by the chloride and the diiodide complexes illustrated in Figure 4a and b, respectively.

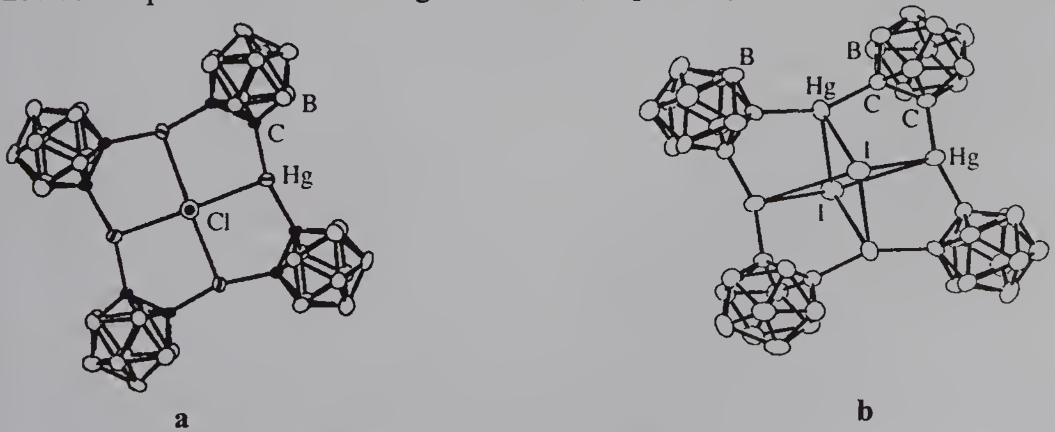

Figure 4 *ORTEP representations of (a) chloride and (b) diiodide complexes of 12-mercuracarborand-4*

In both these structures,[8] the square planar chloride ion and the pair of equivalent iodide ions are held in position by three-center two-electron bonds. The chloride ion employs a degenerate pair of such bonds to achieve strong bonding to the four mercury centers ($K_A \simeq 10^7$). The two iodide ions are each held by one symmetrical and one asymmetrical three-center bonds as described previously. This is exemplified by the 1:1 and 2:1 anion to 12-mercuracarborand-4 compositions thus established with the tetrameric mercuracycle. We now report the isolation and characterization of a "sandwich" iodide ion complex in which an iodide ion is ensconced between the six mercury centers present in a pair of parallel 9-mercuracarborand-3 rings.[9] The resulting complex contains an octahedrally coordinated iodide ion held in position by three three-center, two-electron bonds. Figure 5a shows the X-ray diffraction result while Figure 5b illustrates the proposed multicenter bonding array responsible for octahedral symmetry at iodide by employing the six *p*-electrons supplied by this ion.

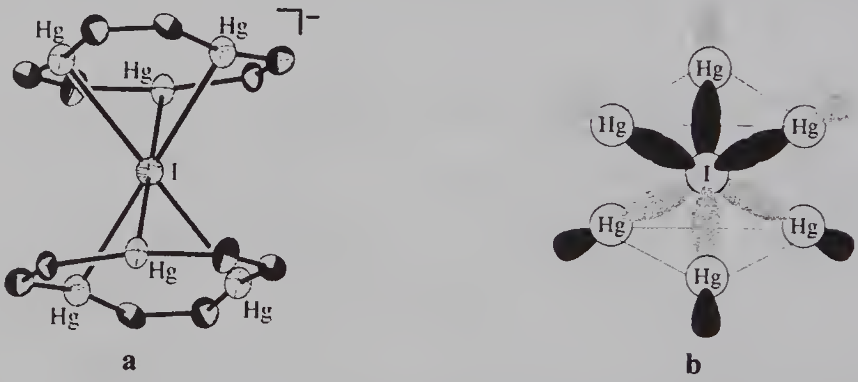

Figure 5 *The bonding environment of an octahedrally coordinated iodide complex: (a) An ORTEP representation (b) schematic showing the three-center, two-electron bonding*

3 CAMOUFLAGED AND TOTALLY FUNCTIONALIZED CARBORANES AND POLYHEDRAL BORANE ANIONS

3.1 Polymethylated carboranes

In 1996 the author reported to the Ninth Imeboron[1] on the possibilities for new chemistry based upon the fully methylated *p*-carborane molecule and other carborane derivatives in which the carborane cage was hidden from view. Hence, such species were described as camouflaged polyhedral boranes and carboranes. Methylation of the BH vertices present in $1,12\text{-}(CH_3)_2\text{-}1,12\text{-}C_2B_{10}H_{10}$ using methyl triflate in triflic acid solvent produced dodecamethyl-*p*-carborane.[10] Photochlorination of another apparent hydrocarbon, decamethyl-*p*-carborane, easily forms deca-(dichloromethyl)-*p*-carborane.[11] Of particular interest is the possible adoption of these camouflaged isosahedral carboranes as pharmacophore groups possessing hydrophobic properties and potential functionalization for further reactions.[12] Figure 6 compares the effective van der Waal diameters of these *p*-carborane derivatives with that of an often mentioned hydrophobe, C_{60}. Assuming that one desired to introduce a pharmacophore group based upon dodecamethyl-*p*-carborane into a new drug, the problem of functionalization of a single B-methyl group could arise. We have solved this problem by the adaptation of the Barton photochemical oximation reaction[13] illustrated in Figure 7. Reactions of the oxime product, which produce a wealth of novel derivatives, are presented in Figure 8.

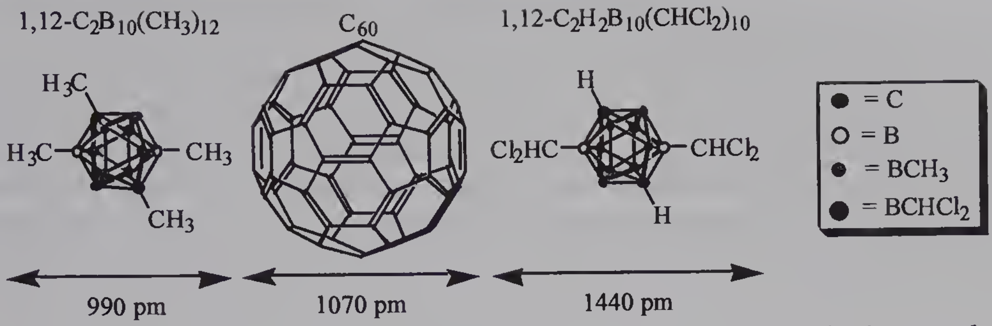

Figure 6 *Comparison of the calculated van der Waals diameters of bulky p-carborane derivatives with that of C_{60}*

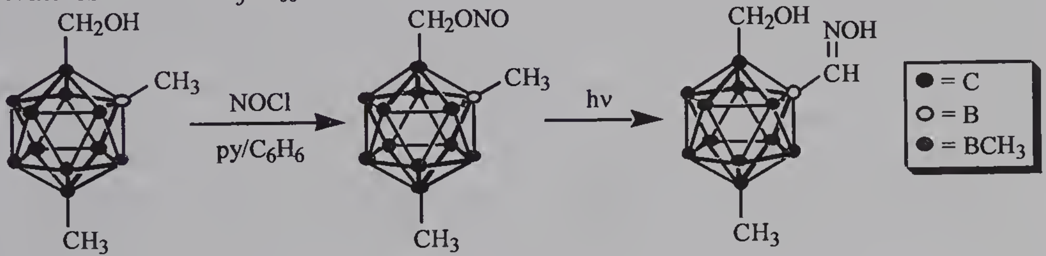

Figure 7 *Application of the Barton oximation reaction to carborane chemistry*

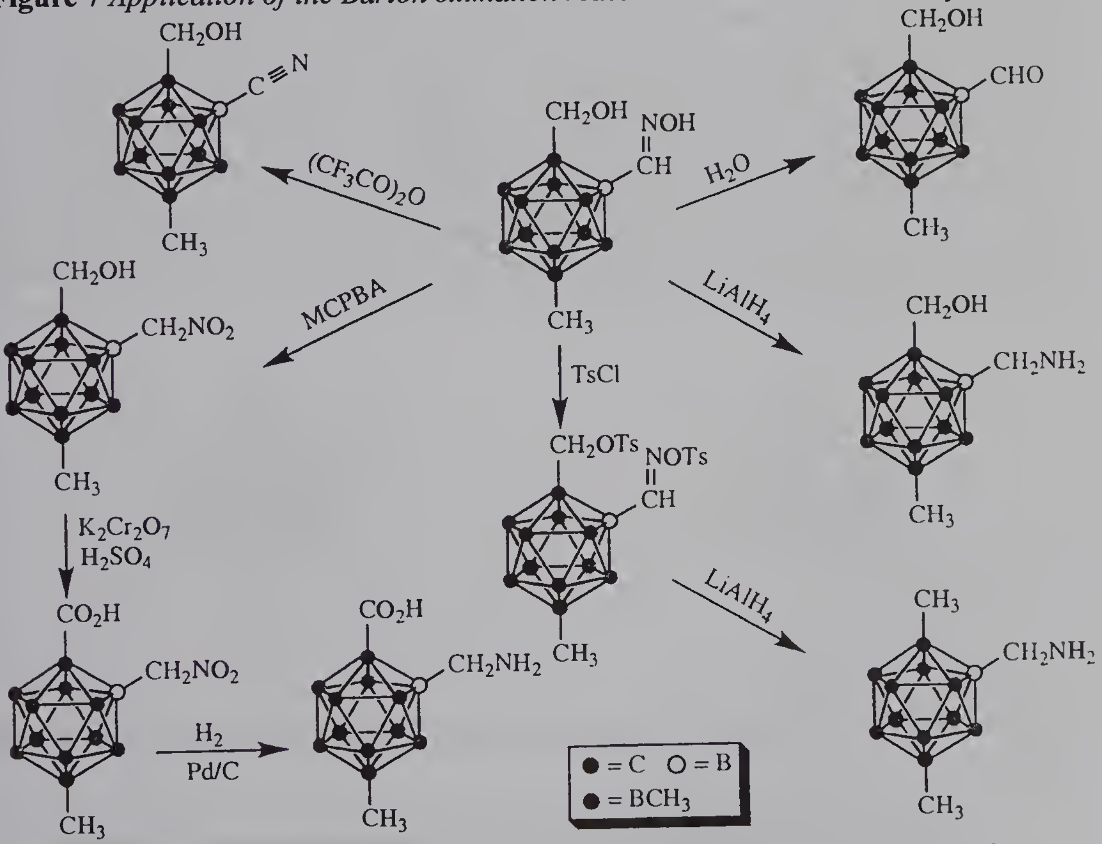

Figure 8 *Possible interconversions of the Barton photochemical oximation product*

Having successfully developed a workable route to dodecamethyl- and decamethyl-*p*-carboranes by triflate-mediated electrophilic methylation of all available BH vertices, it became important to attempt the similar methylation of 1,2- and 1,7-$C_2B_{10}H_{12}$ and at the same time perhaps increase the yields of dodecamethyl- and decamethyl-*p*-carborane. A new procedure employing $AlCl_3$ in neat CH_3I solvent easily methylated *p*-carborane in high yield by substitution of all available BH vertices. However, this procedure only produced the octamethyl derivatives of 1,2- and 1,7-$C_2B_{10}H_{12}$.[14] In both cases the two equivalent BH vertices nearest the 1,2- or 1,7- pairs of CH vertices escaped reaction. This is not an unexpected result due to the reduced electron densities of these unreacted BH vertices in the ground state. The chemistry of the octamethyl-1,2- and 1,7- carboranes has been reported[14] and further work is in progress.

3.2 Polymethylated polyhedral borane anions

Permethylation of the $[CB_{11}H_{12}]^-$ ion was accomplished by Michl and coworkers[15] using an alkylation method based upon methyl triflate. Very recently we reported[16] the discovery of the $[B_{12}(CH_3)_{12}]^{2-}$ ion from the reaction of $Cs_2B_{12}H_{12}$ first with a mixture of methyl iodide and trimethyl aluminum giving $Cs_2B_{12}(CH_3)_{11}I$ followed by the reaction of this intermediate with trimethyl aluminum. Figure 9a presents an ORTEP representation of this new ion. As in the cases of the permethylated carborane and monocarbon anion analogs, the icosahedral surface of $[B_{12}(CH_3)_{12}]^{2-}$ presents a virtual forest of hydrophobic methyl groups even though salts of this species display solubility in water. This ampiphilic ion may serve as a weakly coordinating dianion in a variety of applications. In addition, functionalized modifications of this species could serve as pharmacophores. Of particular interest was the fact that cyclic voltammetry in acetonitrile produced a reversible one-electron oxidation at 0.41 V. Chemical oxidation with Ce^{4+} ion in the same solvent led to the isolation of the bright blue, air-stable anion radical $[B_{12}(CH_3)_{12}]^-$ in good yield.[17] Figure 9b is an ORTEP representation of this anion radical. Bonding features of the diamagnetic dianion and the paramagnetic anion radical are essentially identical. The analogous neutral $[CB_{11}(CH_3)_{12}]$ radical reported by Michl[18] is also bright blue and structurally very similar to the isoelectronic anion radical.

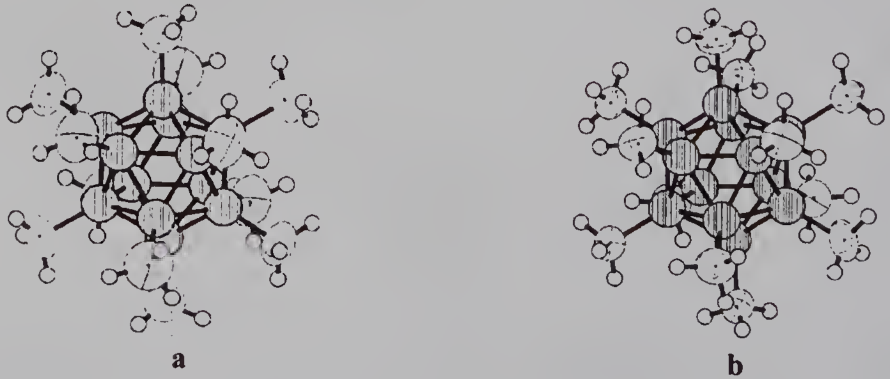

Figure 9 *ORTEP representations of (a)* $[B_{12}(CH_3)_{12}]^{2-}$ *and (b) the* $[B_{12}(CH_3)_{12}]^-$ *radical anion*

The methyl camouflaged species described above demonstrate the amplification of aromatic polyhedral borane chemistry by the prudent application of organic chemistry and the emergence of a novel family of organoboranes.

3.3 Polyhydroxylation of BH vertices in icosahedral species

The development of successful routes for the electrophilic polymethylation of icosahedral carboranes and the $[B_{12}H_{12}]^{2-}$ ion provides species equipped with hydrophobic hydrocarbon surfaces. As a consequence, the possible existence of similar structures presenting hydrophilic surfaces offers a synthetic challenge. While the oxidation of boranes is highly exothermic and reminiscent of high-performance aircraft fuels, rocket propellants and explosives, moderation of this reaction using relatively weak oxidants with stabilized icosahedral borane derivatives offered a challenging approach to polyhydroxylated products. This approach proved to be successful[19] using 30% hydrogen peroxide as both oxidant and solvent elevated temperatures with $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$ and 1,12-$(CH_2OH)_2$-1,12-$C_2B_{10}H_{10}$ as substrates. In each case all BH vertices were converted to BOH counterparts in variable yield. Figure 10 illustrates these synthetic results while Figure 11 presents the structure of $[B_{12}(OH)_{12}]^{2-}$.

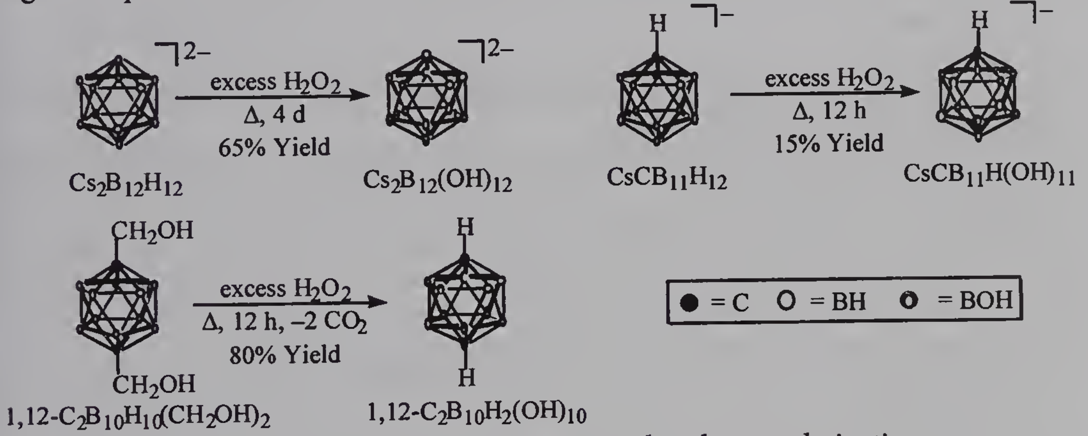

Figure 10 *Hydroxylation of icosahedral borane and carborane derivatives*

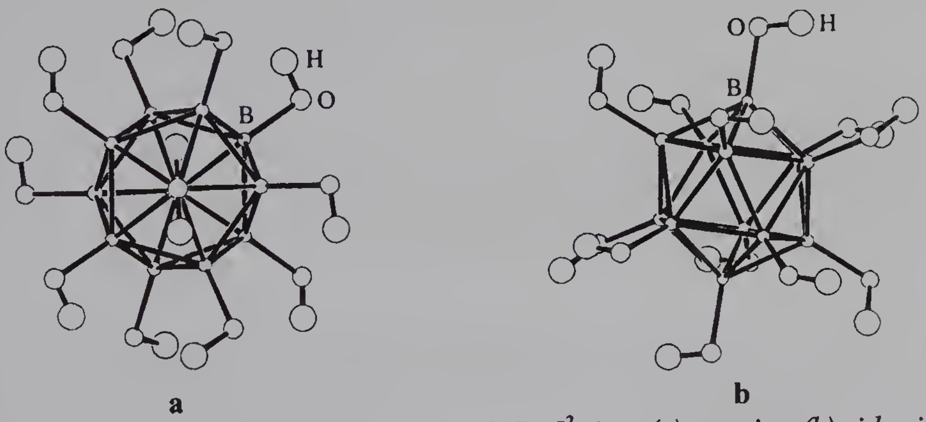

Figure 11 *ORTEP representation of the $[B_{12}(OH)_{12}]^{2-}$ ion, (a) top view (b) side view*

The $-CH_2OH$ substituents present on the *p*-carborane reactant provide some solubility of the carborane derivative and are removed *in situ* by conversion to $-COOH$ groups and subsequent decarboxylation. The properties of the $[B_{12}(OH)_{12}]^{2-}$ ion are of particular interest since this structure offers a number of possible routes to dendritic organic and inorganic derivatives. An unexpected property is the facile aggregation of the disodium salt which has very limited water solubility. Sodium ions appear to coordinate with the $-OH$ surface and provide intercage bonding. The dicesium salt is freely soluble in water since cesium is too large to effectively coordinate to the $[B_{12}(OH)_{12}]^{2-}$ ion. While $[B_{12}(OH)_{12}]^{2-}$ may be viewed as an intermediate in the hydrolysis of $[B_{12}H_{12}]^{2-}$ to boric acid, it still retains aromatic character and twenty-six cage-bonding electrons available for chemical reactions. The chemistry of these novel polyhydroxylated borane derivatives is being actively pursued.

4 CONCLUSIONS

The chemistry described above exemplifies the great similarity between aromatic polyhedral borane chemistry and the aromatic branch of organic chemistry. Modular syntheses with carboranes and the discovery of a variety of camouflaged derivatives clearly reveals the tentacles of organic chemistry reaching into the polyhedral borane field. Thus, the conflux of boron and carbon chemistries is broadened.

References

1. M.F. Hawthorne, in 'Advances in Boron Chemistry', W. Siebert (Editor), the Royal Society of Chemistry 1996, p. 261.
2. X. Yang, W. Jiang, C.B. Knobler, and M.F. Hawthorne, *J. Am. Chem. Soc.,* 1992, **114**, 9719.
3. A. Herzog, T. Wedge, C.B. Knobler, and M.F. Hawthorne, in preparation.
4. W. Jiang, I.T. Chizhevsky, M.D. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, and M.F. Hawthorne, *Inorg. Chem.*, 1996, **35**, 5417.
5. M. Diaz, H. Lee, C.B. Knobler, and M.F. Hawthorne, in preparation.
6. Z. Zheng, W. Jiang, A.A. Zinn, C.B. Knobler, and M.F. Hawthorne, *Inorg. Chem.*, 1995, **34**, 2095.
7. G. Harakas, C.B. Knobler, and M.F. Hawthorne, in preparation.
8. M.F. Hawthorne and Z. Zheng, *Accounts of Chemical Research*, 1997. **30**, 267.
9. M. Diaz, H. Lee, C.B. Knobler and M.F. Hawthorne, in preparation.
10. W. Ziang, C.B. Knobler, M.D. Mortimer and M.F. Hawthorne, *Angew. Chem.,* 1995, **34**, 1332.
11. (a) W. Jiang, C.B. Knobler and M.F. Hawthorne, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 2536. (b) Y. Endo, T. Iijima, Y. Yamakoshi, M. Yamaguchi, H. Fukasawa and K. Shudo, *J. Med. Chem.,* 1999, **42**, 1501.
12. Y. Endo, K. Yaguchi, M. Tsuji, K. Yamaguchi and K. Shudo, *Chem. Phar. Bull,* 1999, **47**, 699.
13. A. Herzog, C.B. Knobler and M.F. Hawthorne, *Angew. Chem*., 1998, **37**, 1552.
14. A. Herzog, A. Maderna, G.N. Harakas, C.B. Knobler and M.F. Hawthorne, *Chem. Eur. J.*, 1999, **5**, 1212.
15. B.T. King, Z. Janousek, B. Gruner, M. Trammell, B.C. Noll and J. Michl, *J. Am. Chem. Soc.*, 1996, **118**, 3313.
16. T. Peymann, C.B. Knobler and M.F. Hawthorne, *J. Am. Chem. Soc.*, 1999, **121**, 5601.
17. T. Peymann, C.B. Knobler and M.F Hawthorne, *Chem. Comm.* (in press).
18. B.T. King, B.C. Noll, A.J. McKinley and J. Michl, *J. Am. Chem. Soc.*, 1996, **118**, 10902.
19. T. Peymann, A. Herzog, C.B. Knobler and M.F. Hawthorne, *Angew. Chem. Int. Ed.*, 1999, **38**, 1061.

Skeletal Rearrangements following Electrophilic Alkylation of 7,8- and 7,9-Dicarbollide Anions (A Review)

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1 INTRODUCTION

In the sixties M.F.Hawthorne and coworkers[1,2] discovered that icosahedral *ortho-* and *meta*-carboranes $C_2B_{10}H_{12}$ underwent selective splitting off one of boron atoms adjacent to both carbon atoms on interaction with strong bases and transformed into 7,8- and 7,9-dicarbaundecaborate(1–) anions having a structure of an icosahedron with one missing vertex. In place of this abstracted boron there was uncovered an “open” pentagonal face, bearing two negative charges, one of which was compensated by adding a proton, so that the whole molecule had only one negative charge. This “excessive” hydrogen, being different from all others – terminal (*exo*) hydrogens, occupies the bridging (*endo*) position above the plane of the pentagonal face. When this proton is torn off by a stronger base, like NaH, BuLi, $NaNH_2$, etc., there is formed a dianion $C_2B_9H_{11}^{2-}$ with the open pentagonal face, which has strong basic and nucleophilic properties and is similar to the aromatic system of cyclopentadienide anion. M.F.Hawthorne named these dianions 7,8- and 7,9-dicarbollide ions, and studied their structures and reactivity.[3]

By the time the alkylation studies were started, the reactivity of the dicarbollide anions toward electrophilic agents had been studied mainly on insertion reactions of boron, or heteroatom, or transition metal into the place of the missing vertex of the icosahedron, restoring its structure. A broad area of metallocarboranes was developed as a result of these studies, which was the subject of many articles and reviews.

1.1 Alkylation of Dicarbollides

It was found that 7,8- and 7,9-dicarbollide dianions, formed on abstraction of a bridging *endo* proton from the corresponding dicarba-*nido*-undecaborate monoanion with sodium metal solution or sodium amide in liquid ammonia or butyl lithium in THF, very easily interact with alkyl halides to yield B-alkyl-7,8- and -7,9-dicarba-*nido*-undecaborates(1–).[4,5] Formally the reaction can be represented by a simple scheme:

$$C_2B_9H_{11}^{2-} + RX \longrightarrow C_2B_9H_{11}R^- + X^-$$
$$R = CH_3,\ C_2H_5,\ C_4H_9,\ CH_2{=}CHCH_2,\ X = Br,\ I$$

which gives almost no information about the essence of the chemical processes involved and does not reflect the complexity of all the reactions accompanying this electrophilic alkylation.

The alkylation reaction is very selective. It yields quantitatively pure B-monoalkyldicarba-*nido*-undecaborate, independent from the excess of alkylating agent. The most active alkyl halides are alkyl iodides and then – bromides. For the alkylation to be complete, 5–10 percent excess of alkyl halide is usually used. And even greater excess makes no difference, since a monoanion formed does not react with RX, and dialkylation does not occur. As a parallel process there could be the proton abstraction from the formed alkylated monoanion with the dicarbollide that has not yet entered the alkylation reaction:

$$C_2B_9H_{11}R^- + C_2B_9H_{11}^{2-} \longrightarrow C_2B_9H_{10}R^{2-} + C_2B_9H_{12}^-$$

In order to avoid this possible side reaction and ensure its selectivity there was used either fast addition of alkyl halide or reversed order of reagent addition. The latter was used particularly with less active alkyl halides.

In many examples with the use of ^{11}B and ^1H NMR and X-ray crystallography it was proved that at the first stage of the reaction there were formed the alkyl derivatives of dicarba-*nido*-undecaborate(–) with bridging (axial or *endo*) alkyl group, that occupies the position above the open pentagonal face.[6–8] With 7,8-dicarbollide they are unstable already in liquid ammonia, while with 7,9-dicarbollide – stable till 0°C.

On raising the temperature of the reaction solutions an intramolecular rearrangement takes place, consisting in migration of the boron atom bearing the alkyl substituent into the site of the missing vertex of the icosahedron (Figures 1 and 2). As a result new isomers of dicarba-*nido*-undecaborate: 11-R-2,7-$C_2B_9H_{11}^-$ (with 7,8-) and 7-R-2,8-$C_2B_9H_{11}^-$ (with 7,9-) are formed, that have been isolated in their protonated form[7,9] and characterized by ^{11}B NMR and X-ray structures (Figures 3 and 4).[7,10]

Being relatively stable at temperatures below 0°C, at room temperature these new anions are easily and irreversibly rearranged into the derivatives of stable 7,8- and 7,9-$C_2B_9H_{12}^-$. For example, 11-R-2,7-$C_2B_9H_{11}^-$ are rearranged by means of migration of the carbon atom of the open face, and then – the boron with the substituent to the place of the missing vertex, yielding 8-R-7,9-dicarba-*nido*-undecaborate(–) (Figure 1).[9,10] Another way of the rearrangement is observed on the abstraction of the *endo*-proton. In presence of a strong base 11-alkyl-2,7- and 7-alkyl-2,8-dicarba-*nido*-undecaborates(–) are completely rearranged, even in liquid ammonia, by migration of the substituted boron and yield respectively 9-alkyl-7,8- and 10-alkyl-7,9-dicarbollides, that are then simply protonated into the *endo*-position, yielding corresponding mono anions (Figures 1 and 2).[7,9,10]

1.2 Investigation and Elucidation of Skeletal Rearrangement Mechanism

The rearrangements mechanism and the sequence of cage atoms migrations were proved unequivocally by carrying out the reactions with selectively deuterated 7,8-dicarba-*nido*-undecaborates(1–), the use of ^{11}B and ^1H NMR spectroscopy and X-ray structures, as well as the counter synthesis of a rearrangement product.

The deuterated anions of 7,8-isomer: 9,11-dideuterio-, 5,6,9,10,11-pentadeuterio- and 1,5,6,9,10,11-hexadeuterio-7,8-dicarba-*nido*-undecaborates(1–) were prepared by a developed method of selective isotope exchange of deuterium for hydrogen in 7,8-dicarba-*nido*-undecaborate(1–) with D_2O at acidic conditions.[12] Since terminal hydrogen atoms are not exchanged in basic media, the deuterium label proved to be quite useful for ^{11}B NMR studies of deuterium distribution in the rearrangement products.

Analysis of the ^{11}B NMR spectra of deuterated derivatives of 8-methyl-7,9-dicarba-*nido*-undecaborate(1–) prepared from the corresponding deuterated 7,8-dicarbollide anions,[9,10] implies that their formation results from exchange of B(9), bearing the substituent, with the adjacent C(8). The other atoms of the polyhedral molecule remain localized. This localization permitted to make assignments of lines in the ^{11}B NMR spectrum of 8-CH_3-7,9-$C_2B_9H_{11}^-$, which did not contradict with that of the nonsubstituted 7,9-$C_2B_9H_{12}^-$.

The structure of the intermediate 11-CH_3-2,7-$C_2B_9H_{11}^-$ (Figure 3) and deuterium distribution in the prepared deuterated 8-CH_3-7,9-isomer, suggest that the reaction forming the latter involves three successive skeletal rearrangements (Figure 1). After formation of an intermediate with a bridge alkyl group, B(9) with this alkyl group migrates to occupy the missing vertex of the icosahedron to form 11-R-2,7-$C_2B_9H_{11}^-$. Because the latter lacks electronic symmetry, and one of the carbon atoms lies in the closed part of the molecule, C(7) migrates to occupy the missing vertex of the icosahedron to form tautomeric 8-R-7,9-$C_2B_9H_{11}^-$, which is very unstable due to the axial position of the alkyl group. It stabilizes

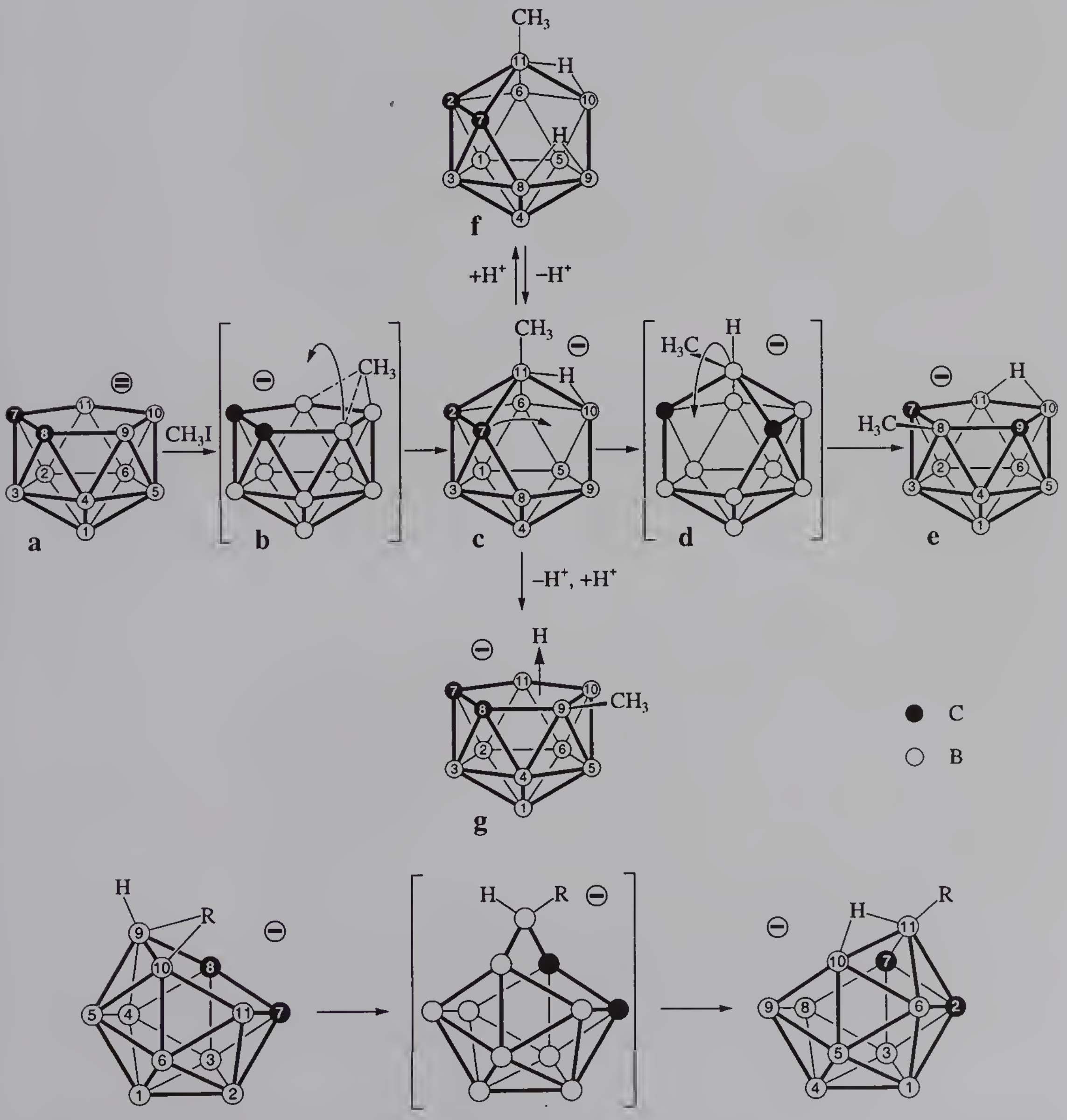

Figure 1. *Reaction of 7,8-dicarbollide anion with methyl iodide.*

by the third rearrangement – one more migration of boron with the substituent to the missing vertex, after which the substituent occupies favorable terminal (*exo*) position and the hydrogen – bridging (*endo*) position (Figure 1). This last step is in complete agreement with the deuterium distribution in the final product.[9,13]

The course and rate of subsequent rearrangements are determined by the electron structure of the open face of 11-R-2,7-C_2B_9-moiety. The open face of *nido*-carborane 11-R-2,7-$C_2B_9H_{12}$ contains two bridge hydrogens, that "freeze" the structure (Figure 3). In the corresponding monoanion the presence of only one hydrogen atom in the open face induces a facile cage rearrangement (at 20–30°C) due to migration of C(7). In the corresponding dianion 11-R-2,7-$C_2B_9H_{10}^{2-}$ a rapid rearrangement occurs with the migration of B(11) with the substituent even below –30°C (in liquid ammonia).

Taking into account the stipulation of the rearrangements of 7,8- and 7,9-monoanions into the respective 2,7- and 2,8-isomers by the chemical activation, i.e. violation of the

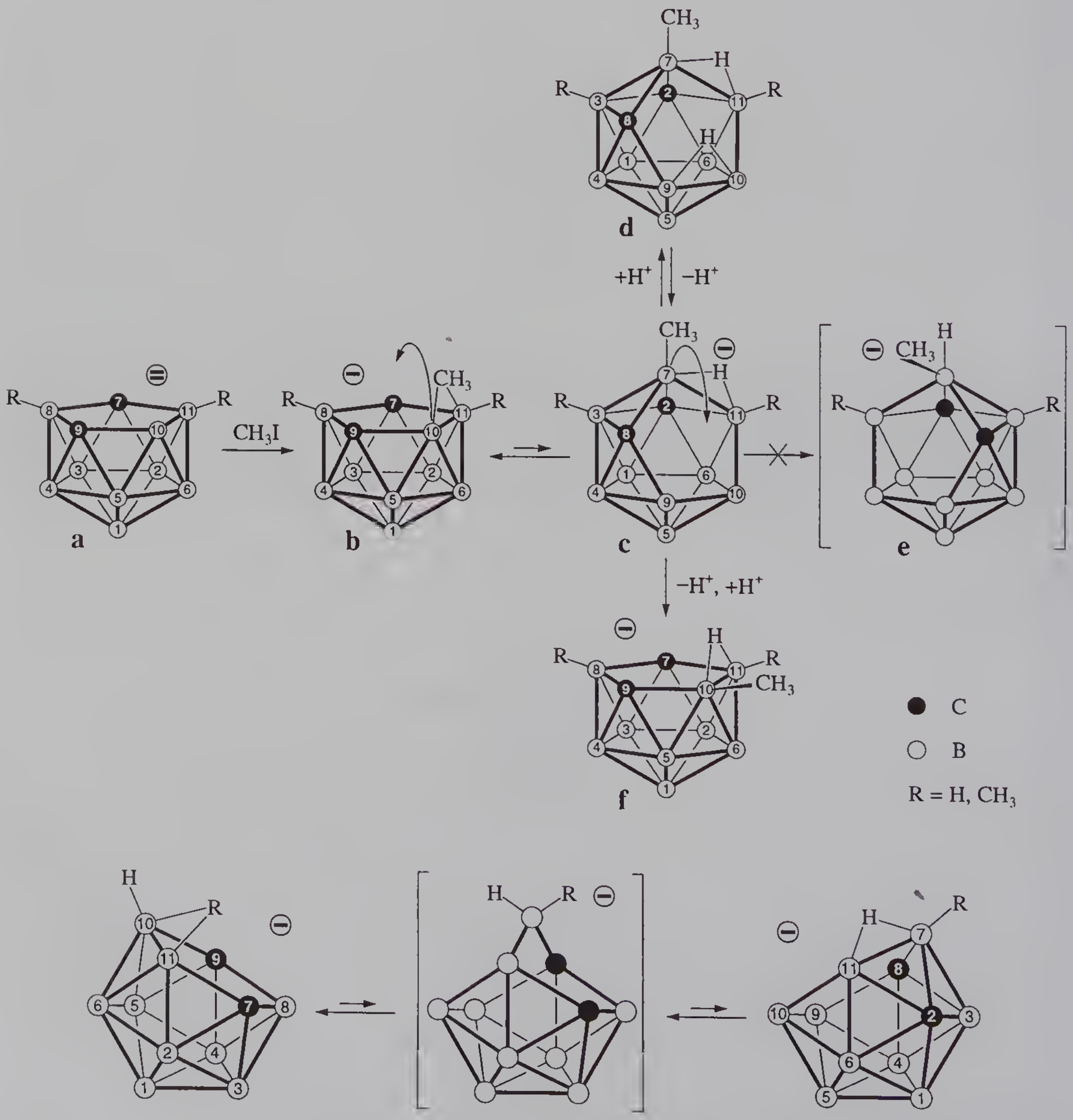

Figure 2. *Reaction of 7,9-dicarbollides with methyl iodide.*

cage electron structure, axial position of the substituent and at the same time maintaining the total number of electrons both in initial and final structures, the authors titled this type of rearrangements – the chemically induced thermal rearrangements.[7] An essential condition for the realization of the rearrangements is their regioselectivity, i.e. maintaining the configuration of the migrating boron atom and excluding its free rotation around one of the bonds (Figures 1 and 2).

In order to confirm the formation of 8-alkyl-7,9-dicarba-*nido*-undecaborate(1–) its counter synthesis was undertaken.[10] For this purpose the dicarbollide, prepared from 7,9-dicarba-*nido*-undecaborate(1–) was introduced into the reaction with *n*-butyl boron

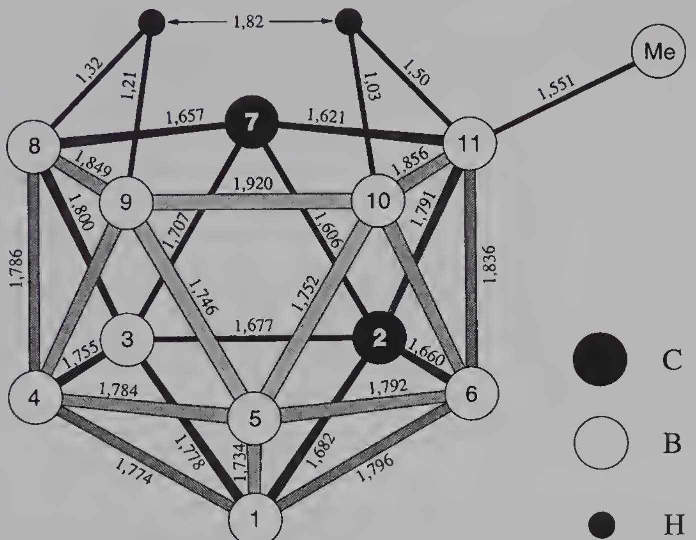

Figure 3. *X-ray structure of nido-carborane* $11\text{-}CH_3\text{-}2,7\text{-}C_2B_9H_{12}$.

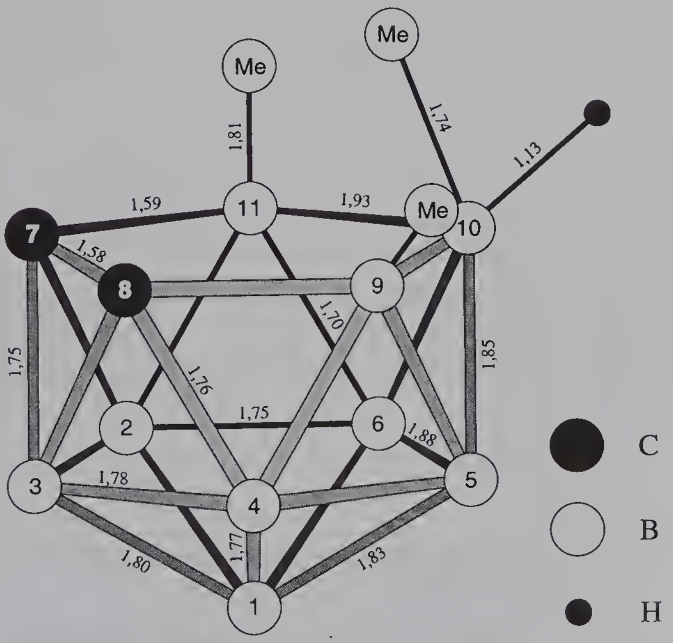

Figure 4. *X-ray structure of nido-carborane* $9,10_a,11\text{-}(CH_3)_3\text{-}7,8\text{-}C_2B_9H_9^-$.

dichloride. The prepared 2-butyl-*meta*-carborane was degraded with potassium hydroxide in butanol and the corresponding authentic 8-butyl-7,9-dicarba-*nido*-undecaborate(1–) isolated as its cesium salt. Its ^{11}B NMR spectrum was identical with that of the respective rearranged product.

1.3 Further Alkylations of Dicarbollides

The interaction of alkyl substituted 7,8- and 7,9- dicarba-*nido*-undecaborates(2–) with alkyl halides proceeds similarly to that of the nonsubstituted ones and follows the same regularities as those described in Figures 1 and 2. For example, alkylation of 9-methyl-7,8-dicarbollide with methyl iodide is directed onto B(11) and results in 6,11-dimethyl-2,7-dicarba-*nido*-undecaborate(1–), whose structure and properties are very similar to that of 11-methyl-2,7-dicarba-*nido*-undecaborate(1–). Its protonation with dilute acetic acid yields the corresponding *nido*-carborane(13). Being kept in THF solution at room temperature the dimethylated anion is rearranged into 8,10-dimethyl-7,9-dicarba-*nido*-undecaborate(1–), but after proton abstraction with a strong base it transforms into 9,11-dimethyl-7,8-dicarba-*nido*-undecaborate(1–):[6,10]

$$9\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_{10}^{2-} + CH_3I \longrightarrow$$

$$\begin{tikzcd}[column sep=large] & 6,11\text{-}(CH_3)_2\text{-}2,7\text{-}C_2B_9H_{11} \\ 6,11\text{-}(CH_3)_2\text{-}2,7\text{-}C_2B_9H_{10}^{-} \arrow[ur, "\text{dil. AcOH}"] \arrow[r, "20^\circ\text{C, THF}"] \arrow[dr, "-H^+/+H^+"] & 8,10\text{-}(CH_3)_2\text{-}7,9\text{-}C_2B_9H_{10}^{-} \\ & 9,11\text{-}(CH_3)_2\text{-}7,8\text{-}C_2B_9H_{10}^{-} \end{tikzcd}$$

Further methylation of 9,11-dimethyl-7,8-dicarba-*nido*-undecaborate(2–) leads to a stable trimethyl derivative, $9,10_a,11$-trimethyl-7,8-dicarba-*nido*-undecaborate(1–), characterized by axial position of the methyl group at B(10). This anion is a direct analog of the mentioned above unstable monoanion with the axial alkyl group, formed at the first step of the alkylation (Figure 1). The structure of this trimethyl derivative was suggested on the basis of NMR spectra and proved by a single crystal X-ray study of its Cs-salt (Figure 4).[8] Such trialkyl compounds do not have a bridging proton, and thus the formation of the corresponding dicarbollide ion is blocked, that hinders further alkylation. Successive introduction of two methyl groups into 8-methyl-7,9-dicarba-*nido*-undecaborate(2–) yields 8,10,11-trimethyl-7,9-dicarba-*nido*-undecaborate(1–), further methylation of which leads to a stable $\mu,8,10,11\text{-}(CH_3)_4\text{-}7,9\text{-}C_2B_9H_8^-$, a compound with a bridging methyl group, that is inert to rearrangements and further alkylation.

It was also shown, that dicarbollide ions could be subjected to similar reactions with other electrophilic agents, such as acyl chlorides,[14] trialkylsilyl chlorides,[15] diphenyl chloro phosphine[16] etc., and yield boron sigma-bonded derivatives of dicarba-*nido*-undecaborates.

1.4 Conclusion

Summarizing the processes, that take place at the electrophilic alkylation of 7,8-dicarbollide ion, the next steps can be noted:

- alkylation into the bridging position in the open pentagonal face; formation of $R_a\text{-}7,8\text{-}C_2B_9H_{11}^-$;

- 1st migration: $R_aB(9)$ – alkyl transfer from bridging to terminal position – formation of $11\text{-R-}2,7\text{-}C_2B_9H_{11}^-$ and its fixation by protonation to the corresponding *nido*-carborane;
- 2nd migration: C(7) – transfer of both C-atoms into the open face – alkyl is again in the disfavorable bridging position;
- 3rd migration: R_aB – transfer of the alkyl group into the terminal position, formation of the stable $8\text{-R-}7,9\text{-}C_2B_9H_{11}^-$;
- 4th migration (after the first migration, as a result of proton abstraction): RB – transfer of both C-atoms into the open face, formation of stable $9\text{-R-}7,8\text{-}C_2B_9H_{11}^-$.

Similarly, after alkylation of 7,9-dicarbollide ion the following steps can be mentioned:

- alkylation into the bridging position in the open face – formation of $R_a\text{-}7,9\text{-}C_2B_9H_{11}^-$;
- 1st migration: $R_aB(10)$ – transfer of alkyl from bridging to terminal position – formation of $7\text{-R-}2,8\text{-}C_2B_9H_{11}^-$;
- 2nd migration: RB(7) (after abstraction of bridging proton) – transfer of both C-atoms into the open face – formation of the stable10-R-$7,9\text{-}C_2B_9H_{11}^-$.

References

1. R.Wiesboeck and M.F.Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642.
2. P.M.Garrett, F.N.Tebbe and M.F.Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 5016.
3. M.F.Hawthorne, D.Young, T.Andrews, *et al.*, *J. Am. Chem. Soc.*, 1968, **90**, 879.
4. V.A.Brattsev, S.P.Knyazev and V.I.Stanko, *Proc. IMEBORON*-2, Leeds, 1973, 174.
5. V.A.Brattsev, S.P.Knyazev and V.I.Stanko, *Zh. Obshch. Khim.*, 1975, **45**, 1192.
6. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Zh. Obshch. Khim.*, 1977, **47**, 2627.
7. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Doklady*, 1978, **239**, 1136.
8. N.I.Kirillova, M.Yu.Antipin, *et al.*, *Izv. Khim. Ser.*, **1979**, 2474.
9. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Doklady*, 1977, **234**, 1093.
10. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Doklady*, 1977, **234**, 837.
11. Yu.T.Struchkov, M.Yu.Antipin, *et al.*, *J. Organomet. Chem.*, 1977, **141**, 133.
12. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Zh. Obshch. Khim.*, 1976, **46**, 2751.
13. S.P.Knyazev, V.A.Brattsev and V.I.Stanko, *Doklady*, 1979, **246**, 368.
14. V.A.Brattsev, S.P.Knyazev and V.I.Stanko, *Zh. Obshch. Khim.*, 1976, **46**, 1419.
15. L.I.Zakharkin, G.G.Zhigareva, *et al.*, *Metalloorg. Khim.*, 1990, **3**, 556.
16. L.I.Zakharkin, V.A.Ol'shevskaya, *et al.*, *Metalloorg. Khim.*, 1989, **2**, 1274.

New Routes to Carboranes

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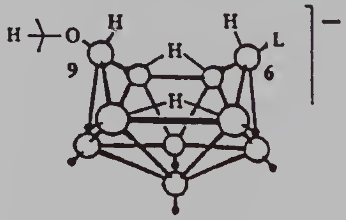
Although hydroborating reactions with smaller hydroborates are widely used as powerful tools in everyday chemistry, much less is known about the hydroborating abilities of higher boranates.

The chemistry of a whole range of arachno-decaboranates $B_{10}H_{13}(L)^-$ (L= H^-, OH^-, CN^-, NH_3, NEt_2H, NEt_3, PPh_3) has been thoroughly studied. The interest focused on the hydroborating abilities of this class of polyhedral boranates towards various ketones RR'CO (R/R'= Me/Me. Me/Ph. Me/Et) and aldehydes RC(H)O (R= H, Me, Ph, C(H)O; hydroxy- and amino-aldehydes). All ketones and most aldehydes lead to 6-*exo*-L-9-R,R'C(H)O-$B_{10}H_{12}^-$, 9-*exo*-alkoxy-substituted anions (figure 1).

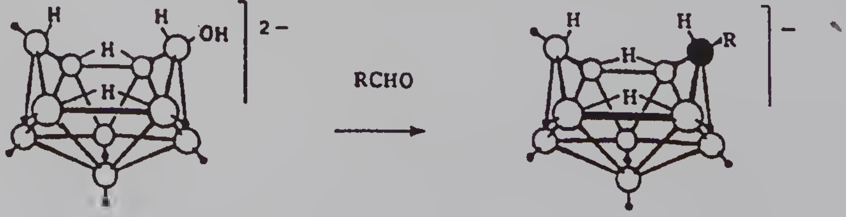


$6,9\text{-}B_{10}H_{12}(L)(OR)^-$

Figure 1

A general feature of these compounds is the retention of the stereochemistry on B_6-(L) and the introduced alkoxy-substituent on B_9 is always *exo*-situated.

A surprising role in this series of *arachno*-decaboranates plays $B_{10}H_{13}(OH)^{2-}$ (in situ generated via $B_{10}H_{14}/OH^-$ in water). A degradation-insertion reaction opens the direct high yield entry to a line of *arachno*-carbadecaboranates $6\text{-}RC(H)B_9H_{12}^-$ (scheme 1, R= H,[1] Me, Ph, C(H)O). $B_9H_{14}^-$ (from $B_{10}H_{13}(OH)^{2-}/H^+$ in water) can be used as starting material as well.

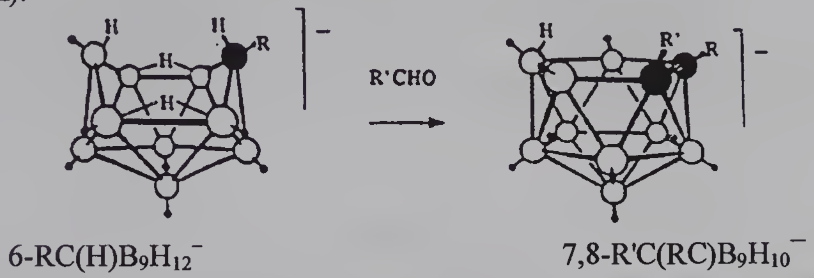


$B_{10}H_{13}(OH)^{2-}$

$6\text{-}RC(H)B_9H_{12}^-$

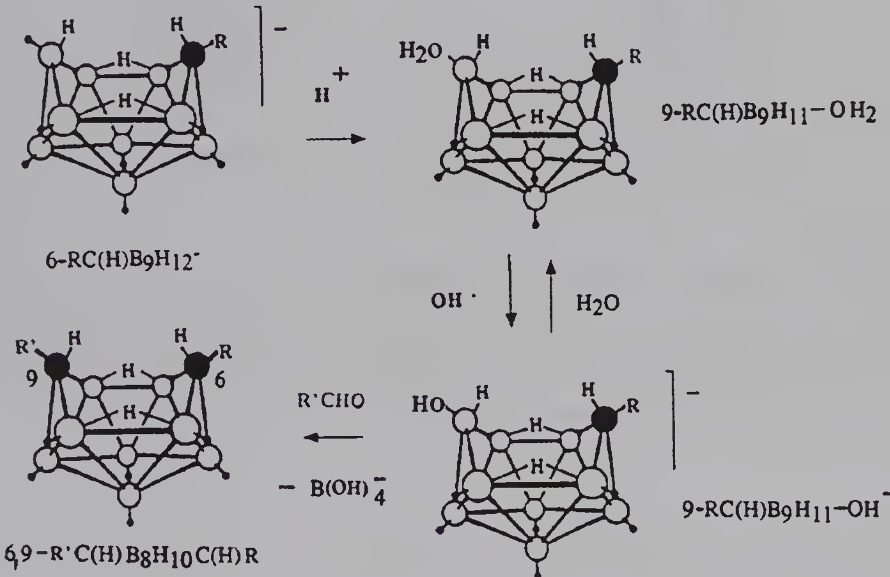
Scheme 1

A second R'C-fragment can be introduced into the 6-carba-decaboranates in a subsequent cluster-insertion reaction with a second aldehyde R'C(H)O (scheme 2, R/R'= H/H, H/Me, H/Ph, Me/Ph).



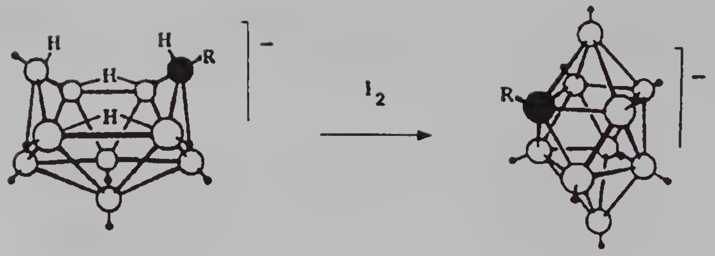
Scheme 2

This leads to di-C-substituted carbollide anions (*nido*-7,8-R,R'$C_2B_9H_{10}^-$) in high yields. This approach is of general use. Its major advantage is the avoidance of seeking for appropriate alkynes for the preceding closo-carboranes R,R'$C_2B_{10}H_{10}$. Especially for unsymmetrically C-substituted carbollides RC- and R'C-vertices can be introduced in a very easy and systematic way.



Scheme 3

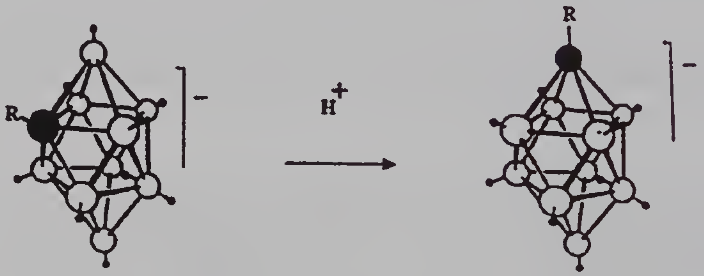
A second row of dicarbaboranes (*arachno*-6,9-R,R'$C_2B_8H_{12}$) with 10 vertices can be synthesized through a sophisticated acid/base-degradation-insertion reaction (cf. scheme 3).Starting from $B_{10}H_{13}(OH)^{2-}$, react to *arachno* RC(H)B_9H_{12}, with RC(H)O, acidify the water solution to gain 9-H_2O-6-RC(H)$B_9H_{11}^-$ deprotonate with OH^- to proceed to 9-OH-6-RC(H)$B_9H_{11}^-$. A degradation-insertion reaction with the second aldehyde R'C(H)O follows, to gain the neutral *arachno*-6,9-RC(H),R'C(H)B_8H_{10} (R/R'= H/H, H/Me, Me/Me) Oxidizing agents (I_2/OH^-, H_2O_2/OH^-), in alkaline water solution, give access to a high yield route from arachno-RCB_9H_{13} to a new class of *closo*-2-$RCB_9H_9^-$ carbadecaboranates (scheme 4, R= H, Me, Ph).



$RC(H)B_9H_{12}^-$ $2\text{-}RCB_9H_9^-$

Scheme 4

These closo-2-isomers can be quantitatively converted to the corresponding *closo*-1-$RCB_9H_9^-$ isomers (scheme 5). This needs the reaction with strong acids (CF_3SO_3H, CH_3SO_3H) in organic solvents like CH_2Cl_2, $CHCl_3$, or $CH_2Cl\text{-}CH_2Cl$.



$2\text{-}RCB_9H_9^-$ $1\text{-}RCB_9H_9^-$

Scheme 5

References

1. B. Stibr, T. Jelinek, J. Plesek and S. Hermanek, *J. Chem. Soc., Chem. Comm.*, 1987, 963
2. B. Stibr, Z. Janousek, J. Plesek, T. Jelinek and S. Hermanek, *Coll. Czech. Chem. Comm.*, 1987, **52**, 103.
3. W. H. Knoth, *Inorg.Chem.*,1971, **10**, 598.

New Routes to Small Carboranes

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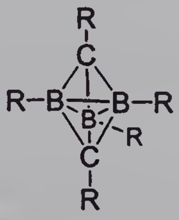
1 INTRODUCTION

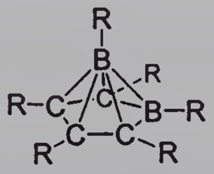
About four decades ago, carborane chemistry has started with reactions of polyboranes with alkynes,[1] and this route is still an active field of investigation.[2] In the case of some *closo*- and *nido*-carboranes (e.g., *closo*-1,2-$C_2B_{10}H_{12}$, *nido*-2,3-$R_2C_2B_4H_6$) this approach is straightforward. However, small carboranes synthesised by this route generally have to be isolated via tedious separation procedures from complex mixtures and are accessible in low yields only. In contrast with the majority of unsubstituted carboranes their alkylated or peralkylated congeners are much more stable, and there may be alternative routes to obtain such derivatives. Therefore, synthetic strategies aiming for greater selectivity and starting from simple organoboranes are of considerable interest. Attempts in this direction have already been successful in the sixties.[3,4] Thus it proved possible to prepare the smallest *closo*-carborane **A** and the carbon-rich *nido*-carborane **B** in large quantities starting from readily available organoboranes.

A



1,5-dicarba-*closo*-pentaborane(5)

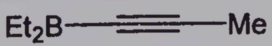
R = alkyl



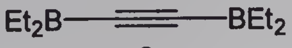
B

2,3,4,5-tetracarba-*nido*-hexaborane(6)

The synthesis of **A**, in particular, prompted us to reinvestigate the mechanism of its formation, bearing in mind that there might be *nido*- or even *arachno*-carborane cages as potential precursors of the *close*-cage of **A**. In the following, the route to various carboranes is reported, starting from diethyl(propyn-1-yl)borane **1**, Et_2B-C≡C-Me, and bis(diethylboryl)ethyne **2**, Et_2B-C≡C-BEt_2. An important role in this context plays tetraethyldiborane(6) ("Köster´s reagent" [5]; short: Et_2BH).



1



2

2 RESULTS AND DISCUSSION

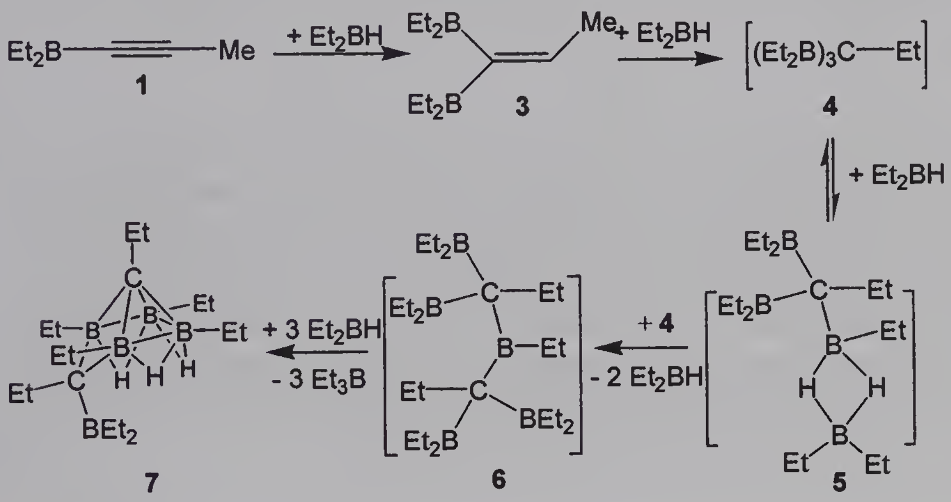
2.1 Tetraethyldiborane(6)

Tetraethyldiborane(6) ($Et_2BH_2BEt_2$), short Et_2BH, cannot be used as a pure reagent. It is prepared from the reaction of Et_3B with diborane(6) in the absence of any solvent, but in the presence of a catalytic amount of Et_2BH.[5] The ^{11}B NMR spectra of equilibrated mixtures [6] show the presence of $Et_2BH_2B(H)Et$, $Et_2BH_2BEt_2$, $Et(H)BH_2B(H)Et$ in small amounts, $Et_2BH_2BEt_2$ as the major component together with an excess of Et_3B. The concentration of the various hydride species depends on the concentration of Et_3B and is readily determined by measuring either the volume of gaseous H_2 after hydrolysis [5] or by quantitative ^{11}B NMR spectroscopy.[6] In all reactions of Et_2BH with borylated alkynes, such as **1** or **2**, leading to carboranes, a large excess of these diborane/Et_3B mixtures ("hydride bath") was used; generally these mixtures served as the solvent. The presence of THF or ether changes the course of the reactions, and carboranes were detected only in trace quantities.

Tetraethyldiborane(6) serves as a hydroborating reagent in the usual way. Furthermore, exchange of B-C bonds is catalysed by Et_2BH which means that condensation of different organoboranes can easily take place, e.g. by elimination of R_3B. Finally, the large excess of Et_2BH provides a hydride reservoir if B-H bonds become essential for the stabilisation of polyhedral frameworks. Attempts to use tetramethyldiborane(6), $Me_2BH_2BMe_2$, instead of Et_2BH were not successful with respect to the synthesis of carboranes in appreciable yield. It is conceivable that the B-H-B bonding is stronger in the methyl derivative. Tetrapropyldiborane(6) has similar properties as Et_2BH, however, the thermal stability of the respective products from hydroboration and condensation is lower. Although the formation of carboranes can be confirmed by ^{11}B NMR spectra, their separation from mixtures and their purification appears to be difficult and has been achieved only for a few examples.

2.2 Reaction of Diethyl(propyn-1-yl)borane (1) with Et_2BH

The 1:1 reaction of Et_2BH with diethyl(propyn-1-yl)borane **1** (readily available from the reaction of Et_2BCl with $Bu_3Sn\text{-}C{\equiv}C\text{-}Me$) gives mainly the 1,1-diborylated alkene **3**. A very small quantity (< 3 %) of a 1,2-diborylated alkene may be present. The reaction of **1** with two equivalents of Et_2BH should lead to the triborylated species **4** which, however, could not be isolated or even detected under the reaction conditions. [The compound $(Et_2B)_3CH$ is known and has been prepared by a completely different route, in the absence of species containing B-H bonds.[7] If $(Et_2B)_3CH$ is added to an excess of Et_2BH, carborane formation was observed, although the mixture turned out to be fairly complex [8]]. It can be assumed that **4** either undergoes dehydroboration to **3** or that **4** reacts fast with Et_2BH to give new types of diborane(6) derivatives such as **5**. The latter assumption is more likely, since **5** would be an ideal starting point for further condensation reaction by elimination of Et_2BH. If there are no other organoboranes present, the condensation of **5** with **4** can take place, leading to a polyborylated hydrocarbon **6** (which may react with Et_2BH in the same way as **4**). The next step in the reaction is the threefold BEt/BH exchange, and the 1-carba-*arachno*-pentaborane(10) derivative **7** is formed. These reactions are summarised in Scheme 1.[9] Interestingly, only one isomer of **7** is present if the reaction mixture is not heated at >80 °C for prolonged time; the carborane **7** is >85 % pure after removing all readily volatile material. The proposed structure of **7** is based on a consistent set of NMR data, and it is supported by comparing its NMR data with those for similar compounds.[8,10-12] Heating of **7** at >100 °C gives the pentaethyl derivative of **A** in high purity and high yield (the molecular structure of Et_5-1,5-C_2B_3 has been determined [9]). This process is accompanied by the formation of ethyldiborane(6) derivatives.

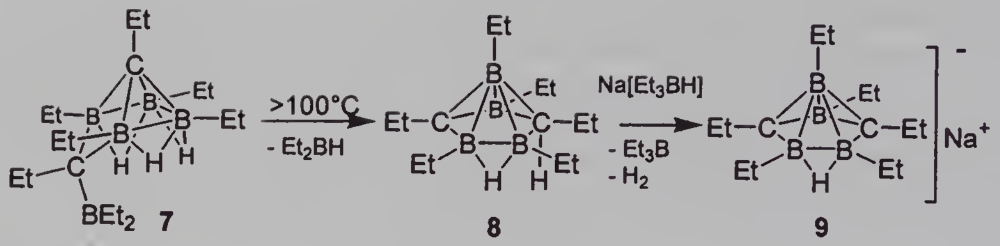


Scheme 1

If the reaction mixture contains boranes which are more reactive than **4**, other condensation products will be formed, and therefore, other carboranes can be prepared. This useful reaction principle will be shown later on.

2.3 Conversion of the 1-Carba-*arachno*-pentaborane(10) Derivative 7 into a *nido*-Carborane and Formation of Sodium Hexaethyl-2,4-dicarba-*nido*-hexaborate(1$^-$)

The *arachno*-structure of **7** in which the carbon atom is forced into the apical 1-position with high connectivity should easily rearrange into a *nido*-structure if a suitable leaving group is present. The inspection of the structure of **7** indicates that Et_2BH can be eliminated. By this the former bridging carbon atom becomes part of the carborane cage, and the former apical CEt unit changes its place with a BEt group and accomodates one of the bridging hydrogen atoms (Scheme 2). The result of elimination and rearrangement is the 2,4-dicarba-*nido*-hexaborane(8) derivative **8**,[13] an isomer of the well known [1] 2,3-dicarba- *nido*-hexaborane(8) cage. If one does not count the carbon atom bearing the ethyl group and the hydrogen atom in **8** as part of the cluster, this would be a pentaborane(9) analogue. However, *ab initio* MO calculations have shown that the structure with six cage atoms is much more stable,[14] and therefore, the C-H bond is required for the correct electron count of a *nido*-structure. These calculations also reproduce ^{13}C and ^{11}B chemical shifts in reasonable agreement with the experimental NMR data.

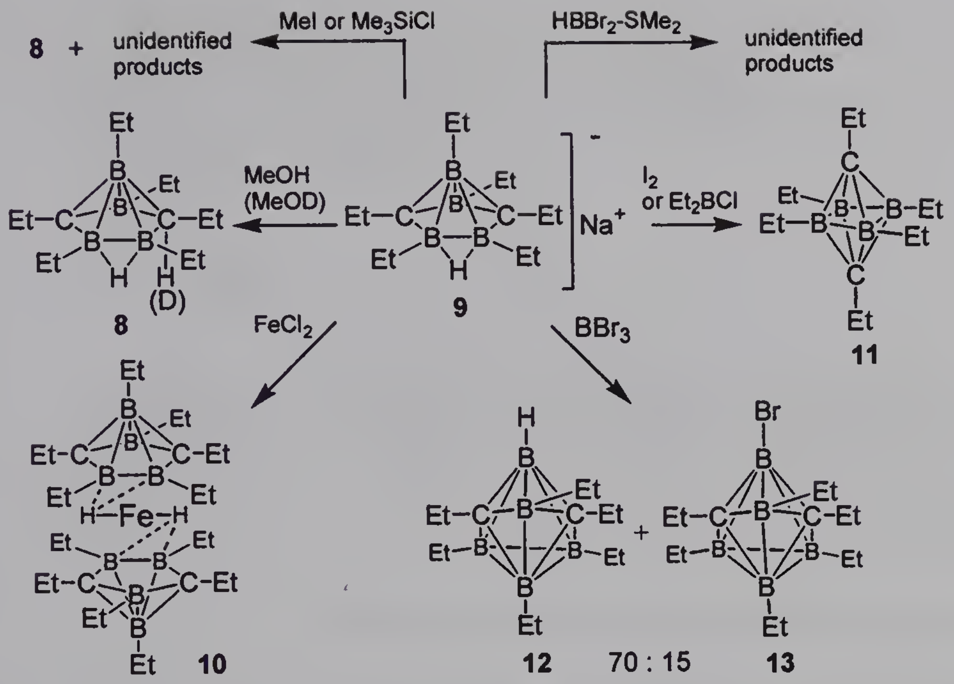


Scheme 2

Deprotonation of **8** is readily achieved by treatment of **8** with $Na[Et_3BH]$ in hexane. The sodium 2,4-dicarba-*nido*-hexaborate(1⁻) **9** has been characterised in solution by ^1H, ^{11}B and ^{13}C NMR, including various $^1H\{^{11}B\}$ double and $^{13}C\{^1H,^{11}B]$ triple resonance experiments and also in the solid state by X-ray structural analysis.[13] In the solid state, **9** crystallises from toluene without solvent as a dimer in which the two sodium cations are imbedded into a cave formed by the ten basal ethyl groups of the two anions. There are numerous close contacts between the sodium cations and the ethyl groups; the B-H-B hydrogen atoms are not involved in those contacts. The electron balance of the anion **9⁻** is comparable to that of cyclopentadienyl anions.

2.4 Reactivity of Sodium Hexaethyl-2,4-dicarba-*nido*-hexaborate(1⁻) (9)

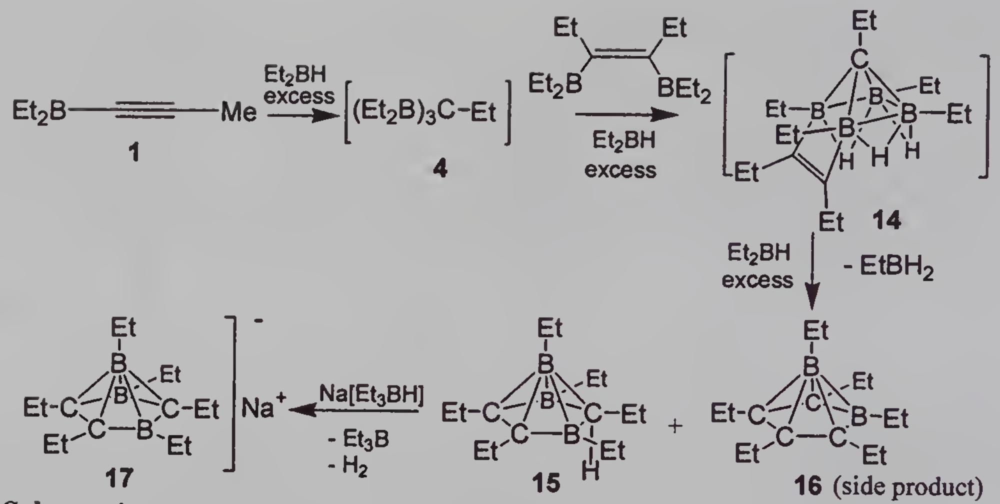
We have only started to explore the reactivity of the sodium 2,4-dicarba-*nido*-hexaborate(1⁻) **9**.[15] Some results are given in Scheme 3. The deprotonation of **8** is reversible, and there is no H/D exchange of the bridging hydrogen atom if the methanolysis is carried out with deuterated methanol. So far, we have failed to obtain species with a C_4B_8 cage by oxidative fusion.[16,17] A potential intermediate could have been the iron sandwich complex **10** which, however, turned out to be a very stable and chemically almost inert compound (fully characterised by NMR in solution and X-ray structural analysis in the solid state).[15] The NMR data indicate that the B-H-B bridging hydrogen atom in **9⁻** is now triply bridging the iron and the two boron atoms in 5,6 positions in **10** [δ^1H = -6.11, and sharpening of the ^1H NMR signal by selective $^1H\{^{11}B(5,6)\}$ double resonance experiments). Instead of oxidative fusion, **9** reacts with iodine to give the hexaethyl-1,6-dicarba-*closo*-hexaborane(6) **11**. The same product is obtained from the reaction of **9** with Et_2BCl, when it was attempted to replace the hydrogen atom by another substituent. By using other electrophiles such as MeI or Me_3SiCl, complex mixtures were obtained, in which **8** could be identified. So far all attempts at the synthesis of a derivative of **8** in which the C(5)-H bond is replaced by a C(5)-element bond have failed. Enlargement of the cage was observed when **9** reacted with BBr_3. This leads to a mixture of the 2,4-dicarba-*closo*-heptaborane(7) derivatives **12** and **13**. Surprisingly, the hexaethyl derivative **12** is formed in excess, whereas the expected 1-bromo-substituted hexaethyl derivative **13** is present only as a minor component. Experiments aiming in the same direction, using $HBBr_2$-SMe_2 as an electrophile, failed completely. The carboranes **11** – **13** are readily identified by their characteristic ^1H, ^{11}B and ^{13}C NMR parameters.[15]



Scheme 3

2.5 Reaction of Et$_2$B-C≡C-Me (1) in the Hydride Bath in the Presence of (Z)-3,4-Bis(diethylboryl)hex-3-ene

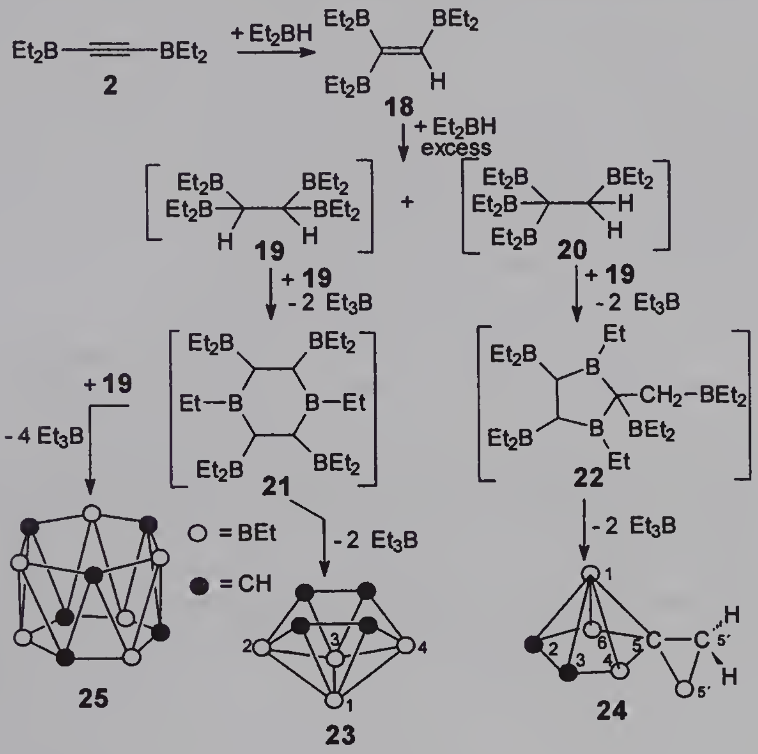
The intermediacy of **4** or **5** is supported by condensation reactions with various geminal bis(diethylboryl)-substituted alkanes [e.g. $(Et_2B)_2C(H)Me$; $(Et_2B)_2C(H)SiMe_3$] leading to 1-carba-*arachno*-pentaborane(10) derivatives analogous to **7**, .in which the Et_2B group is replaced by other substituents.[8] Therefore, it was of interest to find out about the condensation with vicinal bis(diethylboryl)-substituted alkenes. (Scheme 4). The proposed intermediate **14** with the 1-carba-*arachno*-pentaborane(11) cage could not be detected. However, a comparable analogue with a benzo group instead of the EtC=CEt unit has already been isolated.[11] If $EtBH_2$ is eliminated from **14** and the same rearrangement occurs as described for the conversion of **7** into **8**, the formation of **15** is readily explained. A side product, the 2,3,4,5-tetracarba-*nido*-hexaborane(6) **16**, is also formed. This carborane results from the known reaction of (Z)-3,4-bis(diethylboryl)hex-3-ene in the presence of Et_2BH.[4a] Since **16** does not react with $Na[Et_3BH]$, the hexaethyl-2,3,5-tricarba-*nido*-hexaborate(1^-) **17** can be separated and its reaction with methanol affords the pure hexaethyl-2,3,5-tricarba-*nido*-hexaborane(7). Such carboranes have been made before,[18] however the yield was poor and they could not be isolated in pure state. The present synthesis provides a straightforward route to this system.[19] The *endo*-C-H bond is part of the cluster as required by the electron count for a *nido*-cage, and in this case the reduced magnitude of the coupling constant $^{1}J(^{13}C,^{1}H)$ = 100 .Hz is also indicative. Again, the anion **17** is comparable to cyclopentadienyl anions, and one can expect a similarly extended chemistry. The NMR spectroscopic characterisation of the carborane **15** and its anion **17** is reliable,[19] and comparison with known data from the literature [20] serves for the identification of **16**..



Scheme 4

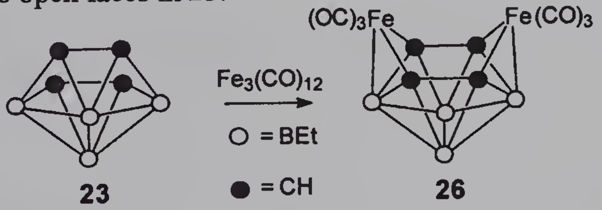
2.6 Reaction of Bis(diethylboryl)ethyne (2) with Et_2BH

Having firmly established the principles of condensation reactions towards polyhedral boranes, we became interested in alkyn-1-ylboranes other than 1. Bis(diethylboryl)ethyne **2** is readily accessible from the reaction of Et_2BCl with $Bu_3Sn\text{-}C{\equiv}C\text{-}SnBu_3$, and its reaction with Et_2BH should provide a route to novel carboranes. Carboranes with a B_4C_4 cage have been described,[21,22] however, their structures have not been assigned with certainty, and the synthetic strategies appeared not very advantageous. According to Scheme 5, the access to the C_4B_4 derivative **23**, starting from **2**, is simple, although the yield is only 20 %.[23] The alkene **18** can be isolated after the 1:1 reaction of **2** with Et_2BH, and it can also serve as starting material. The second hydroboration can lead either to **19** or to **20**. The latter reaction is not preferred. Both **19** and **20** are likely to react with Et_2BH to give diborane(6) derivatives. Condensation of two molecules of **19** should lead to **21**. There are various stereoisomers of **21**. If all Et_2B groups are in *cis*-positions, elimination of Et_3B leads to the *nido*-C_4B_4 cage **23**. Compound **23** is a colourless, air-stable liquid which can be purified by distillation, and the molecular structure was determined by growing a single crystal from the melt, followed by X-ray diffraction analysis.[24] NMR spectra show clearly that all dynamic processes with respect to cage rearrangements are slow on the NMR time scale, and that the solid-state structure is retained in solution. If **20** is formed as a minor product, it is likely to condense with one equivalent of **19** to give the intermediate **22**. If the stereochemistry is correct, elimination of Et_3B will lead to the *spiro*-carborane **24** which belongs to the 2,3,5-tricarba-*nido*-hexaborane(7) family. The novel carborane **24** is extremely reactive owing to the three-membered ring containing a three-co-ordinate boron atom. So far we have not succeeded to isolate **24** in pure state. However, it reacts readily with Lewis-bases at the site of the three-co-ordinate boron atom to give either adducts or to open the ring (e.g. reaction of **24** with one equivalent of BuLi).The NMR data of **24** (also calculated based on optimised geometries) and its derivatives strongly support the proposed structure.[24] The intermediate **21** can condense with a further equivalent of **19**. Again, if the stereochemistry is favourable, elimination of Et_3B leads to the carborane **25** in which six boron and six carbon atoms build the cage. This is an *arachno*-carborane, and the proposed structure is based on consistent spectroscopic data and *ab initio* MO calculations which also reproduce (GIAO or IGLO) the experimental NMR data.[25]



Scheme 5

The open faces in **23** or in **25** invite for adding transition metal fragments. This has been carried out successfully in the case of **23** by adding two $Fe(CO)_3$ units (Scheme 6).[23] The complex **26** has the same electron count as *nido*-decaborane(14) and its structural features, as determined by X-ray analysis, are similar. Work is in progress to make use of the two open faces in **25**.



Scheme 6

3 CONCLUSIONS

The Et_2BH catalysed condensation of polyborylated hydrocarbons offers attractive alternative routes to novel carboranes. Owing to the exceptional thermal stability of the majority of the new carboranes, further useful transformations can be envisaged. The easy access to cyclopentadienyl-analogous borate anions is another promising aspect of the synthetic potential.

Acknowledgement

Support of this work by DFG is gratefully acknowledged.

References

1. R.N. Grimes, ´Carboranes´, Academic Press, London 1970.
2. R. Greatrex, M.A. Fox, in ´The Borane, Carborane, Carbocation Continuum´ (J. Casanova, ed.), Wiley, New York, 1998, pp. 289-305.
3. R. Köster, G.W. Rotermund, *Tetrahedron Lett.* 1964, 1667.
4, (a) P. Binger, *Tetrahedron Lett.* 1966, 2675. (b) R. Köster, M.A. Grassberger, *Angew. Chem* 1967. **79**, 197; *Angew. Chem. Int. Ed. Engl.* 1967, **6**, 218
5. R. Köster, G. Bruno, P. Binger, *Liebigs Ann. Chem.* 1961, **644**, 1.
6. B. Wrackmeyer, H.-J. Schanz, R. Köster, *Fresenius´ J. Anal. Chem.*1998 **362**, 378
7. R. Köster, H.-J. Horstschäfer, P. Binger, P.K. Mattschei, *Liebigs Ann. Chem.* 1975,1339.
8. B. Wrackmeyer, H.-J. Schanz, *Coll, Czech. Chem. Comm.*1997, **62**, 1254.
9. R. Köster, R. Boese, B. Wrackmeyer, H.-J. Schanz, *Chem. Commun.* 1995, 1961.
10. R. Köster, G. Seidel, B. Wrackmeyer, *Angew. Chem.* 1994, **106**, 2380; *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 2294.
11. B. Gangnus, H. Stock, W. Siebert, M. Hofmann, P.v.R. Schleyer, *Angew. Chem.* 1994, **106**, 2382; *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 2296.
12. M.A. Fox, R. Greatrex, M. Hofmann, P.v.R. Schleyer, *Angew. Chem.* 1994, **106**, 2384; *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 2298.
13. B. Wrackmeyer, H.-J. Schanz, W. Milius, *Angew. Chem.* 1997, **109**, 98; *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 75.
14. M. Hofmann, M.A. Fox, R. Greatrex, R.E. Williams, P.v.R. Schleyer, *J. Organomet. Chem.* 1998, **550**, 207.
15. B. Wrackmeyer, H.-J. Schanz, W. Milius, C. McCammon, *Coll. Czech. Chem. Comm.* 1999, **64**, 977.
16. (a) R.N. Grimes, *Chem. Rev.* 1992, **92**, 251. (b) R.N. Grimes, *Coord. Chem. Rev.* 1995, **143**, 71.
17. R. Köster, G. Seidel, B. Wrackmeyer, D. Bläser, R. Boese, M. Bühl, P.v.R. Schleyer, *Chem. Ber.* 1991, **124**, 2715.
18. W. Siebert, in ´Current Topics in the Chemistry of Boron´(G.W. Kabalka, ed.), Royal Society of Chemistry, Cambridge, 1994, pp. 269-275, and literature cited therein.
19. B. Wrackmeyer, H.-J. Schanz, *Main Group Met. Chem.* 1998, **21**, 29.
20. B. Wrackmeyer, *Z. Naturforsch., Teil B,* 1982, **37**, 412.
21. W. Siebert, M.E.M. El-Esawi, *Chem. Ber.* 1979, **112**, 1480.
22. (a) T.P. Fehlner, *J. Am. Chem. Soc.* 1977, **99**, 8345. (b) T.P. Fehlner, *J. Am. Chem. Soc.* 1986, **108**, 3426. (c) M.G.J. Mirabelli, L.G. Sneddon, *Organometallics* 1986, **5**, 1510.
23. B. Wrackmeyer, H.-J. Schanz, W. Milius, *Angew. Chem.* 1997, **109**, 1147; *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 1117.
24. B. Wrackmeyer, H.-J. Schanz, M. Hofmann, P.v.R. Schleyer, R. Boese, *Eur. J. Inorg. Chem.* 1999, 533.
25. B. Wrackmeyer, H.-J. Schanz, M. Hofmann, P.v.R. Schleyer, *Angew. Chem.* 1998, **108**, 1329; *Angew. Chem. Int. Ed. Engl.* 1998, **37**,1245.

Studies of Icosahedral Carboranes with Iminotris(dimethylamino)phosphorane, $HNP(NMe_2)_3$

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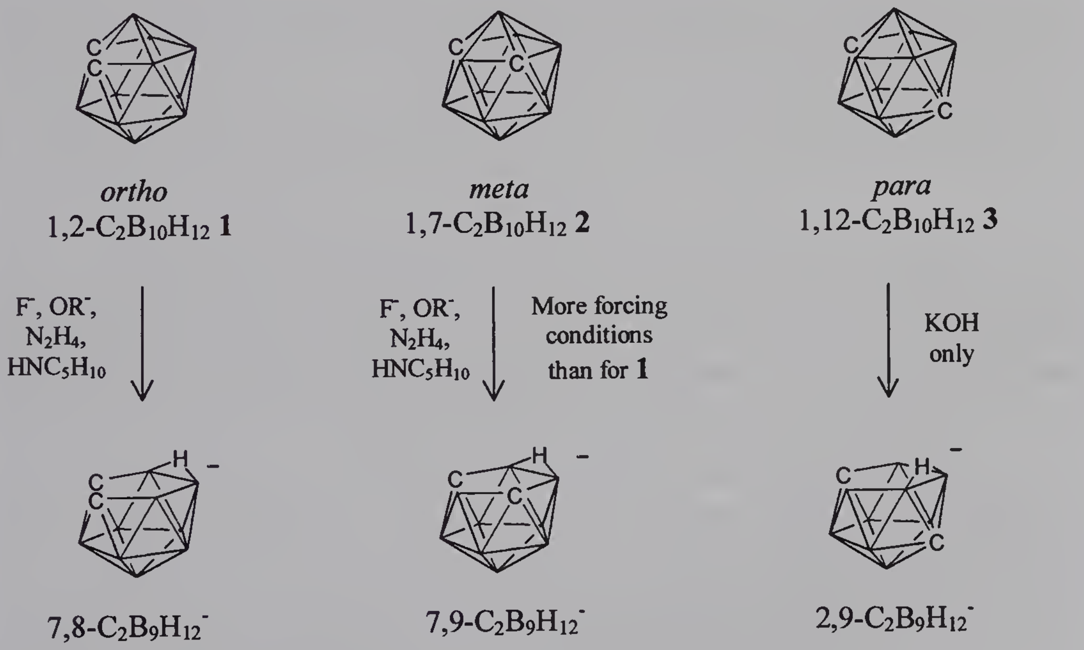
1. INTRODUCTION

The *closo*-icosahedral carboranes $C_2B_{10}H_{12}$ **1-3** are remarkably resilient to heat and oxidising agents but are susceptible to nucleophilic attack by a select few powerful Lewis bases which can remove one of their BH units, formally as BH^{2+}, leaving *nido*-shaped $C_2B_9H_{11}^{2-}$ (or $C_2B_9H_{12}^-$) anionic residues. Alkoxides, fluorides, hydrazines and piperidine convert *ortho* carborane 1,2-$C_2B_{10}H_{12}$ **1** into the *nido* anion 7,8-$C_2B_9H_{12}^-$ and, with more forcing conditions, *meta* carborane 1,7-$C_2B_{10}H_{12}$ **2** into 7,9-$C_2B_9H_{12}^-$.[1-4] The *para* carborane 1,12-$C_2B_{10}H_{12}$ **3** could only be converted into the *nido* anion 2,9-$C_2B_9H_{12}^-$ by potassium hydroxide.[5]

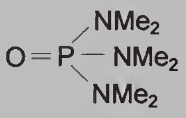


HMPA (hexamethylphosphoramide) $OP(NMe_2)_3$ **4** does not deboronate the $C_2B_{10}H_{12}$ isomers at room temperature but acts as an hydrogen bond acceptor for the acidic hydrogens at the carbon atoms of these clusters to yield 1:1 carborane:HMPA adducts on crystallization.[6] These C-H···O hydrogen bonded supramolecular structures provide the first definitive X-ray structures of the unsubstituted carboranes.

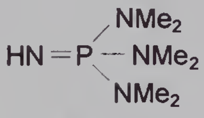
$$\underset{\mathbf{1}}{1,2\text{-}C_2B_{10}H_{12}} + OP(NMe_2)_3 \longrightarrow [1,2\text{-}C_2B_{10}H_{12}\cdot OP(NMe_2)_3]_2$$

$$\underset{\mathbf{2}}{1,7\text{-}C_2B_{10}H_{12}} + OP(NMe_2)_3 \longrightarrow [1,7\text{-}C_2B_{10}H_{12}\cdot OP(NMe_2)_3]_\infty$$

$$\underset{\mathbf{3}}{1,12\text{-}C_2B_{10}H_{12}} + OP(NMe_2)_3 \longrightarrow [1,12\text{-}C_2B_{10}H_{12}\cdot OP(NMe_2)_3]_\infty$$



4



5

This paper discusses reactions between the commercially available base iminotris(dimethylamino)phosphorane $HNP(NMe_2)_3$ **5** and the icosahedral carboranes **1-3** where base **5** is found to be either an effective deboronating agent, a good hydrogen bond acceptor or both.

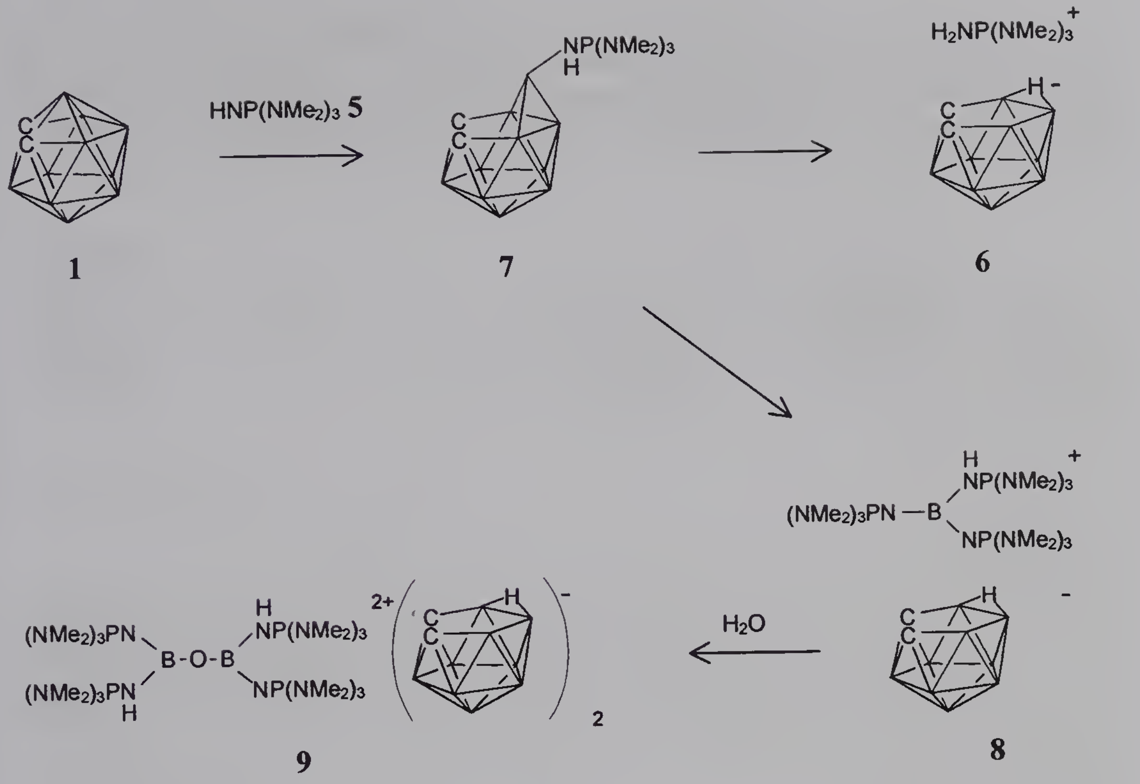
2. *ORTHO* CARBORANE

In the presence of air at 20°C, the reaction of the iminophosphorane **5** with *ortho* carborane **1** resulted in deboronation to yield the $H_2NP(NMe_2)_3^+$ salt **6** of the *nido* anion $7,8\text{-}C_2B_9H_{12}^-$ and boric acid.[7]

$$\underset{\mathbf{1}}{1,2\text{-}C_2B_{10}H_{12}} + \underset{\mathbf{5}}{HNP(NMe_2)_3} + 3\ H_2O \longrightarrow \underset{\mathbf{6}}{7,8\text{-}C_2B_9H_{12}^-\ H_2NP(NMe_2)_3^+} + B(OH)_3 + H_2$$

Crystals formed from the reaction mixture were identified by X-ray crystallography as a 1:1 polymeric adduct of $[H_2NP(NMe_2)_3^+]_2CO_3^{2-}\cdot B(OH)_3$. Unlike HMPA **4**, the iminophosphorane **5** absorbs carbon dioxide and water in the presence of air. Base **5** converts *ortho*-carborane into the *nido*-anion just as effectively in the absence of air indicating that water and CO_2 are not vital ingredients in the deboronation process.

Under nitrogen, slow addition of dry $HNP(NMe_2)_3$ in anhydrous toluene to a solution of **1** in toluene resulted in the formation of a crystalline product overnight. Although this product was identified by boron NMR spectroscopy as a mixture of **1** and $7,8\text{-}C_2B_9H_{12}^-$, a single crystal X-ray determination revealed a carborane adduct $C_2B_{10}H_{12}.HNP(NMe_2)_3$ **7**.[8] Adduct **7** is believed to be the first structurally characterized intermediate in the well known conversion of *closo*-$1,2\text{-}C_2B_{10}H_{12}$ **1** to *nido*-$7,8\text{-}C_2B_9H_{12}^-$. As revealed by the X-ray structure of 7, the first step of the *closo-nido* conversion is the attachment of the base to the most positively charged boron atom near the two neighbouring carbon atoms which pivots about B(10), cleaving the two B-C bonds and stretching the two B-B bonds to B(9) and B(11).



The carborane anion 7,8-$C_2B_9H_{12}^-$ was observed by multinuclear NMR spectroscopy as a 1:1 mixture of salts **6** and **8** containing the cation $H_2NP(NMe_2)_3^+$ and the protonated tris(imino)borane $(Me_2N)_3PNHB[NP(NMe_2)_3]_2^+$ respectively.[8] Monoboron products from the deboronation of *ortho* carboranes have previously been obtained[2,3,9] as neutral or anionic species but in this study the monoboron product in **8** is cationic and of a type previously generated only from monoboron starting materials.[10]

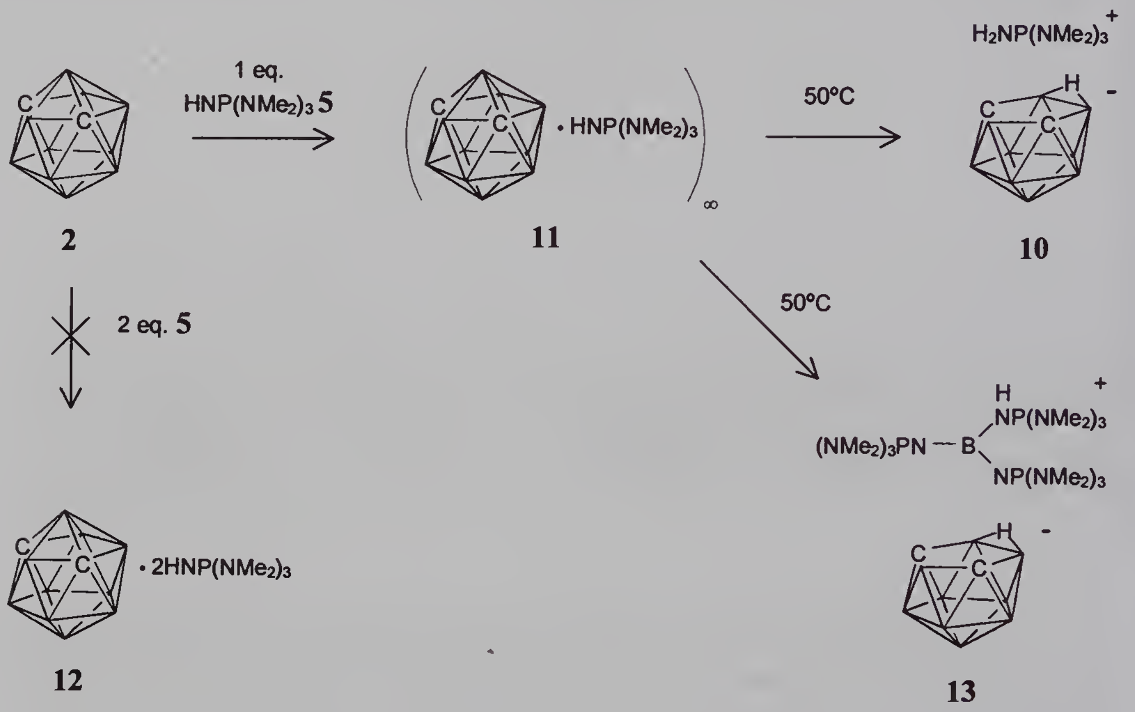
While a crystal structure of the salt **6** has been obtained, attempts to obtain a crystal structure of the salt **8** containing the cation $(Me_2N)_3PNHB[NP(NMe_2)_3]_2^+$ from toluene have not been successful.[8] In one attempted recrystallization of **8** a single crystal was characterized by an X-ray study as a salt **9** containing the dication $[(Me_2N)_3PNHBNP(NMe_2)_3]_2O^{2+}$. The oxygen atom apparently arose from inadequately dried toluene.

3. *META* CARBORANE

In the presence of air at 70°C, the reaction of the iminophosphorane **5** with *meta* carborane **2** resulted in deboronation to yield the $H_2NP(NMe_2)_3^+$ salt **10** of the *nido* anion 7,9-$C_2B_9H_{12}^-$ and boric acid.[5] When isolated in the solid state, the salt **10** degraded further to boric acid residues in the presence of air. Salts containing the 7,9-$C_2B_9H_{12}^-$ anions are characteristically air-sensitive solids.[9,11]

$$\underset{\mathbf{2}}{1,7\text{-}C_2B_{10}H_{12}} + \underset{\mathbf{5}}{HNP(NMe_2)_3} + 3\,H_2O \longrightarrow \underset{\mathbf{10}}{7,9\text{-}C_2B_9H_{12}^-\,H_2NP(NMe_2)_3^+} + B(OH)_3 + H_2$$

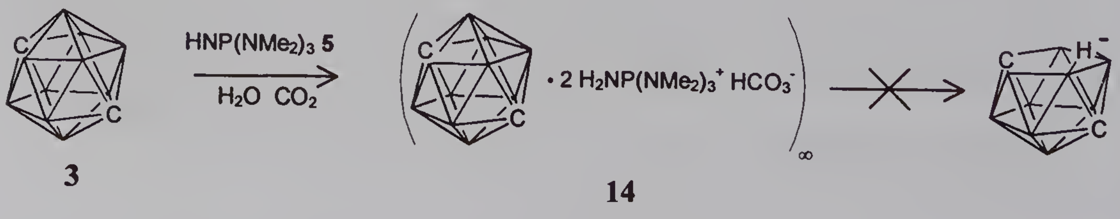
Under nitrogen, a 1:1 ratio mixture of carborane **2** and base **5** in toluene at –20°C gave crystals identified as a 1:1 polymeric adduct **11**.[12] The crystal structure of **11** revealed the presence of two C-H···N hydrogen bonds per molecule. A 2:1 crystalline adduct **12**, where one C-H···N hydrogen bond per base molecule would be expected, could not be obtained.



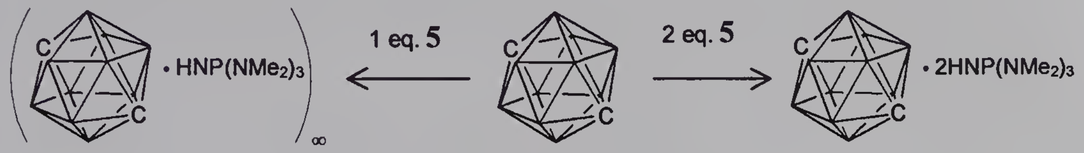
Heating the 1:1 adduct **11** in toluene overnight at 50°C resulted in a third of the *closo* carborane being converted into the *nido* anion 7,9-$C_2B_9H_{12}^-$.[12] The anion was observed by multinuclear NMR spectroscopy accompanied by a 1:3 mixture of the cation $H_2NP(NMe_2)_3^+$ **10** and the protonated tris(imino)borane $(Me_2N)_3PNHB[NP(NMe_2)_3]_2^+$ **13** respectively. The identity of the latter salt **13** was confirmed by an X-ray crystal study.

4. *PARA* CARBORANE

In refluxing toluene, the iminophosphorane **5** did not convert the *para* carborane **3** into the *nido* anion 2,9-$C_2B_9H_{12}^-$ even after several weeks. However crystals obtained from these starting materials were identified by X-ray crystallography as a polymeric adduct $[1,12\text{-}C_2B_{10}H_{12}.2\ H_2NP(NMe_2)_3^+HCO_3^-]_\infty$ **14**.[5]



Under N_2, a 1:1 ratio mixture of *para* carborane **3** and base **5** in toluene at –20°C gave crystals identified by multinuclear NMR spectroscopy as a 1:1 adduct **15.**[12] Likewise, a 1:2 ratio mixture of **3** and **5** gave a 1:2 adduct **16**. An X-ray structural determination of the latter adduct showed two base molecules to be linked solely to one carborane molecule via C-H···N hydrogen bonds.



15 **3** **16**

5. CONCLUSIONS

In this study, the iminophosphorane $HNP(NMe_2)_3$ is shown to be an effective deboronating agent for *ortho* and *meta* carboranes but not for *para* carborane. Under nitrogen, these deboronations provide novel routes to three-coordinate monoboron cations. A carborane intermediate, as $C_2B_{10}H_{12} \cdot HNP(NMe_2)_3$ from *ortho* carborane and $HNP(NMe_2)_3$, is structurally characterized for the first time in the icosahedral carborane *closo-nido* conversion. The iminophosphorane co-crystallizes with *meta* and *para* carboranes to yield adducts with C-H···N bonds.

6. ACKNOWLEDGEMENTS

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REFERENCES

1. R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642; L. I. Zakharkin and V. N. Kalinin, *Tetrahedron Lett.*, 1965, **7**, 407; M. F. Hawthorne, P. A. Wegner and R. C. Stafford, *Inorg. Chem.*, 1965, **4**, 1675; D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen and M. M. Fein, *Inorg. Chem.*, 1963, **2**, 1120; L. I. Zakharkin and V. N. Kalinin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* **1965**, 567; V. I. Stanko, N. S. Titova, A. N. Kashin, K. P. Butin and I. P. Beletskaya, *J. Gen. Chem. USSR, (Engl. Transl.)*, 1970, **40**, 2217; A. F. Zhigach, R. A. Svitsyn and E. S. Sobolev, *J. Gen. Chem. USSR, (Engl. Transl.)*, 1977, **47**, 212.
2. M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862; L. I. Zakharkin and V. S. Kirillova, *Bull. Acad. Sci. USSR, Div. Chem. Sci., (Engl. Transl.)* **1975**, 2484.
3. H. Tomita, H. Luu and T. Onak, *Inorg. Chem.*, 1991, **30**, 812.
4. M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride, K. Wade and H. M. Colquhoun, *Polyhedron*, 1996, **15**, 565.
5. J. Plešek and S. Heřmánek, *Chem. Ind. (London)*, 1973, 381; D. C. Busby and M. F. Hawthorne, *Inorg. Chem.*, 1982, **21**, 4101.

6. M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.*, **1996**, 2285.
7. T.G. Hibbert, *Ph.D. Thesis*, University of Durham, Durham 1997; R. C. B. Copley, M. G. Davidson, F. L. Gray, T. G. Hibbert, J. A. K. Howard and K. Wade, unpublished work.
8. M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, I. S. Neretin and K. Wade, *Chem. Commun.*, **1999**, 1649.
9. M. A. Fox, J. A. H. MacBride and K. Wade, *Polyhedron*, 1997, **16**, 2499; M. A. Fox and K. Wade, *Polyhedron*, 1997, **16**, 2517.
10. P. Kölle and H. Nöth, *Chem. Rev.*, 1985, **85**, 399.
11. M. A. Fox and K. Wade, *J. Organometal. Chem.*, 1999, **573**, 279; J. D. Hewes, M. Thompson and M. F. Hawthorne, *Organometallics*, 1985, **4**,13.
12. A. S. Batsanov, M. G. Davidson, M. A. Fox, J. A. K. Howard and K. Wade, unpublished work.

Novel Organic Derivatives of Carboranes: Synthesis and Chemical Properties

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1 INTRODUCTION

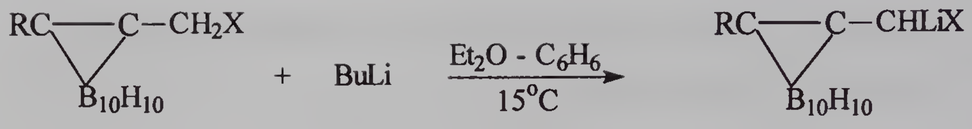
A significant volume of our research is focussed on the synthesis of C- and B-organyl derivatives of carboranes. The metallation reaction of acidic hydrogen atoms at the CH vertices of carborane polyhedron with, *e.g.*, BuLi or $NaNH_2$ followed by the action of electrophilic reagents is one of the most important methods for the synthesis of C-substituted organylcarboranes.[1] In contrast to the CH-groups, hydrogen atoms bonded to boron atoms of the polyhedron are not acidic and are not metallated even by the strongest metallating agents (BuLi, *t*BuOK). In this case, the reaction of electrophilic alkylation in the presence of $AlCl_3$ and cross-coupling reaction are used for introduction of organic groups to boron atoms. In this report we present some new examples of metallation of C-substituted derivatives of *o*-carborane and new methods for the introduction of organic groups to the boron atoms of carboranes.

2 RESULTS AND DISCUSSION

2.1 Synthesis of the Stable Carboranyl-Substituted Carbenoids

Despite the strong electron-withdrawing effect of the 1-*o*-carboranyl group, the alkyl groups bonded to the carbon atom are not metallated with such reagents as BuLi, *t*BuOK, and $NaNH_2$. We have found that substitution of a hydrogen atom in the methyl group of *o*-carborane by a chlorine atom or a methoxy group under the action of BuLi on compounds (1- 3) unexpectedly results in carbenoids (4 - 6) [2,3] stable at room temperature (Scheme 1).The low solubility of compounds (4-6) in a benzene-ether mixture indicates that the C-Li bond is highly polar.

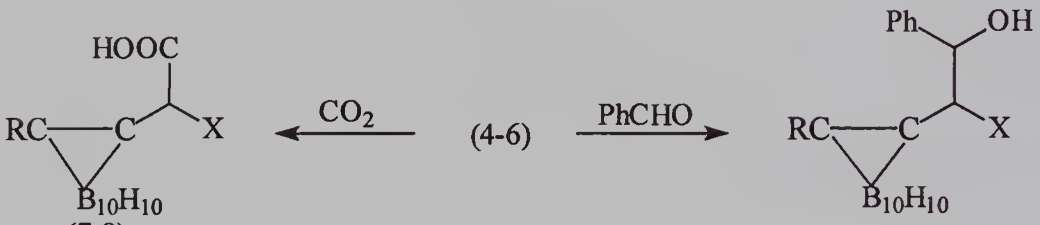
These carbenoids readily react with electrophilic reagents to give new organic carborane derivatives (7-10).



(1-3) (4-6)

X = Cl; R = Me (1, 4)
X = OMe; R = Me (2, 5); R = *i*-Pr (3, 6)

Scheme 1



(7-9) (10-12)

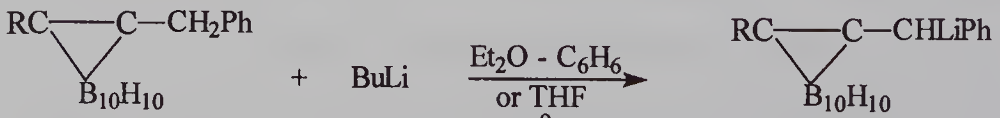
X = Cl; R = Me (7, 10)
X = OMe; R = Me (8, 11); R = *i*-Pr (9, 12)

Scheme 2

2.2 Lithiumbenzyl Carboranes: Preparation and Reactions

We found [4] that the methylene group in 1-methyl-2-benzyl-*o*-carborane is highly acidic (pKa = 19.5). Its acidity is even higher than acidity of *o*-carborane (pKa=23.3) and 1-methyl-7-benzyl-*m*-carborane (pKa = 33.5).

Under the action of BuLi on substituted benzyl-*o*-carboranes (13-15) metallation on the CH_2 group occurs readily to give coloured lithium benzyl-*o*-carboranes (16-18) that are less soluble in aprotic solvents than lithium-*o*-carboranes.[5]



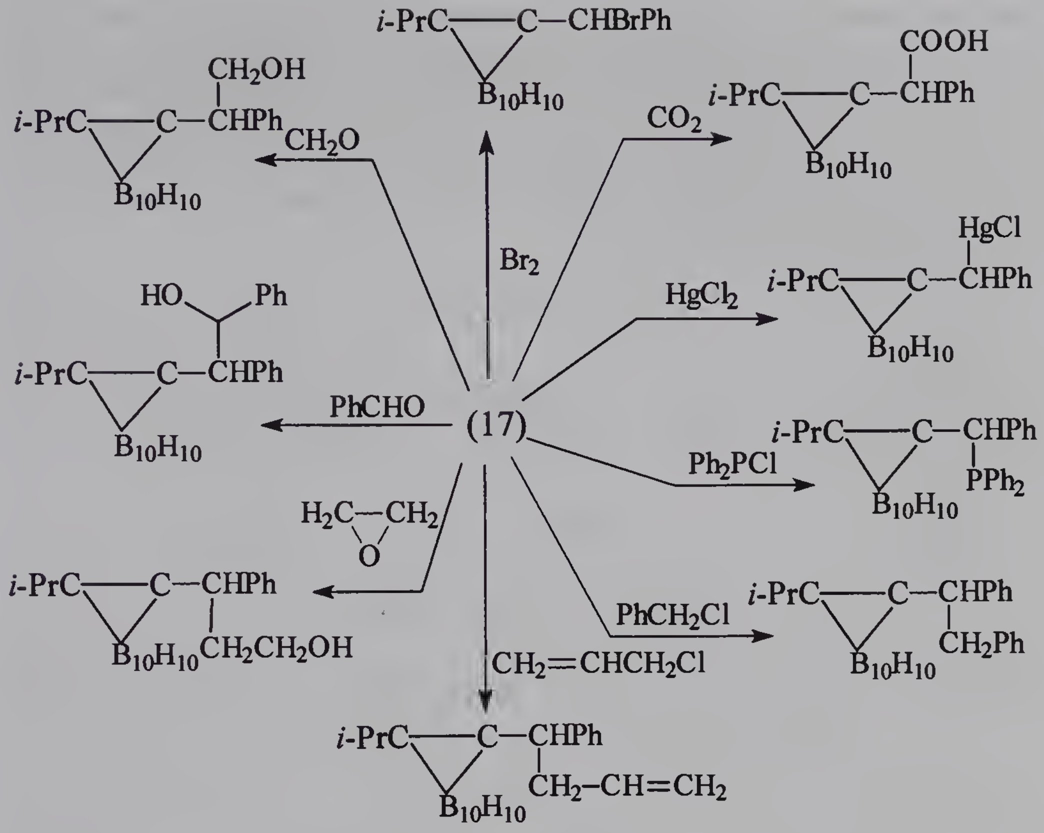
(13-15) (16-18)

R = Me (13, 16); R = *i*-Pr (14, 17); R = Ph (15, 18)

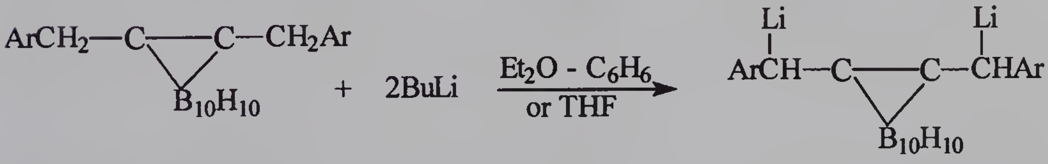
Scheme 3

The lithiumbenzyl carboranes readily react with various electrophilic reagents. This was shown by taking a lithium derivative 17 as an example (Scheme 4). The reactions proceed in high yields and make it possible to obtain various derivatives of *o*-carborane containing a substituted benzyl group.

Similarly to monobenzyl-*o*-carborane, metallation of 1,2-dibenzyl-*o*-carborane and other 1,2-(*o*-carboranylmethyl)diaryls under the action of two moles of BuLi in THF or in a benzene-ether solution results in corresponding intensely coloured dilithium derivatives (Scheme 5).



Scheme 4

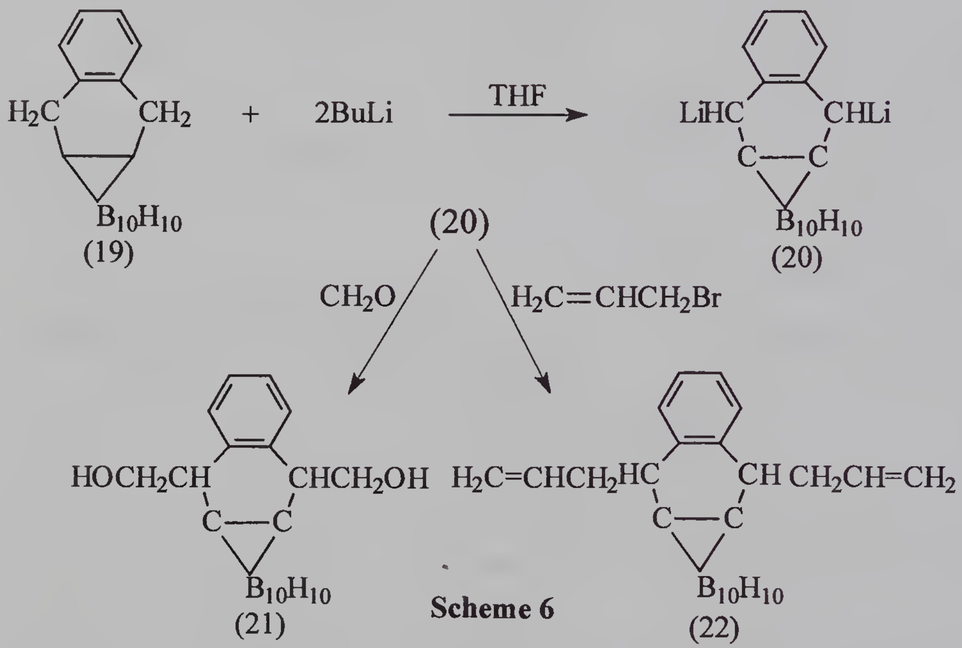


Ar = Ph; *m*- and *p*-$C_6H_4CH_3$; *o*- and *p*-$C_6H_4OCH_3$; α-$C_{10}H_7$

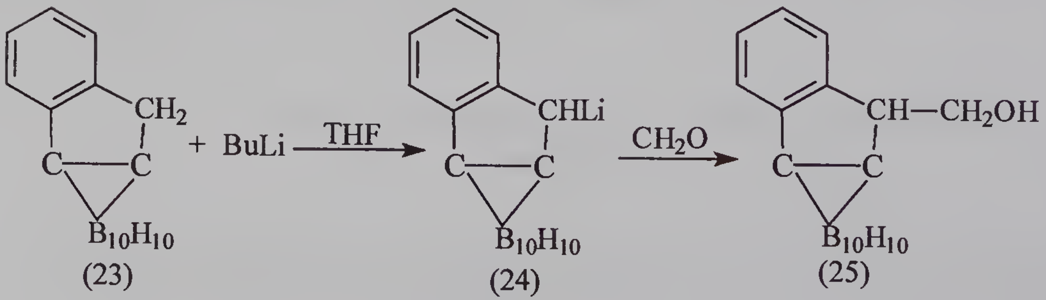
Scheme 5

The analogues of benzyl derivatives also readily undergo metallation under the action of BuLi to give dilithium compounds that also react with electrophilic reagents. 1,2-Benzo-4,5-carboranylcyclohexane (19) is an interesting CH-acid whose metallation by two moles of BuLi results in the formation of the lithium derivative (20), which reacts with CH_2O and allyl bromide to give diol (21) and diallylic compound (22), respectively (Scheme 6). 1,2-Benzo-4,5-carboranylcyclopentane (23), also is a CH-acid and readily undergoes metallation by BuLi to give a lithium derivative (24). The latter is capable of entering into conventional reactions characteristic of organolithium compounds (Scheme 7).

The above examples of reactions mono- and dilithium- substituted compounds show that there are considerable opportunities for using them in the synthesis of various C-organyl substituted *o*-carborane derivatives. The high CH-acidity of *o*-carboranylmethylarenes cannot be rationalized using the data available to date. It is assumed that in the case of *o*-carboranylmethylarenes not only the aromatic system, but also the *o*-carborane cage is involved in delocalization of the negative charge of the carbanion. We believe that partial double bonding in the *o*-carboranylmethyl anion leading to strong delocalization of the negative charge in the case of the lithium benzyl carbanions and dilithium dibenzyl dicarbanions studied. In contrast to *m*-carborane, *o*-carborane is capable[6] of forming a delocalized double bond between the carbon atom of the polyhedron and a neighboring atom.

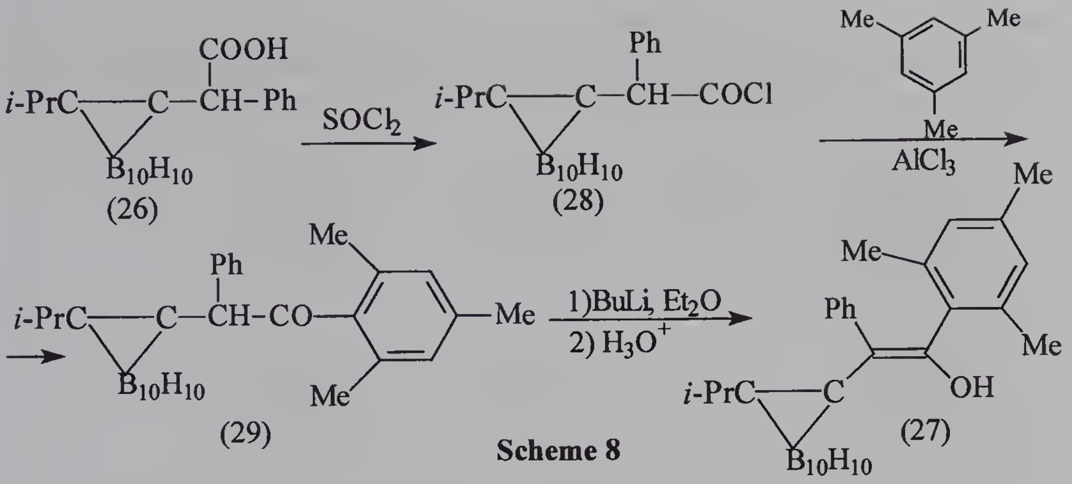


Scheme 6

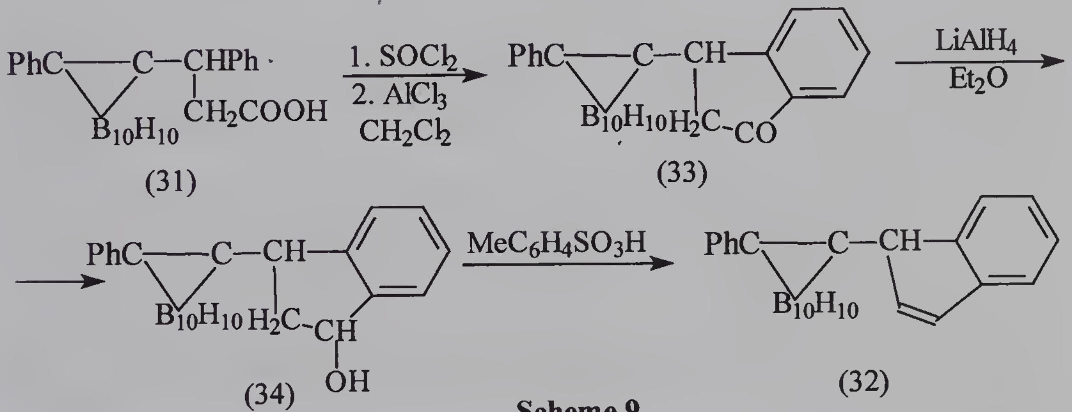


Scheme 7

Based on the benzyl derivative (26), the first stable carborane-containing simple enol (27) was synthesized[7] (Scheme 8). The acid chloride (28) readily enters into a Friedel-Crafts reaction with mesitylene to give ketone (29). Under the action of BuLi on a benzene-ether solution of ketone (29) enolate (30) is formed. Treatment of the latter with diluted HCl solution results in enol (27). Starting from the benzyl derivative (31), carboranyl-substituted indene (32) was synthesized by intramolecular cyclization with a formation of ketone (33), whose reduction (34) followed by dehydration results in (32) (Scheme 9).



Scheme 8

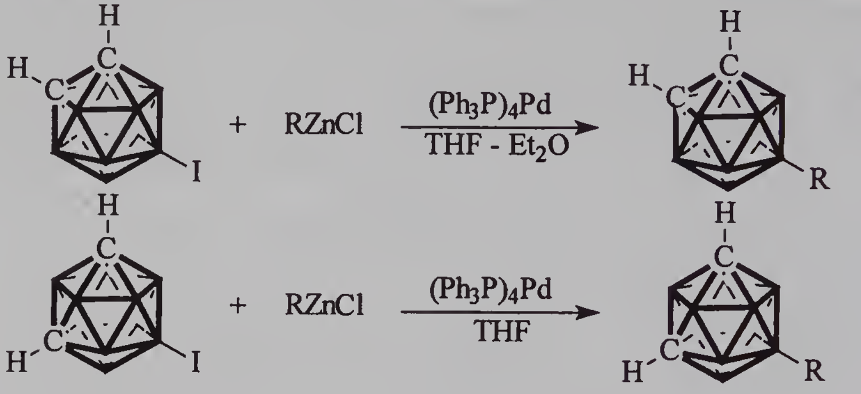


Scheme 9

2.3 Organozinc Compounds in the Cross-coupling Reaction with Iodocarboranes

Earlier, we proposed to synthesize B-substituted organylcarboranes using cross-coupling reactions of B-iodo- and B,B'-diiodocarboranes with organomagnesium compounds catalyzed by palladium complexes we discovered.[8,9] In this work,[10,11] we found that, in contrast to the organomagnesium compounds, organozinc compounds with functionally substituted groups enter into cross-coupling reaction with B-iodocarboranes, which makes it possible to obtain B-substituted organylcarboranes with functional groups. This considerably extends the possibilities of preparing new representatives of B-organylcarboranes. It should be noted that in this case, in contrast to organomagnesium compounds, no metallation on the CH groups of carborane occurs.

Cross-coupling of 9-iodo-*o*-carborane and 9-iodo-*m*-carborane with RZnX proceeds in diethyl ether or THF in high yields following the Scheme 10. Organozinc compounds containing methoxycarbonyl, keto, and nitrile groups were synthesized from the corresponding bromides or iodides and activated zinc, and were used in the cross-coupling reaction with 9-iodo-*o*-carborane and 9-iodo-*m*-carboranes (Scheme 11).

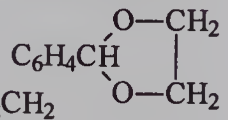


R = Et, C_6H_{13}, $PhCH_2$, Ph, Me_3SiCH_2, CH_2=CH-CH_2, $Me_3SiC{\equiv}C$,
2-thienyl, *o*-$HCB_{10}H_{10}CCH_2$, $C_5H_5FeC_5H_4$, $(CO)_3MnC_5H_4$

Scheme 10

$$o\text{-},m\text{-}HCB_{10}H_9(9\text{-}I)CH \quad + \quad RZnX \xrightarrow[THF]{(Ph_3P)_4Pd} o\text{-},m\text{-}HCB_{10}H_9(9\text{-}R)CH$$

X = Br, I; R = 4-$MeOCOC_6H_4CH_2$, 4-$PhCOC_6H_4CH_2$,
$MeOCO(CH_2)_4CH_2$, $MeOCO(CH_2)_3CH_2$, $CN(CH_2)_2CH_2$



$C_6H_4CH\begin{smallmatrix}O-CH_2\\|\\O-CH_2\end{smallmatrix}$

Scheme 11

Cross-coupling of 9,12-diiodo-*o*-carborane with RZnX catalyzed by palladium complexes also proceeds in high yields; however, a longer time is required for the reaction to go to completion. 9,10-Diorganyl-*m*-carboranes were obtained under the same reaction condition.

$$o\text{-}HCB_{10}H_8(I_2\text{-}9,12)CH \quad + \quad 2\,RZnCl \xrightarrow[THF]{(Ph_3P)_4Pd} o\text{-}HCB_{10}H_8(R_2\text{-}9,12)CH$$

R = Me, Et, Ph

$$m\text{-}HCB_{10}H_8(I_2\text{-}9,10)CH \quad + \quad 2\,RZnCl \xrightarrow[THF]{(Ph_3P)_4Pd} m\text{-}HCB_{10}H_8(R_2\text{-}9,10)CH$$

R = Me, Ph, $PhCH_2$

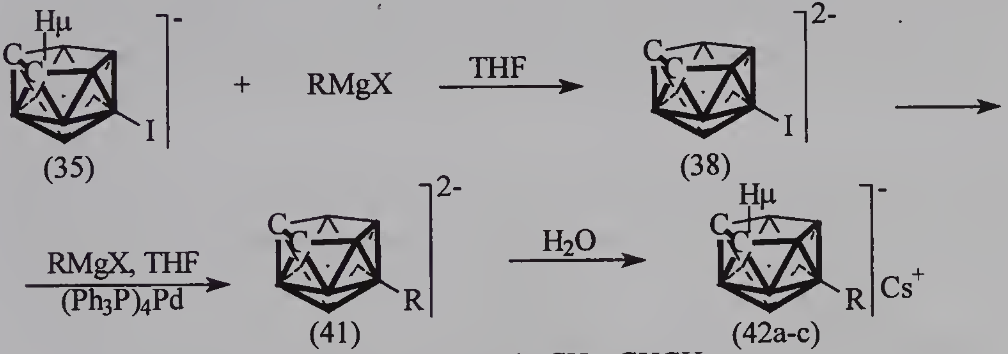
Scheme 12

2.4 Iodo-substituted *nido*-7,8-Dicarbaundecaborates in Cross-coupling Reaction with Organomagnesium and Organozinc Compounds

We have shown for the first time[12] that not only *closo*-carboranes, but also iodo-*nido*-7,8-dicarbaundecaborates containing an iodine atom in the polyhedral skeleton or in the pentagonal plane of the polyhedron enter into cross-coupling reactions with organomagnesium and organozinc compounds catalyzed by palladium complexes. It is known that *nido*-7,8-dicarbaundecaborates are strong BH-acids (pKa = 21.1), due to the presence of the axial hydrogen atom.

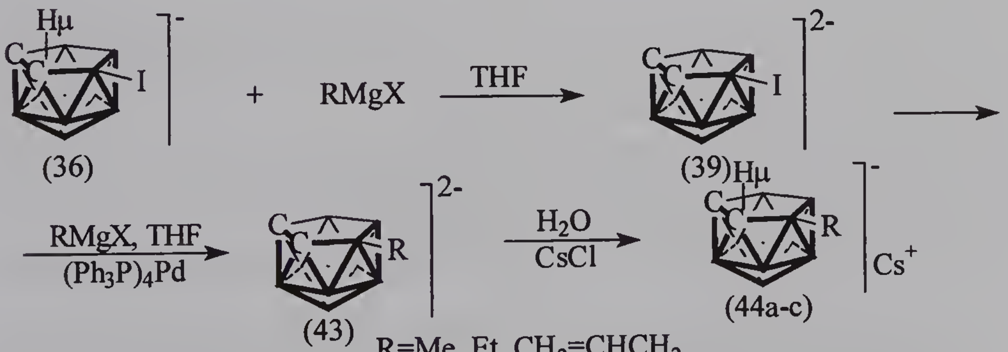
We have shown that the action of a MeMgBr solution on solutions of salts of *nido*-7,8-dicarbaundecaborate, 5-iodo-*nido*-7,8-dicarbaundecaborate (35) and 9-iodo-*nido*-7,8-dicarbaundecaborate (36) and 9,11-diiodo-*nido* 7,8-dicarbaundecaborate (37) in THF results in methane evolution and the corresponding 7,8-dicarbollide anion (38, 39 or 40) is formed, so that cross-coupling reaction with organomagnesium compounds occurs involving the corresponding iodo-substituted 7,8-dicarbollide anion. In this case the cross-coupling reaction of (35) with organomagnesium compounds follows scheme 14 with the formation of 5-organo-7,8-dicarbollide anion (41) as an intermediate that is protonated upon treatment with water to give anions of 5-organo-*nido*-7,8-dicarbaundecaborates (42 a-c) in high yields.

The cross-coupling reaction of (36) and (37) (Scheme 15) with organomagnesium compounds occurs in a similar way, and differs from those above, only in that in these compounds the iodine atom is bonded to the pentacoordinated boron atom in the pentagonal plane. Cross-coupling reactions of organomagnesium compounds with polyhedral B-iodo-substituted compounds containing pentacoordinated boron atoms were previously unknown.



R=Me, Et, C_6H_{13}, Ph, CH_2=$CHCH_2$

Scheme 13



R=Me, Et, CH_2=$CHCH_2$

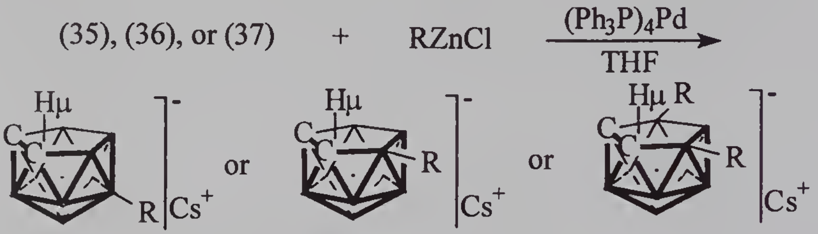
$$9,11\text{-}I_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}^{-} + RMgX \xrightarrow{THF} \underset{(40)}{9,11\text{-}I_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9^{2-}} \xrightarrow[(Ph_3P)_4Pd]{RMgX,\ THF}$$

(37)

$$\longrightarrow \underset{(45)}{9,11\text{-}R_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9^{2-}} \xrightarrow{H_2O} \underset{(46a\text{-}c)}{9,11\text{-}R_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}^{-}}$$

Scheme 14

In contrast to organomagnesium compounds, organozinc compounds do not metallate *nido*-7,8-dicarbaundecaborates. In this case the cross-coupling reaction between iodo-*nido*-7,8-dicarbaundecaborates (35-37) and organozinc compounds in the presence of palladium catalysts proceeds in the corresponding *nido*-7,8-dicarbaundecaborate anion:



R=Me, Ph, $PhCH_2$, CH_2=CH-CH_2

Scheme 15

The structure of all compounds obtained was confirmed by ^1H and ^{11}B NMR spectroscopy.

In present report we developed new approaches to the synthesis of C- and B-organylsubstituted carboranes using both metallation and cross-coupling reactions, that are of doubtless interest for investigations in the field of Boron Neutron Capture Therapy.

Acknowledgements

This research was supported in part by the Russian Foundation for Basic Research (Project No. 97-03-33020) and International. Science Foundation (Grants MSE000 and MSE300).

References

1. R.N. Grimes, "Carboranes", Academic Press, New York and London, 1970.
2. L.I. Zakharkin, V.A. Ol'shevskaya and N.F. Shemiakin, *Russ.Chem. Bull.*, 1994, 1839.
3. L.I. Zakharkin, V.A. Ol'shevskaya and V.V. Guseva, *Russ. Chem. Bull.*, 1996, 243.
4. L.I. Krugliak, E.S. Petrov, V.N. Kalinin, E.G. Rys, L.I. Zakharkin and A.I. Shatenshtein, *Zh. Obchsh. Khim.*, 1972, **42**, 2670.
5. L.I. Zakharkin and V.A. Ol'shevskaya, *Russ. Chem. Bull.*, 1992, 431.
6. D.A. Brown, W. Clegg, H.M. Colquhoun, J.A. Daniels, I.R. Stephenson and K. Wade, *J. Chem. Soc., Chem. Comm.*, 1987, 889.
7. L.I. Zakharkin, V.A. Ol'shevskaya and G.G. Zhigareva, *Russ. Chem. Bull.*, 1996, 1561.
8. L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya and Zh. S. Shaugumbekova, *J. Organometal. Chem.*, 1982, **226**, 217.
9. L.I. Zakharkin, A.I. Kovredov, V.A. Ol'shevskaya and V.A. Antonovich, *J. Organometal.Chem.*, 1984, **267**, 81.
10. L.I. Zakharkin, V.A. Ol'shevskaya and G.G. Zhigareva, *Zh. Obchsh. Khim.*, 1998, **68**, 975.
11. L.I. Zakharkin, V.A. Ol'shevskaya and V.V. Guseva, Russ. Chem. Bull, 1998, 542.
12. L.I. Zakharkin, V.A. Ol'shevskaya and P.V. Petrovsky, *Zh. Obchsh. Khim.*, 1999, in press.

Synthesis and Properties of Some Novel *o*-Carborane-containing Synthons

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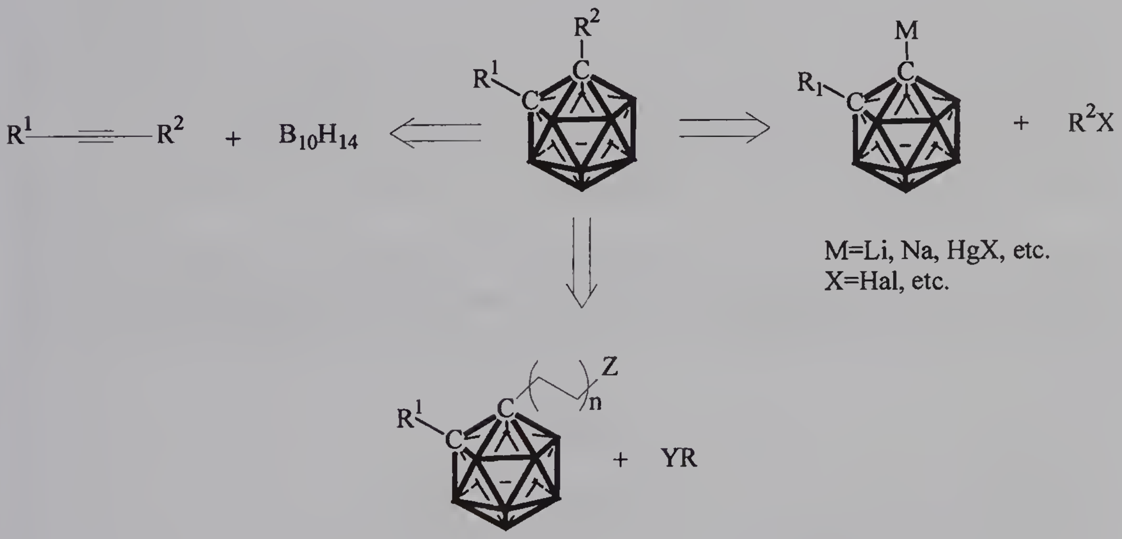
INTRODUCTION

The search for potential BNCT drugs has re-awakened interest in the organic chemistry of the 12-vertex polyhedral boranes.[1] The most widely studied chemistry is of *o*-carborane, where two carbon atoms are available for a number of organic reactions.[2] Most substituted carboranes are prepared either by interaction of alkynes with decaborane,[3] cross-coupling of Li, Na, Mg-carboranes with electrophiles [4] or by the organic reactions on the side chains (Scheme 1).[5]



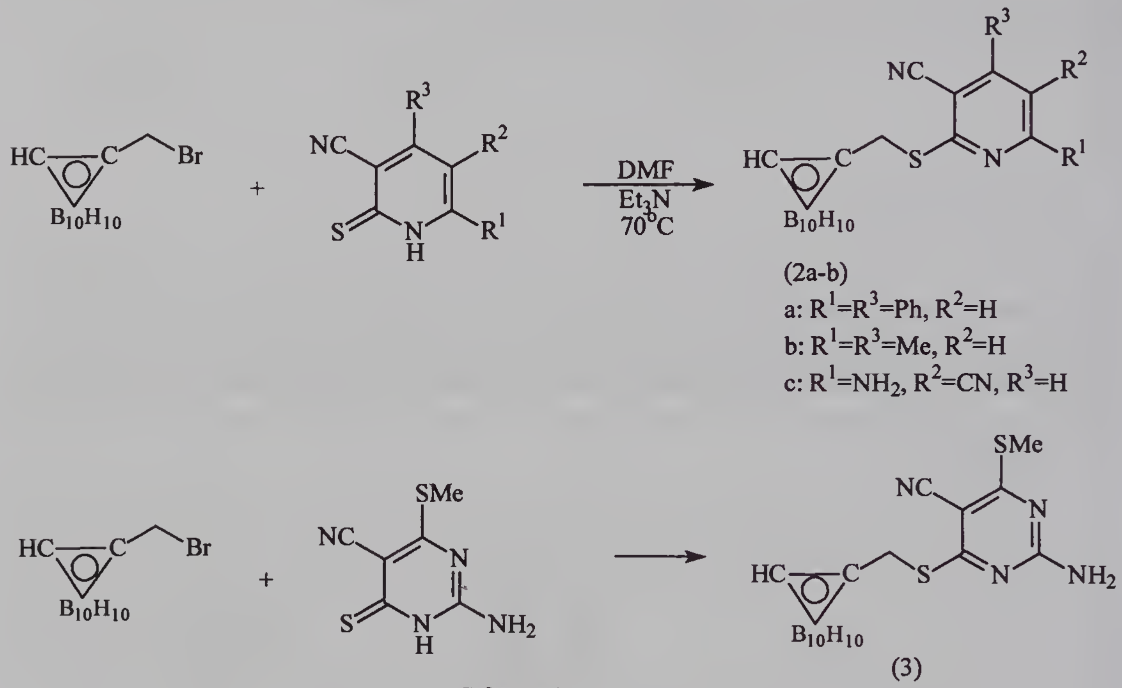
Scheme 1

In the present work the formation of carborane-containing synthons, whose properties are influenced by the carboranyl substituent, will be discussed.

RESULTS AND DISCUSSION

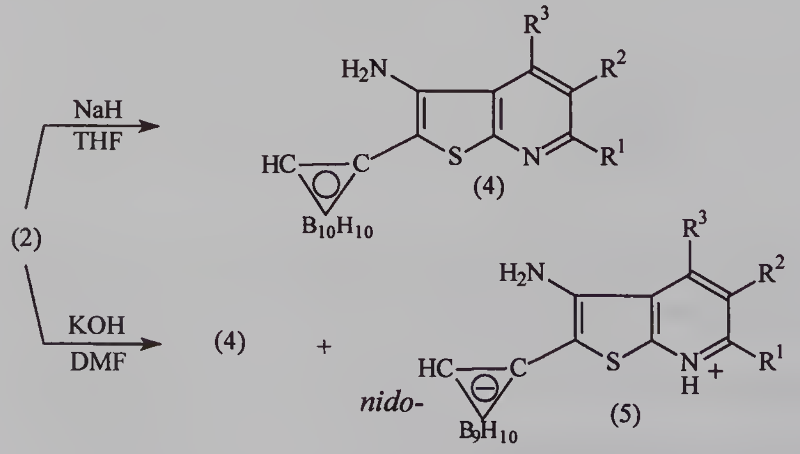
1 Bromomethyl-o-carborane as a Building Block (1)

Usually, alkyl halides are convenient starting materials for organic synthesis. The readily available bromomethyl-*o*-carborane is unfortunately a "dead" synthon for nucleophilic substitution reactions because of the great σ-acceptor effect of the *o*-carborane-1-yl substituent. For example, it does not react with sodium hydrosulfite, potassium phthalimide, etc. The reaction of chloromethyl-o-carborane with sodium iodide proceeds only at 400°C with 70% yield.[6] Still it has proved possible to develop some chemistry based on this compound. We have found that bromomethyl-*o*-carborane reacts with 3-cyanopyridine and pyrimidinethiones in DMF, leading to the following S_N2 reaction products (Scheme 2).[7]



Scheme 2

Compounds 2 and 3 react with sodium hydride in THF to give the products of a Thorpe-Ziegler reaction. The procedure under more conventional conditions (KOH/DMF) results in a mixture of *closo*- and *nido*[8]-carboranyl-thieno-pyridines and -pyrimidines (Scheme 3):

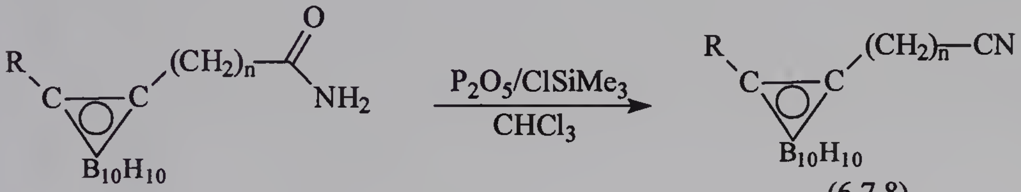


Scheme 3

2 Carborane Nitriles as Building Blocks

2.1 Preparation

The preparation of carborane nitriles was discussed earlier, but sufficiently general methods were not found. For example, the dehydration of the corresponding amides with P_2O_5 does not work in case of amides of carborane carboxylic acids.[9] Such nitriles can be prepared by the action of ClCN or PhOCN on carboranyl lithium, but the yields are poor. Good yields of carborane nitriles can be obtained by using TsOCN,[10] but this reagent is an expensive one. We found that all carborane nitriles can be prepared by the action of the corresponding amides with a $P_2O_5/SiMe_3$-polymer (Scheme 4). The yields in this case are quantitative.



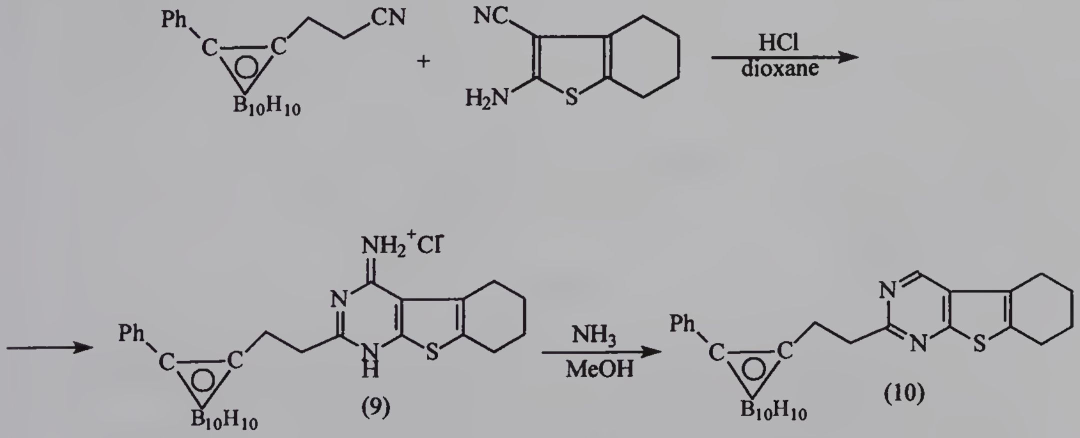
(6,7,8)

(6) : n=0, R=Ph
(7) : n=1, R=H
(8) : n=2, R=Ph

Scheme 4

2.2 Shishoo-Devani reaction

The Shishoo-Devani reaction is a good method for the preparation of pyrimidines by the action of nitriles and ene-aminonitriles[11]. We have studied the reaction of nitriles 6, 7 and 8 with the "Hewald thiophene" and found that only nitrile 8 undergoes this reaction (Scheme 5).[12]



(9)

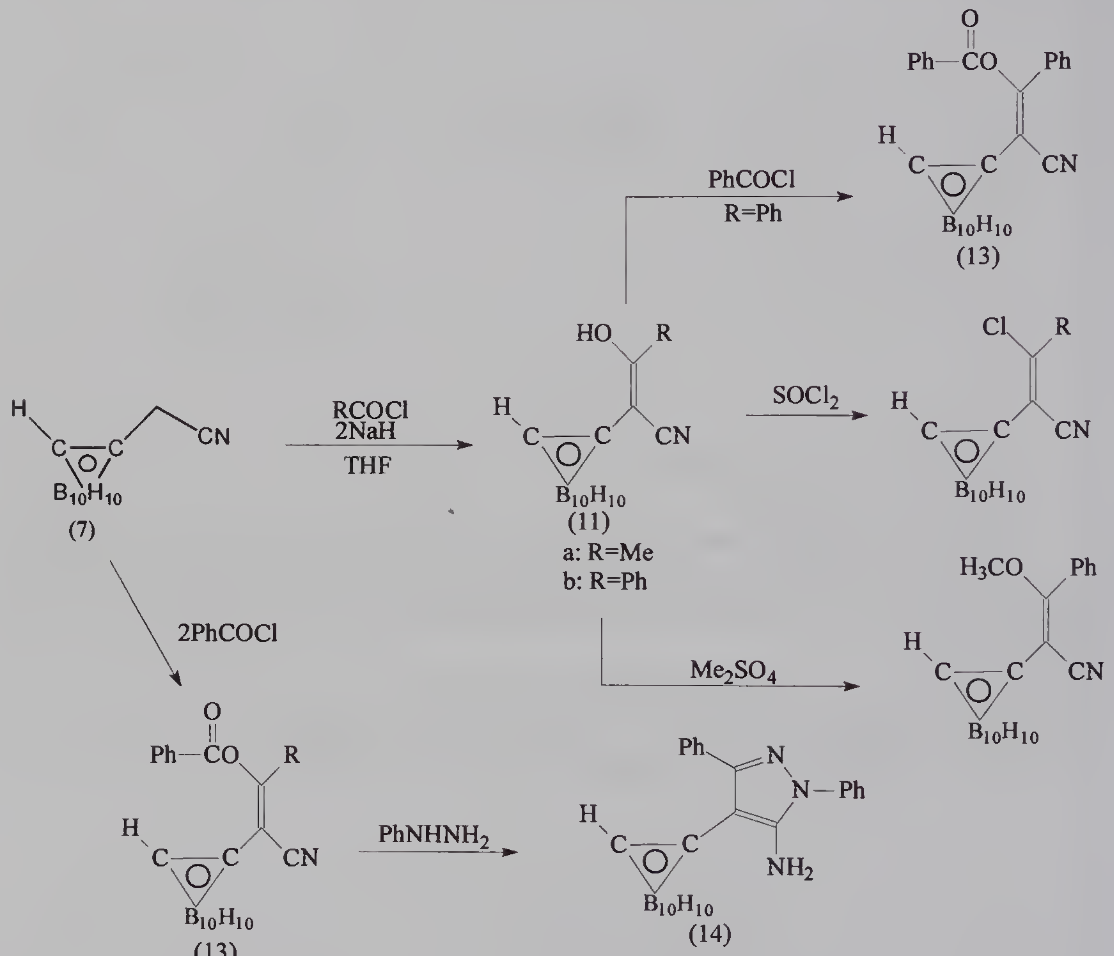
(10)

Scheme 5

Nitriles 6 and 7 do not react, probably due to the σ-acceptor nature of the carboranyl substituent.[10]

2.3 Nitrile 7 as a source of active methylene

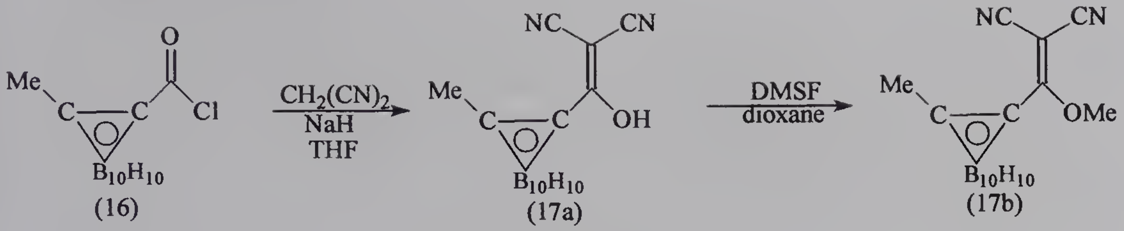
The pK_a of the methylene protons of 7 is close to that of cyanacetic ester. Thus, it was interesting to compare the reactions of these two species. We found that 7 can be acylated by various carboxylic acid halides, leading to compound 11. According to IR and NMR data 11 exists mostly as the enol-form, due to the influence of the carboranyl substituent, which strongly stabilizes conjugated double bonds.[13] Compound 11 is a useful synthon for the preparation of heterocyclic compounds. It can be methylated, chlorinated and acylated twice (compound 13). Compound 13 gives an adduct with phenylhydrazine (scheme 6).



Scheme 6

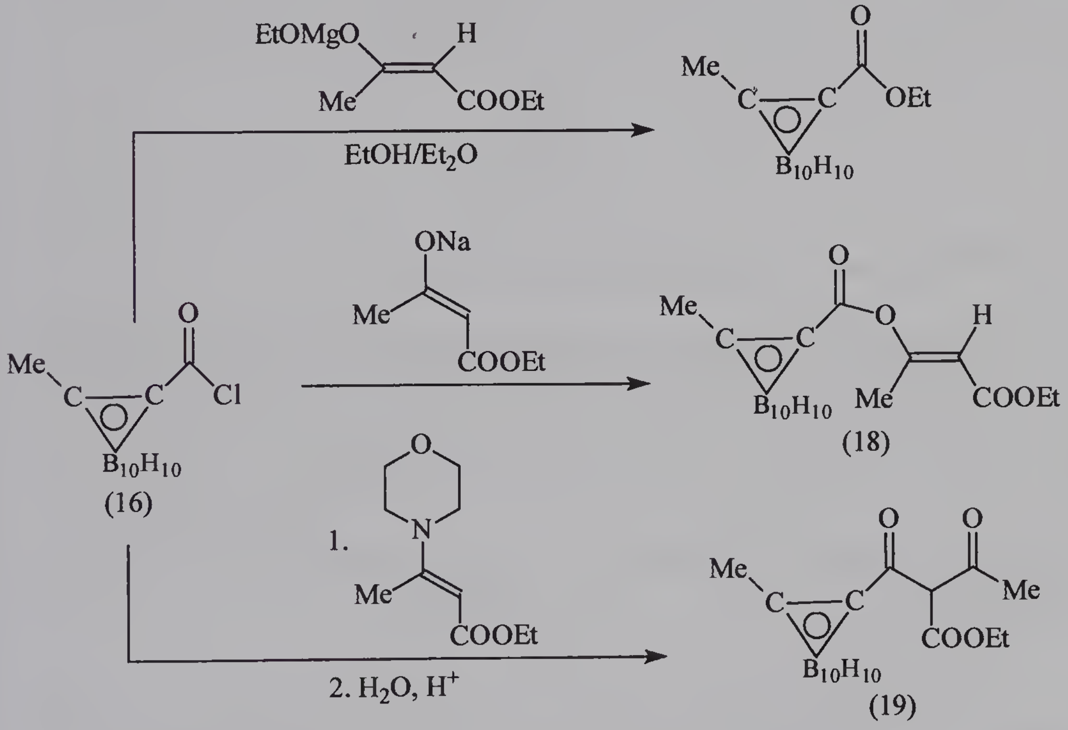
3 Carborane Carboxylic Acid Chlorides as Building Blocks

Carboranyl acid halides can be very easy prepared. We have studied the acylation of malononitrile and acetoacetic ester by methylcarboranyl carboxylic acid chloride (15). The reaction with malononitrile leads to the compound 17a, which exists also as a enol form, similar to compound 13. Compound 17a can be methylated to give compound 17b, a novel synthon for the preparation of wide range of heterocyclic compounds (Scheme 7).



Scheme 7

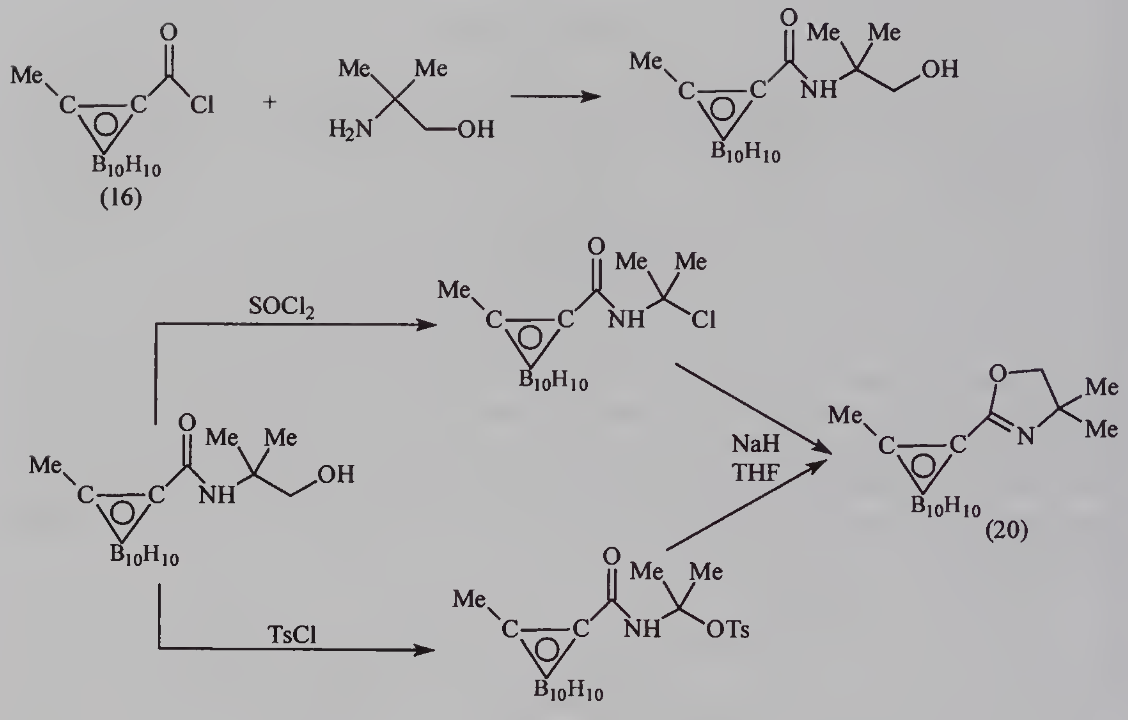
It was a particular interest for us to study the preparation of β,β-carboranyl derivatives, which are synthons for a number of compounds. We found that interaction of compound 16 with the magnesium enolate of acetylacetic ester in Et_2O/EtOH results in esterification of 16 by the EtOH solvent. The same reaction with the sodium enolate of acetylacetonate results in the product of O-acylation. We also found a general method of preparation of carboranyl β,β-diketones (e.g., 19) by reaction of 16 with enamines (Scheme 8).



Scheme 8

4 Carboranyl Oxazolinse. Attempts to Prepare formyl Carboranes

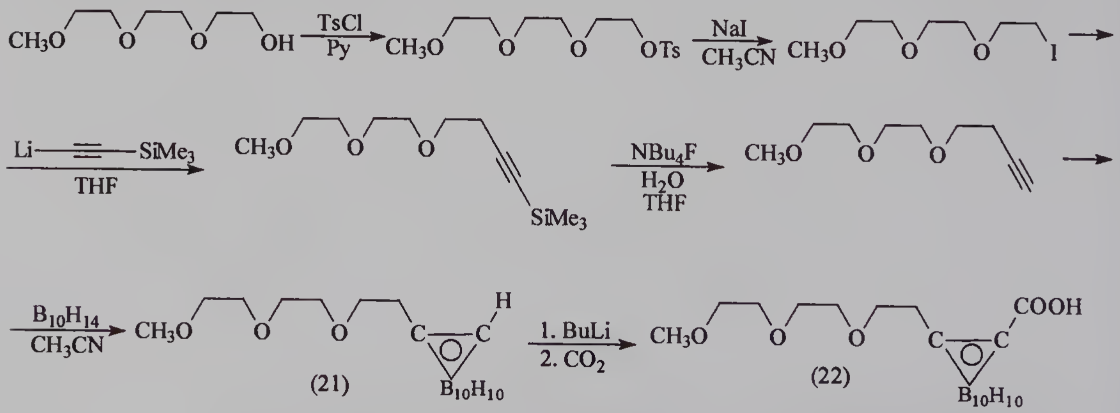
Aldehydes are one of the most impotent synthons in organic chemistry. Many methods of preparation of formyl carboranes have been discussed previously (E. I. Rosemund method,[14] Sonn-Miller reaction,[14] reaction of dodecaborane with diacylal of propargyl aldehyde,[14] Swern Oxidation[15]). Since oxazolines are rather good reagents for the preparation of aldehydes and nitriles, we developed a method of preparation of carboranyl oxazolines (Scheme 9).



Scheme 9

5 Synthesis of Carboranes with Hydrophilic Groups

The main problem with the use of carboranes in BNCT is their high hydrophobity. Thus we synthesized a triethyleneglycol carborane derivative by the following route:



Scheme 10

The acid 22 is a useful synthon for the development of a range of organic chemistry.

ACKNOWLEDGEMENTS. Great thanks to P. Petrovskii, W. Niedermayer and B. Brellochs for NMR spectra, D. Zverev for Mass spectra, V. Artyomov, V. Ivanov, G. Ptashits for cooperation and VW and Russian Foundation for Basic Research for financial support (Grant № 99-03-33073).

REFERENCES

1. M. F. Hawthorne, *Molecular Medicine Today*, 1998, p.174-181
2. R. N. Grimes, "Carboranes", Academic Press, New York and London, 1970.
3. T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, J. W. Szymansky, *Inorg.Chem.*, 1963, 1089-1092; M. Scobie, M. D. Threadgill, *J. Org. Chem.*, 1994, **59**, 7008-7013; D. D. Kelly, S. A. Bateman, R. F. Martin, M. E. Rann, A. M. Rose, A. R. D. Whitter, *Austr. J. Chem.*, 1994, **47**, 247-262.
4. R. Coult, M. A. Fox, W. R. Gill, P L. Herbertson, J. A. H. MacBride, K. Wade, *J. Organomet. Chem.*, 1993, 462, 19-29.
5. M. Scobie, M. D. Threadgill, *J. Chem. Soc., Chem. Comm.*, 1992 (13), 939-942.
6. L. I. Zakharkin, V. A. Brattsev, Yu. A. Chapovskii, *Zh. Obshch. Khimii USSR*, 1965, **35**, 2160-2167.
7. A. A. Semioshkin, G. M. Ptashits, V. L. Ivanov, V. A. Artemov, A. M. Shestopalov, V. I. Bregadze, V. P. Litvinov, *Tetrahedron*, 1997, **53**,. 7911-7916.
8. A. A. Semioshkin, G. M. Ptashits, V. L. Ivanov, V. A. Artemov, A. M. Shestopalov, V. I. Bregadze, V. P. Litvinov, *Russian Journal of Heterocyclic Chemistry*, 1998, N6, 790.
9. A. I. L'vov, Ph.D.(Chem) Thesis, Institute of Organoelement Compounds, USSR Acad. Sci., Moscow, 1967 (in Russian)
10. D. D. Sung, J. A. Jung, G. T. Lim, S. C. Shim, J. G. Shim, M. V. Antonova, V. N. Kalinin, *Mendeleev Commun.*, 1996, 26.
11. C. J. Shishoo, M. B. Devani, V. S. Bhadti, K. S. Jain, S. Ananthan, *J. Heterocyclic Chem.*, 1999, **27**, 119
12. A. Semioshkin, P. Lemmen, S. Inyushin, L. Ermanson, "Advances in boron chemistry", The Royal Society of Chemistry 1997, 311-314.
13. A. A. Semioshkin, P. V. Petrovskii, S. G. Inyushin, V. I. Bregadze, *Russ. Chem. Bull.*, 1998, N7, 1778.
14. V. I. Stanko, V. A. Brattsev, M. E. Al'perovich, N. S. Titov, *Zh. Obshch. Khim.*, 1968, **38**, 1056-1062.
15. X. Lang, M. F. Hawthorne, *Inorg. Chem.*, 1993, **32**, 242-243.

Unusual Double Silylation Reactions of Bis(silyl)metal Complexes with *o*-Carboranyl Unit

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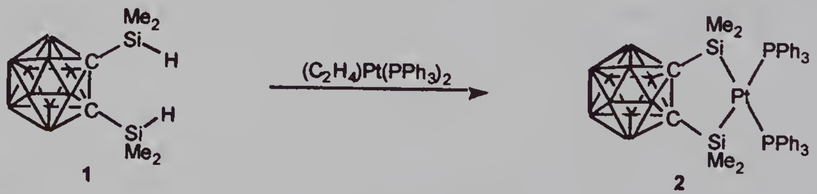
1 INTRODUCTION

The double silylation of unsaturated organic compounds catalyzed by group 10 metals[1] is a convenient synthetic route to disilacyclic compounds. Nickel and platinum complexes, in particular, are excellent catalysts for the transformation of disilanes. Cyclic bis(silyl)metal complexes[2, 3] have been implicated as key intermediates in the metal-catalyzed double silylation of alkynes, alkenes, and aldehydes; however, the intermediates have not been isolated due to their instability. We now describe (i) the isolation of the reactive intermediates cyclic bis(silyl)metal compounds (**1**) with bulky *o*-carborane unit;[4] (ii) the generation of a new class of heterocyclic compounds (**4-5**) by the stoichiometric reaction of the intermediates with a variety of substrates such as an alkyne, dione, and nitrile;[4] and (iii) the facile double silylation of alkenes and alkynes (**10, 12-14**) catalyzed by the intermediate under mild conditions.[5]

2 SOME UNUSUAL REACTION CHEMISTRY WITH UNSATURATED ORGANIC COMPOUNDS

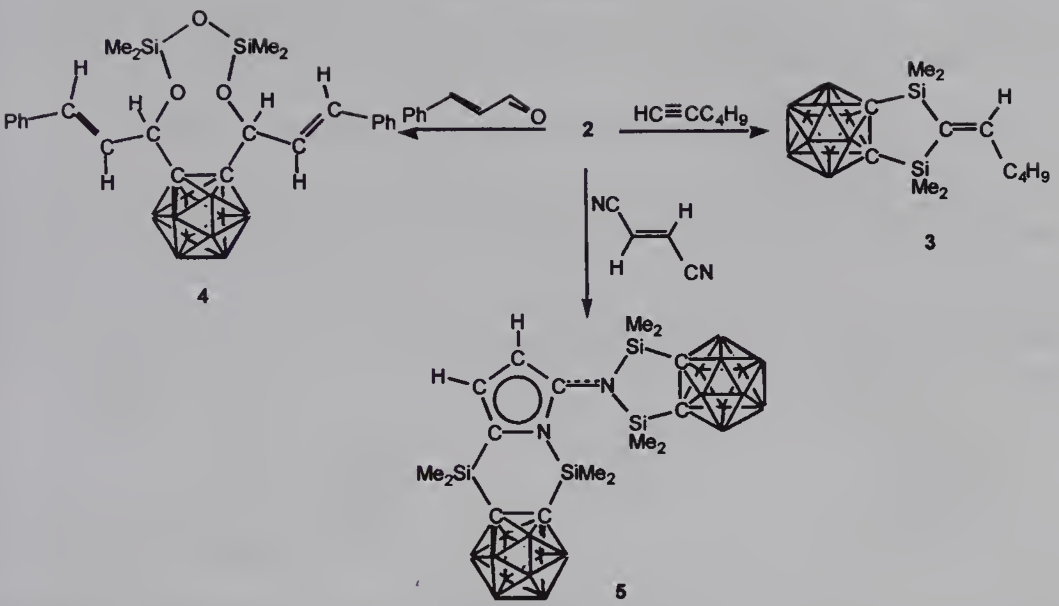
The reaction of $Pt(CH_2{=}CH_2)(PPh_3)_2$ and *bis*(silyl)-*o*-carborane **1** (1.4 equiv) in benzene leads to **2** in good yield (eq 1). The compound **2** is a yellow solid stable to air and to brief heating to 120-130 °C.



(1)

The spectroscopic data for **2** support the proposed structure. In particular, the ^{29}Si NMR chemical shift of 37.17 ppm as a doublet of doublets ($J_{Pt\text{-}Si}$ = 1281.6 Hz, $J_{Si\text{-}P(trans)}$ = 148.82 Hz, $J_{Si\text{-}P(cis)}$ = 12.80 Hz) is close to the literature values for *cis*-$PtSi_2P_2$ complexes.[6] Compound **2** was found to be a good precursor for the double-silylation reaction.[7] Thus, thermolysis of a toluene solution of **2** and 1-hexyne at 120 °C afforded complex **3** as a colorless oil. A key feature in the ^1H NMR spectrum of **3** is a singlet at 6.24 ppm assigned to the vinyl proton. A characteristic low-frequency ^{13}C NMR resonance at δ 138.50 provides evidence for a tethered carbon atom of the two silicon moieties[8] (Scheme 1).

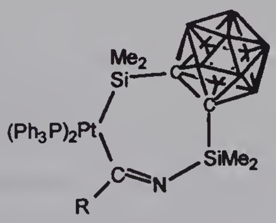
Scheme 1



Treatment of **2** with 3 equiv of 3-phenyl-2-propenal in refluxing toluene-d_8 while the reaction progress was monitored by ^{1}H NMR spectroscopy resulted in the disappearance of the aldehyde hydrogen peak (δ 1.56). The IR spectrum of **4** shows a new absorption due to a $\nu_{C\text{-}O}$ stretch at 1448 cm^{-1}. The mass spectrum of the product shows a molecular ion at m/z 538. To our surprise, an X-ray study of **4** showed it to be the insertion product of the two carbonyl ligands into the C-Si bond in **2**. The reaction has the potential for developing a new method for double C-C bond formation between the carboranyl unit and carbonyl compounds. Such an insertion of the carbonyl functionality into the *o*-carborane has been observed in Yamamoto's work on the chemoselective addition of *o*-carborane to the aldehyde groups by a palladium-catalyzed[9] or a fluoride-promoted reaction.[10]

The reaction between **2** and 4 equiv of fumaronitrile in refluxing toluene produced **5** as colorless crystals. Three singlets (δ 12.53, 4.36, -6.51) in the ^{29}Si NMR spectrum and four singlets (δ 2.20, 0.93, 0.40, -0.047) in the ^{13}C NMR spectrum of **5** assigned to the methyl groups on the silicon atom demonstrate that the four dimethyl groups are not equivalent. The IR spectrum of **5** fails to show a new signal for a terminal CN. An X-ray study revealed **5** to be a cyclization product with two types of disilyl moieties, the imine and *N,N*-bis(silyl)amine, which are connected by a five-membered ring. Such a transformation of nitriles to imines or *N,N*-bis(silyl)enamines has been observed during photochemical reactions[11] or under catalysis by a platinum complex.[7c]

A reasonable mechanism for the formation of **5** involves the initial insertion of the cyano group into one of the platinum-silicon bonds, leading to intermediate **6**, followed by cyclization to the imine **7**.



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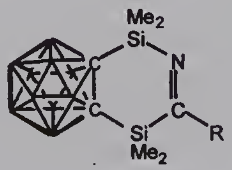

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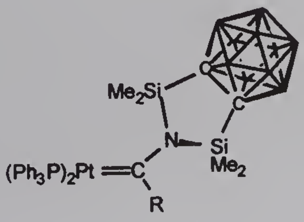
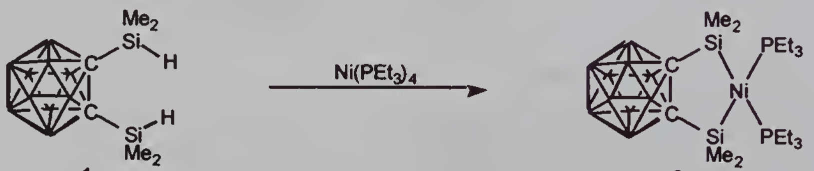


8

This lends some credence to the notion that nucleophilic attack of the imine is at the platinum carbene intermediate **8** formed from the migration of the silicon atom to the nitrogen atom that leads to compound **5**.[12]

3 A FACILE DOUBLE SILYLATION OF ALKENES AND ALKYNES

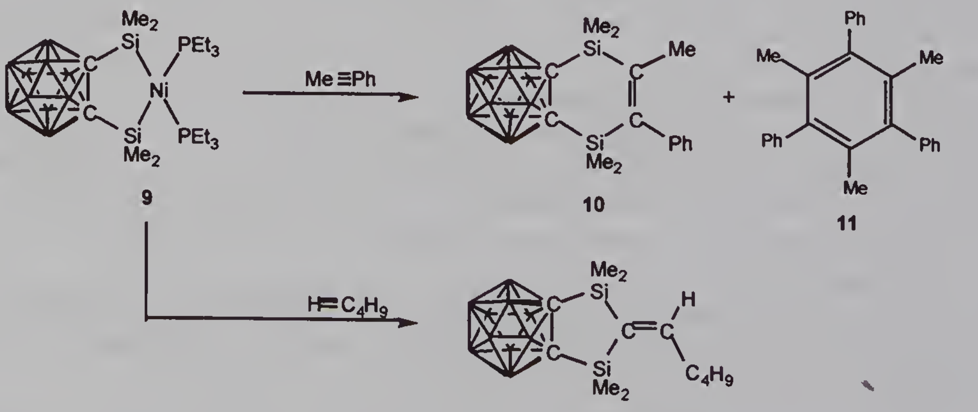
Addition of 1.2 equiv of **1** to $Ni(PEt_3)_4$ in pentane at 25 °C gave a dark red solution, concomitant with the evolution of gas. Standard workup and crystallization from toluene-pentane gave **9** as a spectroscopically pure, dark red crystalline solid sensitive to air and stable during brief heating to 100-110 °C. The unusual thermal stability of the nickel bis(silyl) compound is attributed to the advantageous properties of the carboranyl unit, including electronic and steric effect.



1 **9** (2)

The spectroscopic data for **9** support the proposed structure. In particular, the ^{29}Si NMR chemical shift of δ 43.19 as a triplet ($J_{Si\text{-}P(cis)}$ = 40.11 Hz) resembles the literature value reported for the *cis*-$NiSi_2PC$ complex.[13] Compound **9** was found to be a good reactive intermediate for the double silylation reaction. The reaction of **1** with 1-phenylprop-1-yne (1 equiv) in the presence of a catalytic amount of **9** (0.03 equiv) for 6 h afforded the double-silylated producted **10** in 94 % (GC) yield. The reaction was quite sensitive to the reaction conditions. When the same reaction was carried out at higher temperature (70-75 °C), the major component was identified as the acetylene cyclotrimerization product **11** (Scheme 2), which has been characterized by spectroscopic techniques. When hex-1-yne is employed as a terminal alkyne in the reaction with **1** under the same condition, the five-membered disilyl ring compound **12** is isolated as a colorless liquid in 71 % yield.

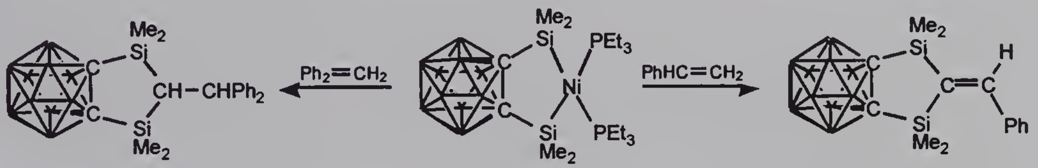
Scheme 2



9 **10** **11** **12**

The reaction of **9** with 1 equiv of styrene takes place at a higher temperature (80 °C) and affords a moderate yield of the five-membered disilyl ring compound **13** (Scheme 3). A key feature in the ^1H NMR spectrum of **13** is a singlet at δ 7.71 assigned to the vinyl proton. A characteristic low frequency ^{13}C NMR resonance at δ 139.75 provides evidence for the carbon atom tethered to the two silicon moieties. Such formation of disilyl ring compound has been observed during the nickel-catalyzed reaction of benzo-disilacyclobutene with styrene.[14] Treatment of **9** with 1 equiv of 1,1-diphenyl-ethylene in toluene at 80 °C resulted in a brown solution from which the five-membered disilyl ring compound **14** was isolated in a yield of 74 %. The formation of **14** was confirmed by a spectrometric analysis. The mass spectrum of the product showed a molecular ion at m/z 440. Two doublets (δ 3.93, 1.81) in the ^{1}H NMR spectrum of **14** are assigned to the methine protons. A low-frequency ^{13}C NMR resonance at δ 49.87 provides evidence for the tethered carbon atom of the two silicon moieties.

Scheme 3



14 **9** **13**

Acknowledgements

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References

1. (a) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (b) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987. (c) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.
2. Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1973**, *63*, 107.
3. (a) Uchimaru, Y.; Lautenschlager, H. J.; Wynd, A. J.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 2639. (b) Tanaka, M.; Uchimaru, Y. *Bull. Soc. Chim. Fr.* **1992**, *129*, 667. (c) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H. J. *Organometallics* **1991**, *10*, 16.
4. Kang, Y.; Ko, J.; Kang, S. O. *Organometallics*, **1999**, *18*, 1818.
5. Kang, Y.; Lee, J.; Kong, Y. K.; Ko, J.; Kang, S. O. *J. Chem. Soc. Chem. Commun.*, **1998**, 2343.
6. (a) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1989**, *117*, 8873. (b) Pham, E.; West, R. *J. Am. Chem. Soc.* **1989**, *111*, 7667.
7. (a) Uchimaru, Y.; Brandl, P.; Tanaka, M.; Goto, M. *J. Chem. Soc., Chem. Commun.* **1993**, 744. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H. J. *J. Organomet.Chem.* **1992**, *428*, 1. (c) Reddy, N. P.; Uchimaru, Y.; Lautenschlager, H. J. J.; Tanaka, M. *Chem. Lett.* **1992**, 45.
8. Naka, A.; Hayashi, M.; Okazaki, S.; Kunai, A.; Ishikawa, M. *Organometallics,* **1996**, *15*, 1101.
9. Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Org. Chem.* **1997**, *62*, 780.
10. Cai, J.; Nemoto, H.; Nakamura, H.; Singaram, B.; Yamamoto, Y. *Chem. Lett.*, **1996**, 792.
11. Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *Organometallics* **1985**, *4*, 623.
12. Gunnoe, T. B.; White, P. S.; Templeton, J. L.; Casarrubois, L. *J. Am. Chem. Soc.* **1997**, *119*, 3171.
13. Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 1250.
14. Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawachuchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114.

Cyclisation of Cage-carborane Compounds using Transition Metal Catalysts and Carbene Intermediates

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1. INTRODUCTION

Boron cluster compounds have many electron deficient sites in them and they possess polyhedral skeleton. The procedure by which the boron cluster compounds are built from small polyhedral skeletons to a big polyhedral skeleton is in wide use for the synthesis of boron neutron capture therapy. The reactivity and reaction mechanism for the formation of the boron cluster compounds from a small cluster to a big cluster have been studied.

Through this study we suggest a useful synthetic procedure for good candidate compounds of a new cage-cluster. The *ortho*-carboranes are very stable chemicals in this research. Carboranyl acetic ester can be easily introduced to the *ortho*- carborane skeleton and then many types of cyclisation of carboranyl cluster can be made to occur. The reactivity and reaction mechanism for cyclisation of carborane cluster have been discussed. The mechanisms for boron cluster expansion reaction and cyclisation at carboranyl edge are summarized as follows.

2. RESULTS AND DISCUSSION

The boron cluster expansion reaction which occurs through the reaction of decaborane with alkynyl pyrimidine is in accord with two path ways of forming *closo*-compounds and *nido*-compounds. Acetonitrile accelerates decaborane to react and to take the role of a good nucleophile.

A very unstable intermediate, *arachno*-$B_{10}H_{12}(CH_3CN)_2$, is formed before decabornae reacts with alkynyl pyrimidine by the acceleration of acetonitrile.

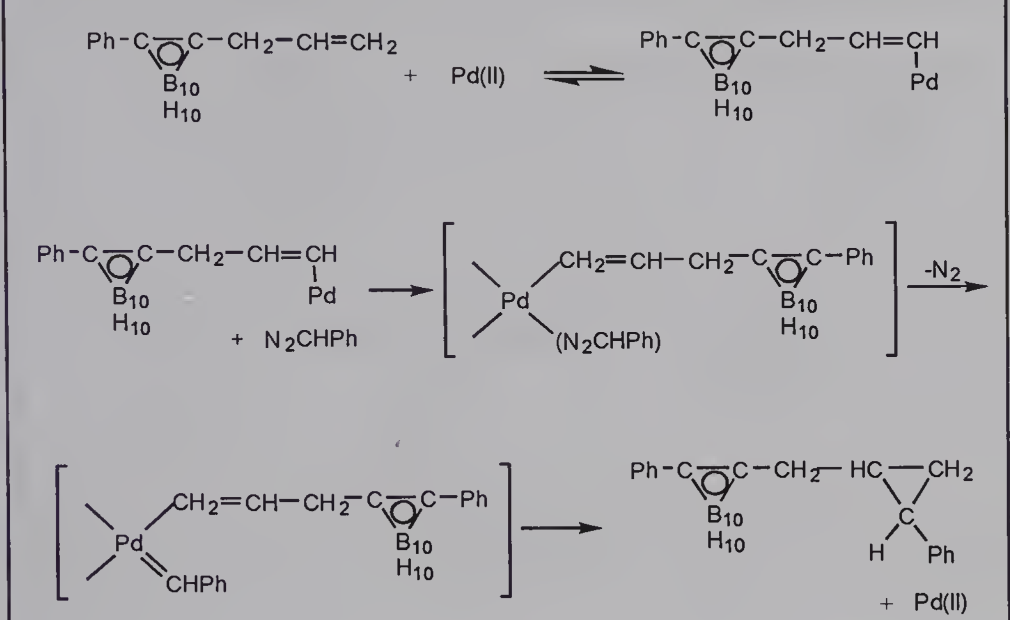
The final product, *closo*-$B_{10}H_{10}CHCR$, is produced through the reaction of *nido*-$B_{10}H_{12}(CH_3CN)$ with alkynyl pyrimidine. The *arachno*-$B_{10}H_{12}(CH_3CN)_2$ results in as a kind of neat product, *nido*-$B_{10}H_{12}(CH_3CN)$, through the reaction of decaborane with acetonitrile.

Alkynyl pyrimidine acts as a strong base and decaborane plays as an important Lewis acid in this reaction series. The electron cloud moves from alkynyl pyrimidine to decaborane. The order of magnitude of reactivity of various alkynyl pyrimidines is proportional to the ability of the electron cloud being supplied to decaborane.

The C-allylation to *ortho*-carborane is accelerated by palladium catalysts.

C–atoms at C–substituted *ortho*–carborane act as nucleophile.

A good yield results when 5mol% of Pd(dba)$_2$ is used as a catalyst as shown in Scheme 1.

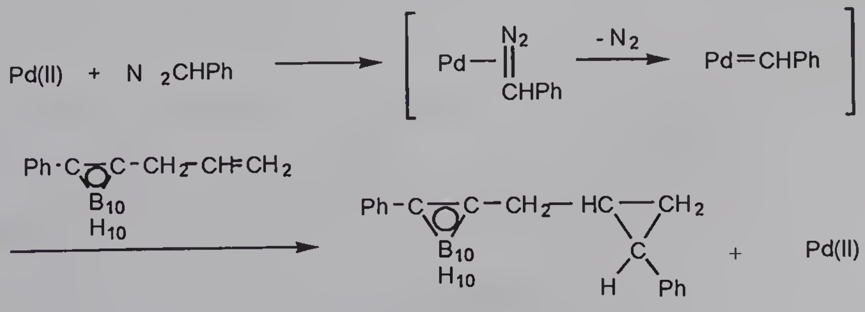


SCHEME 1

C–allylation is dependent on the ligand of palladium catalyst which assists the reaction of C–allylation to *ortho*–carborane.

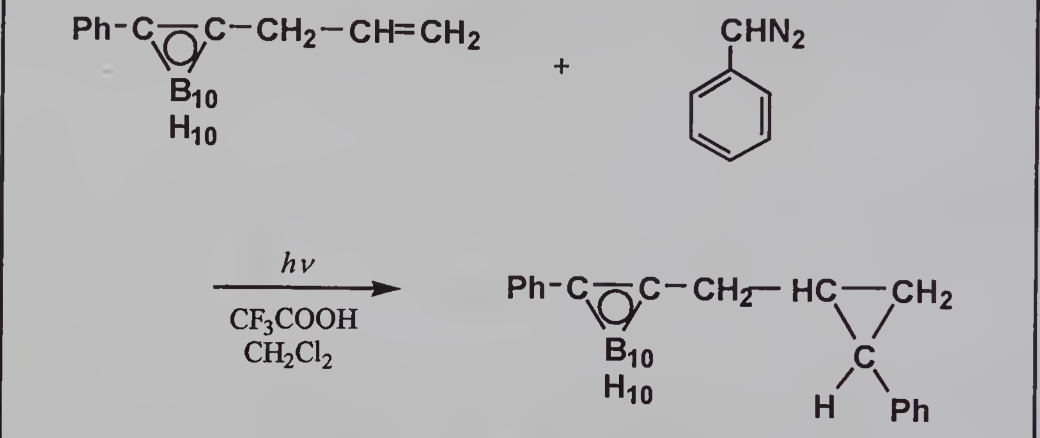
The solvent effect is high in the case of C–allylation to *ortho*–carborane cluster. In non–polar solvents the C–allylation is accelerated, while in polar solvents the C–allylation is decelerated.

The reaction mechanism for the cyclisation at carboranyl edge is so suggested that the β–carbon site in *ortho*–carborane cluster reacts to give carbene intermediate in the first step, and in the second step the carbenoid intermediate is produced, which generates the final product at the end as shown in Scheme 2.



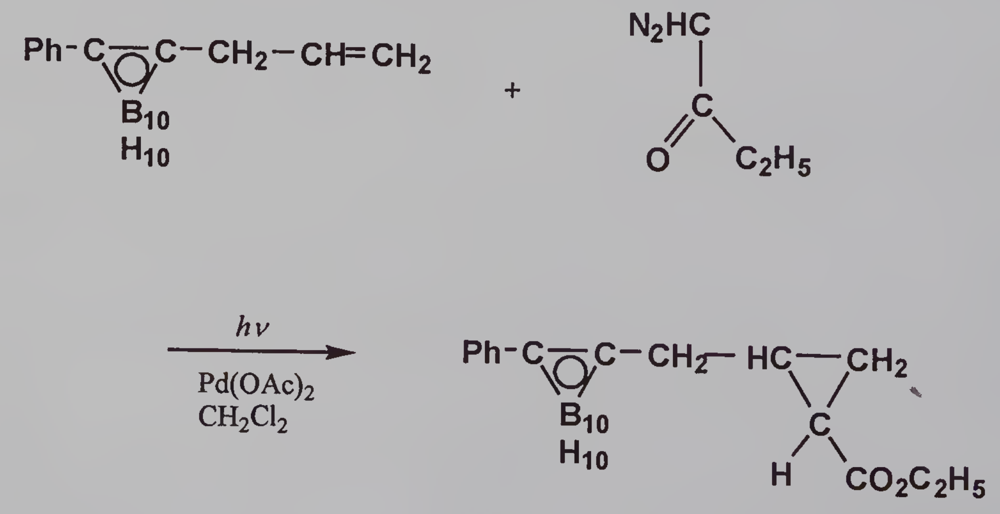
SCHEME 2

In the presence of a strong, non-oxidizing acid, trifluoroacetic acid, the cyclisation at carboranyl edge (Scheme 3.) is less effective compared to Pd catalyst in the carbenoid reaction.



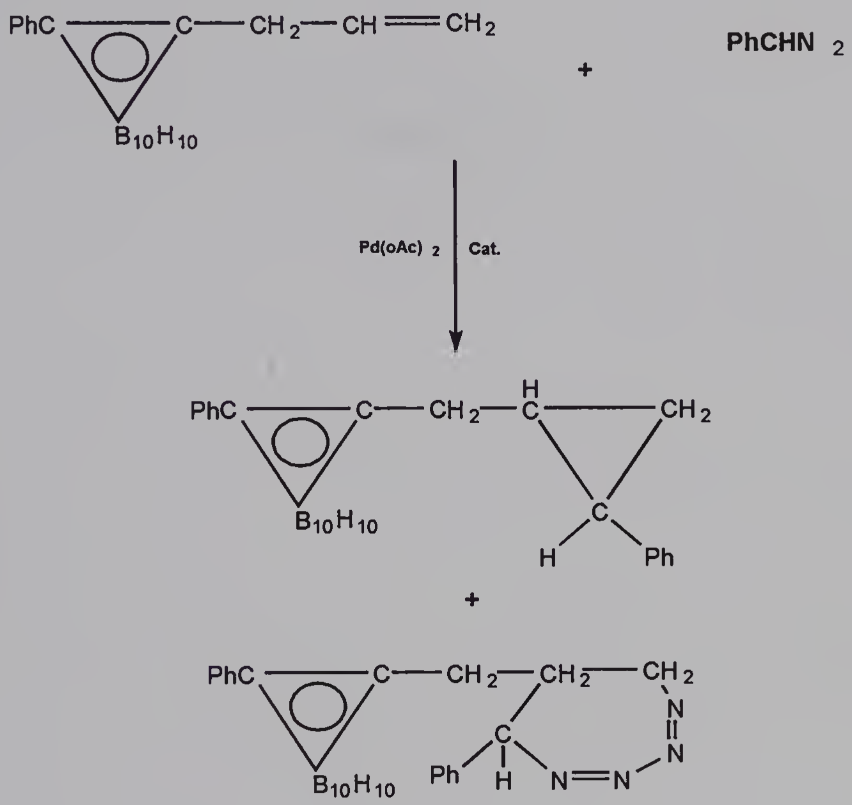
SCHEME 3

In the presence of Pd(OAc)₂, the cyclisation at carboranyl edge occurs effectively through the reaction of *ortho*-carborane cluster with diazomethyl ethyl ketone as shown in Scheme 4.



SCHEME 4

However, totally different reaction products are formed when *ortho*-carborane cluster reacts with phenyl diazomethane in the presence of $Pd(OAc)_2$ and without any other irradiation as shown in Scheme 5.



SCHEME 5

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References

1. D. D. Sung, *Appl. Organomet. Chem,* 1996, 10, 257.
2. L. I. Zakharkin, V. N. Kalinin, A. P. Snyakin and B. A. Kvasov, *J. Organomet. Chem.* 1969, 18, 19.
3. R. E. Williams, *in Progress in Boron Chemistry*, Pergamon, Oxford. 1970, Vol. 2, Ch. 2, 36.
4. D. D. Sung, C. S. Kim, J. D. Lee, G. T. Lim. T. S. Uhm, Y. T. Park, *J. Photosci.* 1994, 1, 89.

Metallaboranes

Intercomparison of Syntheses and Structures of Mono- and Dimetallaboranes Containing Transition Metals from Groups 5–9

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1 INTRODUCTION

Metallaboranes mirror the metal hydrocarbyl complexes of organometallic chemistry and offer the promise of a similar rich chemistry.[1] Indeed there are a number of strictly isoelectronic borane and hydrocarbon complexes in which a C atom is formally replaced with a B^- or BH moiety.[2] Comparison of the structure and properties of these compound pairs highlights interesting similarities and differences between the organic and inorganic derivatives.[3]

Although there are exceptions, notably from the work of Shore[4] and Gaines,[5] previous synthetic routes to compounds containing more than a single metal atom depend more strongly on serendipity than reason. Indeed many routes, including one of our early ones, were characterized as "the result of either genius or inspired guesswork!".[6] A consequence is chromatographic separation of complex mixtures and low yields. Although intriguing stoichiometries and structures abound for group 8 and 9 metals,[7, 8] derivative chemistry and mechanistic insight is scarce. Further, metallaboranes of the earlier transition metals, for which chromatography is often not an option, are practically non existent.

Stimulated by the work of Ting and Messerle,[9] Kathryn Deck began her Ph.D. thesis with me in 1991 with the objective of utilizing the reaction of monocyclopentadienyl metal halides with monoboranes as a new route to metallaboranes. The work has continued and now encompasses examples from metals of groups 5 - 9. As it developed so too did our understanding of the reaction pathway. In the following, I summarize our present knowledge and establish the basis for considering the reaction a truly general route to metallaboranes containing monocyclopentadienyl metal fragments.[10]

2 LITHIUM BOROHYDRIDE

The reaction of metal halides with borohydride salts constitutes a general route to transition metal borohydrides.[11] Further, in the presence of Lewis bases, borohydrides may be converted into metal hydrides which, depending on the metal, may lose dihydrogen thereby reducing the metal center. Less well recognized is the fact that a metal polyborohydride generated from a polyhalide has an alternative to hydride formation namely H_2 elimination with the formation of metal-boron and boron-boron direct bonds (Figure 1). The compounds

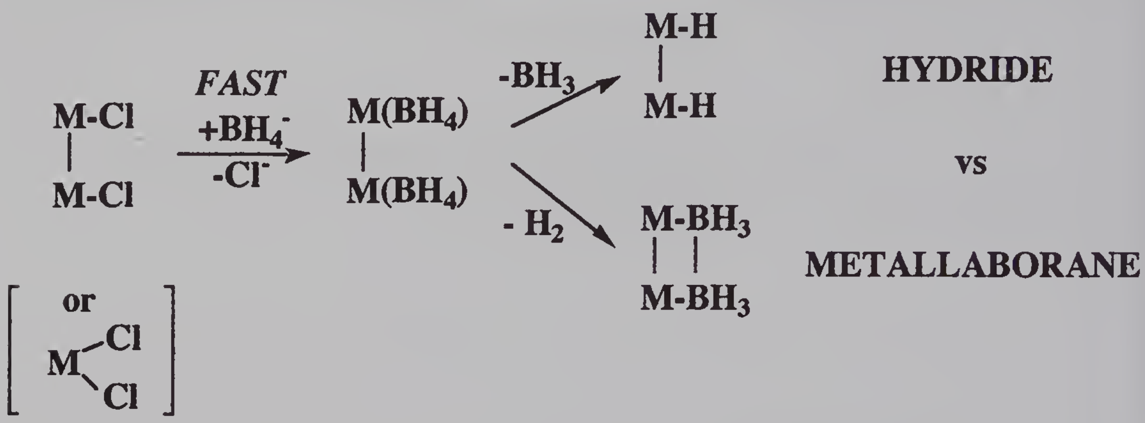

Figure 1 *Competition between hydride and metallaborane formation in the decomposition of a metal polyborohydride*

generated by the latter pathway are metallaboranes. This is illustrated nicely by Simon Aldridge's molybdenum system shown in part in Figure 2.[12] Reaction of Cp^*MoCl_4, $Cp^* = \eta^5\text{-}C_5Me_5$, with $LiBH_4$ presumably forms $Cp^*MoCl_2(BH_4)_2$ which rapidly loses BH_3 and H_2 to give the reduced $[Cp^*MoCl_2]_2$ dimer. Contrariwise, the subsequent $[Cp^*MoCl(BH_4)]_2$ intermediate formed eliminates H_2 more rapidly than BH_3 thereby forming the metallaborane $(Cp^*MoCl)_2B_2H_6$ in a process entirely analogous to that observed by Ting and Messerle for the synthesis of $(Cp^*TaCl)_2B_2H_6$.[9] This appears to be a general reaction and we have confirmed the formation of dimetallatetraboranes of this type for tungsten[13], cobalt[14], rhodium[15] and iridium.[16] However, this compound is not always the final product, e.g., for molybdenum $(Cp^*Mo)_2(B_2H_6)_2$ is the final product. Further, Andrew Weller showed that for Cp^*WCl_4 reduction to $[Cp^*WCl_2]_2$ is slow permitting metallaboranes derived from the putative $Cp^*W(BH_4)_4$ intermediate, e.g., $Cp^*WH_3B_4H_8$, to be formed.[13] Similarly, in Xinjian Lei's chemistry reduction of $[Cp^*RuCl_2]_2$ is incomplete leading to $(Cp^*RuH)_2B_3H_7$ as the first formed metallaborane.[15] Finally, with iridium, where H_2 elimination from hydrides is not observed, $(Cp^*Ir)_2Cl_4$ and $(Cp^*Ir)_2HCl_3$ lead to a metallaborane containing three boron atoms whereas $(Cp^*Ir)_2H_2Cl_2$ yields one with two boron atoms.[16] Hence, the interplay of metal characters provides variations in the first formed metallaborane that are easily understood on the basis of the simple reaction chemistry of Figure 1

3 BORANE·THF

On a study visit to Notre Dame, Yasushi Nishihara observed that the reaction of BH_3THF with $[Cp^*CoCl]_2$ was facile and lead to the formation of metallaboranes, e.g., 2,4-

$(Cp^*Co)_2B_3H_7$, with the generation of one mole of BH_2Cl per mole of Cl lost.[14] Except for the chromium system[17], this coproduct has been observed accompanying the formation of metallaboranes in the reaction of all other monocyclopentadienyl metal chlorides with BH_3THF examined. Our present understanding of its origin is given in Figure 3. There is literature precedent for the first step. Chloroborohydride salts form from the reaction of borane with chloride salts and have been fully characterized.[18] In addition a mononuclear chloroborohydride ruthenium complex has been reported.[19] We suggest that a metal borohydride is formed and that metallaboranes are then generated as indicated in Figure 1. With the exception of the rhodium system (see below) chlorine is not found in the metallaborane products. There are two reasonable routes from the chloroborohydride to the borohydride. At the moment we favor loss of BH_2Cl to yield a hydride followed by addition

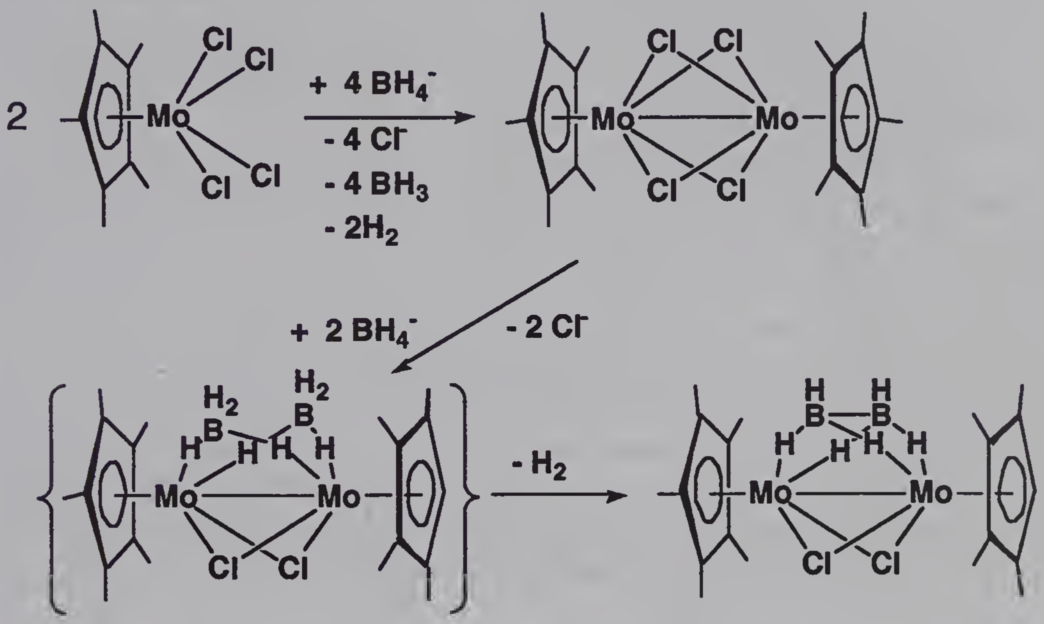

Figure 2 *Synthesis of a molybdaborane with LiBH4*

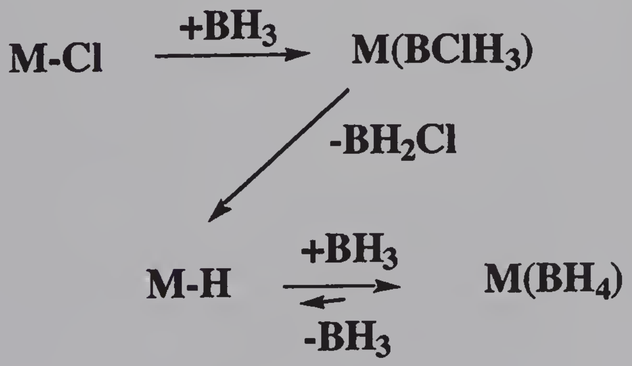

Figure 3 *Proposed formation of a borohydride from the reaction of BH3THF with a metal chloride*

to BH_3 to give the metal borohydride as shown in Figure 3. However, although a direct exchange cannot be excluded, recent work in the tungsten system has shown that a deficiency of borane leads to hydride formation which, on the addition of more borane, smoothly converts to the same product observed with excess borane. A polyborohydride appears to be an intermediate in both metathesis of the monocyclopentadienyl metal chloride by borohydride salts and its reaction with BH_3THF.

There are two important differences between these monoborane reagents that affect the outcome of the overall reaction and provide some control of product formation. First, the presence of a large excess of borane reduces the possibility of metal hydride products. Second, the reaction of borane with the first formed metallaborane can be facile thereby leading to addition of one or more BH fragments and cluster expansion. Indeed, we have now explicitly demonstrated examples of cluster expansion for $M_2B_{2+y} \rightarrow M_2B_{3+y}$; y = 0, M = Rh[15]; y = 1, M = Ru[15]; and y = 2, M = Cr.[20] Thus, it is understandable that, in contrast to borohydride, the reaction of borane generally leads to metallaboranes containing a higher boron content, e.g., the reaction of BH_3THF with Cp^*MoCl_4 leads ultimately to $(Cp^*Mo)_2B_5H_9$ (Figure 4). Note that two intermediates in this process, $(Cp^*MoCl)_2B_3H_7$ and $(Cp^*MoCl)_2B_2H_5(B_2H_5)$, have been isolated and characterized.[12]

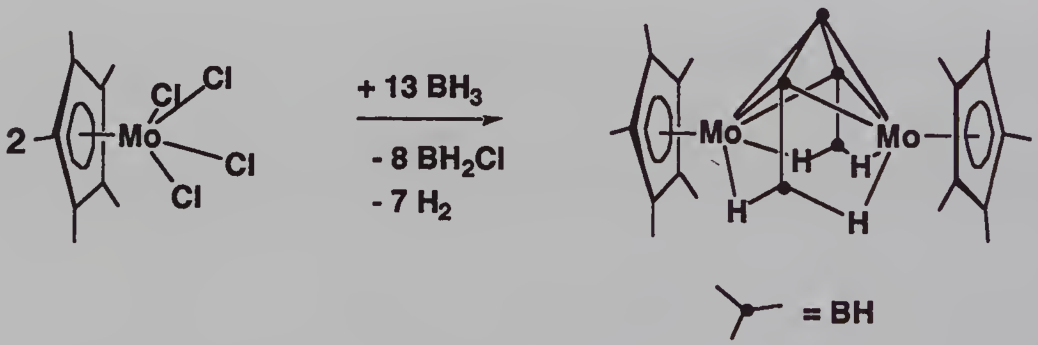

Figure 4 *Synthesis of molybdaboranes with* BH_3THF

As illustrated in Figure 5 for the rhodium system,[15] the two reagents, used in sequence, provide considerable control of product boron content. Reaction of $[Cp^*RhCl_2]_2$ with $LiBH_4$ leads to rapid reduction followed by the generation of $(Cp^*Rh)_2B_2H_6$ presumably via $[Cp^*Rh(BH_4)_2]_2$. As the chlorides are used up, this is where the reaction stops. Addition of BH_3THF to $(Cp^*Rh)_2B_2H_6$ leads to the formation of 2,3-$(Cp^*Rh)_2B_3H_7$. Reaction of borane directly with $[Cp^*RhCl_2]_2$ leads to 1-Cl-2,3-$(Cp^*Rh)_2B_3H_6$ via 3-Cl-2,3-$(Cp^*Rh)_2B_3H_6$ with no sign of a diboron intermediate. The incorporation of one chlorine atom in the product suggests that, in this instance, H_2 elimination from the chloroborohydride is competitive with formation of the borohydride. Similarly, reaction of BH_3THF with $[Cp^*RuCl_2]_2$ leads to a mixture of 1,2-$(Cp^*RuH)_2B_3H_7$ and 1,2-$(Cp^*Ru)_2B_4H_{10}$ whereas reaction with $LiBH_4$ cleanly gives 1,2-$(Cp^*RuH)_2B_3H_7$ which may be quantitatively converted to 1,2-$(Cp^*Ru)_2B_4H_{10}$ with BH_3THF.[15] Similar routes to these ruthenium compounds have been found by others.[21] In summary, choice of metal oxidation state (number of chlorides), monocyclopentadienyl metal chloride oligomer type (monomer vs dimer), stoichiometry, and the monoborane ($LiBH_4$ vs BH_3THF) provides considerable control of product type.

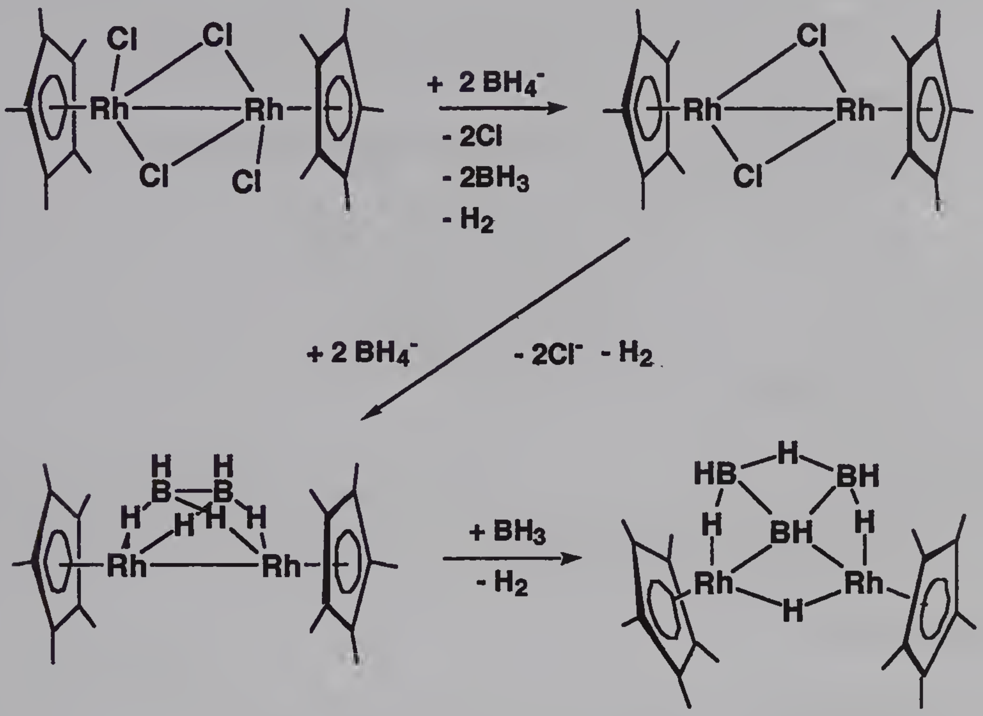

Figure 5 *Selectivity utilizing borohydride vs borane in the formation of rhodaboranes*

4 COMPOUNDS ACCESSIBLE

To date, the following mono and dinuclear metal compounds have been synthesized in our laboratory via the route described above using ordinary Schlenk systems and commercially available solutions of $LiBH_4$ and BH_3THF and syringe techniques. Several of the reactions have been successfully carried out by undergraduates. In some cases the monocyclopentadienyl metal halides can also be purchased. Isolated yields of crystalline materials range from ≈ 30% to quantitative. The compounds listed below without brackets were spectroscopically and crystallographically characterized whereas those in brackets were only spectroscopically characterized. Generally the structures obey the electron counting rules[22, 23]; however, there are notable exceptions that have been discussed elsewhere.[10, 24] Conspicuous by their absence are Mn, Fe and Ni. In our hands, the first two yield only the metallocene whereas the last yields a metal powder. Clearly product stabilities and/or facile reduction are a problem yet to be overcome for these elements.

4.1 Group 5[25]

$Cp^*TaCl_2B_4H_8$

4.2 Group 6 [12, 13, 17, 20]

$(Cp^*Cr)_2B_4H_8$; $(Cp^*Cr)_2B_5H_9$
$(Cp^*MoCl)_2B_2H_6$; $\{Cp^*Mo)_2(B_2H_6)_2\}$
$\{(Cp^*Mo)_2B_5H_9\}$; $(Cp^*MoCl)_2B_3H_7$; $Cp^*MoCl)_2B_2H_5(B_2H_5)$
$Cp^*WH_3B_4H_8$
$\{(Cp^*WCl)_2B_2H_6\}$; $\{Cp^*W)_2(B_2H_6)_2\}$; $\{(Cp^*WH_3)_2B_2H_6\}$;
$\{(Cp^*W)_2(H)(Cl)B_2H_6\}$
$(Cp^*W)_2B_5H_9$

4.3 Group 7[26]

$(Cp^*Re)_2B_4H_8$

4.4 Group 8[15]

$(Cp^*Ru)_2B_4H_{10}$; $(Cp^*RuH)_2B_3H_7$

4.5 Group 9[14, 15, 16]

$Cp^*CoB_4H_{10}$
$(Cp^*Co)_2B_3H_7$; $(\eta^4\text{-}C_5Me_5H)Co(H)\{Cp^*Co\}B_3H_7$
$\{(Cp^*Rh)_2B_2H_6\}$; $(Cp^*Rh)_2B_3H_7$; $(Cp^*Rh)_2B_3H_6Cl$
$\{Cp^*IrH_2B_3H_7\}$; $(Cp^*IrH)_2B_2H_6$

5 DERIVATIVE CHEMISTRY

The synthesis of metallaboranes in quantity permits the examination of reaction chemistry and we have already described a considerable number of reactions of chroma-,[27, 28, 29, 30] molybda-,[20] ruthena-,[15], cobalta-,[31] and rhodaboranes.[15] This work constitutes a true study of the effects of the transition metal on chemistry as the metal ancillary ligand (Cp*) is unchanged. Space does not permit more than a single example that serves to illustrate the type of new chemistry that has been revealed by these new metallaboranes.

For heavier group 6, 7, and 8 metallaboranes the Wade cluster count is often satisfied by the presence of extra endo hydrogen atoms, e.g., $Cp^*WH_3B_4H_8$ has the same formal count as $Cp^*CoB_4H_8$.[32] Based on related organometallic chemistry Andrew Weller surmised that H_2 loss from $Cp^*WH_3B_4H_8$ might be facile thereby leading to unsaturated clusters with high reactivities. Indeed, this is the case and some of the products isolated have extraordinarily low Wade cluster electron counts, e.g., $(Cp^*W)_3HB_8H_8$.[33] This compound formally has 7 skeletal electron pairs, four or five less than observed previously for 11 fragment closo metallaboranes. Further, it possesses a highly condensed geometry which is unprededented in borane and metallaborane chemistry. In fact, the core structure (Figure 6) closely resembles that of a high-nuclearity transition metal cluster with a hexagonal close-packed core. We have shown for this and related compounds[33] that the early transition metal

Cp*M fragment withdraws electrons from the skeletal bonding system effectively collapsing the normal closo structure into a highly capped closed cluster core of lower vertex number. These hypoelectronic[34] metallaboranes constitute a new structure type in metallaborane chemistry and promise an interesting focus for future research.

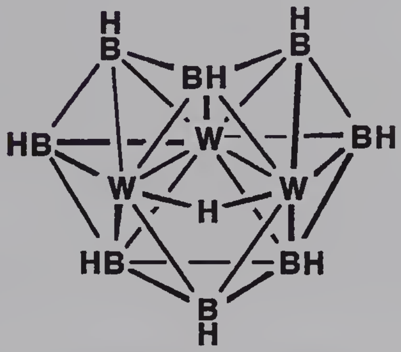

Figure 6 *The core structure of* $(Cp^*W)_3HB_8H_8$

6 SUMMARY

Metallaboranes containing polyboron fragments can be synthesized in high yield from the reaction of $[CpMCl_n]_x$; M = Ta, Cr, Mo, W, Re, Ru, Co, Rh, Ir, with monoboranes. Choice of n, x, stoichiometry, and the monoborane ($LiBH_4$ vs BH_3THF) provides considerable control of product type. Reactions of these new compounds illustrate the significant effects of transition metal variation on metallaborane structure and properties.

Acknowledgments
It was with the fine experimental work of my talented co-workers, who are named in the references, and the generous support of the National Science Foundation, that this chemistry was created.

References

1. T. P. Fehlner, in *Electron Deficient Boron and Carbon Clusters* G. A. Olah, K. Wade and R. E. Williams, Eds. (Wiley, New York, 1991) pp. 287.
2. T. P. Fehlner, in *The Synergy Between Dynamics and Reactivity at Clusters and Surfaces* L. J. Farrugia, Ed. (Kluwer Academic Publishers, Dordrecht, 1995), vol. 465, pp. 75.
3. T. P. Fehlner, Ed., *Inorganometallic Chemistry* Plenum, New York, 1992.
4. T. J. Coffy, G. Medford, J. Plotkin, G. J. Long, J. C. Huffman and S. G. Shore, *Organometallics*, 1989, **8**, 2404.
5. D. F. Gaines and S. J. Hildebrandt, *Inorg. Chem.*, 1978, **17**, 794.

6. J. D. Woollins, *Non-Metal Rings, Cages and Clusters.* Wiley, New York, 1988.
7. J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519.
8. J. D. Kennedy, *Prog. in Inorg. Chem.*, 1986, **34**, 211.
9. C. Ting and L. Messerle, *J. Am. Chem. Soc.*, 1989, **111**, 3449.
10. T. P. Fehlner, *J. Chem. Soc., Dalton Trans.*, 1998, , 1525.
11. T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
12. S. Aldridge, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1998, **120**, 2586.
13. A. S. Weller, M. Shang and T. P. Fehlner, *Organometallics*, 1999, **18**, 53.
14. Y. Nishihara, K. J. Deck, M. Shang, T. P. Fehlner, B. S. Haggerty and A. L. Rheingold, *Organometallics*, 1994, **13**, 4510.
15. X. Lei, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1999, **121**, 1275.
16. X. Lei, A. K. Bandyopadhyay, M. Shang and T. P. Fehlner, *Organometallics*, 1999, **18**, 0000.
17. J. Ho, K. J. Deck, Y. Nishihara, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1995, **117**, 10292.
18. S. H. Lawrence, S. G. Shore, T. F. Koetzle, J. C. Huffman, C.-Y. Wei and R. Bau, *Inorg. Chem.*, 1985, **24**, 3171.
19. Y. Kawano and M. Shimoi, *Chem. Lett.*, 1998, , 935.
20. S. Aldridge, T. P. Fehlner and M. Shang, *J. Am. Chem. Soc.*, 1997, **119**, 2339.
21. Y. Kawano, H. Matsumoto and M. Shimoi, *Chemistry Letters*, 1999, , submitted.
22. K. Wade, *Adv. Inorg. Chem. & Radiochem.*, 1976, **18**, 1.
23. D. M. P. Mingos and D. J. Wales, *Introduction to Cluster Chemistry.* Prentice Hall, New York, 1990.
24. T. P. Fehlner, *J. Organomet. Chem.*, 1998, **550**, 21.
25. S. Aldridge, H. Hashimoto, M. Shang and T. P. Fehlner, *Chem. Comm.*, 1998, , 207.
26. S. Ghosh, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, submitted, , .
27. H. Hashimoto, M. Shang and T. P. Fehlner, *Organometallics*, 1996, **15**, 1963.
28. H. Hashimoto, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1996, **118**, 8164.
29. K. Kawamura and T. P. Fehlner, *Organometallics*, 1998, **17**, 1904.
30. K. Kawamura, M. Shang, O. Wiest and T. P. Fehlner, *Inorg. Chem.*, 1998, **37**, 608.
31. X. Lei, M. Shang and T. P. Fehlner, *Organometallics*, 1998, **17**, 1558.
32. R. Weiss, J. R. Bowser and R. N. Grimes, *Inorg. Chem.*, 1978, **17**, 1522.
33. A. S. Weller, M. Shang and T. P. Fehlner, *Organometallics*, 1999, **18**, 853.
34. S. C. Sevov and J. D. Corbett, *Inorg. Chem.*, 1991, **30**, 4875.

Reactions of Bidentate Phosphines with Metallaboranes: Possible Routes to Linked Cluster Systems

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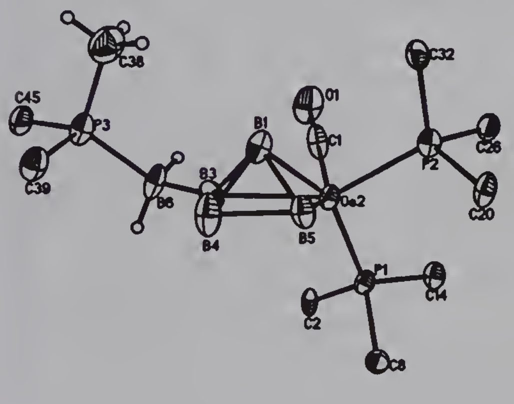
1. INTRODUCTION

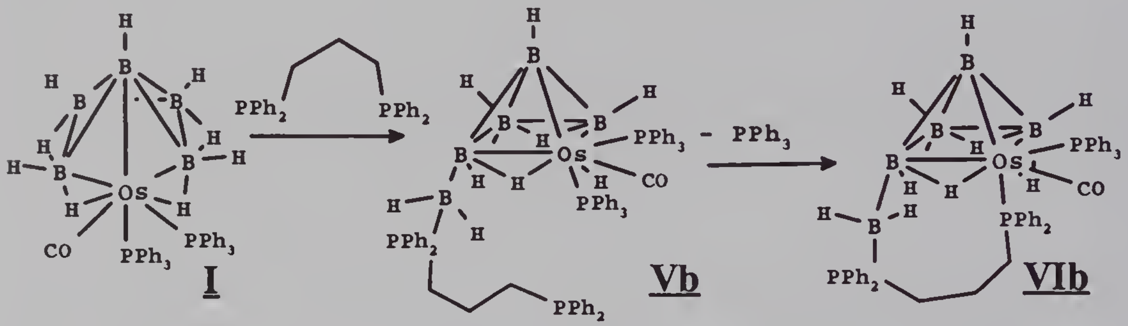
A new mode of metallaborane degradation was discovered in our laboratory recently and the preliminary details have been published.[1] The metallahexaborane [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_5H_9], (I)[2] reacts with the phosphines, PR_3, to give products of the type [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$BH_2{\cdot}PR_3$] (II). These novel species are metallapentaboranes with a BH_2PR_3 group attached to a basal boron atom. A representation of the crystal structure of **II**, where R_3 = Ph_2Me, is shown. Compound **II** degrades, thermally, to the osmapentaborane [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_8] (III) and $BH_3{\cdot}PR_3$. This paper extends this work to reactions of **I** with the bidentate bases [$(CH_2)_n(PPh_2)_2$], where n = 1, 2 or 3, (abbreviated as dppm, dppe and dppp, respectively). A further extension is a study of analogous reactions with the unsaturated cluster [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (IV).[3] The use of bidentate bases provides an opportunity to see if linked cluster systems can be prepared from **II** and **IV** and this paper describes our progress in this area. Some of this work has appeared as preliminary communications[1,4a] and more complete accounts have recently been submitted.[4b,c]



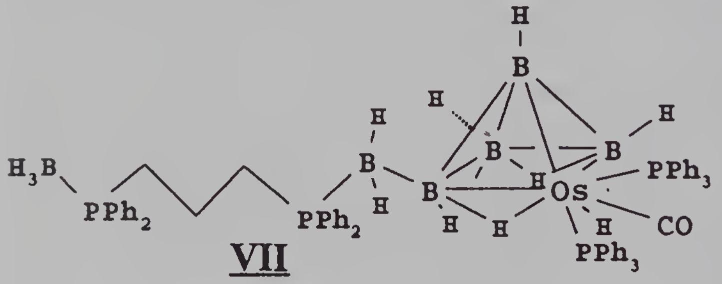
II

2. REACTIONS OF BIDENTATE PHOSPHINES WITH [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_5H_9] (I)

The reactions of [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_5H_9] (I) with bidentate phosphines take place, initially, in similar processes to the reactions with monodentate phosphines. Thus reaction of **I** with dppe or dppp forms the species [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-($BH_2{\cdot}$dppe)] (**Va**) or the analogous dppp compound (**Vb**). Spectroscopic and analytical data suggest an osmapentaborane with a structure very similar to that shown above as **II**. Thus there is a dangling PPh_2 group, easily recognized by its ^{31}P NMR chemical shift which is very similar to that for free ligand. A second species (**VI**) is always observed in the product mixture and, over time, **V** slowly converts to [2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-η^2-3,2-(BH_2·dppe)] (**VIa**), or (**VIb**) the dppp analogue. Compound **VI** is identified by spectral and analytical methods as the product of intramolecular substitution



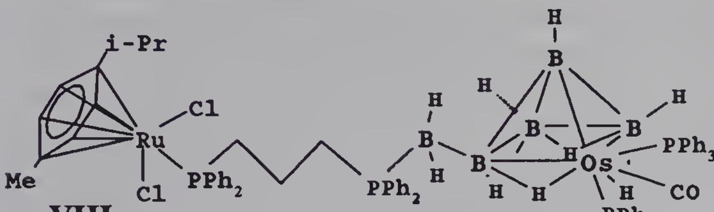
at the Os atom. Spectral data for **VI** are very similar to those for **II** and differ, principally, in one important aspect from the data for compound **V**. They do not contain the ^{31}P resonance for the dangling PPh_2 group. A proposed reaction pathway illustrating the formation of the species **V** and **VI** is given in the scheme above. The process shown requires the release of a mole of PPh_3, which is observed. Under the conditions of our study an alternative reaction, involving attack of another cage in an intermolecular process, has not been observed although we do have preliminary evidence for such products when rigid backbone bidentate bases are used.[5] Reactions of **I** with dppm afford only one product, [2,2,2-(PPh_3)$_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppm] (**Vc**), which is analogous to **Va** and **Vb**. Again it was characterized by analytical and spectroscopic methods, and an important diagnostic feature of the molecule was the presence of a ^{31}P NMR resonance at –25.83 ppm, close to the value for free dppm of –22.26 ppm, measured under the same conditions. We conclude from this that the free PPh_2 end of the dppm is not long enough to attack the Os atom effectively and thus only compound **Vc** is observed.



VII

The presence of the pendent PPh_2 group in compounds **Va-c** affords a basic site in these molecules which should be amenable to further reaction with electrophilic species. Thus, in order to see if we could form derivatives at the free phosphine moiety in **Va-c**, we allowed **Vb** to react with a tenfold excess of BH_3·thf in CH_2Cl_2. Chromatographic separation allowed the isolation of the new species [2,2,2-(PPh_3)$_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2-dppp·BH_3)] (**VII**) in 70% yield, optimized by using a chromatron. Compound **VII** was characterized by ^{11}B, ^1H and ^{31}P NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The proposed structure is given in the illustration above. The formation of **VII** portends well for the possible synthesis of linked borane and metallaborane clusters using this system since there are well-established methods for the incorporation of BH_3 into borane or metallaborane clusters.[6] Attempts to extend this work to other electrophiles have also seen success. We decided to see if **I** would react with [(*p*-cym)$RuCl_2$]$_2$ which is cleaved by phosphines to give adducts of the type [(*p*-

cym)-$RuCl_2·PR_3$].[7] Stirring a 1:2 molar equivalent mixture of **Vb** and [Ru(*p*-cym)Cl_2]$_2$ in CH_2Cl_2 at room temperature followed by workup, affords [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2·dppp·(*p*-cym)$RuCl_2$] (**VIII**) in ca. 15% yield. NMR spectra (^{1}H, ^{31}P and ^{11}B) are consistent with the structure shown below. δ ^{31}P: 9.2d, 14.03t, 19.12br, 24.33s; ^{11}B 2.91(2B), -14.8(1B), -29.3(1B), -37.9(1B) and ^{1}H spectra showed the correct Hμ resonances. Although attempts to obtain elemental analysis and an X-ray crystal structure study to be unsatisfactory, we are convinced that **VIII** is the species represented in the illustration. We believe that the formation of both **VII** and **VIII** suggest that this approach has promise for the formation of a range of linked cluster systems.

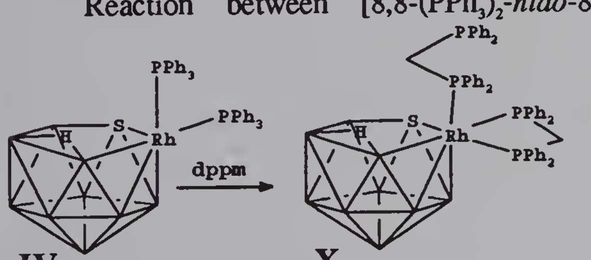


VIII

3. REACTIONS OF BIDENTATE BASES WITH [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (IV)

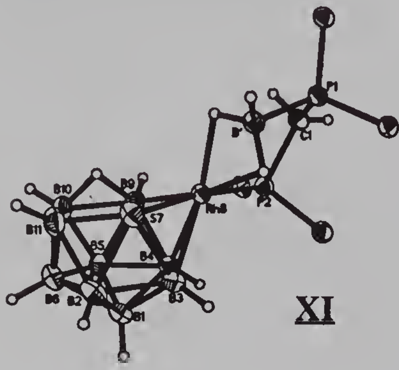
On the basis of our success with the smaller metallaboranes, we decided to extend our work by exploring the reactivity of larger unsaturated clusters with bidentate phosphine ligands. Two substrates came to mind for such a study: [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (IX)[8] and [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (IV),[3] compounds which are formally isoelectronic and are two electrons short of the number notionally required to satisfy the polyhedral skeletal electron pair theory.[9] Since our goal was not to focus on metallacarboranes, we selected the latter species. Unlike the rhodacarborane which is unstable, easily rearranging to a more closed configuration,[10] the rhodathiaborane, IV, is stable, easily prepared, has been more extensively studied and is known to add bases to form stable products.[3,11] IV is shown in the scheme below.

Reaction between [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (IV) and dppm (ie. [$CH_2(PPh_2)_2$]), in CH_2Cl_2 at room temperature, affords the saturated rhodathiaborane cluster [8,8-(η^2-dppm)(η^1-dppm)-*nido*-8,7-RhS-B_9H_{10}], (**X**). Compound **X**, shown here, contains both a bi- and a mono-dentate dppm ligand, and was obtained as a yellow crystalline solid in 48 % yield. It was identified by high-resolution mass spectrometry, multinuclear NMR spectroscopy and a single crystal structure determination. In order to see if compound **X**, which contained a dangling PPh_2 group, like that in **Vb**, would also form links to other main group moieties, we treated **X** with excess BH_3·thf in CH_2Cl_2 at room temperature. An air stable orange crystalline solid **XI** was obtained in 71% yield, along with an equimolar amount of [dppm$(BH_3)_2$]. Compound **XI** was characterized by NMR spectroscopy, elemental analysis, mass spectrometry and a crystal structure determination, to be [8,8-η^2-{η^2-$(BH_3)Ph_2PCH_2PPh_2$}-*nido*-8,7-$RhSB_9H_{10}$]. The structure of **XI** is unique in that it contains the [$(BH_3)Ph_2PCH_2PPh_2$] ligand which chelates to the Rh as a six-electron donor. The ligand bonds to the rhodium atom through a phosphine group and a borane unit. The BH_3

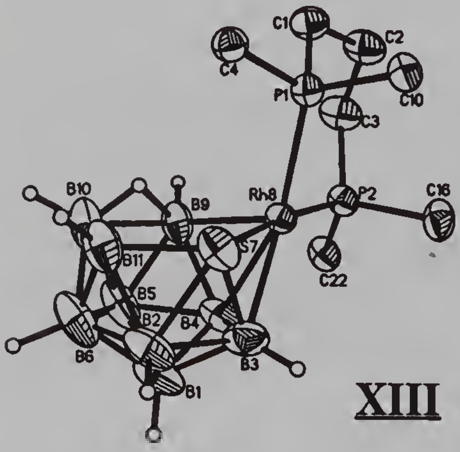


IV **X**

terminus of this ligand can be regarded as a neutral phosphine-borane that coordinates the rhodium atom, through the BH_3 in a bidentate mode, *via* two Rh-H-B three-center two-electron bonds. The $^1H\{^{11}B\}$ NMR spectrum of **XI**, at room temperature, exhibits a single resonance for the H atoms of the BH_3 group at –1.37 ppm. As the temperature is lowered this peak broadens and finally splits into three signals at +2.73, -0.24 and –0.52 ppm. This suggests that the BH_3 group is fluxional in solution, probably undergoing rotation about the B-P bond rendering the two Hμ and the terminal H equivalent on the NMR time-scale ($\Delta G^{\neq} \approx 37$ kJmol^{-1}).



XI

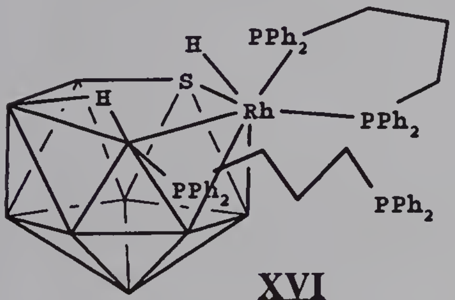


XIII

Reactions of $[8,8$-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}]$ (**IV**) with dppe or dppp (ie. $[(CH_2)_n(PPh_2)_2]$, where n = 2 or 3, respectively) proceed quite differently. When a 1:1 molar ratio of phosphine to rhodathiaborane is used, simple substitution to form $[8,8$-$(\eta^2$-dppe)-*nido*-8,7-$RhSB_9H_{10}]$ (**XII**) or $[8,8$-$(\eta^2$-dppp)-*nido*-8,7-$RhSB_9H_{10}]$ (**XIII**), as orange and yellow air stable solids, respectively, is observed. Compound **XII** is known and was prepared previously from the reaction between $[RhCl(dppe)]_2$ and Cs[6-arachno-$SB_9H_{12}]$,[11d] but compound **XIII** is new and the crystal structure is shown herein. The properties of compounds **XII** and **XIII** are quite similar to those of the starting material **IV**. NMR spectra for **XIII** at different temperatures suggest an intramolecular dynamic process, which resembles the fluxional behavior of the previously studied species, **IV** and **XII**, the isoelectronic platinacarborane, $[8,8$-$(PMe_2Ph)_2$-*nido*-8,7-$PtCB_9H_{11}]$[12] and the rhodaazaborane, $[8,8$-$(PPh_3)_2$-*nido*-8,7-RhN-$B_9H_{11}]$.[13] The activation energy, $\Delta G^{\ddagger}$, calculated for the process observed for **XIII** at the coalescence temperature of 310 K in the ^{31}P NMR spectrum, is 53 kJmol^{-1}. This compares well with values for the previously studied species. A mechanism that may account for the dynamic processes observed for this family of isoelectronic eleven-vertex metallaheteroboranes has been proposed and it is easily extended to the new species. Details may be found elsewhere.[3,13] It involves a shift and rotation of the $[(\eta^2$-dppp)Rh] moiety above the six-membered face, {S(7)B(3)B(4)B(9)B(10)B(11)}. The transition state for this fluxional process is considered[12] to be an eleven-vertex *closo*-type intermediate of C_s symmetry, with the bridging hydrogen now bonded terminally to the metal atom. This is comparable to the solution equilibrium for the *nido*-metallacarborane, $[9,9$-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}]$ (**IX**) and its *isonido*-isomer,[8] $[1,1,1$-$H(PEt_3)_2$-1,2,4-$RhC_2B_8H_{10}]$ (**IXa**), and the formation of the *isonido*-species, $[1,1,1$-$H(PMe_3)_2$-1,2,4-$IrC_2B_8H_{10}]$, from the thermolysis of $[9,9,9$-$CO(PMe_3)_2$-*nido*-9,7,8-$IrC_2B_8H_{11}]$.[10b,c] Further support for the *closo*-type transition state comes from the observation of a reversible *nido* to *closo* change that compound **XII** undergoes on deprotonation.[11c,d]

The reaction of **XIII** with EtOH in CH_2Cl_2:EtOH, in 1:1 molar ratio, affords the ethoxy-derivative, [8,8-(η^2-dppp)-9-(OEt)-*nido*-$RhSB_9H_9$] (**XIV**); behavior which is seen in the series of related compounds.[12,11b] This suggests that the boron vertex at the 9-position in **XIII**, and the related series of compounds, is prone to nucleophilic substitution reactions. **XIV** was characterized by NMR spectroscopy, mass spectrometry and X-ray diffraction. In contrast to the parent rhodathiaborane **IV**, and **XIII**, compound **XIV** does not feature fluxional behavior, even at 373 K; implying, perhaps, $\Delta G^{\neq}$ values greater than 64 $kJmol^{-1}$ for a possible dynamic process in **XIV**. The apparent large difference in the activation energy for the substituted versus the unsubstituted species may be due to either electronic or steric effects. The differences in the structures of **XIII** and **XIV** are minimal except for the B(9)-B(10) distances which differ by 0.083 Å.[4b] This tends to suggest a role for this bond in the fluxional process although a purely steric influence of the substituent at the 9-position in **XIV** cannot be ruled out.

When the reactions of compound **IV** with dppe and dppp are carried out in 1:3 metallathiaborane to phosphine molar ratios, compounds **XII** and **XIII** are formed together with the yellow *nido*-rhodathiaboranes, [8,8-(η^2-dppe)-9-(η^1-dppe)-*nido*-8,7-$RhSB_9H_{10}$] (**XV**) and [8,8-(η^2-dppp)-9-(η^1-dppp)-*nido*-8,7-$RhSB_9H_{10}$] (**XVI**). The new species, **XV** and **XVI**, are formed by substitution reactions at the metal center, and the addition of a second ligand at the 9-position in the cluster. They were characterized by NMR spectroscopy and mass spectrometry. The proposed structure for **XVI** is illustrated below. The ^{11}B NMR spectra consist of five broad peaks of relative intensity 1:1:4:2:1 for **XV**, and seven peaks of relative intensity 2:1:1:1:1:2:1 for **XVI**. $^1H\{^{11}B(sel)\}$ experiments assigned eight different terminal hydrogen atoms to their directly bound boron atoms, indirectly resolving the boron-11 spectra. One of the boron atoms has no terminal hydrogen atom, since it bears a PPh_2 terminus of the monodentate diphosphine substituent. The ^1H NMR spectra include peaks at –1.39 and –11.97 ppm for **XV**, and at –2.39 and –11.96 ppm for **XVI**. The signals at the highest frequencies in the negative region of the spectra, which are broad singlets, are assigned to B-B bridging hydrogen atoms on the cluster, whereas the peaks at the lowest frequencies, observed as multiplets, are assigned to the rhodium bonded hydrides. The ^{103}Rh-^1H coupling is clearly visible. The proton NMR spectra also confirm the presence of two *exo*-polyhedral phosphine ligands in each compound. In addition, the ^{31}P NMR spectra exhibit doublets assigned to the phosphorous atoms of the chelating ligands on the rhodium atom, very broad signals due to the phosphorus atom directly bonded to a cage boron atom, and a sharp doublet for **XV** and a singlet for **XVI** arising from the pendent PPh_2 groups. The observed spectroscopic data suggest molecular structures as shown in the illustration for **XVI**. These conclusions were supported by LRMS data both for **XV** and **XVI** which also indicated the presence of species for both compounds containing one extra O atom from oxygenation of the pendent PPh_2 groups. As indicated later, the pendent PPh_2 groups in these compounds have a strong propensity to form the phosphine oxide.

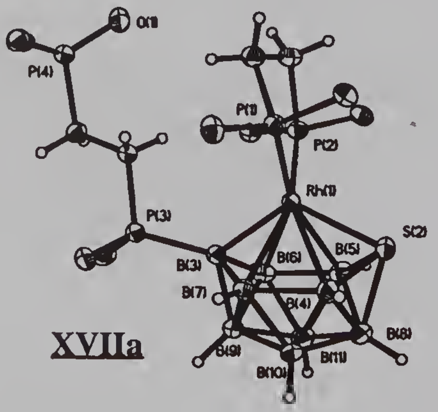


<u>**XVI**</u>

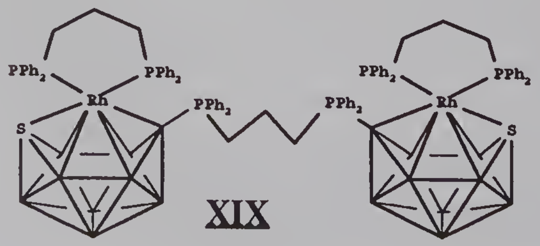
The formation of **XV** and **XVI** from **IV** would appear to involve substitution of the PPh_3 groups by a chelating ligand followed by the addition of a second ligand at the 9-position with concomitant migration of the H atom to the rhodium atom. However we cannot rule out a mechanism with an initial step, similar to the formation of **XI**, in which two ligands first coordinate to the metal followed by transfer of the unidentate one to the electrophilic site at B(9). The higher nucleophilicity of the PPh_2 group on dppe or dppp and a more favorable stereochemistry mitigate in favor of a higher tendency for concerted transfer of a ligand to the cage than would be the case for dppm from compound **XI**. Otherwise, we have no explanation for the different behaviors of the dppm-coordinated clusters with respect to the dppe- and dppp-coordinated systems.

Compounds **XV** and **XVI** are unstable in solution and tend to lose H_2 to form 11-vertex *closo*-clusters. Indeed and the latter species are often formed during attempts to isolate **XV** and **XVI**. However the situation is more complex. When a dilute solution of **XV** is heated at reflux temperature, in CH_2Cl_2 for one day, the resultant solution contains a mixture of the parent rhodathiaborane, **XII**, and free phosphine, dppe, as major components, together with a new species, **XVII**, as minor component. Under the same conditions, compound **XVI** affords a mixture of only the parent **XIII** and free phosphine, dppp. By contrast, when a concentrated solution of **XV** in $CDCl_3$ is heated at 40° degrees in an NMR tube, the new species **XVII** is obtained almost quantitatively. Under the same conditions, **XVI**, gives a mixture of **XIII** and free dppp, this time as minor products, and two new compounds, **XVIII** and **XIX**.

The new species were identified by multinuclear NMR spectroscopy and mass spectrometery. **XVII**, which was identified spectroscopically as [1,1-(η^2-dppe)-3-(η^1-dppe)-*closo*-1,2-$RhSB_9H_8$], also afforded crystals suitable for X-ray analysis and the structure, actually determined as the phosphine oxide, **XVIIa**, is shown here. For all the derivatives of **IV** which contain a dangling PPh_2 group, we always observe the phosphine oxide species in their mass spectra, indicating their strong susceptibly to oxidation. NMR spectra for **XVIII** and **XIX** are very similar to each other and indeed very similar to those for **XVII**. The ^{11}B NMR spectra consist of five resonances of relative intensity 1:1:3:2:2 and $^1H\{^{11}B(sel)\}$ data show eight terminal hydrogen atoms in a 1:1:2:1:2:2 relative intensity pattern, indirectly resolving the ^{11}B spectra. The ^{31}P NMR spectra are diagnostic of the molecular structures of these compounds. For compounds **XVII** and **XVIII**, a sharp doublet is found in the region corresponding to the chelating phosphine ligands, a doublet and a singlet due to the dangling PPh_2 groups, for **XVII** and **XVIII**, respectively, and a broad signal for the phosphorous atom bonded to a cage boron atom are observed. The ^{31}P NMR spectrum of **XIX** exhibits a doublet, assigned to a dppp chelating ligand, and a very broad signal typical of a phosphorous atom directly bonded to boron; the two signals appearing in 2:1 relative intensity ratio, respectively. The ^{31}P NMR spectrum of **XIX** does not exhibit signals corresponding to either dangling PPh_2 or PPh_2O groups. These data and the X-ray structure for **XVIIa**, suggest that



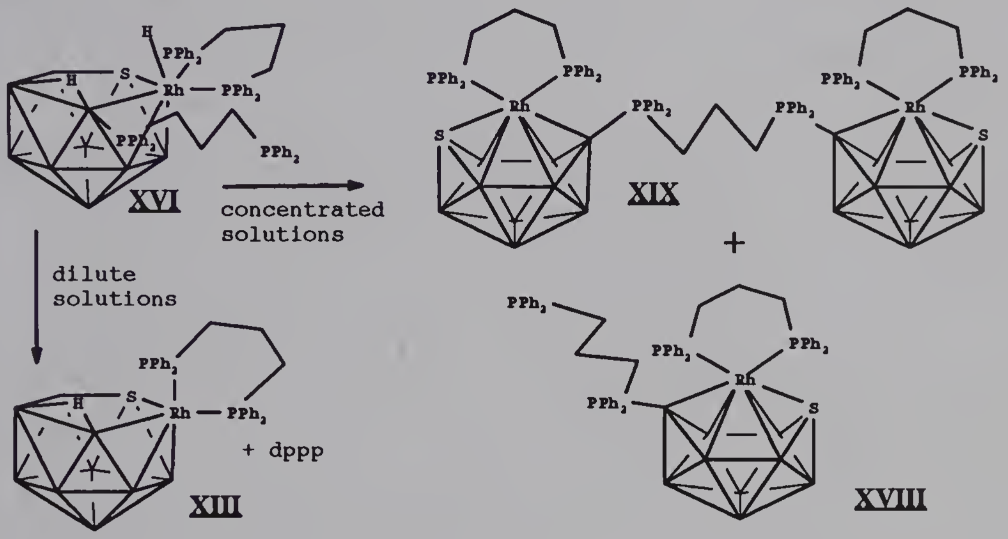
XVIIa



XIX

XIX is composed of two eleven-vertex *closo*-clusters linked by an inter-cage bridging dppp ligand, as shown in the illustration. This conclusion is supported by mass spectrometry, which shows the correct molecular ion, $[M]^+$, centered at 1718.9 a.m.u., with an isotopic distribution which conforms to the calculated values for the proposed formulation of **XIX**.

The series of reaction products obtained from the mild thermolysis of **XV** or **XVI** are summarized for **XVI** in the following scheme. Again we conclude that the formation of species such as **XIX** portends well for the development of chemistry based on larger borane clusters linked by phosphines.



4. SUMMARY

I have described some base-promoted degradation reactions for small metallaboranes. The proposed mechanism may have relevance to other degradation and rearrangement processes in borane and metallaborane chemistry. The work with small metallaboranes has led to the possibility of forming linked clusters and it was extended to the larger cluster, $[(PPh_3)_2RhSB_9H_{10}]$. Different reaction pathways are observed for dppm, compared to the longer ones such as dppe and dppp, when allowed to react with $[(PPh_3)_2RhSB_9H_{10}]$. During this work we discovered a unique example of phosphine-borane to metal coordination. For $[(PPh_3)_2RhSB_9H_{10}]$ we note, as have others,[3,11d] that there are two reactive centers on the $RhSB_9$ cluster. Reactions of the products substituted on both sites, which are concentration dependent, can give rise to linked clusters. Although the idea of linking cluster systems through bidentate phosphine ligands is not new,[14] we believe we have made a notable contribution to this area. This work continues.

Acknowledgments

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References

1. (a) L. Barton, J. Bould, H. Fang, K. Hupp, N. P Rath and C. Gloeckner, *J. Am. Chem. Soc.* 1997, **119**, 631. (b) L. Barton, J. Bould, H. Fang, K. Hupp and N. P. Rath, Advances in Boron Chemistry. W. Siebert, Ed.; Special Publication. Royal Society of Chemistry, 1997, **201**, 476.
2. J. Bould, N. N. Greenwood, J. D. Kennedy, *J. Organomet. Chem.* 1983, **249**, 11.
3. (a) G. Ferguson, M. C. Jennings, A. J. Lough, S. Coughlan, T. R. Spalding, J. D. Kennedy, X. L. R. Fontaine and B. Štíbr, *J. Chem. Soc., Chem. Commun.* 1990, 891. (b) S. Coughlan, T. R. Spalding, G. Ferguson, J. F. Gallagher, A. J. Lough, X. L. R. Fontaine, J. D. Kennedy and B. Štíbr, *J. Chem. Soc., Dalton Trans.* 1992, 2865.
4. (a) R. Macías, N. P. Rath and L. Barton, *Angew. Chem., Int. Ed., Engl.* 1999, **38**, 162. (b) R. Macías, N. P. Rath and L. Barton, *Organometallics*, (in press). (c) P. McQuade, K. Hupp, J. Bould, H. Fang, N. P. Rath, R. Ll. Thomas and L. Barton, *Inorganic Chemistry*, (submitted).
5. P. McQuade and L. Barton, unpublished results. Poster No. PA.17, IMEBORON, Durham, UK, June 11 – 15, 1999.
6. (a) H. D. Johnson and S. G. Shore, *J. Am. Chem. Soc.* 1971, **93**, 3796. (b) S. G. Shore, in "Boron Hydride Chemistry", Muetterties, E. L., Ed., Academic Press, New York, 1975. Chapter 3.
7. S. A. Serron, S. P. Nolan, Yu. A. Abramov, L. Brammer and J. L. Petersen, *Organometallics*, 1998, **17**, 104.
8. C. W. Jung and M. F. Hawthorne, *J. Am. Chem. Soc.* 1980, **102**, 3024.
9. R. E. Williams, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67. (b) K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 60. (c) R. W. Rudolph, *Acc. Chem. Res.* 1976, **9**, 446. (d) D. M. P. Mingos, *Acc. Chem. Res.* 1984, **17**, 311.
10. (a) M. Bown, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Organometallics*, 1987, **6**, 2214. (b) J. Bould, N. P. Rath and L. Barton, Organometallics, 1996, 15, 4915. (c) J. Bould, N. P. Rath and L. Barton. *Acta Crystallogr., Sect C: Cryst. Struct.Commun.*, 1997, **C53**, 416.
11. (a) G. Ferguson, A. L. Lough, S. Coughlan and T. R. Spalding. *Acta Crystallogr., Sect C: Cryst. Struct.Commun.*, 1992, **C48**, 440. (b) M. Murphy, T. R. Spalding, G. Ferguson and J. F. Gallagher, *Acta Crystallogr., Sect C: Cryst. Struct.Commun.*, 1992, **C48**, 638. (c) K. J. Adams, T. D. McGrath, R. Ll. Thomas, A. S. Weller and A. J. Welch, *J. Organomet. Chem.* 1997, **527**, 283. (d) K. J. Adams, T. D. McGrath, G. M. Rosair, A. S. Weller and A. J. Welch, *J. Organomet. Chem.* 1998, **550**, 315.
12. B. Štíbr, T. Jelínek, J. D. Kennedy, X. L. R. Fontaine, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.* **1993**, 1261.
13. R. Macías, R. Ph.D. Thesis, University of Leeds, **1996**.
14. See, for example: (a) U. Honrath, L. Shu-Tang, H. Vahrenkamp, *Chem. Ber.* 1985, **118**, 132. (b) T. Adatia, I. D. Salter, *Polyhedron*, 1995, **15**, 597. (c) D. Imhof, U. Burckhardt, K-H. Dahmen, F. Joho, R. Nesper, *Inorg. Chem.* 1997, **36**, 1813. (d) C. E. Housecroft, A. L. Rheingold, A. Waller, G. P. A. Yap, *J. Organometal. Chem.* 1998, **565**, 105.

Preparation of Bidentate Phosphine Derivatives and their Reactions with *nido*-$[(PPh_3)_2(CO)OsB_5H_9]$: Crystal and Molecular Structure of $[(p\text{-cym})RuCl_2{\cdot}PPh_2CH_2C_6H_4CH_2Ph_2P{\cdot}BH_3]$

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1. Introduction

The reaction between the hexaborane(10) analogue $[2,2,2\text{-}(PPh_3)_2(CO)\text{-}\mathit{nido}\text{-}2\text{-}OsB_5H_9]$ (1)[1] and monodentate phosphines of the type PR_3 (R_3= Ph_3, Ph_2Me and Me_3) generate the species $[2,2,2\text{-}(PPh_3)_2(CO)\text{-}\mathit{nido}\text{-}2\text{-}OsB_5H_7\text{-}3\text{-}BH_2{\bullet}PR_3]$ (2)[2,3]. Spectroscopic analysis of species **2** indicated the presence of a terminal $BH_2{\bullet}PR_3$ moiety, which was later confirmed by a crystal structure determination for the PPh_2Me adduct. This chemistry was extended to bidentate phosphines of the type $[PPh_2(CH_2)_nPPh_2]$. Reactions between phosphines of this type and **1** afford an analogous species to **2**, i.e., $[(PPh_3)_2(CO)\text{-}\mathit{nido}\text{-}2\text{-}OsB_4H_7\text{-}3\text{-}BH_2{\bullet}PPh_2(CH_2)_n(PPh_2)]$ (**3**). However in solution **3** undergoes an intramolecular substitution reaction to generate $[(PPh_3)(CO)\text{-}\mathit{nido}\text{-}2\text{-}OsB_4H_7\text{-}\eta^2\text{-}3,2\text{-}BH_2{\bullet}PPh_2(CH_2)_n(PPh_2)]$ (**4**) and free PPh_3. It was also discovered that **3** could also undergo reaction with electrophiles to afford species in which the free end of the attached bidentate phosphine is bonded to, for example, BH_3 or metal-containing groups. Yields are quite low due to the competing intramolecular substitution so in an effort to avoid this a modified approach was adopted. Our strategy was to functionalize the phosphine prior to reaction with **1**, or to use rigid phosphines, to preclude the formation of species analogous to **4**. This paper describes our efforts to prepare modified bidentate phosphines and to study their reactions with **1**.

2. Results and Discussion

In one series of reactions, phosphines were treated with the species $[(p\text{-cym})RuCl_2]_2$[4] to generate monometallated bidentate phosphines of the type $[PPh_2XPPh_2{\bullet}Ru(p\text{-cym})Cl_2]$ (X= rigid group such as $CH_2C_6H_4CH_2$[5] or C_6H_4[6]). These monometallated phosphines still have an uncoordinated phosphine available for reaction with **1** to generate species of type **3**, only this time with a metal moiety attached to the distal end of the ligand.

2.1 Synthesis of $[PPh_2CH_2C_6H_4CH_2PPh_2{\bullet}Ru(p\text{-cym})Cl_2]$.

Illustrated in Figure 1 is the synthetic pathway that was utilized to generate the monometallated bidentate phosphine $[PPh_2CH_2C_6H_4CH_2PPh_2{\bullet}Ru(p\text{-cym})Cl_2]$ (**5**).

Obviously for this reaction pathway to generate high yields of **5**, a large excess of free phosphine, i.e. [$PPh_2CH_2C_6H_4CH_2PPh_2$] (**6**), had to be used. Typically this was in the order of a five-fold excess so that **5** could be isolated in a 62% yield. Species **5** was characterized by a range of spectroscopic methods and by elemental analysis. During the spectroscopic investigation of **5** it was shown that there is long-range coupling between P(1) and P(2) with $^7J_{P\text{-}P}$= 4.10 Hz. This coupling is confirmed in 2D [^{31}P-^{31}P]-COSY experiments.

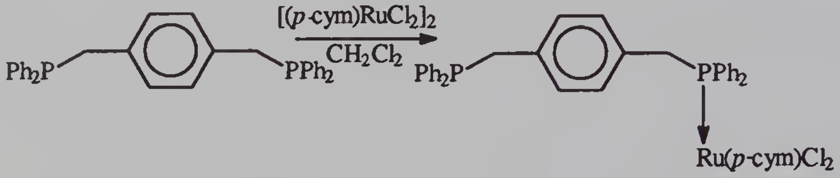

Figure 1. *Synthesis of [$PPh_2CH_2C_6H_4CH_2PPh_2$•Ru(p-cym)Cl_2].*

2.2 Synthesis of [BH_3•$PPh_2CH_2C_6H_4CH_2PPh_2$•Ru(*p*-cym)Cl_2].

To check the reactivity of the uncoordinated phosphine in **5**, the latter was allowed to react with BH_3•thf to produce the bifunctional species [BH_3•$PPh_2CH_2C_6H_4CH_2PPh_2$•Ru(*p*-cym)Cl_2] (**7**). The reaction scheme is shown below in Figure 2.

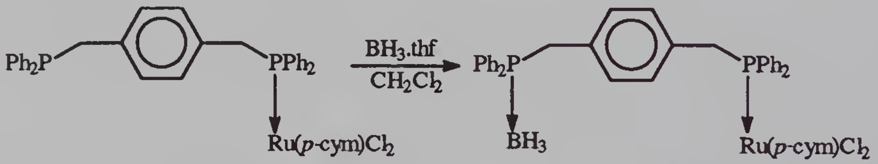

Figure 2. *Synthesis of [BH_3•$PPh_2CH_2C_6H_4CH_2PPh_2$•Ru(p-cym)Cl_2].*

Bright red rectangular crystals of **7**, containing two moles of CH_2Cl_2 solvent, were grown from a toluene/CH_2Cl_2/Et_2O solution at –5°C, and a projection of the determined X-ray structure is shown below in Figure 3.

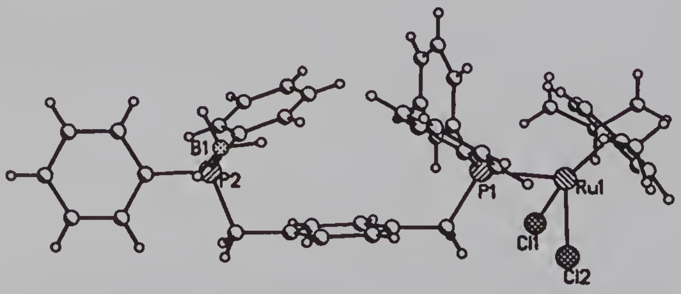

Figure 3. *Crystal structure of [BH_3•$PPh_2CH_2C_6H_4CH_2PPh_2$•Ru(p-cym)Cl_2].*

The two P atoms in **7** are essentially *syn* to each other with the C_6H_4-$C_{methylene}$-P planes having a dihedral angle of 4.5° indicating two effectively coplanar linkages perpendicular to the connecting C_6H_4 ring. This conformation appears to be the least sterically hindered, and this can be seen by examining Figure 3. Species **7** was characterized fully by a variety of spectroscopic methods, elemental analysis and HRMS, and, as in the case with **5**, there is long range coupling observed between P(1) and P(2) with $^7J_{P\text{-}P}$= 5.58Hz.

2.3 Comparison of the ^{1}H NMR spectra of the methylene protons in free, mono and bifunctionalized phosphine.

An interesting feature in this series of compounds is seen by examining the ^{1}H spectra for the methylene protons. These are shown below in Figure 4.

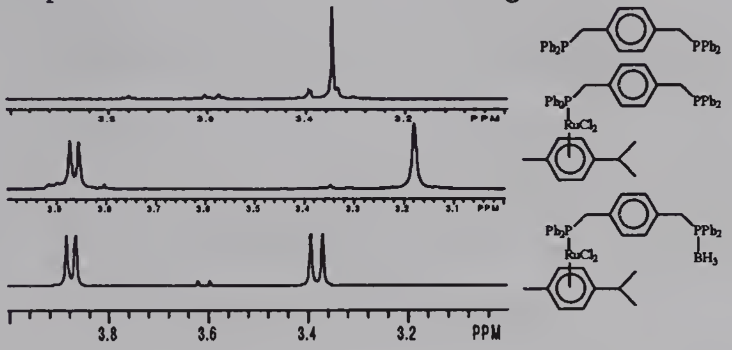

Figure 4. *Comparison of methylene proton resonances in* **5**, **6** *and* **7**.

Presumably the differences observed in the ^{1}H-^{31}P coupling in the series of compounds shown in Figure 4 can be attributed to the hybridization of the phosphorus atom. When the phosphorus is trigonal pyramidal (PR$_3$) the hybridization of the phosphorus atom is essentially p^3, with the s orbital primarily located on the lone pair. However, when the phosphorus becomes four coordinate (i.e. pseudotetrahedral) the hybridization changes to approximately sp^3. Thus, since coupling information is communicated via the s electrons, the more s character a bond has the higher the coupling between the atoms, and this series of compounds demonstrates this.

2.4 Reaction of [PPh$_2$CH$_2$C$_6$H$_4$CH$_2$PPh$_2$•Ru(*p*-cym)Cl$_2$] with [(PPh$_3$)$_2$(CO)OsB$_5$H$_9$].

The reaction of **5** with BH$_3$•thf to generate the bifunctional species **7** demonstrated the reactivity of the uncoordinated phosphine. The next step was to allow **5** to react with [(PPh$_3$)$_2$(CO)OsB$_5$H$_9$] and see if **5** behaves similarly to phosphines of the type [PPh$_2$(CH$_2$)$_n$PPh$_2$] to generate the species [(PPh$_3$)$_2$(CO)-*nido*-2-OsB$_4$H$_7$-3-BH$_2$•PPh$_2$CH$_2$C$_6$H$_4$CH$_2$•Ru(*p*-cym)Cl$_2$] (**8**). The reaction scheme proposed is shown below,

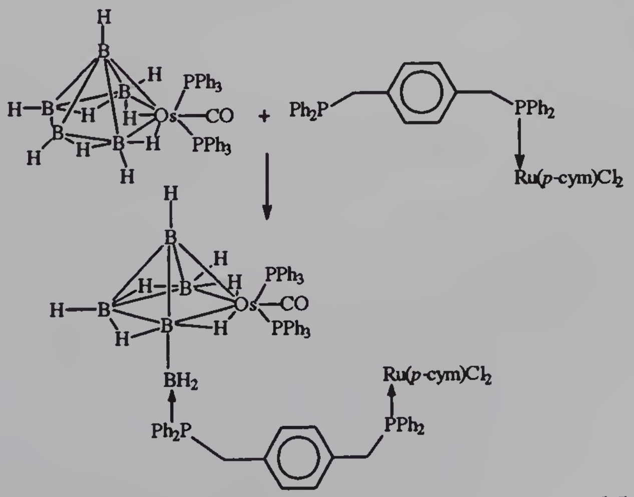

Figure 5: *Proposed scheme for the reaction between* **5** *and* **1**.

The reaction between **5** and **1** occurs readily at room temperature and **8** is isolated in 54% yield. This compound was characterized by extensive spectroscopic and elemental analysis. The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ spectra of **8** are shown below in Figure 6.

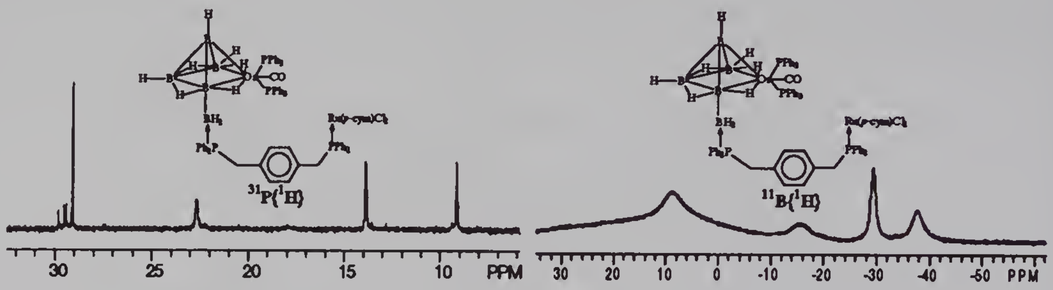

Figure 6. *$^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ spectra of 8.*

3. Summary

We have prepared and characterized the bidentate phosphine [$PPh_2CH_2C_6H_4CH_2PPh_2$] and functionalized it at one end by adding the metal moiety [Ru(*p*-cym)Cl_2], to form **5**. The other, uncoordinated, end is amenable to further derivatization, thus we allowed **5** to react with BH_3•thf to generate **7** and with [$(PPh_3)_2(CO)OsB_5H_9$] to produce species **8**, both in high yields. This chemistry was also applied to more rigid bidentate phosphine [$PPh_2C_6H_4PPh_2$], but due to difficulty in separating the monometallated species and the inherit instability of the species analogous to **8**, this route proved unsuccessful. This chemistry can be extended to examine the possibility of producing linked clusters.

4. Acknowledgements

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5. References

1. Bould, J.; Greenwood, N. N.; Kennedy, J. D. *J. Organomet. Chem.* **1983**, 249, 11.
2. Barton, L.; Bould, J.; Fang, H.; Hupp, K.; Rath, N. P.; Gloeckner, C. *J. Am. Chem. Soc.* **1997**, 119, 631.
3. McQuade, P.; Hupp, K.; Bould, J.; Fang, H.; Rath, N. P.; Thomas, R. Ll.; Barton, L. *Inorg. Chem* (submitted).
4. Bennett, M. A.; Huang, T.-N.; Matteson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, 21, 74.
5. Imhof, D.; Burckhard, U.; Dahmen, K.-H.; Joho, F.; Nesper, R. *Inorg Chem.* **1997**, 36, 1813.
6. Baldwin, R. A.; Cheng, M. T. *J. Org. Chem.* **1967**, 32, 1572.

Metal Borides: Interstitial Boron at the Molecular Level

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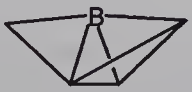
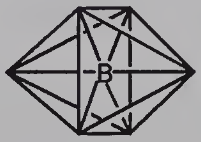
1 INTRODUCTION

This article reviews strategies that we have used to link transition metal boride clusters of types **1** (semi-interstitial boron, M_4B cage) and **2** (fully interstitial boron, M_5B cage), and addresses some of the problems of competing reactions.



(1)



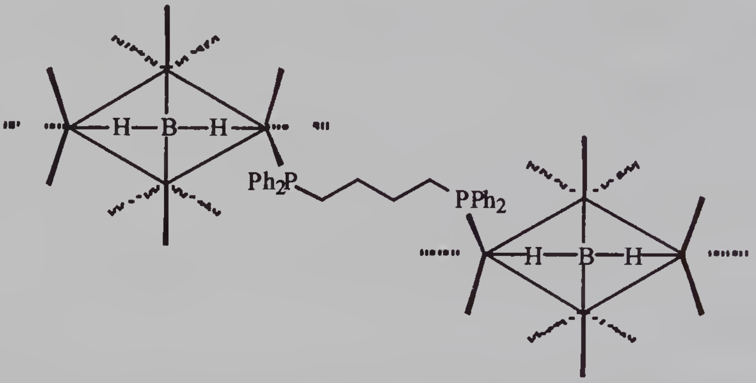
(2)

2 $Ph_2P(X)PPh_2$ LINKERS

Initial studies were carried out using the type-**1** cluster $HRu_4(CO)_{12}BH_2$; the boron atom is relatively protected against attack and preliminary work indicated that competing boron extraction was not a problem as had been observed in reactions of clusters containing M_3B or M_3B_2 cores.[1,2] The use of a bisphosphine $Ph_2P(X)PPh_2$ where X is a variable spacer provides four possible modes of coordination:

- chelating to one Ru;
- edge-bridging two Ru atoms
- monodentate to one cluster (pendant);
- monodentate to each of two clusters (linkage).

The choice of spacer X is clearly important, e.g. use of a rigid spacer such as C≡C (i.e. the ligand dppa) reduces the options of bonding mode, while use of a flexible spacer leaves more options open: dppm, for example, might be expected to favour edge-bridging modes, while for dppb and dppf it is difficult to predict the dominant coordination modes. Of the ligands studied, dppb gave the highest yields of a linked cluster, i.e. $\{HRu_4(CO)_{11}BH_2\}_2(\mu\text{-dppb})$ (**3**). However, even here where the yield was 45%, the reaction was complicated by the formation of $HRu_4(CO)_{11}BH_2(dppb)$ (pendant). Preferences for other ligands can be summarized as follows: dppe favoured an edge-bridging mode, with competition for cluster linkage; dppp and dppf behave similarly with the formation of clusters containing the ligands in pendant or chelating modes (linked species could only be obtained under photolytic conditions); dpph behaved in a similar manner to dpph but gave lower yields of the linked product; the rigid dppa yielded products containing the ligand in linkage and pendant modes and in addition disubstitution on a single cluster was observed.[3]



Hinge μ-H omitted

(3)

3 $\{AuPh_2P(X)PPh_2Au\}^{2+}$ LINKERS

The compound $HRu_4(CO)_{12}BH_2$ contains three cluster protons which can, in theory, be replaced by $\{AuPR_3\}^+$ units.[4,5] Several years ago, we showed that, in practice, replacement of one or two protons is facile giving products of type $HRu_4(CO)_{12}B(AuPR_3)_2$ but, with the bisphosphine dppf, there is competition between the formation of $HRu_4(CO)_{12}B(Au_2dppf)$ and the linked cluster. $\{HRu_4(CO)_{12}BHAu\}_2(\mu\text{-}dppf)$.[6,7] In some reactions, further complication is the formation (dependent on the

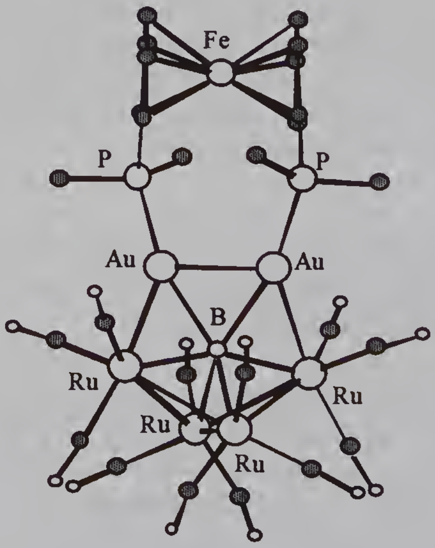
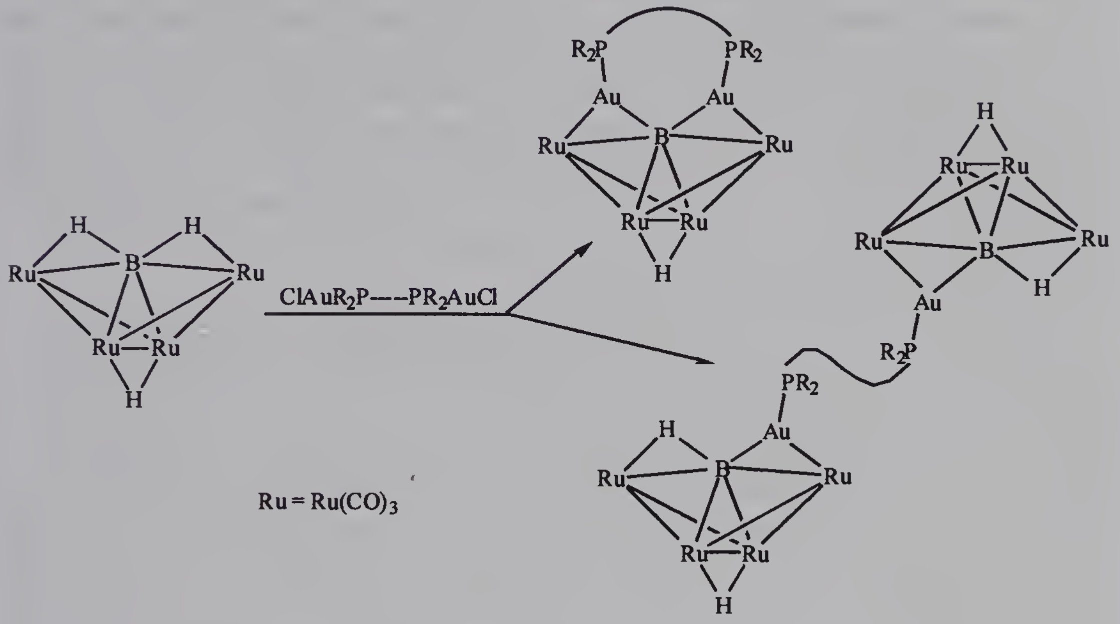


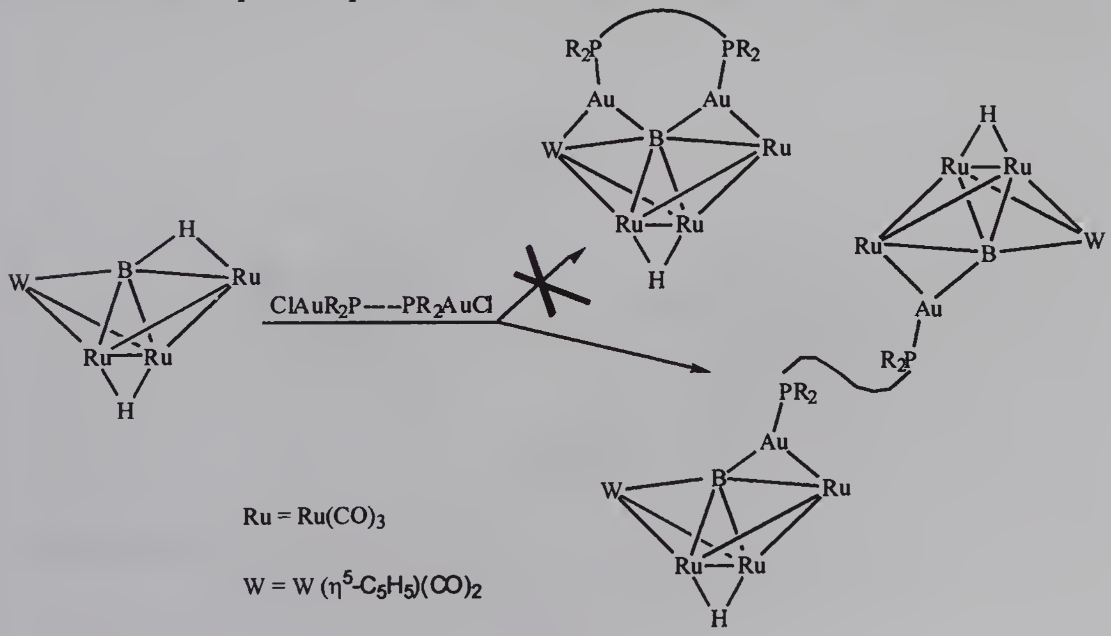
Figure 1 *Structure of* $HRu_4(CO)_{12}B(Au_2dppf)$ *determined by X-ray diffraction (ref. 7); only the ipso-C of each Ph ring is shown.*

organic group in the phosphine) of the gold(I)-fused dicluster $[\{HRu_4(CO)_{12}BH\}_2Au]^-$.[8] We have focused attention on the competition between the formation of $HRu_4(CO)_{12}B(Au_2dppf)$ (Figure 1) and $\{HRu_4(CO)_{12}B\text{-}HAu\}_2(\mu\text{-}dppf)$ (Scheme 1).



Scheme 1

One way of driving the competition in favour of the linked dicluster-type product is to remove the potential for the second site of attack by Au(I) on the first cluster, i.e. provide the cluster with only one B–H–M site rather than two. This can be achieved by changing one of the cluster metal fragments so as to increase *by one* the valence electrons provided by that fragment (compared to $Ru(CO)_3$) and thereby decrease by one the number of cluster H atoms required to provide the total number of valence electrons for the cluster.



Scheme 2

For example, $Ru(CO)_3$ is a 14 electron fragment, and the electron count for $HRu_4(CO)_{12}BH_2$ is (4 × 14) + 3 + 3 = 62 (the electron count for an M_4-butterfly framework); $W(\eta^5\text{-}C_5H_5)(CO)_2$ is a 15 electron fragment, and $HW(\eta^5\text{-}C_5H_5)Ru_3(CO)_{11}BH$ is a 62-butterfly cluster analogous to $HRu_4(CO)_{12}BH_2$. Initial studies of the reaction of the conjugate base of $HW(\eta^5\text{-}C_5H_5)Ru_3(CO)_{11}BH$[9] with Ph_3PAuCl showed the preferential formation of a *monogold* derivative (something that is hard to achieve starting from $HRu_4(CO)_{12}BH_2$), and crystallographic data for $HW(\eta^5\text{-}C_5H_5)Ru_3(CO)_{11}BAuPPh_3$ confirmed that the $AuPPh_3$ unit bridges an $Ru_{wingtip}$-B edge. With ClAu(dppf)AuCl, $[HW(\eta^5\text{-}C_5H_5)Ru_3(CO)_{11}B]^-$ reacts to give $\{HW(\eta^5\text{-}C_5H_5)Ru_3(CO)_{11}BAu\}_2(\mu\text{-dppf})$ in 70% yield, and this preferential formation of the linked dicluster (Scheme 2) follows the expectations from the reduced availability of boron-attached cluster protons in the precursor.

The hexametal boride anions $[Ru_6(CO)_{17}B]^-$ and $[Rh_2Ru_4(CO)_{16}B]^-$ (structure type **2**) are attractive precursors for the preparation of diclusters linked by a $\{AuPh_2PXPPh_2Au\}$-spacer since they are monoanions with no further sites of deprotonation. The reaction of $[Ru_6(CO)_{17}B]^-$ with ClAu(dppm)AuCl gives two products, the major one being the fused dicluster $[\{Ru_6(CO)_{17}B\}_2Au]^-$; the desired linked $\{Ru_6(CO)_{17}B\}_2\{\mu\text{-Au(dppm)Au}\}$ is formed only in low yield. Increasing the bisphosphine chain length had the effect of tipping the reaction in favour of the linked dicluster, e.g. using ClAu(dppb)AuCl resulted in the formation of $\{Ru_6(CO)_{17}B\}_2\{\mu\text{-Au(dppb)Au}\}$ in 70% yield.[10] This chain length was also found to be a favourable choice for the linkage of the heterometallic $[Rh_2Ru_4(CO)_{16}B]^-$ clusters and Figure 2 shows the structure of $\{Rh_2Ru_4(CO)_{16}B\}_2\{\mu\text{-Au(dppb)Au}\}$.[11]

An obvious choice of bisphosphine for cluster linkage is dppa; it has a rigid PCCP-backbone, and the reaction of $[Ru_6(CO)_{17}B]^-$ with ClAu(dppa)AuCl gives $\{Ru_6(CO)_{17}B\}_2\{\mu\text{-Au(dppa)Au}\}$ in 50% yield. Another choice of linker was the $\{Au((E)\text{-dppet})Au\}^{2+}$ unit, but despite its rigidity, the linked cluster $\{Ru_6(CO)_{17}B\}_2\{\mu\text{-Au}((E)\text{-dppet})\text{Au}\}$ could only be obtained in ≤20% yield. In this case, spectroscopic data indicated the formation of $Ru_6(CO)_{17}BAu((E)\text{-dppet})AuCl$, but its slow conversion to $\{Ru_6(CO)_{17}B\}_2\{\mu\text{-Au}((E)\text{-dppet})\text{Au}\}$ made isolation and full characterisation of the former impossible.

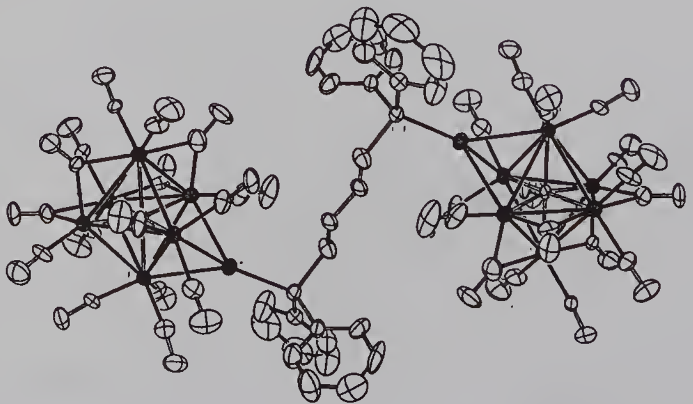
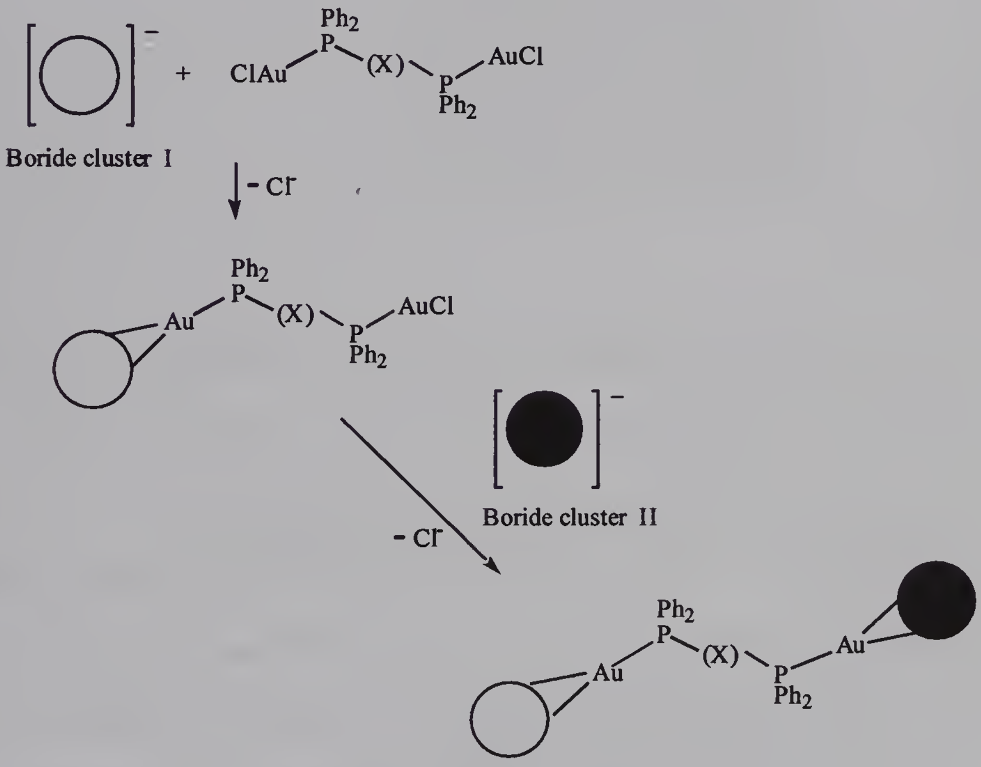


Figure 2 *Structure of* $\{Rh_2Ru_4(CO)_{16}B\}_2\{\mu\text{-Au(dppb)Au}\}$ *determined by X-ray diffraction (ref. 11). The Rh atoms in each cluster are mutually trans.*

The formation of asymmetrical diclusters, i.e. two different clusters linked by a spacer, has been another aim in our studies. Using the {AuPh$_2$P(X)PPh$_2$Au}-spacer would require the sequence of reactions shown in Scheme 3, but the problematical feature of this scheme has been the formation of isolable intermediate clusters bearing pendant arms terminating in a Au(I)Cl functionality. As already mentioned, Ru$_6$(CO)$_{17}$BAu((*E*)-dppet)AuCl can be separated but converts to {Ru$_6$(CO)$_{17}$B}$_2${μ-Au((*E*)-dppet)Au} on standing. Similarly, we have isolated Ru$_6$(CO)$_{17}$BAu(dppe)AuCl, but in solution, this converts to {Ru$_6$(CO)$_{17}$B}$_2${μ-Au(dppe)Au}. With the rigid spacer dppa, formation of the linked dicluster is more favourable than forming Ru$_6$(CO)$_{17}$BAu(dppa)AuCl even with a 1:1 cluster:ClAu(dppa)AuCl ratio.



Scheme 3

CONCLUSIONS

The synthesis of linked diclusters containing interstitial boron can be achieved using bisphosphine ligands or {AuPh$_2$PXPPh$_2$Au}$^{2+}$ linkers. Greatest success has been with the latter method provided that one removes the possiblity of competing routes of multiple gold(I) attachment to the initial cluster, i.e. use clusters which have only one site of ready deprotonation. The synthesis of asymmetrical diclusters requires the formation of an intermediate cluster carrying a pendant {AuPh$_2$PXPPh$_2$AuCl} unit; in all cases studied, conversion of such species to symmetrical linked diclusters precludes their efficient use for the synthesis of asymmetrical products.

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ABBREVIATIONS

dppa	bis(diphenylphosphino)acetylene
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppet	1,2-bis(diphenylphosphino)ethene
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane

REFERENCES

1. C.E. Housecroft and T.P. Fehlner, *J. Am. Chem. Soc.*, 1986, **108**, 4867.
2. C.E. Housecroft, D.M. Matthews, A.J. Edwards and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1993, 2727.
3. S.M. Draper, C.E. Housecroft, J.S. Humphrey and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1995, 3789.
4. J.W. Lauher and K. Wald, *J. Am. Chem. Soc.*, 1981, **103**, 7648.
5. K.P. Hall and D.M.P. Mingos, *Prog. Inorg. Chem.*, 1984, **32**, 237.
6. A.K. Chipperfield, C.E. Housecroft and A.L. Rheingold, *Organometallics,* 1990, **9**, 681.
7. S.M. Draper, C.E. Housecroft and A.L. Rheingold, *J. Organomet. Chem.*, 1992, **435**, 9.
8. S.M. Draper, C.E. Housecroft, J.E. Rees, M.S. Shongwe, B.S. Haggerty and A.L. Rheingold,*Organometallics*, 1992, **11**, 2356.
9. C.E. Housecroft, D.M. Matthews, A.L. Rheingold and X. Song, *J. Chem. Soc., Dalton Trans.*, 1992, 2855.
10. C.E. Housecroft, A.L. Rheingold, A. Waller and G.P.A. Yap, *J. Organomet. Chem.*, 1998, **565**, 105.
11. A.D. Hattersley, C.E. Housecroft and A.L. Rheingold, *Inorg. Chim. Acta*, 1999, in press.

Metallaheteroboranes

Boron-functionalized MC_2B_4 and MC_2B_3M' Clusters and their Applications

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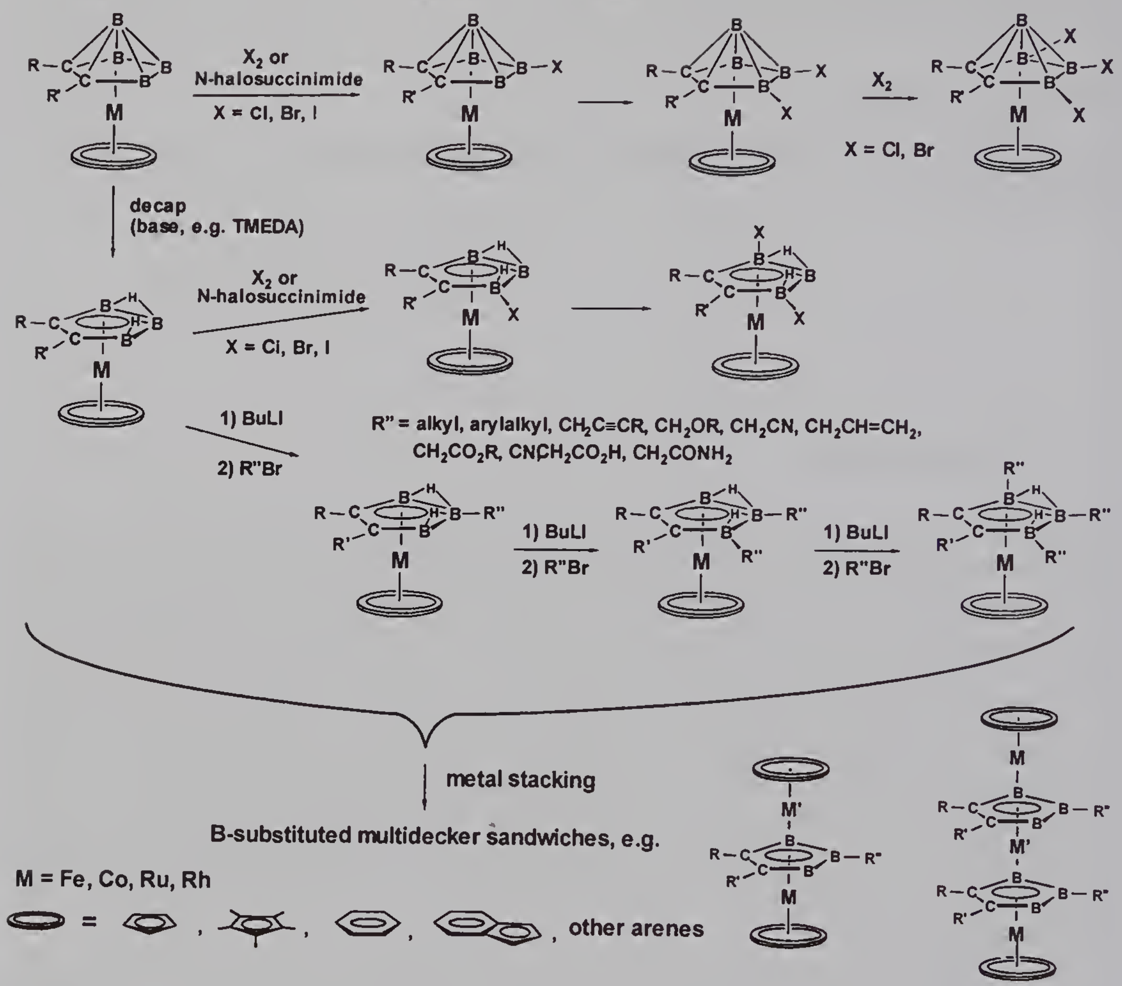
1. INTRODUCTION

One of the more important challenges presented by carborane chemistry in its 40-year history has been to develop controlled methods for introducing substituents at the carbon or boron vertices in the cage framework.[1] Derivitization is a prerequisite for many if not most carborane and metallacarborane applications,[2] including polymer synthesis, boron neutron capture therapy, catalysis, incorporation in nonlinear optical (NLO) materials, and agents for metal ion extraction, to cite a few examples. In closed polyhedral (closo) carboranes, organic substitution is usually effected at the carbon rather than boron atoms, because the cage C-H bonds are considerably more polar than the B-H groups and readily undergo proton removal on treatment with alkyllithium reagents and other strong bases. For the icosahedral $C_2B_{10}H_{12}$ isomers[1] as well as smaller homologues such as $C_2B_5H_7$[3] and $C_2B_4H_6$,[4] such reactions afford a straightforward route to C-functionalized derivatives.

Substitution at boron is a different story. Halogenation at BH vertices occurs readily in carboranes via electrophilic and photochemical processes,[1] but the introduction of organic functional groups presents a synthetic challenge, especially when attachment at specific boron locations is desired. General, nonspecific B-alkylation of $C_2B_{10}H_{12}$ clusters can be accomplished by several routes,[5] and indeed Hawthorne and co-workers[5c] have prepared peralkylated $C_2B_{10}Me_{12}$ carboranes via the treatment of 1,12-$C_2B_{10}H_{12}$ with methyl triflate and triflic acid. The placement of substituents at pre-selected boron locations, however, is a difficult challenge in large carboranes having many BH vertices, and is likely to remain so. In the smaller 3-and 4-boron clusters that are the focus of our research, this problem is much more tractable. We are interested in B-substitution in these compounds for two reasons: first, as a way to modify the electronic (and in some cases steric) properties of the ligands and thus allow tailoring of their complexes for catalytic and other purposes, and second, to prepare functionalized building block compounds for assembling polymetallacarborane chains and networks.[6]

Methods for regiospecific introduction of halogens at boron vertices in 7-vertex MC_2B_4 clusters, and for organosubstitution at boron in *nido*-MC_2B_3 compounds, have been developed in recent years[6] and are summarized in Scheme 1. The approaches shown, combined with available routes to C-substituted derivatives, have been used to advantage in preparing B- and C-functionalized multidecker complexes and linked dimers. However, recent synthetic objectives in our program require more versatility; in

Scheme 1

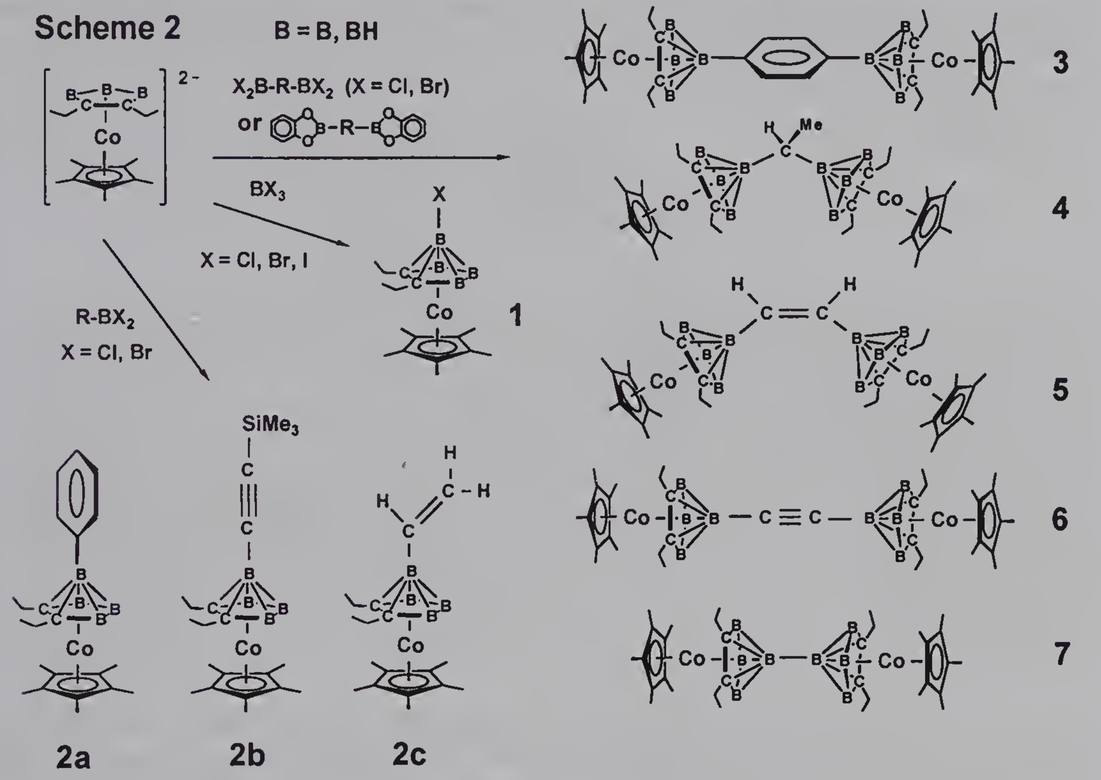


particular, we have sought methods for attaching organic linking groups to MC_2B_4 boron vertices, including the apex (B7) and equatorial (B4, B5, B6) positions. This report describes some recent progress in this area and briefly outlines some of our current synthetic objectives based on this chemistry.

2. APEX-FUNCTIONALIZED CLUSTERS

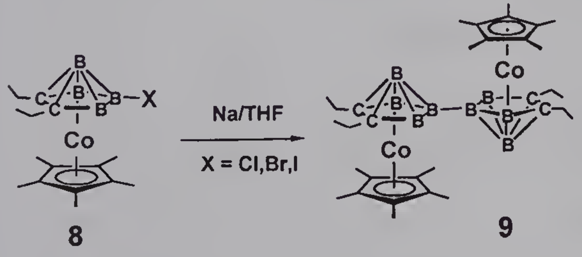
In contrast to the relatively facile halogenation[7] of equatorial boron atoms in MC_2B_4 cages (see Scheme 1), the apex hydrogen is essentially unreactive toward nucleophilic or electrophilic substitution, even under forcing conditions (the apex BH unit is, of course, extracted in base-promoted decapping reactions[6] that convert MC_2B_4 into *nido*-MC_2B_3 clusters, as shown in the top left of Scheme 1). Recognizing the potential utility of apex-substituted derivatives in constructing metallacarborane oligomers and polymers, we found a general, albeit indirect, route to such compounds via "recapitation" of *nido*-MC_2B_3 complexes.[8] As shown in Scheme 2, RBX_2 reagents undergo metathesis with $Cp^*Co(R_2C_3B_3H_3)^{2-}$ dianions, releasing 2 X^- and forming $Cp^*Co(R_2C_3B_4H_3\text{-}7\text{-}R)$ derivatives (**1** - **3**). In collaboration with Siebert and co-workers, this approach was broadened[9] via the use of organoborane reagents (Scheme 2), generating a variety of dimeric products in which the apices are linked by organic moieties having sp^3-, sp^2-, or sp-hybridized carbon (**4** - **6**) or are directly connected (**7**); all of those shown have been structurally confirmed by X-ray crystallographic studies. The electronic properties of these and other apically-linked dimers, especially with respect to metal-metal communication in paramagnetic species, are currently under investigation.

Scheme 2



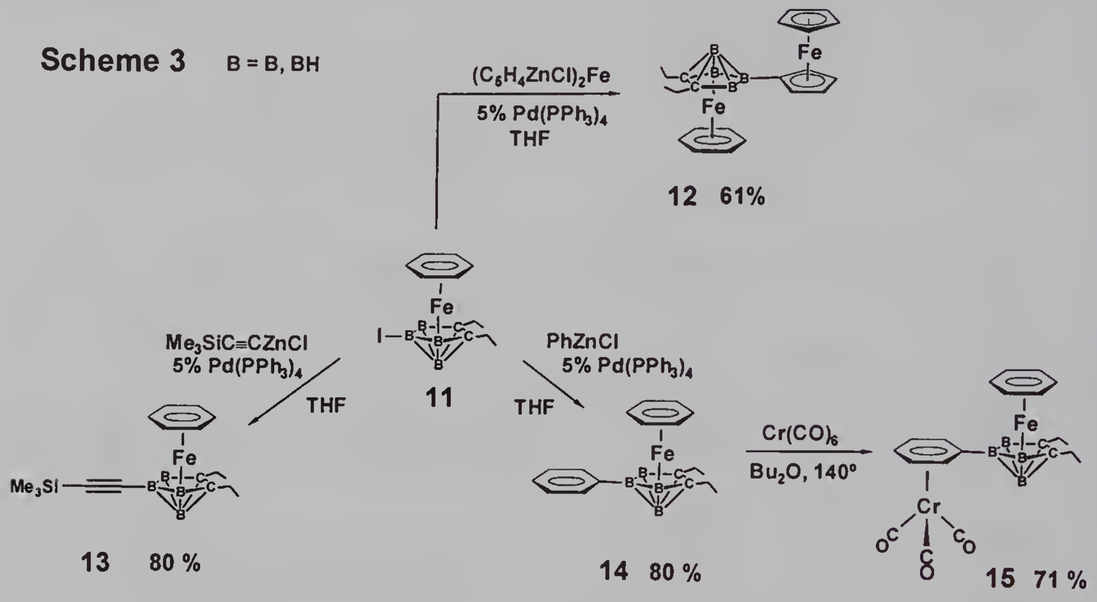
3. COUPLING REACTIONS OF COBALT AND IRON METALLACARBORANES

The method described above for preparing apically derivatized complexes is complemented by techniques for equatorial substitution. Several years ago, Wong, Sabat and Grimes[10] found that 5-halo cobaltacarborane derivatives (**8**) undergo a so-called "inorganic Wurtz reaction" with sodium metal to generate the dimer **9**, a red-orange solid. Of interest in this context is the fact that **9** and **7** are isomers, allowing a comparison of the effects of equatorial vs. apical B-B linkage on electronic behavior. A third "isomer" of this system is the bis(cobaltacarborane) fulvalene complex $(Et_2C_2B_4H_4)Co(C_5H_4)$—$(C_5H_4)Co(Et_2C_2B_4H_4)$ (**10**), linked via a Cp-Cp bond, whose electronic properties have been studied in detail via spectroelectrochemical techniques.[11] The electrochemically generated anion $\mathbf{10}^-$, a d^6d^7 bimetallic system, was found to be a fully delocalized (Day and Selbin Class III) complex; the behavior of **7** and **9** is currently under investigation.



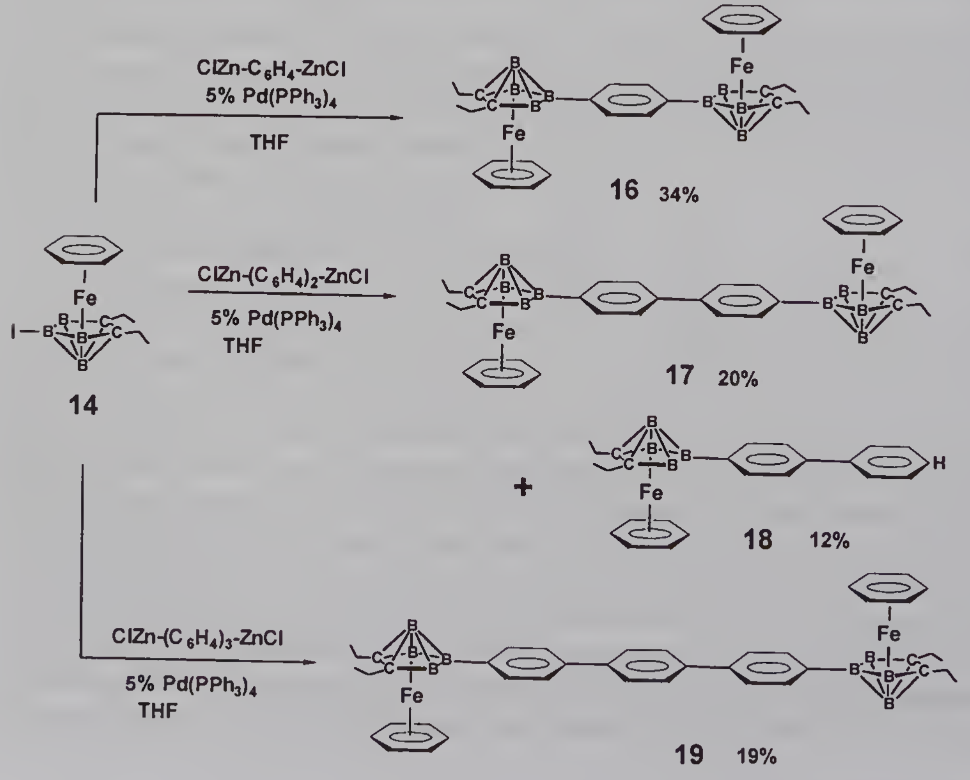
Very recently our group has explored metal-promoted cross-coupling reactions of small metallacarboranes. The 5-iodo ferracarborane **11**, on treatment with $(C_5H_4ZnCl)_2Fe$ in the presence of a palladium catalyst, somewhat unexpectedly formed the B-monoferrocenyl derivative **12**, a yellow-orange air-sensitive solid, rather than the anticipated diferrocenyl compound (Scheme 3).[12] Palladium-catalyzed cross-coupling also works with other reagents as shown, affording the red crystalline TMS-ethynyl derivative **13** and the brown crystalline phenyl complex **14**, both in good yield. As is further discussed below, these compounds have considerable potential as synthetic agents; for example, **14** readily adds chromium tricarbonyl to give the yellow air-sensitive heterobimetallic complex **15**.

Scheme 3 B = B, BH



A similar approach using bis(chlorozinc)polyphenylene reagents has yielded a series of phenylene-bridged bisferracarboranes, isolated as yellow air-stable solids (Scheme 4).[12] An X-ray crystallographic study on the triphenylene complex **19**

Scheme 4 B = BH, B

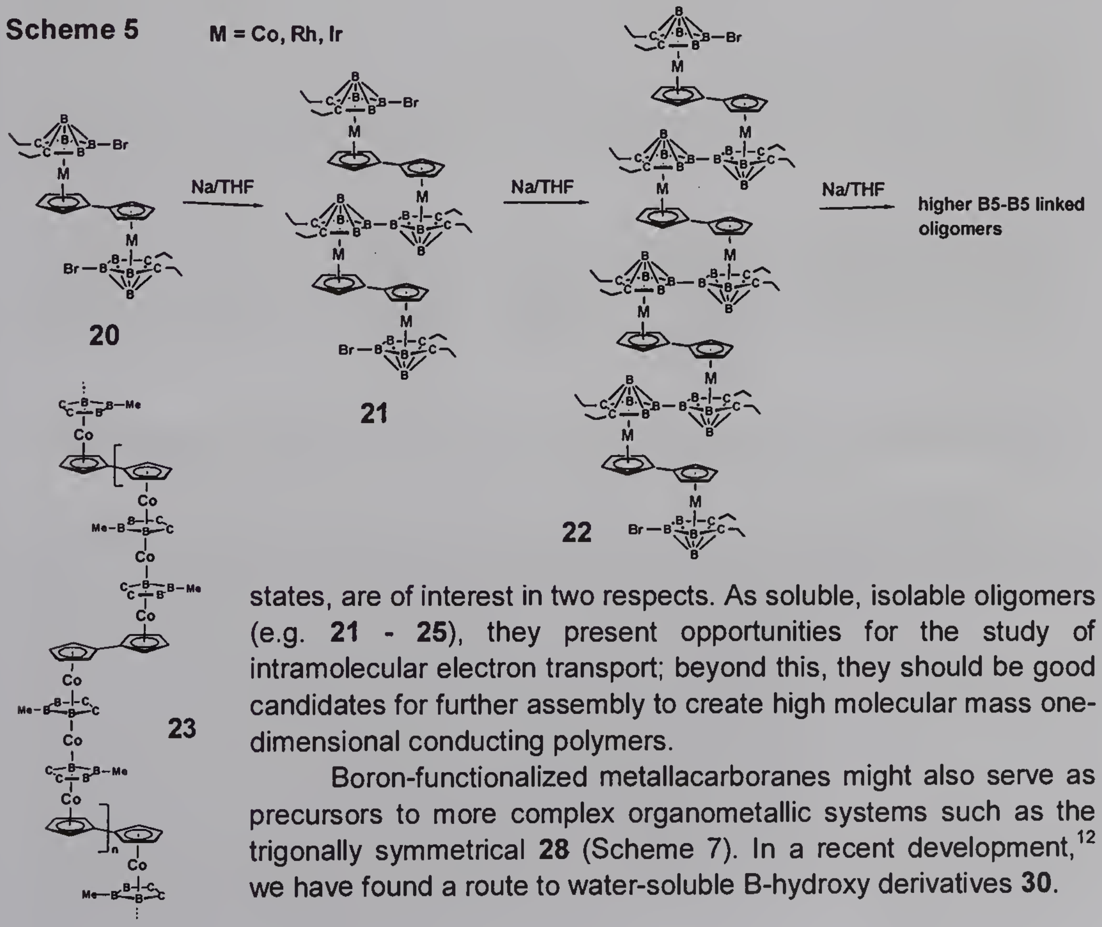


established the solid-state structure[12] which has the centrosymmetric "anti" geometry depicted; however, conformers arising from rotation on the inter-ring C-C and C-B single bonds are presumed to be present in solution in all of these species. The binuclear complexes **16**, **17**, and **19** are diamagnetic Fe^{II}-Fe^{II} d^6d^6 systems that are expected to be oxidized and/or reduced to paramagnetic mixed-valence states. Consequently, they are excellent subjects for the study of metal-metal communication via delocalization of unpaired electrons, a subject of considerable general interest in transition metal chemistry. At this writing, electrochemical data for this series are available only on **16**,[13] and are consistent with some delocalization.

4. CONSTRUCTION OF B-B LINKED OLIGOMERS AND POLYMERS

Linkage of small metallacarboranes via intercluster B-B bonds, in combination with methods described elsewhere for forging C-C or metal-metal connections, opens the way to the assembly of a large variety of extended chains and networks from bifunctional synthon complexes. In principle, all that one requires are soluble, stable species that are capable of some type of linkage — e.g., boron-boron bond formation or stacking of C_2B_3 faces with metal ions — at both ends of the molecule. Schemes 5 and 6 illustrate two approaches to metallooligomer target compounds based on equatorial and apical B-B linkage, respectively, of bis(metallacarboranyl)fulvalene complexes that are available from earlier work.[14] Known fulvalene-linked tetradecker-sandwich oligomers such as **23**, prepared via metal stacking with metal ions,[15] are highly electron-delocalized.[16] Extended polymetallic chains of this kind, when oxidized or reduced to paramagnetic states, are of interest in two respects. As soluble, isolable oligomers (e.g. **21** - **25**), they present opportunities for the study of intramolecular electron transport; beyond this, they should be good candidates for further assembly to create high molecular mass one-dimensional conducting polymers.

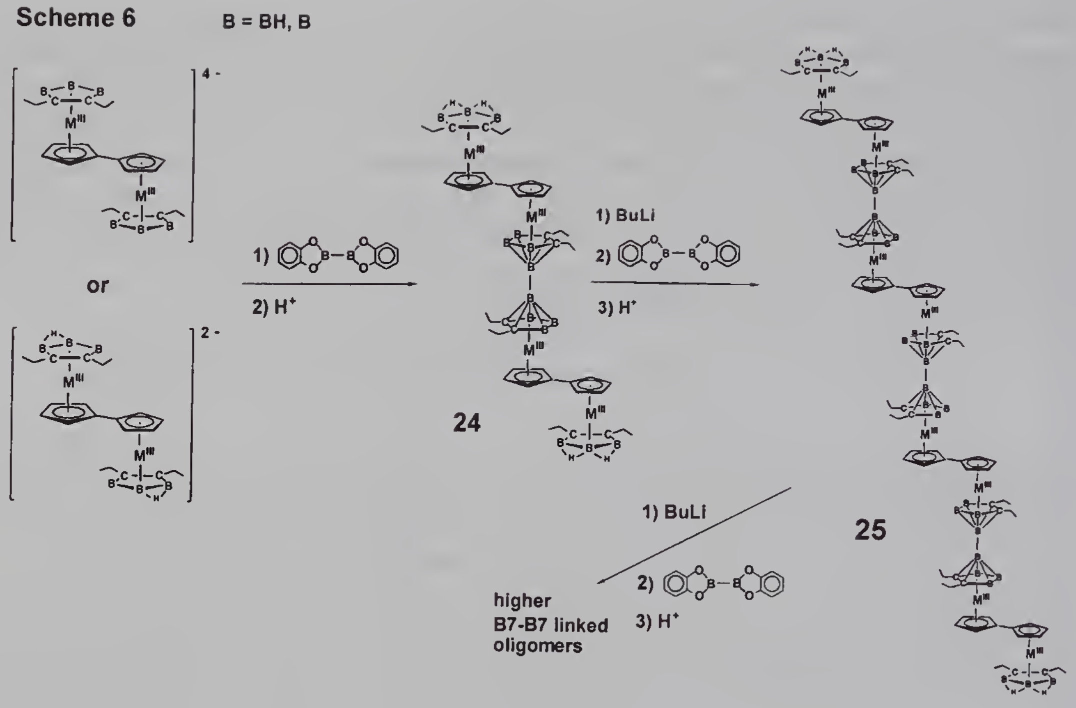
Scheme 5



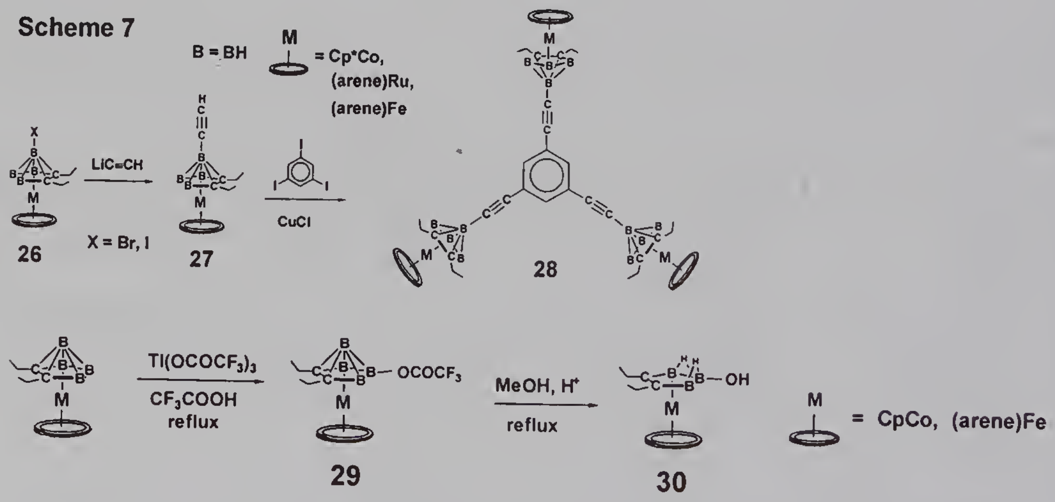
20 **21** **22** **23**

Boron-functionalized metallacarboranes might also serve as precursors to more complex organometallic systems such as the trigonally symmetrical **28** (Scheme 7). In a recent development,[12] we have found a route to water-soluble B-hydroxy derivatives **30**.

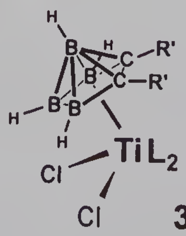
Scheme 6



Scheme 7



5. SUBSTITUTION AT BORON IN EARLY TRANSITION METAL COMPLEXES



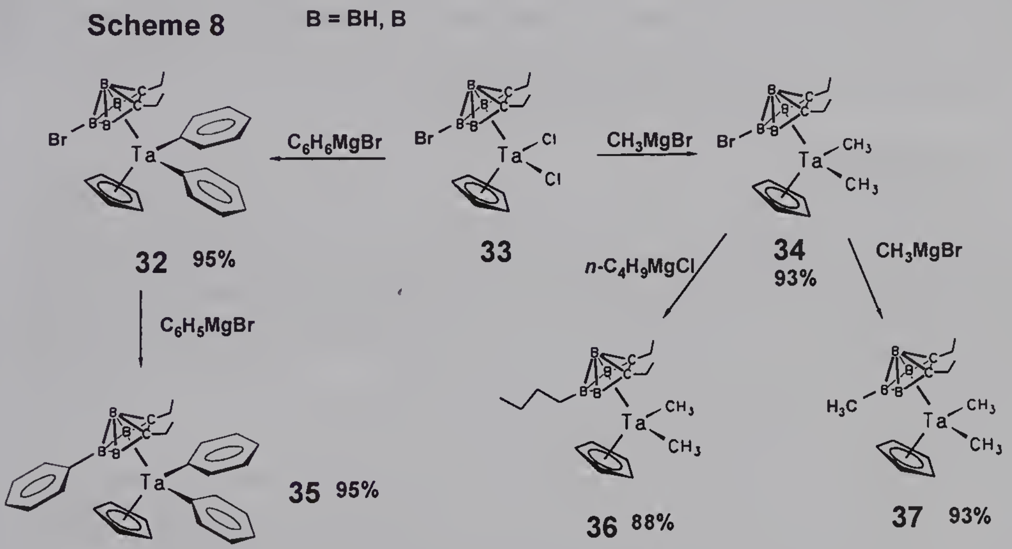
31

$L_2 = 2PR_3, (R_2P)_2(CH_2)_n$
R = alkyl, Ph
R' = Me, Et, $SiMe_3$

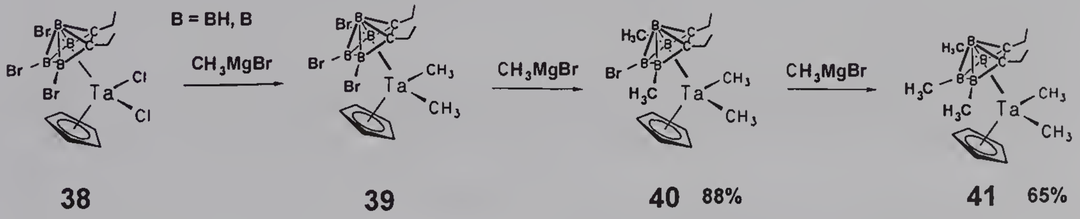
Small carborane complexes of tantalum, titanium, niobium, and other early metals are of interest to us as potentially useful reagents for organic transformations, especially in the area of olefin polymerization catalysis under mild conditions. These complexes are invariably bent-sandwich species having metal-bound η^1-coordinated ligands such as halogens or alkyl groups.[17] The motivation for introducing halogens and/or organic substituents to the carborane ligand in these early-metal complexes is different from that underlying the work on late-metal systems described above. The intent here is to manipulate the reactivity at the metal center via derivatization of the ligand — specifically, to optimize the metal electron density for specific olefin polymerization applications. As an example, phosphino-titanium complexes such as **31** are precatalysts for the formation of polyolefins from ethylene or other alkenes at 25 °C and 1 atm.[18] Replacement of one or more of the BH hydrogens by halogen atoms may enhance the catalytic activity by reducing the donation of electron density from the carborane ligand to the metal, a prospect that is currently under investigation.

When halogens are simultaneously present on the metal and on the carborane cage, the former are found to be more reactive toward Grignards and organolithium reagents, so that organosubstitution occurs first at the metal and then at the B-halo vertices (Scheme 8).[19]

Scheme 8



This reactivity pattern is maintained in polyhalo derivatives, as shown by the conversion of the Ta-dichloro-tri-B-bromo species **38** (prepared as in Scheme 1) to the tri-B-methyl compound **41**.[19]



6. CONCLUSIONS

The development of methods for placing halogens and organic functional groups on cage boron atoms in MC_2B_4 and MC_2B_3 complexes, and for effecting intercluster B-B linkage, supplement other approaches that allow substitution at cage carbon and metal vertices. Together, these procedures comprise an array of synthetic tools that allow access to many different varieties of small metallacarborane derivatives and multicluster assemblies. In addition to the applications briefly discussed above, several families of small metallacarborane complexes are currently under investigation as anticancer agents. This study, in collaboration with Prof. Iris Hall and co-workers,[20] has demonstrated that mixed-ligand sandwich complexes of the type $Cp'Cl_2M(R_2C_2B_4H_4)$, where M is Ta or Nb, Cp' is η^5-C_5H_5 or η^5-C_5Me_5, and R is Et or $SiMe_3$, and which have the bent-metallocene geometry of **33** (Scheme 8), are active cytotoxic agents against several cancer cell lines including murine L1210 lymphoid leukemia, Tmolt$_4$ leukemia, HI-60 leukemia, HuT-8 lymphoma, THP-1 acute monocyclic leukemia, and suspended HeLa-S^3 uterine carcinoma, among others. Further studies are under way in this area.

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REFERENCES

1. (a) T. Onak, in: E. Abel, F. G. A. Stone, G. Wilkinson (Eds.), 'Comprehensive Organometallic Chemistry II', Vol. 1, Chap. 6, Pergamon Press, Oxford, England, 1995, p. 217. (b) T. Onak, in: E. Abel, F. G. A. Stone, G. Wilkinson (Eds.), 'Comprehensive Organometallic Chemistry', Pergamon Press, Oxford, England, 1982, p. 411. (c) R. N. Grimes, 'Carboranes', Academic Press, New York, 1970.
2. J. Plesek, *Chem. Rev.* 1992, **92**, 269.
3. R. R. Olsen and R. N. Grimes, *J. Am. Chem. Soc.* 1970, **92**, 5072.
4. R. R. Olsen and R. N. Grimes, *Inorg. Chem.* 1971, **10**, 1103.
5. Recent examples: (a) L. I. Zakharkin, V. A. Ol'shevskaya, and G. G. Zhigareva, *Russ. J. Gen. Chem.* 1998, **68**, 975. (b) L. I. Zakharkin, V. A. Ol'shevskaya, E. V. Vorontsov, and P. V. Petrovsky, *Russ. Chem.* Bull. 1996, **45**, 2614. (c) W. Jiang, C. B. Knobler, M. D. Mortimer, and M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 1332. (d) A. Herzog, C. B. Knobler, M. F. Hawthorne, A. Maderna, and W. Siebert, *J. Org. Chem.* 1999, **64**, 1045.
6. (a) R. N. Grimes, *Appl. Organometal. Chem.* 1996, **10**, 209, and references therein. (b) R. N. Grimes, *Chem. Rev.* 1992, **92**, 251.
7. K. E. Stockman, D. L. Garrett, and R. N. Grimes, *Organometallics* 1995, **14**, 4661.
8. M. A. Curtis, M. Sabat, and R. N. Grimes, *Inorg. Chem.* 1996, **35**, 6703.
9. M. A. Curtis, T. Müller, V. Beez, H. Pritzkow, W. Siebert, and R. N. Grimes, *Inorg. Chem.* 1997, **36**, 3602.
10. X. Wang, M. Sabat, and R. N. Grimes, *Organometallics* 1995, **14**, 4668.
11. (a) T. T. Chin, S. R. Lovelace, W. E. Geiger, C. M. Davis, and R. N. Grimes, *J. Am. Chem. Soc.* 1994, **116**, 9359. (b) T. T. Chin, R. N. Grimes, and W. E. Geiger, *Inorg. Chem.* 1999, **38**, 93.
12. J. M. Russell, M. Sabat, and R. N. Grimes, manuscript in preparation.
13. P. Zanello, private communication to R.N.G.
14. J. H. Davis, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.* 1989, **111**, 4776; *Ibid.*, p. 4884.
15. X. Meng, M. Sabat, and R. N. Grimes, *J. Am. Chem. Soc.* 1993, **115**, 6143.
16. W. E. Geiger, private communication to R.N.G.; W. E. Geiger, T. T. Chin, and R. N. Grimes, manuscript in preparation.
17. (a) K. E. Stockman, K. L. Houseknecht, E. A. Boring, M. Sabat, M. G. Finn, and R. N. Grimes, *Organometallics.* 1993, **14**, 3014. (b) E. A. Boring, M. Sabat, M. G. Finn, and R. N. Grimes, *Organometallics.* 1998, **17**, 3865. (c) R. N. Grimes, *J. Organometal. Chem.* 1999, 581, 1.
18. (a) M. A. Curtis, M. G. Finn, and R. N. Grimes, Abstracts of Papers, BUSA IV, Guanajuato, Mexico, May 1996, Abstract 7. (b) T. Dodge, M. A. Curtis, M. G. Finn, and R. N. Grimes, manuscript submitted for publication.
19. E. A. Boring, Ph.D. thesis, 1999; E. A. Boring, K. E. Stockman, M. Sabat, and R. N. Grimes, manuscript in preparation.
20. I. H. Hall, C. E. Tolmie, B. J. Barnes, M. A. Curtis, J. M. Russell, M. G. Finn, and R. N. Grimes, manuscript submitted for publication.

The Ligating Properties of the Anionic Rhenacarboranes $[\mathrm{Re(CO)_3}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]^-$ and $[\mathrm{Re(CO)_3}(\eta^5\text{-}7\text{-}\mathrm{CB_{10}H_{11}})]^{2-}$

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1 INTRODUCTION

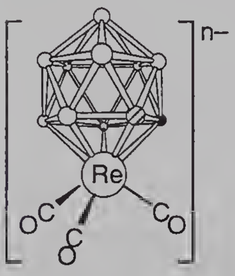
The recognition that the ligating properties of $[\textit{nido}\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}}]^{2-}$ and $[\textit{nido}\text{-}7\text{-}\mathrm{CB_{10}H_{11}}]^{3-}$ groups would mimic those of $[\mathrm{C_5H_5}]^-$ led to the discovery of metallacarborane chemistry,[1] a field which now encompasses most of the d-and f-block elements.[2] Even so our knowledge of metallacarboranes as synthons in organometallic chemistry is much less developed than that of the cyclopentadienyl metal complexes. Thus it has been stated that more than 80% of all organometallic complexes of the transition elements contain the cyclopentadienyl ligand or a derivative thereof.[3] Moreover cyclopentadienyl and carbonyl ligands are often present in the same metal complex leading to an extensive use of such species in synthesis. Carbon monoxide and $[\textit{nido}\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}}]^{2-}$ groups are also known to share co-ordination sites on metal centers but examples are fewer than with metallacyclopentadienyl chemistry. This suggests that carbonyl metallacarboranes could play a larger role in synthesis particularly as the isolobal mapping of $[\mathrm{C_5H_5}]^-$ with $[\textit{nido}\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}}]^{2-}$ leads to interesting correlations between the two systems, *e.g.*

(i) $[\mathrm{W(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]^- \xleftrightarrow[\text{o}]{} [\mathrm{W(CO)_3}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]^{2-}$
(ii) $[\mathrm{Ru_2}(\mu\text{-}\mathrm{CO})_2\mathrm{(CO)_2}(\eta\text{-}\mathrm{C_5H_5})_2] \xleftrightarrow[\text{o}]{} [\mathrm{Ru_2}(\mu\text{-}\mathrm{CO})_2\mathrm{(CO)_2}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})_2]^{2-}$
(iii) $[\mathrm{Mn(CO)_3}(\eta\text{-}\mathrm{C_5H_5})] \xleftrightarrow[\text{o}]{} [\mathrm{Ru(CO)_3}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]$
(iv) $[\mathrm{Ru(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]^- \xleftrightarrow[\text{o}]{} [\mathrm{Rh(CO)_2}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]^-$
(v) $[\mathrm{Ir(CO)_2}(\eta\text{-}\mathrm{C_5H_5})] \xleftrightarrow[\text{o}]{} [\mathrm{Pt(CO)_2}(\eta^5\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]$

Because the chemistry of carbonyl metallacarborane complexes has been little studied we believe this area merits attention. In this we have been stimulated by the differences in the donor abilities and steric requirements of carborane and cyclopentadienyl ligands,[4] and by the numerous observed reactions where the carborane ligands adopt non-spectator roles due to activation of BH vertices in the *closo*-3,1,2-$\mathrm{MC_2B_9H_{11}}$ and *closo*-2,1-$MCB_{10}H_{11}$ frameworks.[5] In this paper we address the chemistry of the species $[Re(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ (**1**) and $[Re(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^{2-}$ (**2**)[6] which are isolobal with the well studied complex $[Re(CO)_3(\eta\text{-}C_5H_5)]$.

2 RESULTS†

2.1 Preparation of Salts of the Tricarbonyl Rhenacarborane Anions



	▨	n
1	CH	1
2	BH	2

Complex **1** was first isolated as its Cs^+ salt over 30 years ago[7a] by treating $[ReBr(CO)_5]$ with Na_2[*nido*-7,8-$C_2B_9H_{11}$] in refluxing THF (tetrahydrofuran) followed by addition of CsCl, and its crystal structure was determined.[7b] The $[N(PPh_3)_2]^+$ salt of **2** has been recently synthesized in this Laboratory by the reaction between Na_3[*nido*-7-$CB_{10}H_{11}$] and $[ReBr(CO)_3(THF)_2]$ followed by addition of $[N(PPh_3)_2]Cl$. An X-ray diffraction study of the $[NEt_3(CH_2Ph)]^+$ salt of the dianion **2** confirmed that its structure is very similar to that of the monoanion **1**.[8]

2.2 Protonation and Oxidation of $[Re(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ and $[Re(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^{2-}$

Unexpectedly salts of **1** and **2** do not protonate $[HBF_4{\cdot}Et_2O$, $HCl(Et_2O)$, $CF_3CO_2H]$ to give neutral hydrido complexes, nor do they react with $[Au(PPh_3)]^+$ to afford isolable products with Re–Au bonds. This contrasts with the behavior of the evidently more electron rich species $[Pt(PEt_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^-$ which with $HBF_4{\cdot}Et_2O$ and with $[AuCl(PPh_3)]$ gives $[PtH(PEt_3)_2(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ and $[PtAu(PEt_3)_2(PPh_3)(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$, respectively.[9] It seems likely that the inertness of the rhenium centers in **1** and **2** is due to the dispersion of the anionic charge within the superaromatic cage frameworks. Simple molecular orbital analyses of **2** are in accord with this supposition.[8]

It was not possible to form stable complexes of the type $[Re(L)(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (L = THF, MeCN, CO, PR_3, alkynes) by treating **2** with various oxidants in the presence of ligands L. Low temperature treatment with just under 1 equiv. of I_2 did however give $[N(PPh_3)_2][ReI(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]$ (**3**). Interestingly **1** is oxidized by $[NO][BF_4]$ to give $[Re(CO)_2(NO)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ (**4**),[10] isolobal with $[Re(CO)_2(NO)(\eta\text{-}C_5H_5)]^+$.

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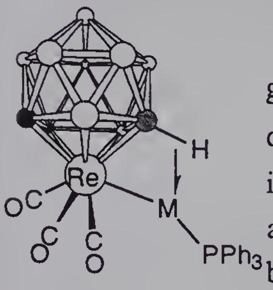
† Diagram key: ○ BH ◉ B ● CH unless otherwise indicated.

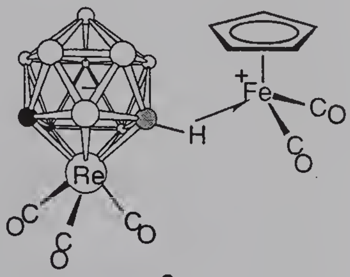
2.3 Reactions of $[Re(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]^-$ and $[Re(CO)_3(\eta^5\text{-}7\text{-}CB_{10}H_{11})]^{2-}$ with Electrophilic Metal-Ligand Fragments



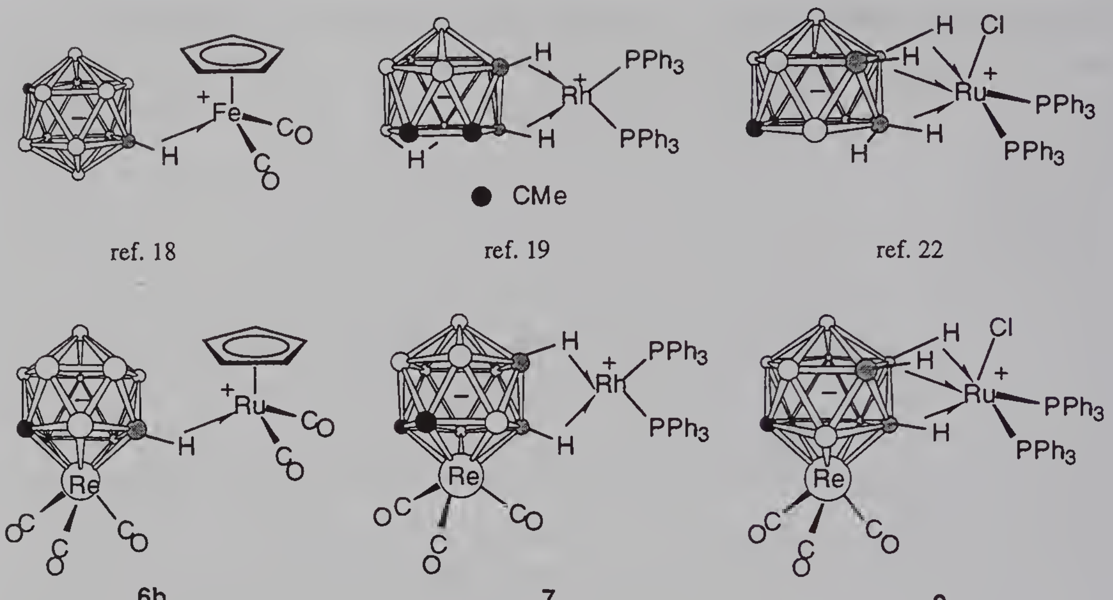
5 M = Cu or Ag

The Cs^+ salt of **1** reacts with CuCl in the presence of PPh_3 to give $[ReCu(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3(PPh_3)]$ (**5a**). An X-ray diffraction study revealed that while the *nido*-7,8-$C_2B_9H_{11}$ ligand is pentahapto bonded to the Re atom in the usual manner it forms an exopolyhedral B–H ⇀ Cu linkage to the copper using the boron vertex at the β-site with respect to the carbons in the $\overline{\mathrm{CCB}B\mathrm{B}}$ ring ligating the rhenium atom. This agostic interaction spans a Re–Cu bond [2.6583(6) Å]. Attachment of $Cu(PPh_3)$ fragments to *closo*-3,1,2-$MC_2B_9H_{11}$ structures both by Cu–M and either by one or by two B–H ⇀ Cu bonds is well established.[9,11,12] In CH_2Cl_2 solutions **5a** is highly dynamic, undergoing a process that involves migration of the $[Cu(PPh_3)]^+$ fragment about the metallacarborane cage surface. Rapid exchange of BH vertices involved in multiple (2 or 3) B–H ⇀ Cu bonds is preceded by heterolytic Re–Cu bond fission. Using a similar synthetic methodology, the complex $[ReAg(\mu\text{-}10\text{-}H\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_{10})(CO)_3(PPh_3)]$ (**5b**) is formed by reaction of Cs[**1**] with $AgBF_4$ in the presence of PPh_3. Complexes with Re–Ag bonds are exceedingly rare[13] and we have been unable to find another example of a structurally characterized rhenium-silver binuclear complex. An X-ray diffraction study of **5b** revealed that it is isostructural with **5a** in the solid state and in solution the dynamic behavior of **5b** mirrors that of **5a**.

Treatment of Cs[**1**] with the salts $[M(CO)_2(THF)(\eta\text{-}C_5H_5)][BF_4]$ affords the complexes $[Re(CO)_3(\eta^5\text{-}10\text{-}(\mu\text{-}H)\text{-}exo\text{-}\{M(CO)_2(\eta\text{-}C_5H_5)\}\text{-}7,8\text{-}C_2B_9H_{10})]$ [M = Fe (**6a**), or Ru (**6b**)]. The *closo*-3,1,2-ReC_2B_9 cage system behaves as a monodentate ligand and there are no metal-metal bonds in these zwitterionic species. An X-ray diffraction study of **6b** revealed a Ru–B distance of 2.695(13) Å. A range of polyborane compounds are known with B–H ⇀ ML_n interactions.[14] However, for those species studied by X-ray diffraction the Ru–B distances are significantly shorter than that found in **6b**, falling in the range 2.15–2.48 Å. The molecules **6** are reminiscent of ion pair complexes formed by the anions $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ (ref. 15, 16) and $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ (ref. 17) with metal-ligand fragments. Indeed an interesting structural comparison can be made between the species **6** and $[12\text{-}\mu\text{-}H\text{-}exo\text{-}\{Fe(CO)_2(\eta\text{-}C_5H_5)\}\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]$ (Figure 1).[18] It is noteworthy that from both NMR and X-ray measurements it was firmly established that the complexes **6** employ β-



6a



ref. 18 ref. 19 ref. 22

6b **7** **9**

Figure 1. Zwitterionic molecules.

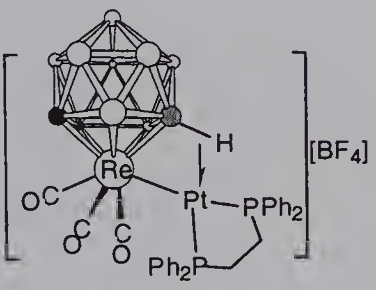
boron atoms in the co-ordinating $\overline{\mathrm{CCB}B\mathrm{B}}$ face of the cage for the interactions with the group VIIIB metal. If $[Fe(CO)_2(THF)(\eta\text{-}C_5Me_5)][BF_4]$ is the reagent used, the nature of the product is the same, but a 1:1 mixture of α and β isomers is formed.

The anionic complex **1** can also function as a bidentate ligand towards cationic rhodium species as in the complexes $[Re(CO)_3(\eta^5\text{-}5,10\text{-}(\mu\text{-}H)_2\text{-}exo\text{-}\{Rh(PPh_3)_2\}\text{-}7,8\text{-}C_2B_9H_9\})]$ (**7**) and $[Re(CO)_3(\eta^5\text{-}5,10\text{-}(\mu\text{-}H)_2\text{-}exo\text{-}(Rh\{Fe(\eta\text{-}C_5H_4PPh_2)_2\})\text{-}7,8\text{-}C_2B_9H_9)]$ (**8**), and as a tridentate ligand in the compound $[Re(CO)_3(\eta^5\text{-}2,3,10\text{-}(\mu\text{-}H)_3\text{-}exo\text{-}\{RuCl(PPh_3)_2\}\text{-}7,8\text{-}C_2B_9H_8)]$ (**9**). An *exo* mode of attachment of $[Rh(PPh_3)_2]^+$ fragments to $[nido\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = H, alkyl, aryl) anions via two B–H ⟶ Rh bonds was established several years ago by Hawthorne and co-workers[19] and thereafter replicated in this Laboratory using the anion $[10\text{-}endo\text{-}\{Au(PPh_3)\}\text{-}7,8\text{-}Me_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]^-$.[20] In CH_2Cl_2 solutions at ambient temperatures complexes **7** and **8** undergo dynamic behavior similar to that described above for the complexes **5**. Such a process has already been documented for $[Rh(PPh_3)_2]^+$ fragments bound to carborane and metallacarborane cages.[19,20] NMR spectra of complex **7** at –90 °C strongly suggest that a low temperature limit has been reached, resulting in the formation of a major species with a near-static $exo\text{-}[Rh(PPh_3)_2]^+$ group bound to the anion **1** in addition to a minor product which has a Re–Rh bond supported by a bridging B–H ⟶ Rh interaction. A bidentate mode of bonding has also been previously identified for other transition metals as in the complex $[9,10\text{-}(\mu\text{-}H)_2\text{-}exo\text{-}\{W(CO)_2(\eta\text{-}C_5R_5)\}\text{-}7,8\text{-}Me_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_8]$ (R = H or Me),[21] which was an unexpected product from the reaction between the alkylidyne complexes $[NEt_4][Mo(\equiv CC_6H_4Me\text{-}4)(CO)\{P(OMe)_3\}(\eta^5\text{-}7,8\text{-}$

Me_2-*nido*-7,8-$C_2B_9H_9$)] and [W(≡CR)$(CO)_2$(η-C_5R_5)] (R = C_6H_4Me-4 or Me) in the presence of $HBF_4 \cdot Et_2O$ in CH_2Cl_2 at −78 °C.

In contrast with the complexes **5**, **7** and **8**, compound **9** is not dynamic in solution, the *exo*-[RuCl$(PPh_3)_2$] group showing no propensity to migrate about the metallacarborane surface. Thus the ^{1}H NMR spectrum measured at ambient temperatures clearly displays signals due to two types of agostic B–H ⇀ Ru protons, a feature not observed at room temperature with the more dynamic congeners described above. The ability of the carborane anions [*nido*-7,8-$C_2B_9H_{12}$]$^-$ and [*closo*-1-$CB_{11}H_{12}$]$^-$ to function as tridentate ligands to cationic metal-ligand groups is unusual but has been demonstrated with the isolation and structural characterization of [2,3,10-$(\mu\text{-H})_3$-*exo*-{RuCl$(PPh_3)_2$}-*nido*-7,8-$C_2B_9H_9$][22] and [7,8,12-$(\mu\text{-H})_3$-*exo*-{Zr$(Me)_2$(η-C_5Me_5)}-*closo*-1-$CB_{11}H_9$].[23] A collage of these zwitterionic molecules is shown in Figure 1.

Reactions between Cs[**1**] and [Pt$(NCMe)_2$(dppe)]$[BF_4]_2$, and between $[N(PPh_3)_2]_2$[**2**] and [$PtCl_2(PPh_3)_2$] in the presence of $TlPF_6$, afford the species [RePt(μ-10-H-η^5-7,8-$C_2B_9H_{10}$)$(CO)_3$(dppe)][BF_4] (**10**) and [RePt(μ-9-H-η^5-7-$CB_{10}H_{10}$)-$(CO)_3(PPh_3)_2$] (**11**), respectively. In contrast with the molecules **6**–**9**, where there are no heteronuclear metal-metal bonds, the metal atom separations in **10** [2.8126(10) Å][24] and **11** [2.7931(4) Å][8] are typical of those for Re–Pt bonds in other compounds with this type of linkage. In both molecules there are also exopolyhedral B–H ⇀ Pt bonds which employ boron vertices in the β-sites with respect to the carbons in the $\overline{\mathrm{CCB}\mathit{B}\mathrm{B}}$ and $\overline{\mathrm{CB}\mathit{B}\mathrm{BB}}$ rings ligating the Re atoms. Complex **10** may be deprotonated (LiPh or K-Selectride) to yield two neutral isomeric complexes [RePt{μ-σ(*n*),η^5-7,8-$C_2B_9H_{10}$}$(CO)_3$(dppe)] [*n* = 9 (**12a**), or 10 (**12b**)], the ratio **12a**:**12b** being determined by the reaction conditions.



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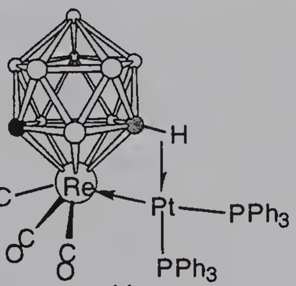
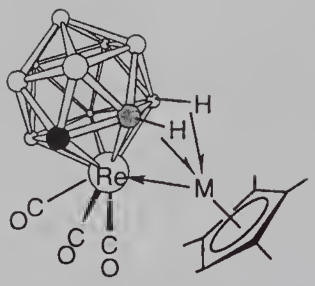


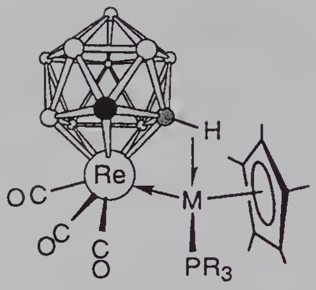
11

Reactions between $[N(PPh_3)_2]_2$[**2**] and the rhodium and iridium complexes [M$(NCMe)_3$(η-C_5Me_5)]$[BF_4]_2$ have also been studied.[5b] The initially formed products are [ReM{μ-8,9-$(H)_2$-η^5-7-$CB_{10}H_9$}$(CO)_3$(η-C_5Me_5)] [M = Rh (**13a**), or Ir (**13b**)] where the *nido*-7-$CB_{10}H_{11}$ cage functions, via two B–H ⇀ M bonds, as a bidentate



13

M = Rh or Ir

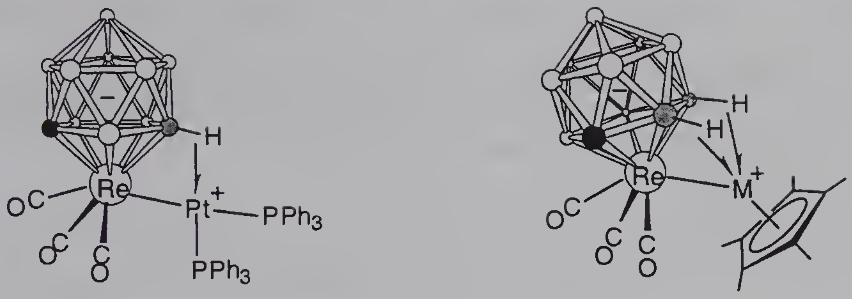


14 (*α-anti* isomer shown)

ligand to the rhodium or iridium centers. Reactions of **13** with tertiary phosphines result in a lifting of one of the B–H$\rightharpoondown$M bonds to give the compounds $[\mathrm{ReM}(\mu\text{-}n\text{-H-}\eta^5\text{-7-}\mathrm{CB_{10}H_{10}})(\mathrm{CO})_3(\mathrm{PR_3})(\eta\text{-}\mathrm{C_5Me_5})]$ [M = Rh (**14a**), or Ir (**14b**); n = 8 or 9] formed as mixtures of isomers. These isomers arise according to whether the exopolyhedral B–H$\rightharpoondown$M bond involves a BH vertex in an $\alpha\,(\overline{\mathrm{C}\mathit{B}\mathrm{BBB}}, n = 8)$ or $\beta\,(\overline{\mathrm{CB}\mathit{B}\mathrm{BB}}, n = 9)$ site in the ring pentahapto co-ordinated to rhenium. The situation is further complicated because the η-C_5Me_5 ligand can lie either *syn* or *anti* to the cage carbon, and in most instances both isomers are observed. While the α/β isomers can be chromatographically separated, it is not possible to further separate the *syn/anti* forms. X-Ray diffraction and NMR studies have been used to elucidate the stereochemistry of the isomers and their dynamic behavior in solution, particularly for complex **13a**,[5b] which at ambient temperatures in CH_2Cl_2 solutions undergoes a migratory process where an *exo*-$[\mathrm{Rh}(\eta\text{-}\mathrm{C_5Me_5})]^{2+}$ moiety scrambles about the *closo*-2,1-$\mathrm{ReCB_{10}H_{11}}$ polyhedral surface.

3 CONCLUSIONS

It is evident that the anionic rhenacarboranes **1** and **2** have a rich chemistry despite our initial observation of low basicity at the metal center, *i.e.* failure to protonate. However, the BH vertices in these species readily ligate electrophilic metal-ligand fragments via exopolyhedral B–H$\rightharpoondown$M bonds thus forming dipolar complexes. Indeed it may be that formation of a B–H$\rightharpoondown$M interaction occurs as the first step in the synthesis of the complexes **5**, **10**, **11** and **13** which have metal-metal bonds. Such an ion pair intermediate would collapse forming the Re–M bonds. In this connection it is noteworthy that **11** and **13** can be formulated as zwitterionic molecules (Figure 2) with the negative charge delocalized over the cage system.



11 **13**

Figure 2. Ion-pair formulations.

4 ACKNOWLEDGMENT

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5 REFERENCES

1. K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, 1976, **14**, 1452.
2. R. N. Grimes in 'Comprehensive Organometallic Chemistry II'; E. W. Abel, F. G. A. Stone and G. W. Wilkinson Eds. Pergamon Press, Oxford, U.K., 1995; Vol. 1, C. E. Housecroft Ed., Chapter 9.
3. C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, 1991, **33**, 291.
4. T. P. Hanusa, *Polyhedron*, 1982, **1**, 663.
5. (a) P. A. Jelliss and F. G. A. Stone, *J. Organomet. Chem.*, 1995, **500**, 307. (b) J. C. Jeffery, P. A. Jelliss, L. H. Rees and F. G. A. Stone, *Organometallics*, 1998, **17**, 2258.
6. The new compounds described in this paper have a rhenium atom incorporated into *closo*-1,2-dicarba-3-rhenadodecaborane or *closo*-1-carba-2-rhenadodecaborane structures. However, to avoid a complicated nomenclature for the complexes reported, and to relate them to the many known rhenium species with η-co-ordinated cyclopentadienyl ligands, we treat the cages as *nido*-11-vertex ligands with numbering as for an icosahedron from which the twelfth vertex has been removed.
7. (a) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879. (b) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, 1966, **5**, 1189.

8. I. Blandford, J. C. Jeffery, P. A. Jelliss and F. G. A. Stone, *Organometallics*, 1998, **17**, 1402.

9. S. A. Batten, J. C. Jeffery, P. L. Jones, D. F. Mullica, M. D. Rudd, E. L. Sappenfield, F. G. A. Stone and A. Wolf, *Inorg. Chem.*, 1997, **36**, 2570.

10. P. A. Jelliss and F. G. A. Stone, unpublished results.

11. (a) Y. Do, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1987, **109**, 1853. (b) H. C. Kang, Y. Do, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1988, **27**, 1716.

12. (a) J-L. Cabioch, S. J. Dossett, I. J. Hart, M. U. Pilotti and F. G. A. Stone, *J. Chem. Soc. Dalton, Trans.*, 1991, 519. (b) J. C. Jeffery, F. G. A. Stone and I. Topaloğlu, *J. Organomet. Chem.*, 1993, **451**, 205. (c) D. D. Ellis, S. M. Couchman, J. C. Jeffery, J. M. Malget and F. G. A. Stone, *Inorg. Chem.*, 1999, **38**, in press. (d) D. D. Ellis, A. Franken, and F. G. A. Stone, *Organometallics*, 1999, **18**, in press.

13. (a) N. G. Connelly, J. A. K. Howard, J. L. Spencer and P. K. Woodley, *J. Chem. Soc., Dalton Trans.*, 1984, 2003. (b) T. Beringhelli, G. D'Alfonso, M. Freni, G. Ciani and A. Sironi, *J. Organomet. Chem.*, 1985, **295**, C7.

14. J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1993, 2545.

15. C. A. Reed, *Accns. Chem. Res.*, 1998, **31**, 133.

16. R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.

17. G. G. Hlatky, H. W. Turner and R. R. Eckman, *J. Am. Chem. Soc.*, 1989, **111**, 2728.

18. D. J. Liston, Y. J. Lee, W. R. Scheidt, and C. A. Reed, *J. Am. Chem. Soc.*, 1989, **111**, 6643.

19. C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc,*, 1984, **106**, 2990.

20. J. C. Jeffery, P. A. Jelliss, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1993, 1073.

21. S. A. Brew, J. C. Jeffery, M. D. Mortimer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1992, 1365.

22. I. T. Chizhevsky, I. A. Lobanova, V. I. Bregadze, P. V. Petrovskii, V. A. Antonovich, A. V. Polyakov, A. I. Yanovskii and Y. T. Struchkov, *Mendeleev Commun.*, 1991, 48.

23. D. J. Crowther, S. I. Borkowski, D. Swenson, T. Y. Meyer and R. F. Jordan, *Organometallics,* 1993, **12**, 2897.

24. D. D. Ellis, J. C. Jeffery, P. A. Jelliss and F. G. A. Stone, *Organometallics*, 1999, **18**, in press.

Carboranes and Metallacarboranes: Chemistry in New Directions

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1 INTRODUCTION

There has been extensive research reported on the chemical and structural properties of the metallacarboranes in the pentagonal bipyramidal (MC_2B_4) and the icosahedral (MC_2B_9)cage systems.[1] These complexes are generally synthesized by the reaction of the mono- or dianions of the *nido*-C_2B_4 or C_2B_9carboranes with suitable metal reagents. Much of the emphasis for these studies comes from the fact that the two *nido*-carboranes have 6 π electrons delocalized on a C_2B_3 open pentagonal face that are very similar to the primary metal-bonding orbitals of the cyclopentadienide ligand, $[C_5H_5]^-$. Our research in this area has involved synthetic, structural, reactivity and theoretical studies on the full- and half-sandwich metallacarboranes derived from the interactions of [*nido*-2-($SiMe_3$)-*n*-(R)-2,*n*-$C_2B_4H_4$]$^{2-}$ [$n = 3$, 4; R = $SiMe_3$, Me, H] with main group,[2] *d*-group,[3] and *f*-group metals.[4] Here we report some of our latest results in this fascinating area of carborane research.

1.1 Syntheses of C_2B_4 and C_4B_8-carboranes

The reaction of the 2,3-C_2B_4-carborane dianion with $NiCl_2$ in hexane did not give the nickelacarborane but instead underwent oxidative cage closure reactions to produce the corresponding *closo*-1-($SiMe_3$)-2-(R)-1,2-$C_2B_4H_4$ (see **Figure 1**) and nickel metal.[5] In addition,

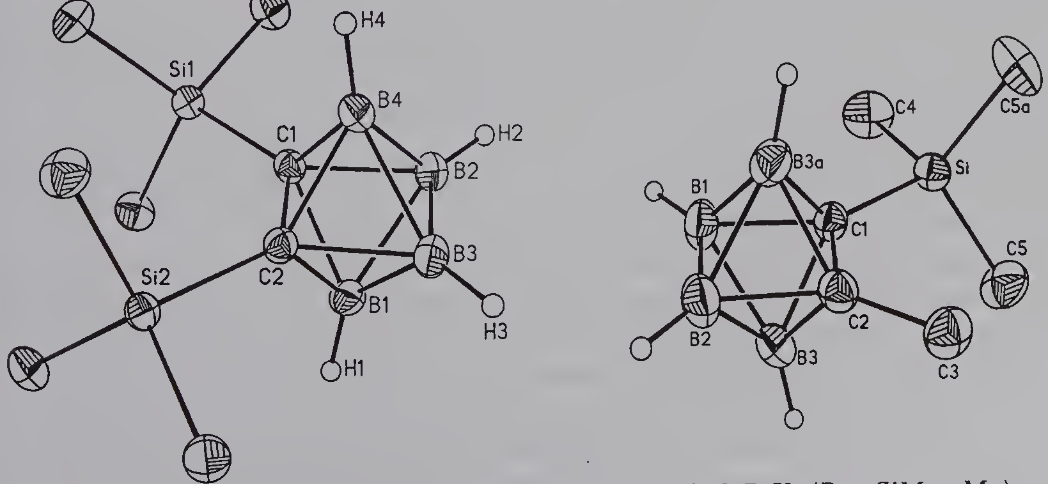
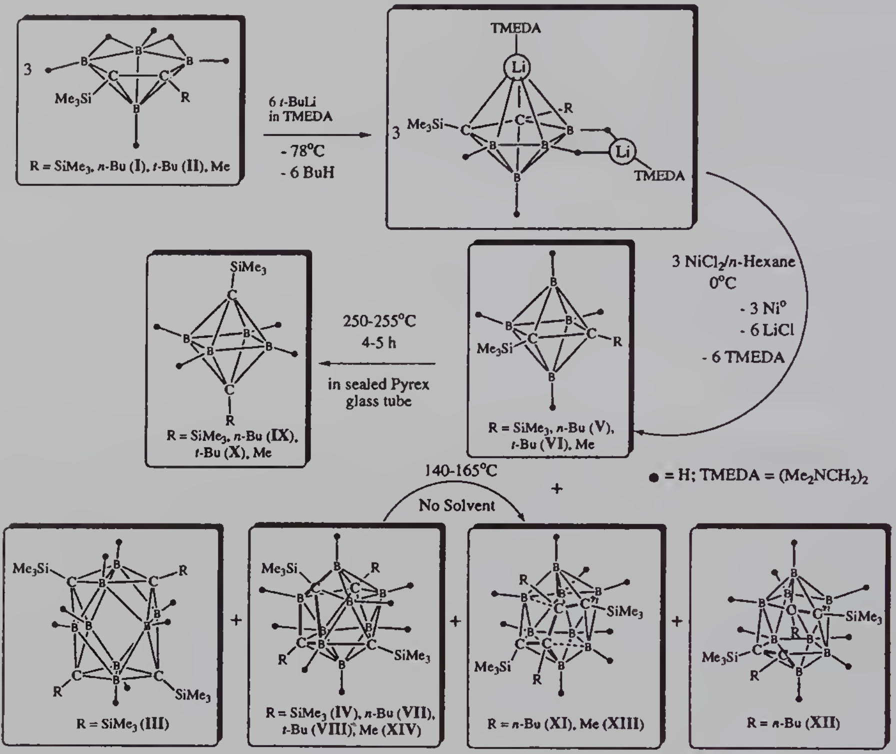


Figure 1 *Crystal structures of* closo-*1-($SiMe_3$)-2-(R)-1,2-$C_2B_4H_4$ (R = $SiMe_3$, Me).*

we observed an accompanying oxidative cage fusion process that led to the formation of the novel tetracarbon carboranes, *nido*-2,4,x,y-$(SiMe_3)_4$-2,4,x,y-$C_4B_8H_8$ (x = 7, y = 9, [**III** in **Scheme 1**]; x = 6, y = 12, [**IV** in **Scheme 1**]).[6,7] Since all cage carbon atoms are separated by at least one boron atom, they will subsequently be referred to as the "carbons apart" isomers. Grimes and co-workers first reported on the syntheses, structures and reactivities of several tetracarbon carboranes, all of which possessed the common structural feature in that the cage carbons were localized on one side of very distorted icosahedral cages.[8-12] In one of these "carbons adjacent" isomers the carbon atoms were bonded contiguously in a Z-shaped pattern,[10] while in the other, the middle C–C bond was ruptured leading to a more open structure.[11] However, the proximate locations of the cage carbons were maintained in all isomers. These "carbons adjacent" compounds were obtained as the products from the mild air oxidation of the metal-hydride complexes, $(R_2C_2B_4H_4)_2MH_x$ (M = Fe (x = 2), Co (x =1); R = CH_3, C_2H_5, n-C_3H_7 and $CH_2C_6H_5$).[8,9,12] On the other hand, when the dianions, $[nido\text{-}2\text{-}(SiMe_3)\text{-}3\text{-}(R)\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (R = $SiMe_3$, n-Bu or t-Bu) were oxidized by $NiCl_2$ a completely different set of tetracarbon carboranes were produced.[6,7]



Scheme 1 *Syntheses of* closo-C_2B_4- *and* nido-C_4B_8-*carboranes*

In these trimethylsilyl-substituted compounds, the cage carbons were more evenly dispersed throughout the cage, being separated by at least one boron, to give the so-called "carbons apart" compounds. One of these, *nido*-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8$, is of particular interest in that it is a 12-vertex cage whose structure is based more on a cuboctahedron than an icosahedron (**Figure 2**).[6,7] This geometry is of interest in that a cuboctahedral structure was proposed by Lipscomb for the key intermediate in the diamond-square-diamond (DSD) mechanism for the rearrangement of *closo*-1,2-$C_2B_{10}H_{12}$ to *closo*-1,7-$C_2B_{10}H_{12}$.[13] The

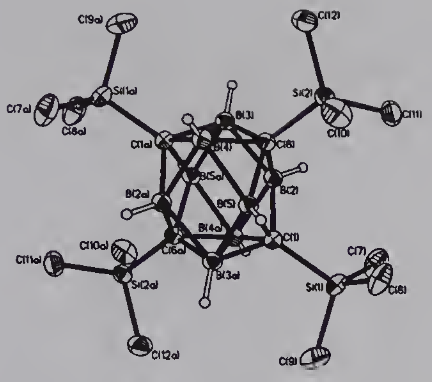


Figure 2 *nido*-2,4,7,9-$(SiMe_3)_4C_4B_8H_8$

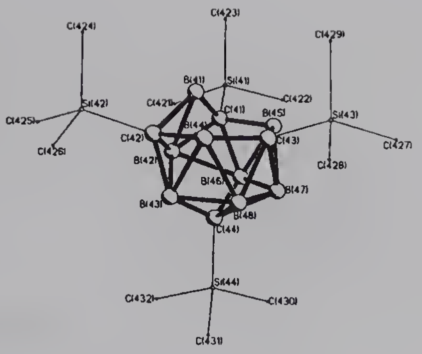


Figure 3 *nido*-2,4,6,12-$(SiMe_3)_4C_4B_8H_8$

other isomer, exemplified by *nido*-2,4,6,12-$(SiMe_3)_4$-2,4,6,12-$C_4B_8H_8$, had a more traditional *nido*-cage structure with an open C_3B_3 face surmounting a B_5 ring and an apical cage carbon (**Figure 3**).[7] Most of the C_4B_8 carboranes exhibit nonrigid stereochemistry, showing multiple isomerization or fluxional behavior in solution.[7,8,11] When less bulky *n*-butyl groups were substituted for two of the $SiMe_3$ moieties, both "carbons adjacent" and "carbons apart" isomers of C_4B_8-carborane were isolated. Moreover, the geometries of these "carbons adjacent" isomers are identical to those observed by Grimes (**Figures 4** and **5**).[7]

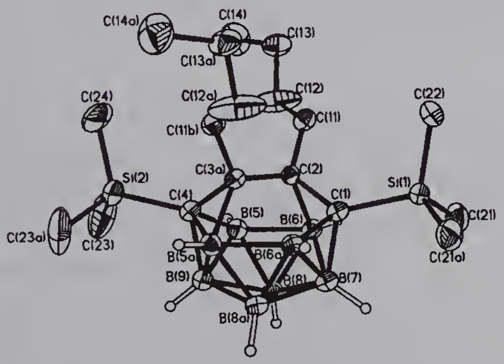


Figure 4 1,4-$(SiMe_3)_2$-2,3(n-$Bu)_2C_4B_8H_8$

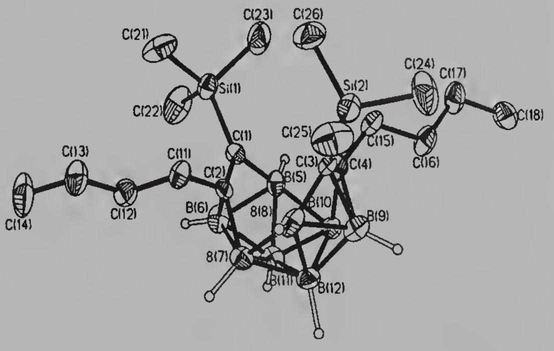
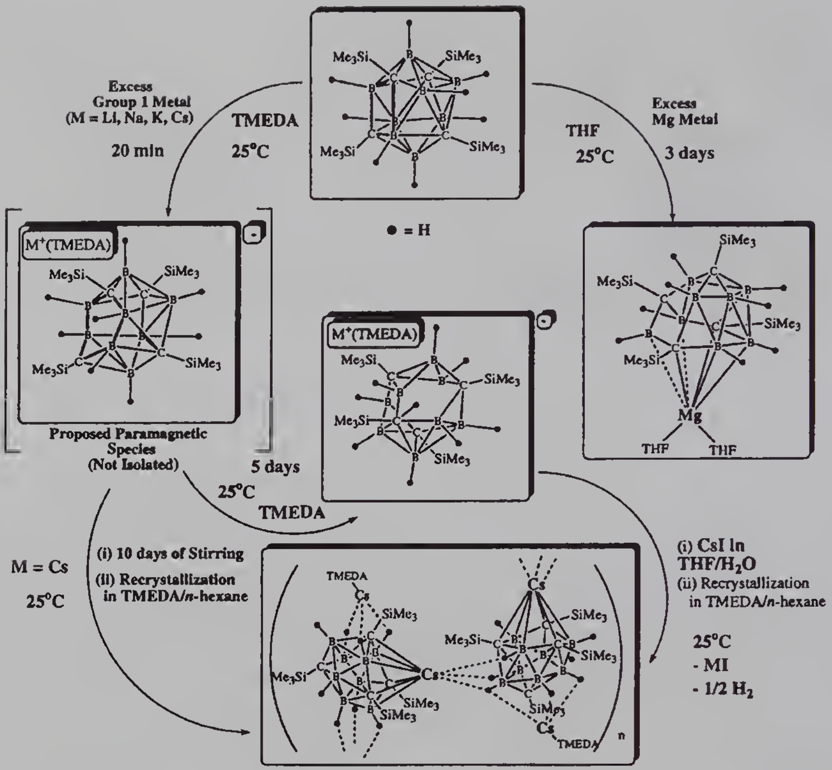


Figure 5 2,8-$(SiMe_3)_2$-3,9-(n-$Bu)_2C_4B_8H_8$

1.2 Reactivities of "Carbons Apart" C_4B_8-carboranes

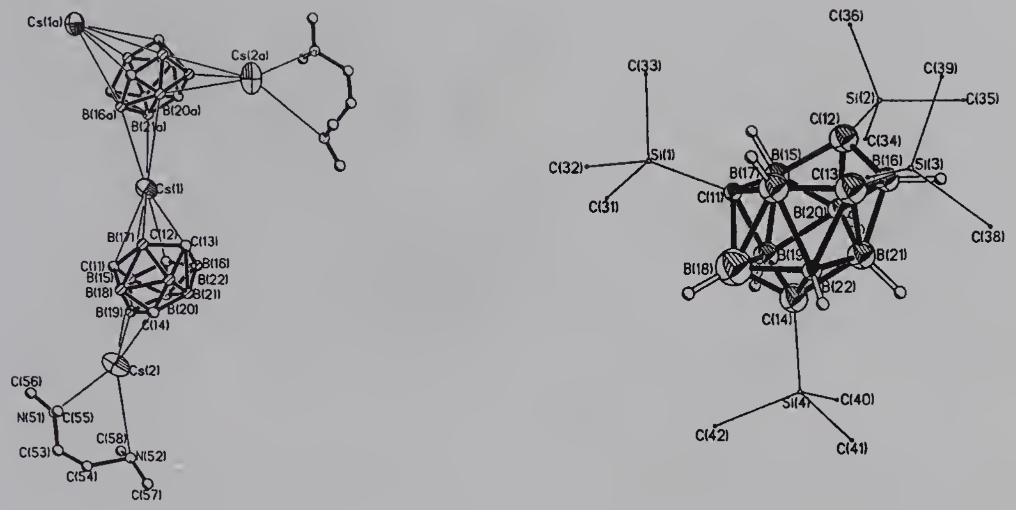
Both "carbons adjacent" and "carbons apart" C_4B_8-carboranes can be reduced to give dianionic cages, which on metallation produced, at least formally, 13-vertex metallacarboranes. Grimes and co-workers have reported the syntheses of a large number of d-block metallacarboranes in the "carbons adjacent" system.[1(a),14,15] Multiple structures were found for a particular carborane and metal group. These were thought to arise from the metal coordination of the numerous isomers of the C_4B_8 dianions that were present in reaction solutions. While the reports on the metallacarboranes derived from the "carbons adjacent" carboranes are fairly extensive, the only metallacarboranes in the "carbons apart" system that have been published are those contained in our preliminary reports on $[(THF)_4Li][(SiMe_3)_4C_4B_8H_9]$, [*exo*-Cs(TMEDA)-1-Cs-2,4,7,9-$(SiMe_3)_4$-2,4,7,9-$C_4B_8H_8$] and $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$ whose synthetic pathways are shown in **Scheme 2**.[16,17]



Scheme 2 *Syntheses of Tetracarbon-carborane Compounds of Group 1 and Group 2 Metals*

According to this scheme the room temperature reaction between a TMEDA solution of 2,4,7,9-tetracarba-*nido*-dodecaborane (12), $(SiMe_3)_4C_4B_8H_8$, and excess cesium metal, in the absence of naphthalene and aromatic solvents, produced the novel EPR-silent species, $[exo\text{-}[(\mu\text{-}H)_2Cs(TMEDA)]\text{-}1\text{-}Cs\text{-}2,4,7,9\text{-}(SiMe_3)_4\text{-}2,4,7,9\text{-}C_4B_8H_8]_n$, the first example of a cesium compound in which the metal interacts with the carborane cage sequentially to form repeating metal-carborane units.[17] An X-ray diffraction study on the cesium complex confirmed its polymeric structure in which each C_4B_8-carborane fragment serves as a ligand to two Cs atoms, bonded to one through an open six-membered face and to the other *via* upper- and lower-belt M-H-E (where E = B or C) interactions (**Figure 6**).[17] This structural feature is somewhat similar to that of the Sr complex of the $[C_2B_{10}H_{12}]^{2-}$ ligand, reported by Hawthorne and coworkers.[18] However, the interatomic distances of Cs to the carborane cages are such that it could be regarded as a cesium-carborane complex in which some degree of interaction exists between the metal and the π-electron density on the carborane cage. Since this cesium compound can also be prepared by an ion-exchange reaction directly from lithium, sodium or potassium salts of the C_4B_8-cage (see **Figure 6b**), further study of this and related compounds in solvent extraction of radioactive cesium metal (^{137}Cs) from nuclear waste is envisioned.

Under similar reaction conditions, the "carbons apart" tetracarbon carborane, *nido*-2,6-$(R)_2$-4,12-$(SiMe_3)_2$-2,4,6,12-$C_4B_8H_8$ (R = $SiMe_3$, *n*-butyl), and several of its B-alkylated derivatives, react with Mg metal in THF to produce magnesacarboranes in yields ranging from 57% to 74% (**Scheme 2**).[16,19] Two types of cages were found, one in $(THF)_2Mg(SiMe_3)_4(B\text{-}Me)C_4B_7H_7$ and the other in $(L)_2Mg(SiMe_3)_2(R)_2(B\text{-}Y)C_4B_7H_7$ (L = THF, R = $SiMe_3$, Y = *t*-Bu; L = THF, R = $SiMe_3$, Y = H; $(L)_2$ = TMEDA, R = *n*-Bu, Y = H).



(a) (b)

Figure 6 *Crystal structures of the dicesiacarborane complex: (a) A cesiacarborane unit in a polymeric chain; (b) A* C_4B_8 *carborane cage without the cesium metals.*

Both cages showed the presence of electron precise carbon and boron atoms, as well as electron deficient fragments. On the other hand, the reactions of *nido*-2,4,6,12-$(SiMe_3)_4$-2,4,6,12-$C_4B_8H_8$ with the group 1 metals followed a different course in which two distinct steps occurred (**Scheme 2**). The first step formed the paramagnetic $[(SiMe_3)_4C_4B_8H_8]^-$ intermediate, which, in a slower step, reacted with a second equivalent of the metal to give the diamagnetic $[(SiMe_3)_4C_4B_8H_8]^{2-}$. For the lighter metals, this dianion picked up a proton to give the products, $[(THF)_4M][(SiMe_3)_4C_4B_8H_9]$ (M = Li, Na or K), in 35%–54% yield.[19] In the case of Cs, no protonation occurred and the final product was a polymeric dicesiacarborane, [*exo*-Cs(TMEDA)-1-Cs$(SiMe_3)_4C_4B_8H_8]_n$, isolated in 41% yield. In group 1 metallacarboranes, the lighter metal was solvated by four THF molecules and was not involved in the cage, while in cesium compound one Cs occupied an apical position above a C_3B_3 open face of one carborane and bonded to a B_3 face of a neighboring carborane. The second Cs, solvated by a TMEDA molecule, occupies an *exo*-polyhedral position and was not part of the polymeric chain (See **Figure 6**).

1.3 Reactivity of "Carbons Adjacent" C_4B_8-carborane

A "carbons adjacent" magnesacarborane, *exo*-$(\mu\text{-H})_3Mg(THF)_3(SiMe_3)_2(Me)_2C_4B_8H_8$ was synthesized, in 81% yield, by the reaction of the metal with the $(SiMe_3)_2(Me)_2C_4B_8H_8$ precursor. Single crystal X-ray diffraction studies showed the compound to be composed of an *exo*-polyhedral $[Mg(THF)_3]^{2+}$ cation that is loosely bound to a $[(SiMe_3)_2(Me)_2C_4B_8H_8]^{2-}$ cage. This carborane polyhedron is best described as ten-vertex *arachno*-$(SiMe_3)_2C_2B_8H_8$ cage that subtends an electron precise MeC=CMe fragment (**Figure 7**).[19]

1.4 Conversion of Carborane Cage into Electron-Precise Heterocyclic Ring

The dominant structural patterns found in alkyl and aromatic hydrocarbons are reflections of the structures of elemental carbon (diamond or graphite) where added hydrogen atom across the C-C bonds gives "electron precise-carbon hydrides." In a similar way the

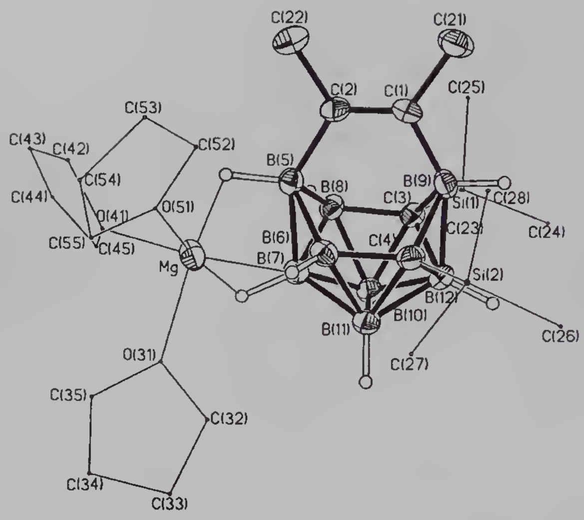
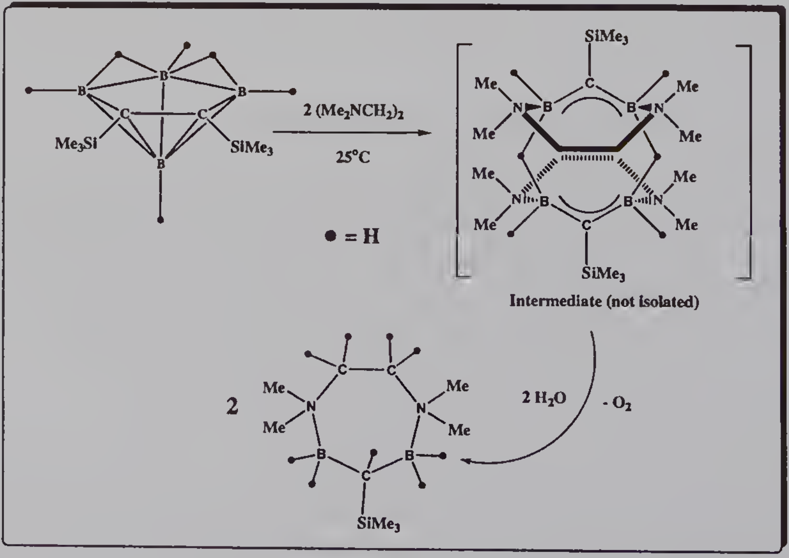
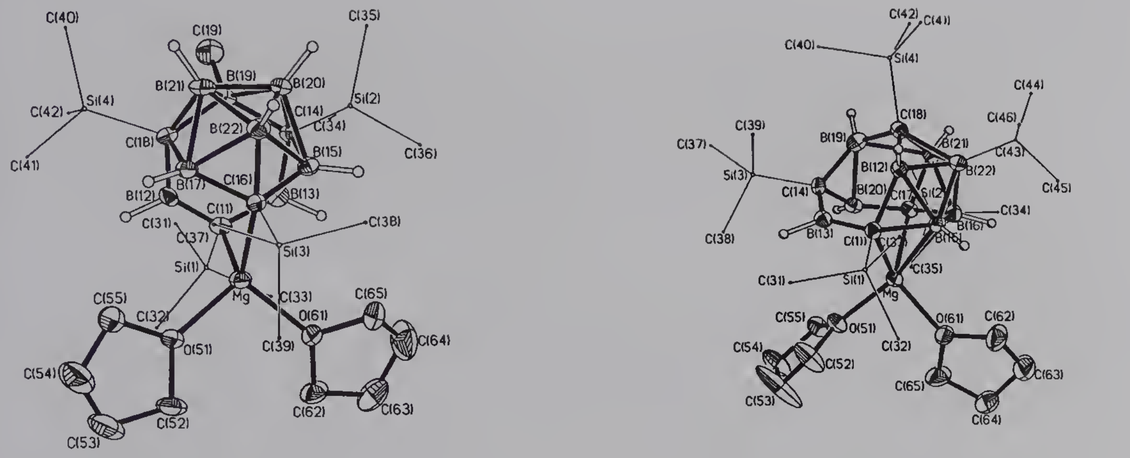


Figure 7 *Crystal structure of* exo-$(\mu\text{-}H)_3Mg(THF)_3(SiMe_3)_2(Me)_2C_4B_8H_8$

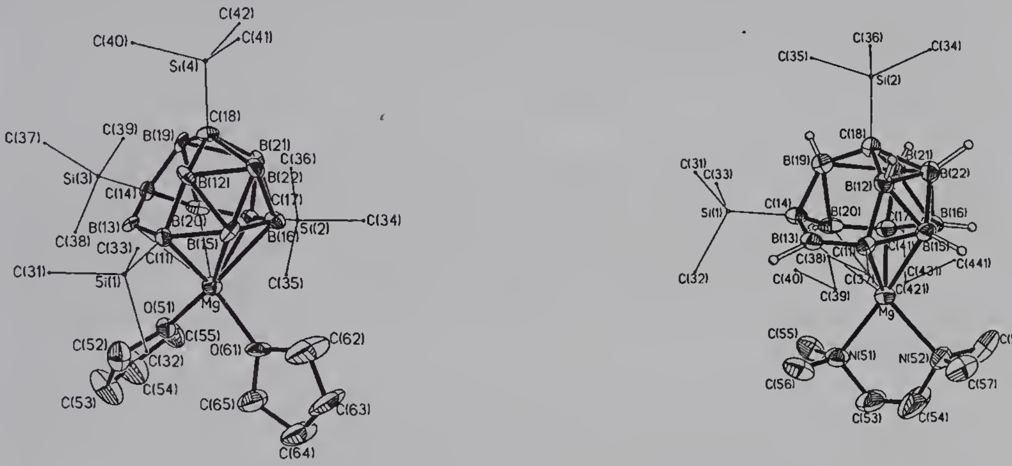
structures of boron hydrides are reflections of the icosahedral units found in elemental boron and the replacement of a $(BH)^-$ unit by a CH or CR unit gives the corresponding "electron deficient" carborane derivatives.[20] Although the magnesacarboranes in **Figure 8** consisted of both electron-precise atoms and an electron-deficient carborane unit in a single cage framework, there have been no reports on the conversion of an electron-deficient carborane cage essentially into an electron-precise heterocyclic ring. As part of our exploration of new methodologies in this area, a neat sample of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ was reacted with a large excess of wet *N,N,N,N*-tetramethylethylenediamine (TMEDA) *in vacuo* with constant stirring at room temperature for 7 days that transformed the "electron-deficient" carborane cage into a seven-membered "electron-precise" heterocyclic ring, 1-trimethylsilyl-3,6-dimethyl-3,6-diaza-1,4,5-tricarbaheptaborane (**Scheme 3**) whose solid state geometry was confirmed by X-ray crystallography (see **Figure 9**).[21]



Scheme 3 *Synthesis of the "electron-precise" carborane ring.*



(a) $(THF)_2Mg(SiMe_3)_4(B\text{-}Me)C_4B_7H_7$ (b) $(THF)_2Mg(SiMe_3)_4(B\text{-}t\text{-}Bu)C_4B_7H_7$



(c) $(THF)_2Mg(SiMe_3)_4C_4B_8H_8$ (d) $(TMEDA)_2Mg(SiMe_3)_2(n\text{-}Bu)_2C_4B_8H_8$

Figure 8 *Crystal structures of magnesacarboranes, (a)-(d), of the C_4B_8-cage systems.*

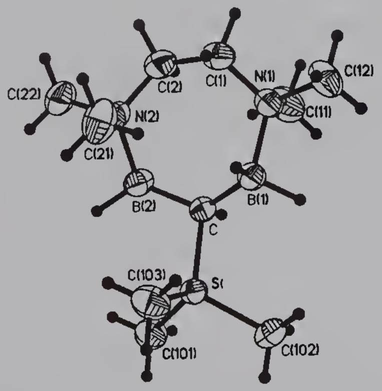


Figure 9 *Electron-precise heterocyclic ring.*

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References

1. For general references see: (a) 'Comprehensive Organometallic Chemistry II', E. W. Abel, F. G.A. Stone and G. Wilkinson, Eds., Elsevier Science Ltd., Oxford, 1995; Vol. 1, Chapters 6-8 9. (b) N. S. Hosmane and J. A. Maguire, in 'Electron-Deficient Boron and Carbon Clusters', G. A. Olah, K. Wade and R. E. Williams, Eds., Wiley, New York, 1991, Chapter 9, pp. 215. (c) N. S. Hosmane and J. A. Maguire, *Adv. Organomet. Chem.*, 1990, **30**, 99.
2. (a) A. K. Saxena, J. A. Maguire and N. S. Hosmane, *Chem. Rev.*, 1997, **97**, 2421 and references therein. (b) N. S. Hosmane, K.-J. Lu, H. Zhang and J. A. Maguire, *Organometallics,* 1997, **16**, 5163. (c) N. S. Hosmane, J. Yang, K.-J. Lu, H. Zhang, U. Siriwardane, M. S. Islam, J. L.C. Thomas and J. A. Maguire, *Organometallics,* 1998, **17**, 2784.
3. (a) N. S. Hosmane, Y. Wang, H. Zhang, K.-J. Lu, J. A. Maguire, T. G. Gray, K. A. Brooks, E. Waldhör, W. Kaim and R. K. Kremer, *Organometallics,* 1997, **16**, 1365-1377. (b) H. Zhang, Y. Wang, A. K. Saxena, A. R. Oki., J. A. Maguire and N. S. Hosmane, *Organometallics,* 1993, **12**, 3933. (c) C. J. Thomas, J. Lei, H. Zhang, U. Siriwardane, J. A. Maguire, V. P. Weiss, K. A. Brooks and N. S. Hosmane, *Organometallics,* 1995, **14**, 1365.
4. (a) N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang, D. Zhu, E. M. McDonald and J. A. Maguire, *Phosphorus, Sulfur, and Silicon,* 1994, **93-94**, 253, and references therein. (b) N. S. Hosmane, Y. Wang, A. R. Oki, H. Zhang and J. A. Maguire, *Organometallics,* 1996, **15**, 626. (c) N. S. Hosmane, Y. Wang. H. Zhang, J. A. Maguire, M. McInnis, T. G. Gray, J. D. Collins, R. K. Kremer, H. Binder, E. Waldhör and W. Kaim, *Organometallics,* 1996, **15**, 1006.
5. N. S. Hosmane, A. K. Saxena, R. D. Barreto, H. Zhang, J. A. Maguire, L. Jia, Y. Wang, A. R. Oki, K. V. Grover, S. J. Whitten, K. Dawson, M. A. Tolle, U. Siriwardane, T. Demissie and J. S. Fagner, *Organometallics*, 1993, **12**, 3001.
6. N. S. Hosmane, H. Zhang, J. A. Maguire. Y. Wang, C. J. Thomas and T. G. Gray, *Angew. Chem. Int. Ed. Engl.,* 1996, **35**, 1000.
7. N. S. Hosmane, T. J. Colacot, H. Zhang, J. Yang, J. A. Maguire, Y. Wang, M. B. Ezhova, A. Franken, T. Demissie, K.-J. Lu, D. Zhu, J. L.C. Thomas, J. Collins, T. G. Gray, S. N. Hosmane and W. N. Lipscomb, *Organometallics,* 1998, **17**, 5294.
8. (a) R. N. Grimes, *Adv. Inorg. Chem. Radiochem.,* 1983, **26**, 55. (b) R. B. Maynard and R. N. Grimes, *J. Am. Chem. Soc.,* 1982, **104**, 5983.
9. (a) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, 1974, **96**, 7116. (b) W. M. Maxwell, V. R. Miller and R. N. Grimes, *Inorg. Chem.,* 1976, **15**, 1343.
10. D. P. Freyberg, R. Weiss, E. Sinn and R. N. Grimes, *Inorg. Chem.,* 1977, **16**, 1847.
11. T. L. Venable, R. B. Maynard and R. N. Grimes, *J. Am. Chem. Soc.,* 1984, **106**, 6187.
12. J. T. Spencer, M. R. Pourian, R. J. Butcher, E. Sinn and R. N. Grimes, *Organometallics,* 1987, **6**, 335.
13. (a) W. N. Lipscomb and D. J. Britton, *J. Chem. Phys.*, 1960, **33**, 275-280. (b) W. N. Lipscomb, *Science,* 1966, **153**, 3734, and references therein.
14. (a) W. M. Maxwell, R. F. Bryan and R. N. Grimes, *J. Am. Chem. Soc.,* 1977, **99**, 4008. (b) W. M. Maxwell, R. Weiss, E. Sinn and R. N. Grimes, *J. Am. Chem. Soc.*, 1977, **99**, 4016.
15. (a) R. N. Grimes, J. R. Pipal and E. Sinn, *J. Am. Chem. Soc.*, 1979, **101**, 4172. (b) W. M. Maxwell and R. N. Grimes, *Inorganic Chem.,* 1979, **18**, 2174.

16. N. S. Hosmane, H. Zhang, Y. Wang, K.-J. Lu, C. J. Thomas, M. B. Ezhova, S. C. Helfert, J. D. Collins, J. A. Maguire and T. G. Gray, *Organometallics,* 1996, **15**, 2425.
17. N. S. Hosmane, T. Demissie, H. Zhang, J. A. Maguire, W. N. Lipscomb, F. Baumann and W. Kaim, *Organometallics,* 1998, **17**, 293.
18. R. Khattar, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.,* 1990, **29**, 2191.
19. N. S. Hosmane, H. Zhang, J. A. Maguire, Y. Wang, T. Demissie, T. J. Colacot, M. B. Ezhova, K.-J. Lu, D. Zhu, T. G. Gray, S. C. Helfert, S. N. Hosmane, J. D. Collins, F. Baumann, W. Kaim and W. N. Lipscomb, *Organometallics,* submitted for publication.
20. (a) W. N. Lipscomb, in 'Boron Hydrides', Benjamin, New York, 1963, p. 89. (b) E. L. Muetterties and W. H. Knoth, in 'Polyhedral Boranes', Marcel Dekker, New York, 1968, p.40. (c) R. W. Parry, in 'The Borane, Carborane, Carbocation Continuum', J. Casanova, Ed., Wiley, New York, 1998, p.191.
21. C. Zheng and N. S. Hosmane, *Acta Cryst.,* **1999**, *C55,* 000.

Pyrrole and *o*-Carborane

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1 INTRODUCTION

Conducting polymers have constituted a major field of chemistry and physics research for the last 20 years.[1,2] Interest in these materials is focused on their unique combination of the attractive mechanical properties of polymers and the electronic properties of metals or semiconductors. Although the engineering of materials based on organic polymers has been developed on a large scale and many organic, conductive polymers have been synthesized[3] the understanding of certain crucial chemical properties of these systems is far from complete. In particular, it would be interesting, from both a theoretical and a practical point of view, to understand the electronic and structural modifications produced in these polymers by the inclusion of doping agents.[4]

1.1 Polypyrrole and the Requirements of its Monomer Precursor

The formation of conductive polypyrrole films takes place electrochemically by the anodic oxidation of pyrrole in acetonitrile at a moderately positive potential ($E_{1/2}$= 1 to 1.3 V *vs* Saturated Calomel Electrode (SCE)). The initially formed radical coupled species is immediately oxidized at the applied potential, since it is more oxidizable than the monomer, leading to a new radical cation. The continuing reaction is a lenghtening of the oligomer chain. Since polymers from pyrrole have markedly lower oxidation potentials (0 to 0.4 V(SCE)) than the monomer, they are obtained in an oxidized state which is electrically conducting, allowing the growth of the film. The important point that it is relevant to this paper is that the resulting polymer contains mainly structural units of 2,5 linkage.

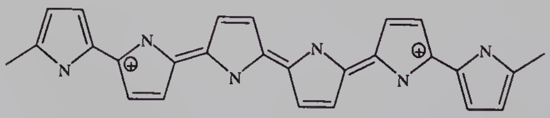


Figure 1 *Polypyrrole showing connectivity through α positions*

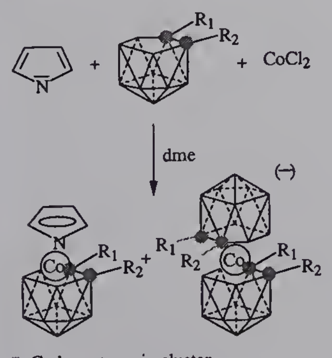
Thus it appears that non-substituted pyrrole at the 2,5 positions is highly recommended to produce good quality polypyrrole (PPy). See Figure 1. Besides, conducting PPy needs to be doped to stabilize the generated positive charges which is equivalent to say that it requires the presence of anions. In this sense pyrrole/pyrrolyl η^5 coordination to a metal may be considered as a way of oxidizing the pyrrole, as part of its electron-density is involved in the coordination to the metal. As it may come out of this introduction we have been aiming at synthesizing robust pyrrolyl complexes which could provide alternative routes to new polypyrrole materials, and as a consequence the need to have the α positions free. The combination of the two negatively charged dicarbollide, the mononegative η^5 pyrrolyl and Co(III) seemed to be an adequate combination to generate such stable sandwich species.

1.2 Pyrrole/Pyrrolyl Complexes

A literature survey suggests that η^5 coordination is widely common with $(C_5H_5)^-$ and $(C_5Me_5)^-$ ligands but it is relatively rare for pyrrolyl since strong competition with N-σ bonding takes place.[5] Consequently, $[(\eta^5\text{-pyrrolyl})\text{metal}(\eta^5\text{-}C_5R_5)]$ (R= H, Me) sandwich species are relatively rare.[6,7] Some examples are $[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}NMeC_4Me_4)]^{2+}$,[8] $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}NMeC_4Me_4)]^+$,[8] $[(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}NC_4Me_4)]$,[9] $[(\eta^5\text{-}C_5Me_5)Ru(\eta^5\text{-}NC_4H_4)]$,[10] and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}NC_4H_4)]$.[11] On the other hand there are several examples of mixed metallacarboranes with $(C_5H_5)^-$ and dicarbollyl ligands $(C_2B_9H_{11})^{2-}$.[12] Though $(C_5H_5)^-$ is electronically equivalent to pyrrole and pyrrolyl the number of mixed pyrrolylmetallacarboranes is very limited and is restricted to small carboranes and dimethyl or tetramethyl substituted pyrrolyl anions. No examples of mixed metallacarboranes with the non-substituted pyrrolyl ligand have previously been reported. It has been suggested that blocking of the pyrrolyl α or α and β positions prevents the N-σ bond formation, thus η^5 coordination is favored.[13] Examples of mixed pyrrolyl/carborane complexes are the double-decker[14] $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_4H_4)]$ (R = Me, H), $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_3H_5)]$ and the triple decker[15] $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_2B_3H_3)Co(C_5H_5)]$ (R = Me, H), $[(\eta^5\text{-}NC_4Me_2R_2)Co(Et_2C_3B_3H_3)Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)]$ (R = Me, H) and $[(\eta^5\text{-}NC_4Me_4)_2Co_2(Et_2C_2B_3H_3)]$. Though a great deal of work in metallacarborane chemistry has been done with $(C_2B_9H_{11})^{2-}$,[16] no examples of mixed pyrrolyl/ $(C_2B_9H_{11})^{2-}$ complexes have ever been reported.

2 ROUTES TO PYRROLYLCOBALTADICARBOLLIDE COMPLEXES

Two procedures have been developed to synthesize these mixed complexes with plain pyrrolyl and dicarbollide derivatives. Procedure A uses the preformed *nido* carborane while procedure B starts directly from the *closo* species.



● Carbon atoms in cluster
Cluster vertexes correspond to B-H

Figure 2 *Procedure A*

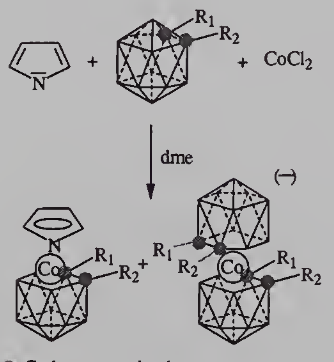
2.1 Procedure A

This consists[17] in performing the reaction starting from the preformed components of the sandwich, to say the dicarbollide, the pyrrolyl and $CoCl_2$, in 1,2-dimethoxyethane (dme). The synthesis of the reported complexes is as follows. Reaction, under nitrogen, of $[NMe_4][7\text{-}R_1\text{-}8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_{10}]$ (R_1 = H, R_2 = H; R_1 = CH_3 R_2 = H; R_1 = CH_3, R_2 = C_4H_9; R_1 = CH_3, R_2 = $C_3H_6OC_2H_5$) in dry dme with $CoCl_2$ and potassium pyrrolyl (Figure 2), in a ratio 1:5:10 respectively, generates, after 48 hours of refluxing, a mixture of sandwich complexes $[(\eta^5$-

$NC_4H_4)Co(7\text{-}R_1\text{-}8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)]$ (a) (**1a**, $R_1 = H, R_2 = H$; **2a**, $R_1 = CH_3, R_2 = H$; **3a**, $R_1 = CH_3, R_2 = C_4H_9$; **4a**, $R_1 = CH_3, R_2 = C_3H_6OC_2H_5$) and the corresponding bisdicarbollyl complexes $[3,3'\text{-}Co(1\text{-}R_1\text{-}2\text{-}R_2\text{-}1,2\text{-}C_2B_9H_9)_2]^-$ **(b) 1b, 2b, 3b** and **4b,** respectively. Separation is achieved by chromatography on silica gel using CH_2Cl_2 / C_6H_{14} (7/3) as mobile phase to provide the pure yellow mixed sandwich complexes: **1a, 2a, 3a,** and **4a** [Rf (anal. silica gel) = 0.21, 0.28, 0.50 and 0.13] in 68, 65, 62 and 60% yield respectively. In all cases, the **a**:**b** molar ratio is approximately 4:1. The solid yellow complexes, **1-4a,** are air-stable and their identification has been based on NMR measurements, mass spectrometry and microanalysis.

2.2 Procedure B

This is basically the same as the one in procedure A but using the *closo* species instead of the *nido* one.[18,19] It is far simpler than the former one since the *nido* species does not need to be synthesized. For $[(\eta^5\text{-}NC_4H_4)Co(C_2B_9H_{11})]$ the procedure is as simple as: the reaction of *o*-carborane with $K(NC_4H_4)$ and $CoCl_2$ in the ratio 1:12:5 in dme yields after working up $[(\eta^5\text{-}NC_4H_4)Co(C_2B_9H_{11})]$ in 76% yield. The reaction is shown in Figure 3.

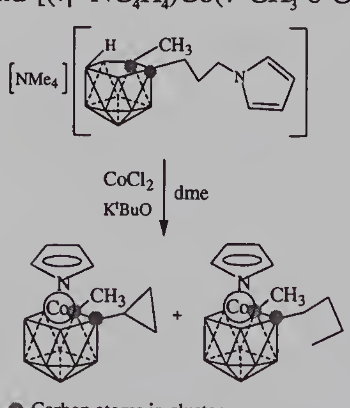


● Carbon atoms in cluster
Cluster vertexes correspond to B-H

Figure 3 *Procedure B*

2.3 Stability of the Mixed Pyrrolylcobaltadicarbollide Species

The tendency for these compounds to be formed can be proven by the reaction of $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$, a compound with a σ bonded pyrrolyl group, with $CoCl_2$ and K*t*BuO in dme. After refluxing for 72 h a mixture of compounds is obtained that is partly resolved by TLC. Complexes $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}CH_3\text{-}8\text{-}C_4H_9\text{-}7,8\text{-}C_2B_9H_9)]$ **(5)** and $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}CH_3\text{-}8\text{-}C_3H_5\text{-}7,8\text{-}C_2B_9H_9)]$ **(6)**. To prove that this reaction was not an isolated case, it was reproduced with the phenyl substituted equivalent $[7\text{-}C_6H_5\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$. The reaction was carried on following the same experimental conditions reported in the synthesis of **5** and **6**, and compounds $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}C_6H_5\text{-}8\text{-}C_4H_9\text{-}7,8\text{-}C_2B_9H_9)]$ **(7)** and $[(\eta^5\text{-}NC_4H_4)Co(7\text{-}C_6H_5\text{-}8\text{-}C_3H_5\text{-}7,8\text{-}C_2B_9H_9)]$ **(8)** were obtained which had similar appearance as **5** and **6,** respectively. The NMR data of **7** and **8** are also very comparable to those of **5** and **6** . The reaction leading to these complexes is indicated in Figure 4. A mechanism explaining their formation was previously discussed.[18] The major differences between complexes **5** and **6** are found on the carbon cluster (Cc) substituents. Compound **5** has a butyl chain while compound **6** has reconverted the original $-(CH_2)_3-$ spacer in ligand $[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ to a cyclopropyl group. The +3 charge of cobalt is compensated by the pyrrolyl (1-) and the dicarbollide (2-) moieties. The source of $(CH_3)^+$



● Carbon atoms in cluster
Cluster vertexes correspond to B-H

Figure 4 *Modification of the substituent on the formation of the mixed sandwhich* for **5** and **7** is the $[N(CH_3)_4]^+$ salt. This was proven by carrying on the same reaction leading to **5** and **6** but starting from $K^+[7\text{-}CH_3\text{-}8\text{-}C_4H_4N\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ instead of the $[N(CH_3)_4]^+$ salt. In this case, compound **6** was found but not compound **5**.

3 MOLECULAR STRUCTURE OF THE MIXED PYRROLYLCOBALTADICARBOLLIDE SPECIES.

The molecular structures of the parent $[(\eta^5\text{-}NC_4H_4)Co(7,8\text{-}C_2B_9H_{11})]$ and **5** and **8,** all having in common that there are no substituents on the η^5 pyrrolyl unit, show that the basic units of all these structures are very similar. The metal is sandwiched by the pentagonal faces of the pyrrolyl ion and the dicarbollide ligand, and the conformation of the faces is staggered with the pyrrolyl nitrogen being placed between the two cluster carbons. Table 1 summarizes the angle deviation (α) from strictly staggered disposition of some of these mixed sandwich complexes. Substituents make reference to Figure 5. Also deviation from planarity (180-θ) of the pyrrolyl and C_2B_3 faces is reported. As it may be seen there, the planes constituted by the pentagonal faces of the pyrrolyl ion and the dicarbollide ligand are never exactly parallel; the largest distortion is observed when the butyl and methyl groups are the substituents of the carbons in the carborane cage. In all cases the nitrogen atom is the more distant atom within the heterocycle from the C_2B_3 plane.

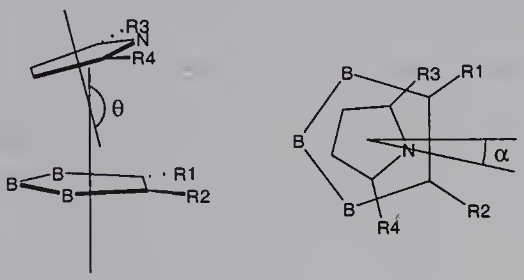


Figure 5 *Definition of α and β structural parameters*

Table 1 *Deviation from planarity of the pyrrolyl and C_2B_3 faces and deviation from strictly staggered disposition of three different complexes.*

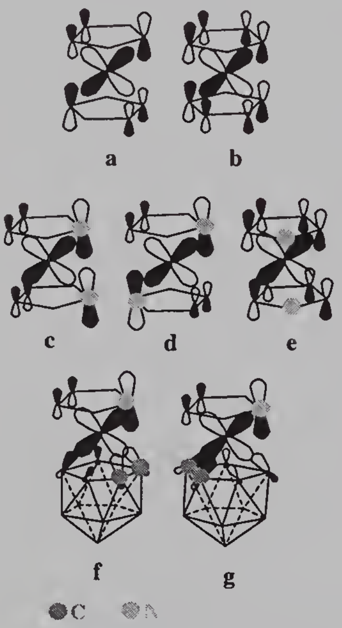
R1	R2	R3	R4	180-θ(°)	α(°)
H	H	H	H	4.09	3.88
n-C_4H_9	CH_3	H	H	7.69	5.45
C_6H_5	C_3H_5	H	H	4.26	-1.75

Concerning the angle deviation (α) from strictly staggered disposition, it can be seen that even the complex with no substituents presents a minor rotation of the pyrrolyl ring.

3.1 The Influence of Metal's d_{xy} and d_{xz} in the Stability of the Staggered Rotamer

As has been indicated in the former section, the nitrogen atom irrespectively of the substituents on the heterocycle or on the dicarbollide closely bisects the C-C cluster connectivity. This can be interpreted just considering the $\mathbf{d_{xz}}$ and $\mathbf{d_{yz}}$ metal orbitals interaction with the $NC_4H_4^{1-}/C_2B_9H_{11}^{2-}$ HOMO levels. To make this more evident we start from the bonding $\mathbf{e_{1g}}$ levels in $[FeCp_2]$ in a staggered configuration. These are shown as **6a** and **6b** in Figure 6. Figures **6c-6e** correspond to the diazoferrocene. Due to the larger electronegativity of N (3.0) *vs* C (2.5), the former degeneracy $\mathbf{e}_{1g}$ found in [$FeCp_2$] is broken and the energy level corresponding to **6c** or **6d** is more stabilized than **6e**. The orbital interaction diagrams shown in **6c** and **6e** have been described for an eclipsed configuration. It can be inferred from **e** that any other rotamers would not have got such a good overlap situations as in **6c** or **6d**. Thus the orbital interaction shown in **6c** or **6d** shows that the indicated rotamers are more stabilized than other possible ones. Following this argument it would be expected that the diazaferrocene molecule would be found as the eclipsed **6c** or the anti rotamer **6d**, and considering the nitrogen-nitrogen lone pair repulsion, the anti rotamer **6d** would be preferred. Indeed this is the structure found for octamethyldiazaferrocene.[13]

A similar description could be applied for the pyrrolyl/dicarbollide species, where the overlap of the $\mathbf{d}_{xz}$ orbital with the $NC_4H_4^{1-}/C_2B_9H_{11}^{2-}$ HOMO level incorporating the atomic orbital contribution of the more electronegative elements (N, C) would be the more stable. This would correspond to Figures **6f** and **6g**. The non-existence of lone pairs on carbon atoms in dicarbollide presumably does not destabilize the staggered disposition shown in **6f** as much as the equivalent in **6c**. Thus the staggered conformation shown in **6f** could be reasonable stable following this argument, as it would be the anti disposition shown in **6g**. Thus no further real arguments are found, based on this qualitative interaction of orbitals, to indicate which is the more stable rotamer, the one corresponding to **6f** or **6g**, although one of these would correspond to the experimental rotamer. As was indicated earlier several crystal structures have shown that the more stable is the one corresponding to **6f**, and as will be seen in the next section the rotamer corresponding to **6g** is the less stabilized of the possible rotamers.



Vertexes are boron in cluster, carbon other cases

Figure 6 *Orbital interaction in pyrrolylcobaltadicarbollide complexes*

3.2 Theoretical Calculations

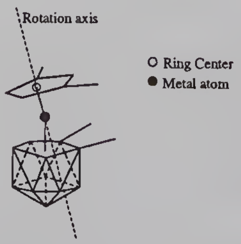


Figure 7 *Basic structure for the RHF-SCF calculations*

As indicated in Table 1, the X-ray diffraction analysis of [(η^5- NC_4H_4)Co($C_2B_9H_{11}$)] confirmed that the nitrogen atom is about 4° displaced from the totally staggered conformation, whereas the two planes formed by both five-membered faces ring are not exactly parallel (4.1°) (see Figure 7).

A molecular modeling RHF-SCF calculation was carried out with [(η^5- N C_4H_4)Co($C_2B_9H_{11}$)]. All calculations were performed by the direct SCF approach on a standard Pentium 200 MHz PC, using the program Gamess95. The pyrrolyl ring was rotated in 36° steps about the ring center-metal axis. X-Ray diffraction data were used as initial structure coordinates. A single point calculation was carried out at each step using STO-3G as basis set.

As can be seen in Figure 8, the conformation corresponding to the staggered situation of $[(\eta^5\text{-NC}_4\text{H}_4)\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})]$ with the nitrogen atom placed between the two cluster carbon atoms corresponds to a minimum (torsion angle 0°), whereas the maximum corresponds to the structure resulting from a ring rotation of 180° (anti rotamer). The energy barrier between both structures is about 5 Kcal/mol. The conformation corresponding to a 144° ring rotation (staggered conformation with the nitrogen atom placed between two boron atoms) corresponds to a local minimum. These results are in agreement with experimental results, where the nitrogen atom has been found to be always between the two carbons in the crystalline state. To find if these calculations were realistic in terms of structure the same kind of calculations were performed with diazaferrocene. The X-ray diffraction interatomic distances (Fe-C, C-C, C-N and N-Fe) obtained for 2,2',3,3',4,4',5,5'-octa-methyl-1,1'-diazaferrocene were used as starting geometry for diazaferrocene, replacing methyl groups by hydrogen atoms. The C-H distance was fixed to 1.104 Å that was obtained for $[(\eta^5\text{- NC}_4\text{H}_4)\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})]$.

As can be seen in Figure 8 the maximum of energy corresponds to the conformation with the nitrogen atoms eclipsed, whereas the conformation rotated 180°, anti, corresponds to a minimum of energy.

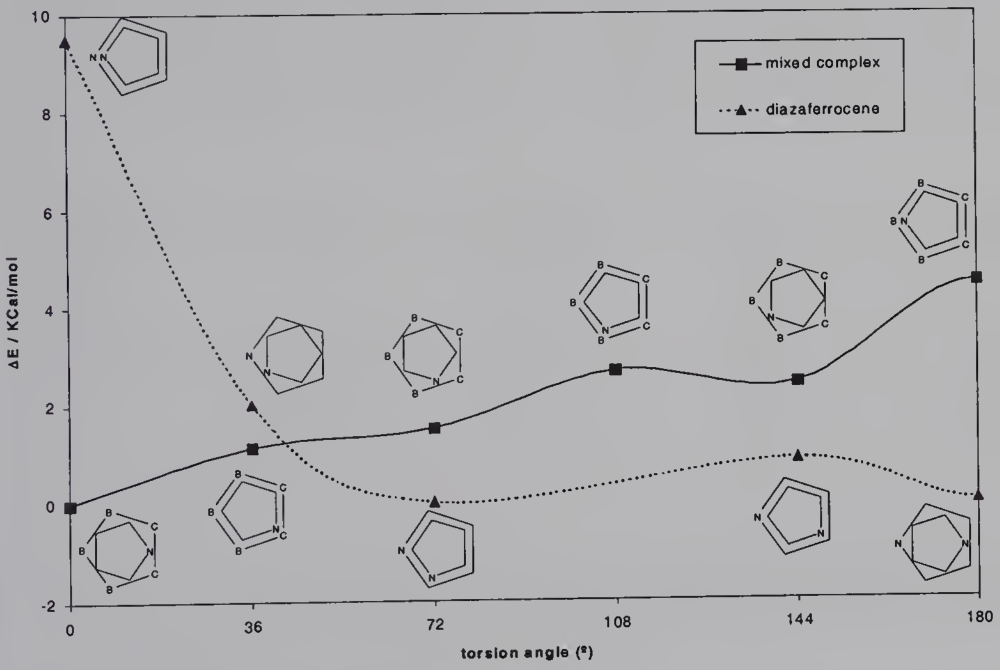
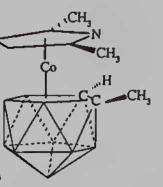


Figure 8 *Torsional diagram based on an RHF-SCF calculation for* $[(\eta^5\text{-NC}_4\text{H}_4)\text{-}\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})]$ *and diazaferrocene. The sketches correspond to the distinct ring rotamers*

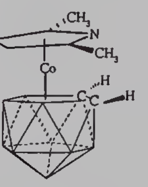
3.3 Behavior in Solution

The solution behavior of these mixed sandwich complexes was studied by ^{1}H and ^{13}C{^{1}H} NMR techniques. Due to the C_s symmetry or lower of these mixed complexes the expected number of resonances should be 2 (C_s) or 4 (lower symmetry). In Table 2 the ^{1}H and ^{13}C{^{1}H} NMR pyrrolyl resonances are indicated. All mixed sandwich complexes described there display the ^{1}H NMR pyrrolyl moiety expected resonances pattern, except **A** that shows one

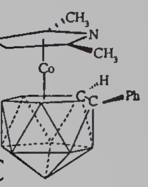
Table 2 *^{13}C{^{1}H} and ^{1}H NMR relevant positions for* **A-F**. *The drawing at the upper part refers to entries in Table 2. Cc are cluster carbons, all others correspond to pyrrolyl group.*



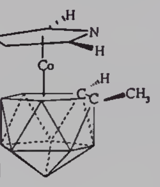
A



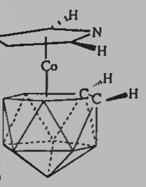
B



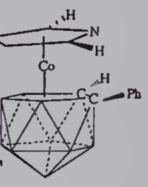
C



D



E



F

^{13}C{^{1}H} NMR	**Cc-R**	**Cc-H**	**CH=C**	**=C-N**	**CH_3-C-N**
A	74.96	60.79	87.57 / 89.55	124.2 / 124.7	14.56
B	------	55.10	89.65	124.2	14.63
D	75.66	60.82	90.37 / 92.20	111.35 / 13.39	------
E		53.01	92.57	110.32	------
F	54.65	53.44	90.91 / 92.61	116.96 / 11.08	------

^{1}H NMR	**Cc-H**	**CH=C**	**HC-N**	**CH_3-C-N**
A	3.86	5.83 / 5.97	-------	2.40 (2)
B	3.91	5.96 (2)	-------	2.33 (2)
C	**4.58**	5.72 /5.89	-------	2.37 / **1.37**
D	4.61	6.21 / 6.39	6.64 / 6.78	-------
E	4.36	6.37 (2)	6.72 (2)	-------
F	**5.20**	6.16 / 6.23	**5.31** / 6.73	-------

resonance integrating two, and two integrating one. This matching between structure and ^{1}H NMR has been found when $HCCl_3$ is used as a solvent. Contrarily, when acetone is the solvent used in **D** (no such test has been done in other sandwich complexes) three resonances are observed at room temperature and four at 200 K. On the other hand when chloroform was used the four signals were already visible at room temperature. This is shown in Figure 9. It has been interpreted as if a hydrogen bond was established between N and $HCCl_3$ increasing the rotation barrier. In Table 2 some resonances have been marked darker than others. They belong to sandwich complexes incorporating phenyl groups on the dicarbollide. If attention is paid to **C**, it is observed that the Cc-H proton resonance shifts downfield and one pyrrolyl CH_3 resonance shifts upfield, while the second CH_3 resonance remains at a regular position. A similar situation takes place at **F**.

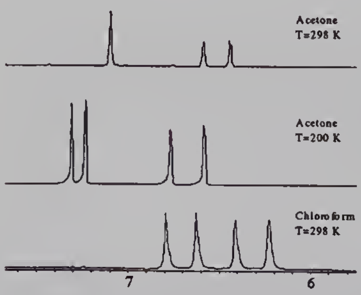


Figure 9 *^{1}H NMR of D at different Temp. and solvent*

Interestingly this phenomenon has not been observed for [(η^5-NC_4H_4)Co(7-C_6H_5-8-C_3H_5-7,8-$C_2B_9H_{11}$)] where the pyrrolyl resonances set has been found near 6.4 ppm, a value similar to all other mixed complexes.

This upfield shift has been attributed to the ring current associated with the phenyl ring which strongly influences the pyrrolyl proton sitting on top of it. This could be a clear indication of a highly restricted rotation of the pyrrolyl moiety, suggesting a good correspondence of the structure in solution and this in the solid state.

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[1] W. R. Salaneck, D. T. Clark and E. J. Saumelsen, Science and application of Conducting Polymers, Adam Hilger; Bristol, 1991.

[2] W. R. Salaneck, I. Lundstron and B. Ranby, Conjugated Polymers and Related Materials: The interconnection of Chemical and Electronic Structure; Oxford University: London, 1993.

[3] Handbook of Conducting Polymers; T. A. Skotheim, Ed.; Marcel Dekker: New York, 1986.

[4] R. Colle and A.Curioni, *J. Am. Chem. Soc.*, 1998, **120**, 4832.

[5] K. H. Pannell, B. L. Kalsotra and C. Parkanyi, *J. Heterocycl. Chem.*, 1978, **15**, 1057.

[6] F. Kvietok, V. Allured and D. M. Rakowski, *Organometallics*, 1994, **13**, 60.

[7] K. Öfele and E. Dozauer, *J. Organomet. Chem.*, 1971, **30**, 211.

[8] N. Kuhn, E. M. Horn, E. Zauder, D. Blaser and R. Boese, *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 579.

[9] W.J. Kelly and W. E. Parthun, *Organometallics*, 1991, **10**, 1965.

[10] R. H. Fish, E. Baralt and H. Kim, *Organometallics*, 1991, **10**, 1965.

[11] K. K. Joshi, P. L. Pauson, A. R. Oazi and W. H. Stubbs, *J. Organomet. Chem.* 1964, **1**, 471.

[12] a) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, 1965, **87**, 3987. b) A. Zalkin, D. H. Templeton and T.E. Hopkins, *J. Am. Chem. Soc.*, 1965, **87**, 3988. c) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjis, L. F. Warn, Jr. and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879. d) H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.* 1968, **7**, 2279. e) R. J. Wilson, L. F. Waren, and M. F. Hawthorne, *J. Am. Chem. Soc.* 1969, **91**, 758.

[13] N. Kuhn, E-M. Horn, R. Boese and N. Augart, *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 1368.

[14] K. J. Chase and R. N. Grimes, *Organometallics*, 1989, **8**, 2492.

[15] K. J. Chase, R. F. Bryan, M. K. Woode and R. N. Grimes, *Organometallics*, 1991, **10**, 2631.

[16] Some exemples are: a) M. F. Hawthorne and H. W. Ruhle, *Inorg. Chem.* 1969, **8**, 176. b) L. F. Warren Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.* 1970, **92**, 1157. c) F. A. Gomez, S. E. Johnson, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1992, **31**, 3558. d) Y.K. Yan, P. D. M. Mingos, *Chem. Soc. Rev.* 1995, 203.

[17] M. Lamrani, S. Gómez, C. Viñas, F. Teixidor, R. Sillapää and R. Kivekäs, *New J. Chem.*, 1996, **20**, 909.

[18] F. Teixidor, S. Gómez, M. Lamrani, C. Viñas, R. Sillanpää and R. Kivekäs, *Organometallics*, 1997, **16**, 1278.

[19] a) S. Gómez, C. Viñas, M. Lamrani, F. Teixidor, R. Kivekäs and R. Sillanpää, *Inorg. Chem.*, 1997, **36**, 3565. b) J. Bertran, C. Viñas, S. Gómez, M. Lamrani, F. Teixidor, R. Sillanpää and R. Kivekäs. *Collect. Czech. Chem. Commun.*, 1997, **62**, 1263.

Metallacarboranes and Metal Amides

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INTRODUCTION

In common with other areas of organometallic and coordination chemistry, the most widely used method of coordinating the dicarbollide ligand, $[C_2B_9H_{11}]$, to a transition metal is the elimination of alkali metal halide, MX, between a metal halide and salts such as $Li_2C_2B_9H_{11}$.[1] Thermodynamics ensures that this reaction proceeds readily, although redox reactions and poor yields can accompany it. In this report we explore an alternative method of preparing metal-dicarbollide bonds, using metal amides.[2] Recently there has been a resurgence of interest in the reactions of metal amides with substituted cyclopentadienes and other acidic reagents as routes to metallocenes and half-sandwich complexes.[3] Jordan and co-workers have extended this chemistry to group 4 dicarbollide complexes.[4] The attraction of metal amides for the synthesis of metal dicarbollide complexes is the potential for higher yields and access to otherwise unavailable complexes.[5]

There is an interest in developing ligands that mimic the bonding of a cyclopentadienyl ligand, especially in the targeting of group 4 metallocene and half-sandwich analogues. The Π_2 ligands[6] relevant to this work are *nido*-7,8-$C_2B_9H_{11}$[7] and the imide, RN, ligand.[8] One distinguishing feature of these ligands is that the π-orbitals of (η-C_5H_5) are degenerate, as are those of a trialkylimide, R_3CN. However, the lower symmetry of *nido*-7,8-$C_2B_9H_{11}$ and arylimide, ArN, mean that the π-orbitals of these ligands are not degenerate, although they may have very similar energies.

Recognising that these ligands present similar orbitals to a metal, but donate different numbers of electrons, we may select a metal with an appropriate number of valence electrons so as to construct isonumeral series of complexes, figure 1.

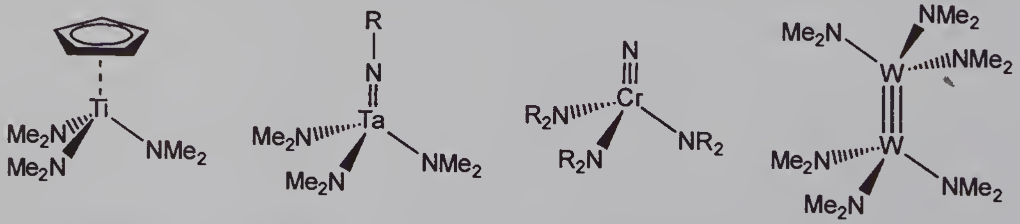

Figure 1 *Isonumeral $\Pi_2M(NMe_2)_3$ complexes of group 4, 5 and 6*

Although these complexes are isonumeral, they are not isostructural. The ditungsten complex $W_2(NMe_2)_6$ has a local C_{3v} arrangement of NMe_2 ligands, with all three NMe_2 ligands "vertical";[9] by contrast a large number of group 4 complexes, including some examples such as $ClTi(NMe_2)_3$ and $[CpFe(CO)_2]Ti(NMe_2)_3$ where the fourth ligand is arguably not a Π_2 ligand,[10] have propeller-like arrangements of NMe_2 ligands with local C_3 symmetry,[11] and remarkably constant pitch of the propeller. Prior to our work, the group 5 $\Pi_2M(NR_2)_3$ complexes were represented by $Me_3CNTa(NMe_2)_3$ which has a propeller geometry,[12] although with a smaller pitch than for the group 4 complexes, and $(2,6\text{-}^iPr_2C_6H_3N)Ta(NMe_2)_3$ which has two "vertical" NMe_2 ligands, and one (whose nitrogen atom is co-planar with the aryl group) "horizontal" NMe_2 ligand.[13]

It should be emphasised that although all these species are apparently 18 electron complexes, there is a need to consider the symmetry of the ligand π-donor orbitals and the metal d orbitals, and it is well established for example that the true electron count of $W_2(NMe_2)_6$ is 16 electrons, with a linear combination of nitrogen p orbitals, containing two electrons, that has no symmetry overlap with a metal d orbital. The geometric preferences of these species will be explored by us in more detail in a future paper, but suffice it to comment at this stage that the observed geometries appear to be a consequence of the energies and symmetries of the available metal-based orbitals.

RESULTS AND DISCUSSION

The reaction of $M(NMe_2)_5$ (M = Nb, Ta) with the neutral carborane *nido*-7,8-$C_2B_9H_{13}$, proceeds with the elimination of two equivalents of Me_2NH to give the $\Pi_2M(NMe_2)_3$ complex, $[M(1,2\text{-}C_2B_9H_{11})(NMe_2)_3]$, in high yield. The molecular structure of the tantalum congener in figure 2, shows that the NMe_2 ligands are in a two "vertical", one "horizontal" array, with the C_2 unit of the ligand located *trans* to the unique NMe_2 ligand. The solution structure is fluxional, and both ^1H and ^{13}C NMR spectra display a single resonance for all the NMe groups down to -80°C.

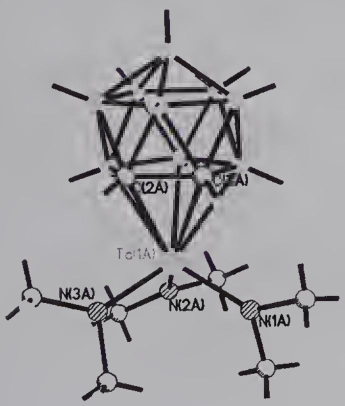

Figure 2 *Molecular structure of* *$[Ta(1,2\text{-}C_2B_9H_{11})(NMe_2)_3]$*

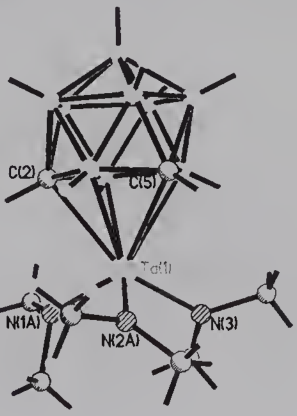

Figure 3 *Molecular structure of* *$[Ta(1,7\text{-}C_2B_9H_{11})(NMe_2)_3$*

By contrast with the established coordination chemistry of the *nido*-7,8-$C_2B_9H_{11}$ ligand, the analogous *nido*-7,9-$C_2B_9H_{11}$ ligand, derived by deboronation of "*meta*-carborane" 1,7-$C_2B_{10}H_{12}$ has been less widely studied. The few studies that have been performed have established that the *nido*-7,8-$C_2B_9H_{11}$ and *nido*-7,9-$C_2B_9H_{11}$ ligands differ in the energies of their π-donor frontier orbitals.[14] The reaction of $M(NMe_2)_5$ (M = Nb, Ta) with the salt [*nido*-7,9-$C_2B_9H_{12}$][NMe_3H], gives [$M(1,7-C_2B_9H_{11})(NMe_2)_3$] in high yield. The molecular structure of the Ta congener has been determined and suffers from some disorder, but the ordered component is shown in figure 3, with the NMe_2 ligands adopting a propeller conformation. Noting that propellers are chiral, the disorder can be accounted for by the location of both enantiomers at the same site in the crystal.

These two complexes, where an apparently small change in the ligand has a large structural effect, prompted us to explore the third easily accessible isomer of *nido*-$C_2B_9H_{11}$ as a ligand. The reaction of $Ta(NMe_2)_5$ with *nido*-2,9-$C_2B_9H_{13}$, obtained by deboronation of "*para*-carborane" 1,12-$C_2B_{10}H_{12}$, gives [$Ta(1,12-C_2B_9H_{11})(NMe_2)_3$], the molecular structure of which appears in figure 4, and reveals a geometry similar to that of the "ortho" complex, with two "vertical" and one "horizontal" NMe_2 ligands.

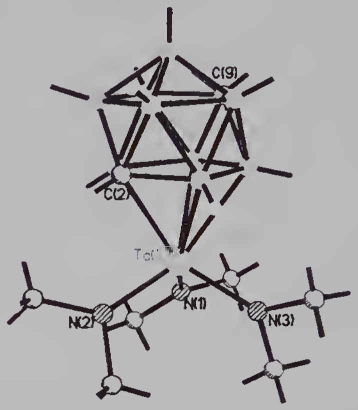

Figure 4 *Molecular structure of [$Ta(1,12-C_2B_9H_{11})(NMe_2)_3$*

These studies suggest that the tuneable electronics of the isomeric $C_2B_9H_{11}$ ligands provide an opportunity to access a range of structures in $\Pi_2M(NMe_2)_3$ complexes which are otherwise only observed by change of ligand **and** metal within the isonumeral series. We have explored the coordination chemistry of [$M(1,2-C_2B_9H_{11})(NMe_2)_3$] (M = Nb, Ta), and we find that the dicarbollide ligand acts as a spectator ligand, with the NMe_2 ligands undergoing their characteristic chemistry. Thus heterocumulenes such as CO_2, CS_2, RCN and RNC insert into the M-N bond, the reactions with CO_2 and CS_2 giving structurally characterised carbamate and dithiocarbamate complexes (figure 5 shows the niobium dithiocarbamate complex). These display a two "horizontal" one "vertical" array of X_2CNMe_2 ligands, which might also be described as a *pseudo*-pentagonal bipyramid geometry. This arrangement of ligands is also observed in the isonumeral (η-

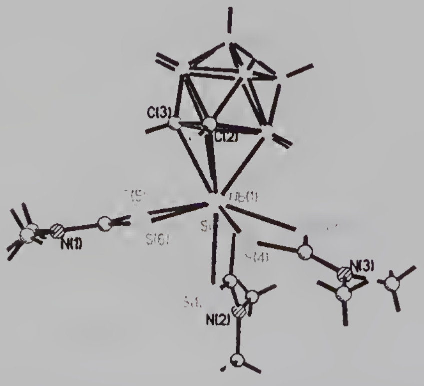

Figure 5 *Molecular structure of [$Nb(1,2-C_2B_9H_{11})(S_2CNMe_2)_3$]*

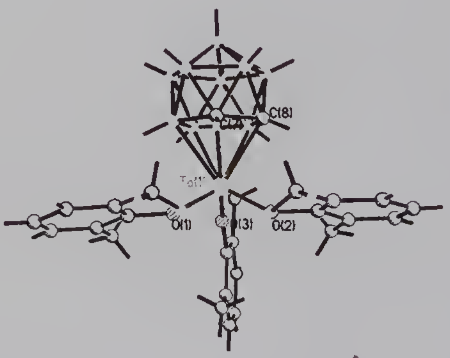

Figure 6 *Molecular structure of [$Ta(1,2-C_2B_9H_{11})(OC_6H_3Me_2)_3$]*

$C_5H_5)M(X_2CNMe_2)_3$ complexes (M = Ti, Zr, Hf; X = O, C).[15] It is again a feature that the unique ligand is approximately *trans* to the C_2 unit of the dicarbollide ligand.

The reaction of $[Ta(1,2\text{-}C_2B_9H_{11})(NMe_2)_3]$ with three equivalents of 2,6-$Me_2C_6H_3OH$ liberates Me_2NH and generates the *tris*-alkoxide complex, $[Ta(1,2\text{-}C_2B_9H_{11})(2,6\text{-}Me_2C_6H_3O)_3]$, whose solid-state structure (figure 6) displays two "horizontal" and one "vertical" aryloxide ligands, with the unique ligand almost trans to the C_2 unit of the dicarbollide ligand, suggesting that π-bonding effects are important.

The success of reactions with group 5 metal amides has prompted us to explore the reactions of tungsten amides. The reaction of *nido*-7,8-$C_2B_9H_{13}$ with $[W(N^tBu)_2(NH^tBu)_2]$ (containing two imide and two amide ligands,[16] and readily prepared from WCl_6 and $^tBuNH_2$) involves the formal replacement of an imide ligand by a dicarbollide to give $[W(N^tBu)(1,2\text{-}C_2B_9H_{11})(NH^tBu)_2]$, as shown in figure 7.

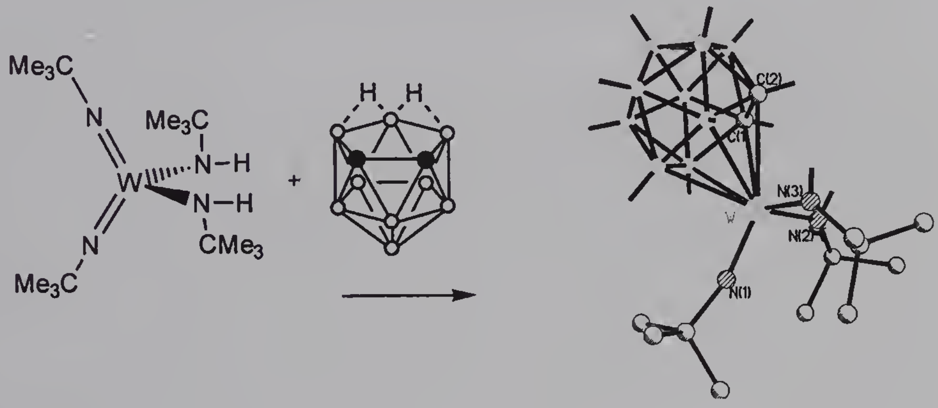

Figure 7 *The synthesis of* $W(N^tBu)(1,2\text{-}C_2B_9H_{11})(NH^tBu)_2$

This complex is *pseudo*-tetrahedral and isonumeral with $[Hf(\eta\text{-}C_5H_5)_2(NR_2)_2]$. Acids such as 2,6-$Me_2C_6H_3OH$ and water can cleave the W-NH^{t}Bu bonds, and W-Cl bonds can be introduced by the use of chloride sources.

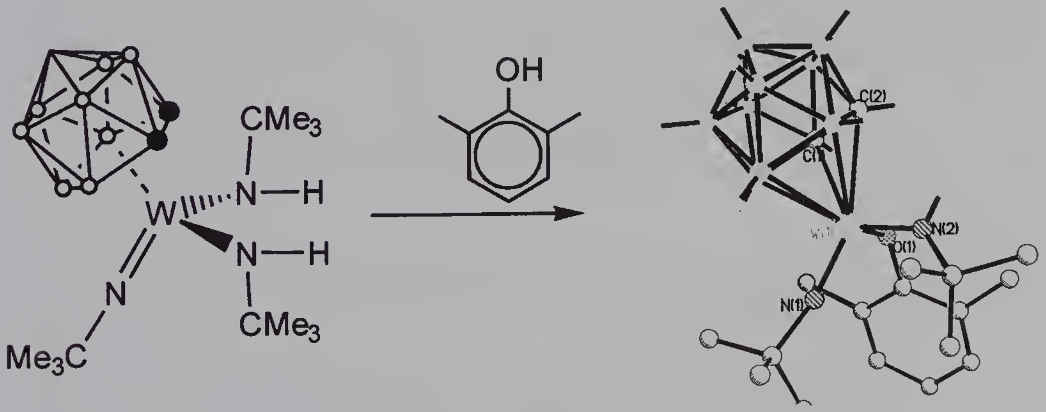

Figure 8 *The synthesis of* $W(N^tBu)(1,2\text{-}C_2B_9H_{11})(NH^tBu)(2,6\text{-}Me_2C_6H_3O)$

In conclusion, we have demonstrated that the reactions of metal amide bonds, M-NR_2, with acidic hydrogen atoms of *nido*-carboranes provide an attractive route to the synthesis of metallacarboranes of the early/middle transition elements. The structural preferences of the amide ligands in the products provide us with valuable lessons on the relationship between electronic and molecular structures. Early transition metal complexes containing $C_2B_9H_{11}$ ligands provide analogues of familiar metallocenes and half-sandwich complexes, and we will continue to explore the consequences of such relationships in the context of catalysis and stoichiometric reactions.

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REFERENCES

1. R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol 1, ch. 9; M. F. Hawthorne, *Acc. Chem. Res.*, 1968, **1**, 281; A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081;

2 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, "Metal and Metalloid Amides: Syntheses, Structures and Physical and Chemical Properties", Ellis Horwood, Chichester, 1980; M. H. Chisholm and I. P. Rothwell in "Comprehensive Coordination Chemistry", eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Volume 2, Chapter 13.4, Pergamon Press, Oxford, 1987.

3. A. K. Hughes, A. Meetsma and J. H. Teuben, *Organometallics*, 1993, **12**, 1936; W. A. Hermann and W. Baratta, *J. Organomet. Chem.*, 1996, **506**, 357; Y. Mu, W. E. Piers, M. A. MacDonald and M. J. Zaworotko, *Can. J. Chem.*, 1995, **73**, 2233; Z. Ziniuk, I. Goldberg and M. Kol, *J. Organomet. Chem.*, 1997, **546**, 441.

4. R. Uhrhammer, D. J. Crowther, J. D. Olson, D. C. Swenson and R. F. Jordan, *Organometallics*, 1992, **11**, 3098; D. J. Crowther, S. L. Borkowsky, D. Swenson, T. Y. Meyer and R. F. Jordan, *Organometallics*, 1993, **12**, 2897; D. J. Crowther, D. C. Swenson and R. F. Jordan, *J. Am. Chem. Soc.*, 1995, 117, 10403.

5 G. M. Diamond, R. F. Jordan and J. L. Petersen, *J. Am. Chem. Soc.*, 1996, **118**, 8024

6 V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1994, 1607.

7 Deboronation of *closo*-1,2-$C_2B_{10}H_{12}$ generates *nido*-7,8-$C_2B_9H_{13}$, which may be coordinated to a metal to give [3,1,2-$Ta(NMe_2)_3C_2B_9H_{11}$], which we prefer to refer to as $Ta(1,2\text{-}C_2B_9H_{11})(NMe_2)_3$, emphasising the relationship of the $C_2B_9H_{11}$ fragment with the planar *arachno* cyclopentadienyl radical, (C_5H_5).

8. Ligands are presented as electrically neutral radicals, the so-called neutral ligand formalism: M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127.

9. M. H. Chisholm, M. W. Extine, F. A. Cotton and B. R. Stults, *J. Am. Chem. Soc.*, 1976, **98**, 4477.

10. D. G. Dick, R. Rousseau and D. W. Stephan, *Can. J. Chem.*, 1991, **69**, 357; W. J. Sartain and J. P. Selegue, *Organometallics*, 1987, **6**, 1812.

11. J. N. Christopher, G. M. Diamond, R. F. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4038.

12. W. A. Nugent and R. L. Harlow, *J. Chem. Soc., Chem. Commun.*, 1978, 579.

13. W. A. Herrmann, W. Baratta and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1951.

14 T. B. Marder, R. T. Baker, J. A. Long, J. A. Doi and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1981, **103**, 2988.

15. R. C. Fay, *Coord. Chem. Revs.*, 1996, **154**, 99

16. W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777

Novel Osmacarboranes: Reactivity and Application to the Syntheses of *exo*-Os-*closo*-M′-Bimetallacarboranes

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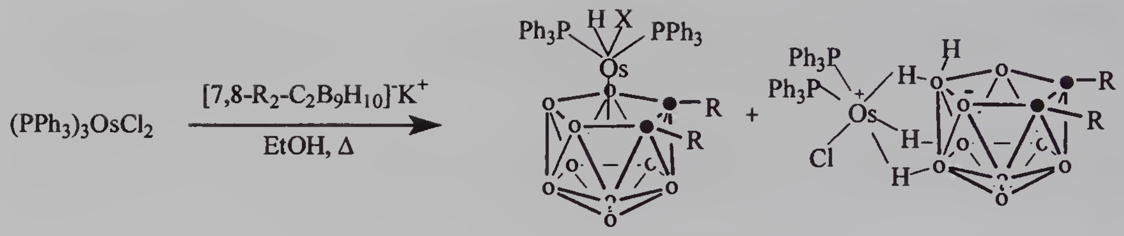
1 INTRODUCTION

Metallacarboranes of platinum metals have long attracted particular attention from the point of view of synthetic as well as structural and theoretical investigations, and, moreover, some of them have already found extensive practical application as efficient homogeneous catalyst precursors.[1-3] Although the chemistry of 12-vertex hydridometallacarboranes of most of the platinum metals is well-documented, information on the syntheses and reactivity of the related osmium complexes remains rather scant. In an attempt to bridge this information gap and extend the scope of known osmacarborane clusters we have performed the syntheses of a series of mononuclear *closo*- and *exo*-*nido*-osmacarboranes derived from *nido*-7,8- and *nido*-7,9-$C_2B_9H_{12}^{2-}$. We have also carried out studies of their reactivity with an emphasis on the reactions of *exo*-*nido*-osmacarborane species leading to the construction of mixed-metal bimetallacarboranes of the novel type, *exo*-Os-*closo*-M′(L-L)-bimetallacarboranes [M′=Rh, Ir; L-L - η^4-cyclodiene ligands].

2 RESULTS AND DISCUSSION

2.1 Syntheses, Structural Characterization and Mechanistic Studies of the Formation of *closo*-Hydridoosmacarboranes

Recently, we have successfully synthesized the first series of *closo*-*bis*(phosphine)hydridoosmacarborane complexes, *closo*-3,3-$(Ph_3P)_2$-3-H-3-X-1,2-R_2-3,1,2-$OsC_2B_9H_9$ [R = H, X = Cl (1); R = X = H (2); R = Me, X = H (3)], by the reaction of $OsCl_2(PPh_3)_3$ with a slight excess of the corresponding $[nido\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_{10}]^-K^+$ under reflux in deoxygenated ethanol[4] (Scheme 1). Comparison of the course and the products of the reactions studied revealed some important differences. Thus, the reaction of $OsCl_2(PPh_3)_3$ with the unsubstituted carborane salt (R = H) produced a 1:1 mixture of monohydrido (1) and dihydrido (2) complexes of the *closo* type, whilst the reaction of the disubstituted salt (R = Me) with $OsCl_2(PPh_3)_3$ yielded only the dihydrido *closo*-osmacarborane (3) along with a small yield of an *exo*-*nido*-$[Cl(Ph_3P)_2Os]$-7,8-$Me_2C_2B_9H_{10}$ species (4) of symmetrical structure (see below).



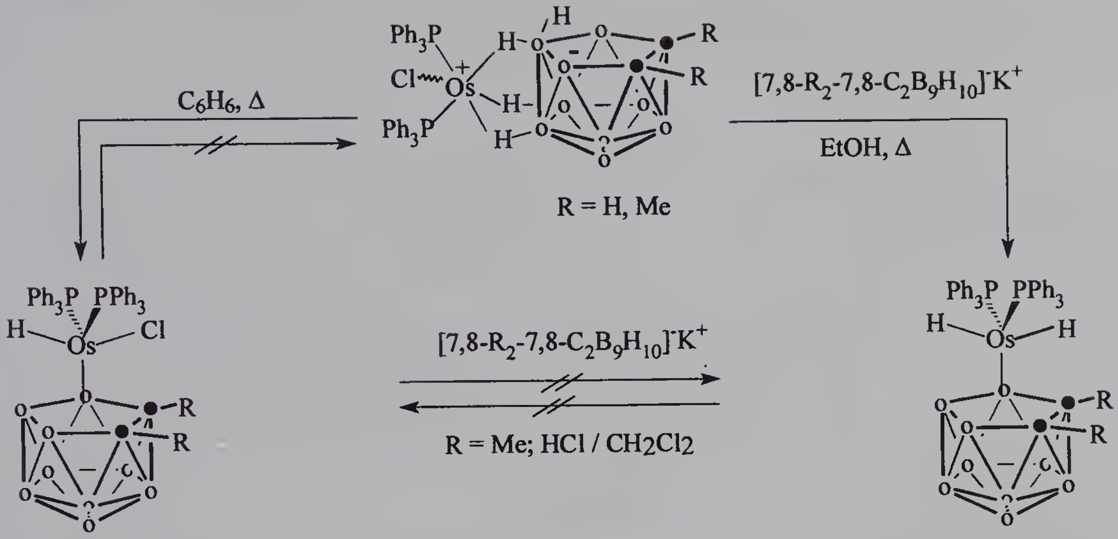
R=H, X=Cl (1); R=X=H (2);
R=Me, X=H (3)

R=Me (4)

Scheme 1

In an attempt to gain better insight into the possible mechanism of formation of complexes (1)-(3) several additional experiments have been carried out (Scheme 2). Since in the crude mixture of products of the reaction of $OsCl_2(PPh_3)_3$ with [*nido*-7,8-$C_2B_9H_{12}]^-$ K^+ no traces of unsubstituted *exo-nido*-[$Cl(Ph_3P)_2Os$]-7,8-$C_2B_9H_{12}$ (5) were detected, one may assume that the formation of *closo*-complex (1, R = H, X = Cl) proceeds *via* thermal *exo-nido* → *closo* rearrangement of (5), which might be expected as an intermediate species in the first stage of the reaction. Indeed, further experiments showed that the *closo*-isomer, (1), could be prepared quantitatively by the irreversible thermal rearrangement of (5) in either benzene or ethanol solutions. In contrast to (5), its dimethylsubstituted analogue *exo-nido*-[$Cl(Ph_3P)_2Os$]-7,8-$Me_2C_2B_9H_{10}$ (4) could not be converted into the corresponding *closo* isomer even upon heating in toluene at elevated temperature. At the same time, when a mixture of the *exo-nido* complexes (5) or (4) and the corresponding carborane salts [*nido*-7,8-R_2-7,8-$C_2B_9H_{10}]^-K^+$ (R = H, Me) was refluxed in ethanol, both dihydrido complexes, (2) and (3) respectively, were formed. This fact indicates that the anionic carborane salts can serve as the source of hydride ligands in the reactions discussed. On the other hand, our attempt to convert (1) into (2) by the reaction with [*nido*-7,8-$C_2B_9H_{12}]^-K^+$ in boiling ethanol solution, or to replace one of the two hydrido ligands in complex (3) by chloride by treatment with gaseous HCl, either in ethanol or CH_2Cl_2 solutions, failed. All these findings, taken together, suggest that the reactions discussed proceed stepwise through the intermediate *exo-nido*-complexes, and the final products are formed from these species by at least two competitive processes.

The structure of the two *closo*-complexes (1) and (3) has been determined by an X-ray diffraction study[4] which showed rather unexpected differences in the solid-state conformations of the apparently related $(Ph_3P)_2OsHX$ (X = H, Cl) moieties with respect to the open cage face of these molecules (Figure 1). Thus, in (3) one of the two PPh_3 groups is disposed not as far away as possible from the cage substituents as one might have expected. At the same time, the orientation of metal-containing group in (1) relative to the C_2B_3 plane of the carborane cage seems to be quite normal, with the chloride ligand occupying a position nearly *trans* to the B(8) atom, and is similar to those found in analogous ruthenium complexes.[5] We believe that the differences in the orientation of the P_2OsHX moieties with respect to the coordinating C_2B_3 planes of the carborane cage in (1) and (3) may reflect possible differences in the optimal overlap of the HOMO-LUMO nodal planes of the metal-containing groups (P_2OsHCl and P_2OsH_2) and dicarbollyl ligand orbitals.



R=H (1)

R=H (2), R=Me (3)

Scheme 2

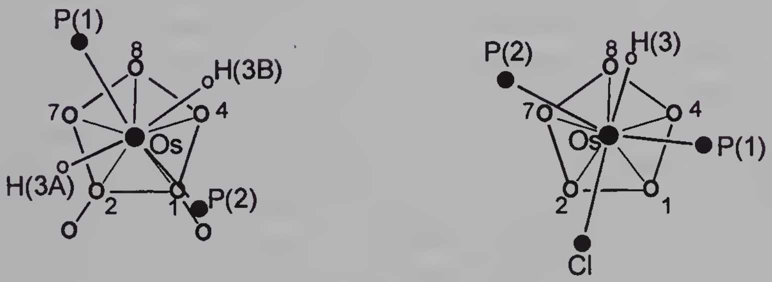
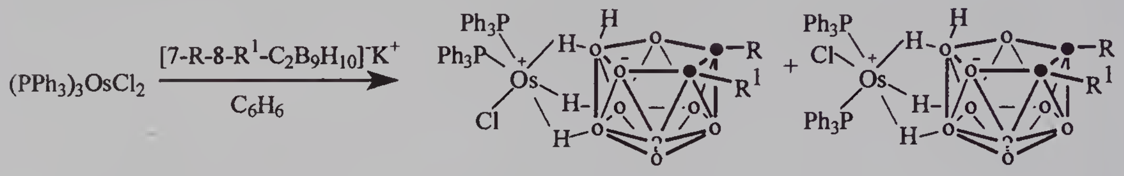


Figure 1 *View of the P_2OsH_2 and P_2OsHCl moieties and the C_2B_3 open carborane face coordinated to osmium in complexes (1) (right) and (3) (left)*

2.2 Direct Synthesis of *exo-nido*-Osmacarboranes and Their Isomerism

We have also developed the direct syntheses of a series of *exo-nido*-osmacarborane complexes with unsubstituted[6], monosubstituted and disubstituted[6] dicarbollyl ligands. Unlike the conditions previously used for the syntheses of *closo*-complexes (1) - (3), the reaction between the same reagents in benzene at room temperature for approximately 3 h afforded *exo-nido* products (5) and (4) in 73 and 85% yields, respectively. Several other mono- and disubstituted *exo-nido*-osmacarboranes (6) - (8) have been successfully prepared by the same method as shown below in the Scheme 3. Remarkably, when the reaction time of $OsCl_2(PPh_3)_3$ with $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-K^+$ was increased to 24 h, a mixture of *exo-nido-* (5) and *closo-* (1) isomers in the ratio of 3:1 was formed. This can apparently be explained by the *exo-nido* → *closo* rearrangement of (5), and was confirmed by ^1H NMR monitoring experiments with the pure unsubstituted *exo-nido*-osmacarborane (5). It was shown that the isomerization of (5) into its *closo*-isomer (1) proceeds in solution under very mild conditions in contrast to those required for the ruthenium congener[5] where the corresponding *closo*-isomer had not been detected in the solution of *exo-nido* species upon monitoring by ^1H NMR.



$R=R^1=Me$ (4); $R=R^1=H$ (5);
$R=R^1=PhCH_2$ (6); R=H, $R^1=Me$ (7);
$R,R^1=1,2\text{-}C_6H_4(CH_2)_2$ (8)

Scheme 3

All “three-bridged” *exo-nido*-osmacarboranes obtained were found to exist as mixture of symmetrical and unsymmetrical isomers both in solution and in the solid state. These seem to possess different thermodynamic and kinetic stabilities; which most probably accounts for our failure to obtain pure unsymmetrical species by fractional crystallization. However, small fractions of complexes (4) and (8) enriched to 90 % unsymmetrical isomers were available after several fractional crystallizations of the corresponding isomeric mixtures. Nevertheless, our attempts to grow crystals of the unsymmetrical isomer (8) suitable for an X-ray diffraction experiment were unsuccessful, and those crystals obtained by slow crystal growth proved to have the symmetrical structure (see Figure 2). Only one pair of absolutely pure isomeric complexes (6a, b) has been successfully prepared, using quantitative separation of (6) using column chromatography on silica-gel. This allowed us to prove the existence of geometrical isomerism of these complexes in solution by a detail examination of their ^1H, $^{31}P\{^1H\}$, ^{11}B NMR spectra and by analysis of long-range coupling constants, $^2J_{P\text{-}H}$, observed in the $^1H\{^{11}B\}$ NMR spectra. Finally, it has been found that in solution the unsymmetrical isomer (6b) undergoes slow isomerisation to the symmetrical isomer (6a). Upon gentle heating in benzene this reaction proceeds much more rapidly, accompanied by some decomposition of (6b).

We have also investigated the reactions of $OsCl_2(PPh_3)_3$ with anionic *nido*-carborane salts derived from $1,7\text{-}C_2B_{10}H_{12}$. It has been found that the reactions of $OsCl_2(PPh_3)_3$ with [*nido*-7-R-7,9-$C_2B_9H_{11}$]$^-$$K^+$, when carried out in benzene at ambient temperature, resulted in the formation of the novel complex *exo-nido*-[$(Ph_3P)_2OsHCl$]-7-R-10,11-$(\mu\text{-}H)_2$-7,9-$C_2B_9H_{10}$ [R=H (9), R=Ph (10)] along with some amount of the zwitterionic side product *nido*-7-R-7,9-$C_2B_9H_{10}PPh_3$ (Scheme 4).

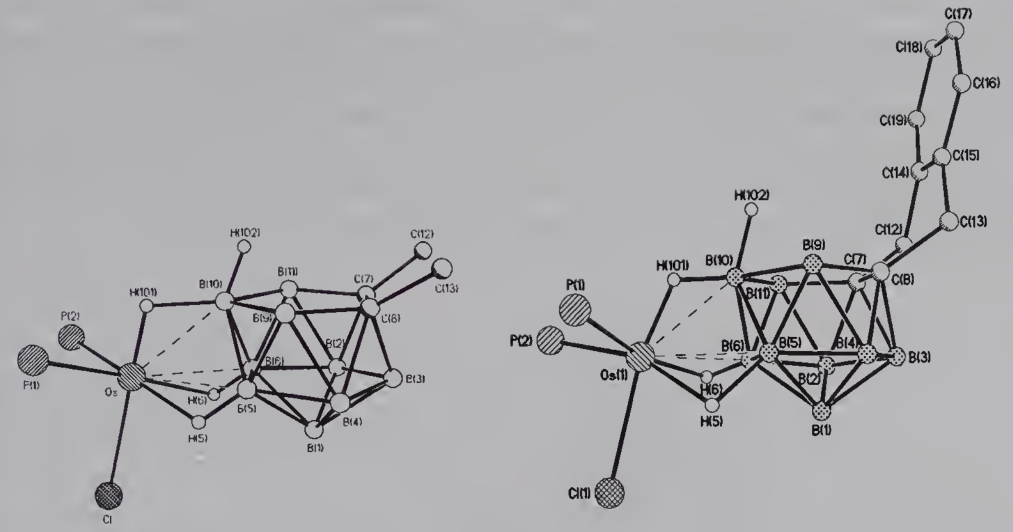
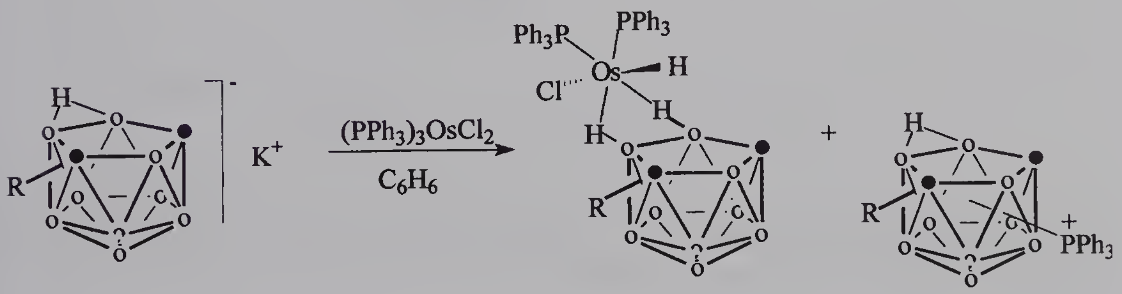


Figure 2 *Molecular structures of symmetrical isomers of complexes (4) (left) and (8) (right), respectively*



R=H (9),
R=Ph (10)

R=H, Ph

Scheme 4

The structure of complex (9) which has been determined by X-ray diffraction study (Figure 3) proved to be rather unusual. The high quality of single crystal of (9) allowed us to locate and reliably refine all hydrogen atoms in the molecule including the terminal hydride at the metal center [Os-H, 1.64(8) Å]. Nevertheless, it was impossible to elucidate the positions of "extra-hydrogen" atoms which by analogy with other known *exo-nido*-metallacarborane complexes are believed to be located over the cage open face. The ^1H and $^1H\{^{11}B\}$ NMR spectra of (9) also revealed the absence of these "extra-hydrogen" atoms in this molecule. These spectra showed only two high-field resonances at δ -5.8 (2H, BH) and -13.6 (1H, OsH) ppm with a 2:1 intensity ratio. Taking this into account, complex (9) may be formally regarded as 16e Os^{IV} species, such as has not previously been characterized in organoosmium chemistry. Alternatively, one may consider the H-atom attached to the metal vertex in (9) as a "semi-bridging" hydrogen which is participating in a weak bonding interactions with the two cage boron atoms B(10) and B(11) thus forming a four-center [OsHB(10)B(11)] two-electron bond system. Complex (9) may be regarded, therefore, as a zwitterionic Os^{II} species where the osmium atom has a saturated 18e shell. Since the chloride ligand at the metal center in (9) occupies a position *trans* to the "semi-bridging" hydrido ligand, we believe that the structural *trans*-influence of the former might have played a crucial role in the strengthening of a bridging B(10)...H...B(11) interaction [B(10)...H(Os), 2.17 Å, B(11)...H(Os), 2.34 Å] and the shortening of the Os...H distance in the structure of (9). Such an effect, moreover, is responsible for the observed octahedral configuration preferred by an Os^{II} atom in various organoosmium compounds.

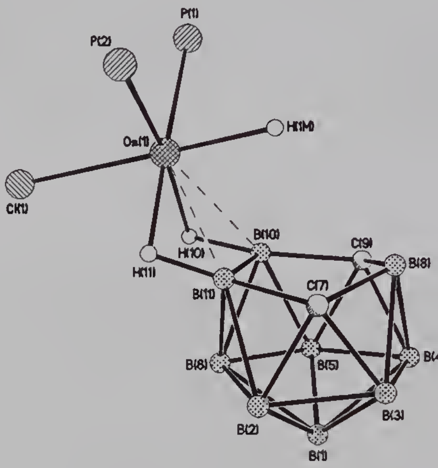


Figure 3 *Molecular structure of complex (9)*

2.3 *exo-nido*-Osmacarboranes as "Osmadicarbollide-ions" Precursors in the Synthesis of Mixed-Metal Bimetallacarboranes

Recently, we have published a convenient syntheses of a series novel bimetallic Ru-Rh carborane complexes (η^4-diene)M(μ-H)Ru(PPh_3)$_2$(η^5-$C_2B_9H_{11}$) (M = Rh, diene = COD, NBD; M = Ir, diene = COD) using the unsubstituted *exo-nido*-[Cl(Ph_3P)$_2$Ru]-7,8-$C_2B_9H_{12}$ as a precursor[7]. The reactions proceed in the presence of a base (KOH/EtOH) acting as a "sponge" for the "extra-hydrogen" atom from the starting *exo-nido*-ruthenacarborane and result in the formation of an apparent intermediate "*exo*-ruthenadicarbollide-ion". If this anionic species could be obtained as a stable salt, it would be a new convenient reagent for the selective η^5-bonding of other metal-containing moieties. However, when *exo-nido*-ruthenacarborane loses the "extra-hydrogen" atom, another intermediate anionic species *closo-bis*(phosphine)hydridoruthenacarborane is formed instead which then readily reacts with μ-halide rhodium or iridium dimers of the type [(η^4-diene)MCl]$_2$ to give the final binuclear products.

In contrast, we have now found that *exo-nido*-[Cl(Ph_3P)$_2$Os]-7,8-$C_2B_9H_{12}$ (5) when reacts with the same reagents (KOH with subsequent treatment by μ-halide rhodium or iridium dimeric complexes [(η^4-diene)MCl]$_2$) and under the same conditions (EtOH, room temperature) to produce bimetallacarboranes with a different structure, namely, *closo*-3,3-(η^4-diene)-8,9,12-{*exo*-[Cl(Ph_3P)$_2$Os]}-8,9,12-(μ-H)$_3$-3,1,2-M-$C_2B_9H_8$ [M = Rh, diene = COD (11); M = Rh, diene = NBD (12); M = Ir, diene = COD (13)]. From the results of the X-ray diffraction study of complex (11) (Figure 4), the osmium atom in (11) retains the same *exo*-position as in the starting cluster (5) relative to the carborane cage and is connected with the cage boron atoms by means of three 2e-3c bridging B-H...Os bonds, while the Rh atom coordinated by η^4-COD ligand is η^5- coordinated to the cage open face.

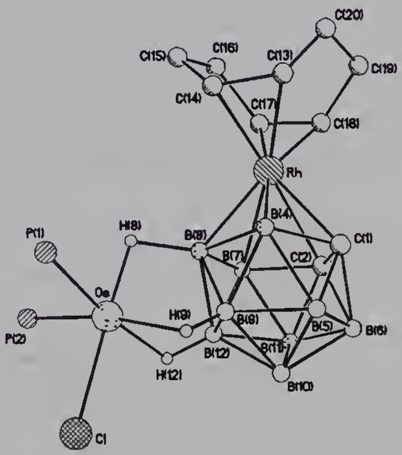


Figure 4 *Molecular structure of symmetrical isomer of complex (11)*

It should be noted that the complexes (11)-(13) were also found to exist as a mixture of symmetrical and unsymmetrical isomers but, in this case, with significant predominance of the latter in the crude isomeric mixtures (ratio of ~95:5). Once again, however, the X-ray diffraction experiment performed for the crystal of unsymmetrical isomer of (11b) after its thorough separation and slow crystallization, failed to provide direct evidence for the unsymmetrical structure. This stimulated us to undertake the study of solution behavior of individual isomeric complexes (11a) and (11b) by monitoring their ^1H NMR spectra in the hydride region under non-kinetic conditions. It was found that the isomeric complex (11a) after storage for some time in CH_2Cl_2 solution was in equilibrium with (11b). The same was true when an analogous experiment was carried out with pure isomer (11b). Interconversion between isomers appears to be slow on the ^1H NMR timescale, and is both solvent and temperature dependent. Thus, after heating of each isomer in CH_2Cl_2 at 35-36 °C for three days, the final ratio of (11a) to (11b) was ca. 2.5:1, respectively. The equilibrium with K_{eq} ~2.5 is reached much more rapidly from the unsymmetrical isomer (11b).

ACKNOWLEDGMENTS.

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REFERENCES

1. J. A. Belmond, J. Soto, R. E. King III, A. J. Donaldson, J. D. Hewes, M. F. Hawthorne, *J. Am. Chem. Soc*, 1989, **111**, 7475 and references therein.
2. A. Felekidis, M. Goblet-Stachow, J. F. Liégeois, B. Pirotte, J. Delarge, A. Demonceau, M. Fontaine, A. F. Noels, I. T. Chizhevsky, T. V. Zinevich, V. I. Bregadze, F. M. Dolgushin, A. I. Yanovsky and Yu. T. Struchkov, *J. Organomet. Chem.,* 1997, **536-537**, 405 and references therein.
3. F. Teixidor, M. A. Flores, C. Viñas, R. Kivekäs, R. Sillanpää, *Angew. Chem. Int. Ed. Engl.,* 1996, **35**, 2251.
4. I. T. Chizhevsky, P. V. Petrovskii, P. V. Sorokin, V. I. Bregadze, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, A. Demonceau and A. F. Noels, *Organometallics*, 1996, **15**, 2619.
5. I. T. Chizhevsky, I. A. Lobanova, V. I. Bregadze, P. V. Petrovskii, A. V. Polyakov, A. I. Yanovsky and Yu. T. Struchkov, *Organomet. Chem. U.S.S.R.*, 1991, **4**, 469 (*Engl. Transl.*).
6. G. D. Kolomnikova, P. V. Sorokin, I. T. Chizhevsky, P. V. Petrovskii, V. I. Bregadze, F. M. Dolgushin and A. I. Yanovsky, *Izv. Akad. Nauk, Ser. Khim.,* 1997, **46**, 1971 (*Engl. Transl.*).
7. I. T. Chizhevsky, I. A. Lobanova, P. V. Petrovskii, V. I. Bregadze, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, A. L. Chistyakov, I. V. Stankevich, C. B. Knobler and M. F. Hawthorne, *Organometallics,* 1999, **18**, 726.

Towards Experimental Mapping of the Mechanism of Heteroborane Isomerisation

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1 INTRODUCTION

The classic isomerisation in heteroborane chemistry is the 1,2 → 1,7 and → 1,12 isomerisation of the icosahedral carborane $C_2B_{10}H_{12}$ (Figure 1). King [1] has shown that the icosahedron is an inherently rigid cluster, and, fully consistent with this, it has been known for many years that high temperatures are required to isomerise $C_2B_{10}H_{12}$. Thus 1,2-$C_2B_{10}H_{12}$ isomerises to the 1,7 isomer at 450 °C, [2] and to the 1,12 isomer at >600 °C, [3] and for the former process an activation energy of *ca.* 260 kJ mol^{-1} has been measured. [4]

Figure 1 *Isomerisation of* $C_2B_{10}H_{12}$

Even before the first report of the isomerisation of $C_2B_{10}H_{12}$, and certainly ever since, there have been numerous theories advanced for the mechanism of heteroborane isomerisation. A summary of some of the key developments follows. The earliest suggestion, Lipscomb's "hextuple concerted diamond-square-diamond" (dsd) mechanism, [5] proceeding *via* a cube-octahedral intermediate, elegantly accounts for the 1,2 → 1,7 isomerisation and is still frequently cited in textbooks on inorganic chemistry. Lipscomb was later to modify this mechanism to allow for rotation of the triangular faces in the cube-octahedral intermediate. [6] Early alternative suggestions were the "pentagonal twist" [2] and the "triangle face rotation" (tfr) [7] mechanisms. A development of the latter is the "extended tfr" mechanism of Wu and Jones [8], whilst Wong and Lipscomb [9] and later Edvenson and Gaines [10] have suggested the involvement of nido intermediates. Finally, Wales and co-workers have considered that these isomerisations might occur *via* a series of stepwise dsd processes involving both transition states and intermediates of relatively low symmetry. [11] It transpires that it is these mechanistic predictions of Wales to which our experimental studies, described herein, stand most comparison.

In spite of a plethora of theories, definitive experimental work on the mechanism of heteroborane isomerisation is lacking, for two basic reasons. Firstly, labelling studies (in which substituents are attached to various cluster vertices and the fate of these vertices in the isomerised form determined by structural study) are flawed because the high temperatures usually required mean that the integrity of the vertex—substituent bond cannot be guaranteed. Secondly, until very recently no intermediate in the isomerisation process, the structural identification of which would have provided an important signpost in the isomerisation pathway, had ever been isolated. In the studies described below we describe heteroborane systems that isomerise at room temperature or below (thus allowing labelling studies to be performed with confidence) and which have isolatable isomerisation intermediates.

2 METALLACARBORANES

Our work involves the isomerisation of metallacarboranes. Figure 2a shows the isomerisation of 3-(η-C_5H_5)-3,1,2-*closo*-$CoC_2B_9H_{11}$ to the 2,1,8-CoC_2B_9 isomer, [12] demonstrating that this mirrors the isomerisation of 1,2 → 1,7 $C_2B_{10}H_{12}$ – in both species the net change is 1,2 → 1,7 C atom isomerisation, and the isomerisation temperatures are very similar. However, as early as 1984 Hawthorne had shown that pre-organising for the starting metallacarborane to be sterically crowded could lead to a dramatic reduction in isomerisation temperatures, the ^{t}Bu-substituted 3,1,2-RhC_2B_9 species of Figure 2b isomerising (also in 1,2 → 1,7 fashion) at only 65 °C. [13]

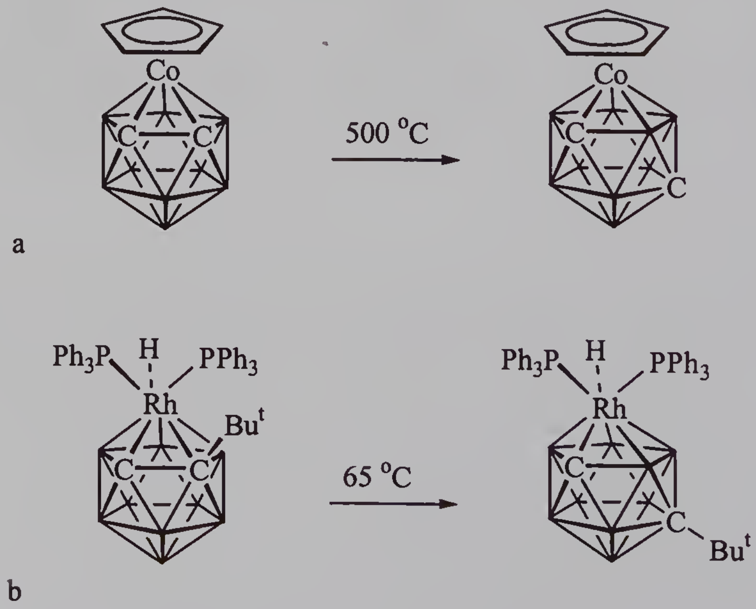


Figure 2 *Isomerisation of metallacarboranes*

This outlines the approach we have adopted. We begin with a nido 7,8-C_2B_9 carborane ligand with bulky substituents (usually Ph groups) attached to the cage C atoms. Metallation with a sterically demanding {ML_x} fragment affords the transient 3,1,2-MC_2B_9 species, which isomerises at low temperature to relieve overcrowding (Figure 3a). An actual example is shown in Figure 3b. Treatment of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$ with a source of {$Pt(PR_3)_2$}$^{2+}$ (PR_3 = wide variety of phosphines) yields only the net 1,7 C isomerised platinacarborane at room temperature, presumably *via* the transient 3,1,2-PtC_2B_9 species shown.

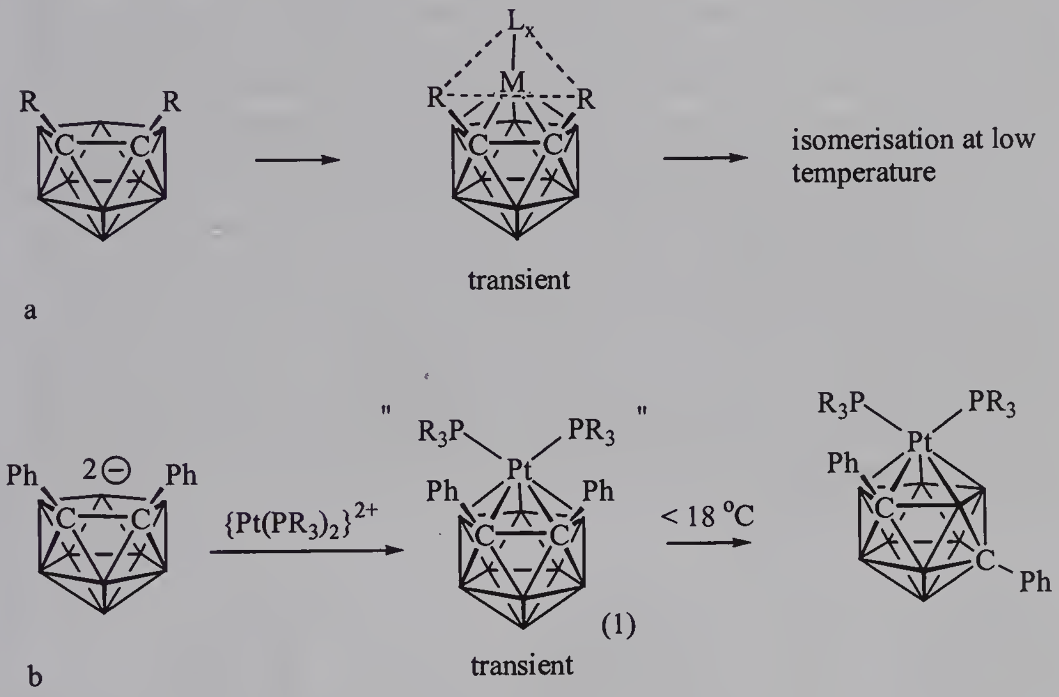
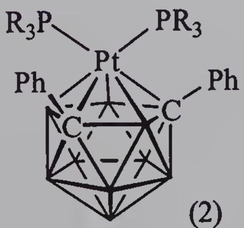


Figure 3 *Low-temperature isomerisation of transient, overcrowded, metallacarboranes*

This simple result already provides an opportunity to test one of the established isomerisation mechanisms. If the hextuple concerted dsd mechanism operates, the transient platinacarborane (1) would transform into the C-separated species (2) which, since it is not observed, must also be transient. However, we have synthesised (2) by an alternative strategy and shown it to be stable to further isomerisation in refluxing toluene.[14] Therefore we can rule out the hextuple concerted dsd mechanism in this system at least.

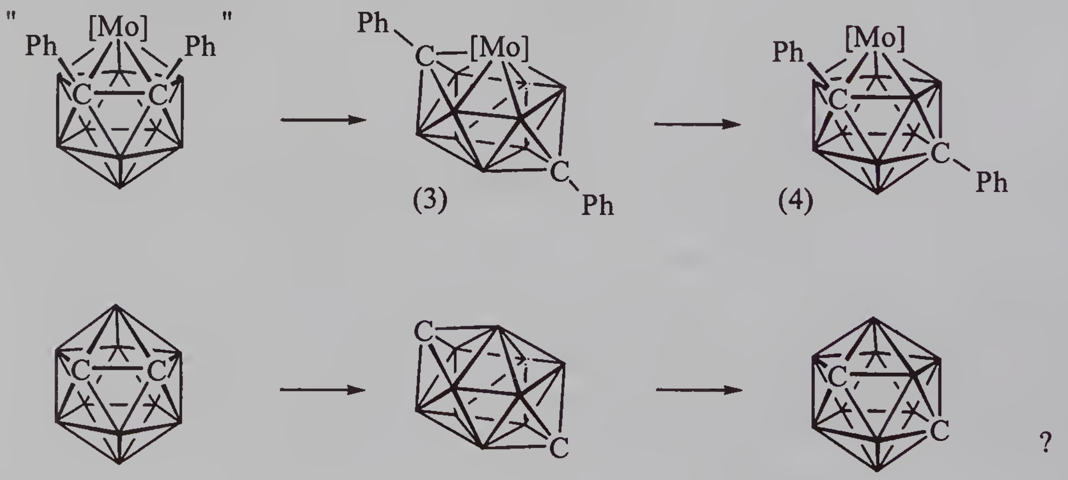


(2)

3 ISOLATION OF INTERMEDIATES

It is only partially satisfying to disprove one mechanism and clearly better to be able to say something positive about another. This we have done *via* the isolation, for the first time, of an intermediate in the isomerisation of one icosahedral heteroborane into another.

Metallation of $[7\text{-Ph-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^{2-}$ with a source of $\{Mo(\eta\text{-}C_3H_5)(CO)_2\}^+$ at room temperature yields the expected $3,1,2\text{-}MoC_2B_9$ icosahedron, characterised by spectroscopic and crystallographic techniques. In particular ν(CO) occurs at *ca.* 1920 and 1830 cm^{-1} for this species, and it turns out that these frequencies are diagnostic of this type of anionic icosahedral molybdacarborane. However, similar metallation of $[7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$ does not form an icosahedral product, as evidenced by ν(CO) values of *ca.* 1950 and 1890 cm^{-1}. Crystallographic study revealed structure (3), a closed but non-icosahedral species in which the Mo atom and one B atom are 6-connected with respect to the cage, and both the cage C atoms are 4-connected and substantially separated (*ca.* 390 pm). Most importantly, (3) is only the kinetic product of the reaction. In solution it slowly transforms at room temperature (rapidly with gentle warming) into a new product displaying ν(CO) values typical of an icosahedron (*ca.* 1920 and 1830 cm^{-1}) and ultimately shown to be the 1,7 C isomerised species (4). Assuming that the first product of the reaction is the (overcrowded) $3,1,2\text{-}MoC_2B_9$ species, these results identify (3) as an intermediate in the isomerisation of a $3,1,2\text{-}MC_2B_9$ heteroborane into its $2,1,8\text{-}MC_2B_9$ isomer (Scheme 1).[15] Does $1,2\text{-}C_2B_{10}H_{12}$ isomerise to $1,7\text{-}C_2B_{10}H_{12}$ *via* an intermediate of similar-shape?



Scheme 1 *Intermediate isolated in the isomerisation of a metallacarborane*

We believe that the answer to this question is almost certainly "Yes", since a carborane of this shape has previously been identified by Wales[11] as a relatively stable intermediate in a theoretical study of the 1,2 → 1,7 isomerisation of $C_2B_{10}H_{12}$. Wales finds that $1,2\text{-}C_2B_{10}H_{12}$ isomerises through a series of sequential dsd steps (Figure 4) *via* low symmetry intermediates (C_s, C_2, C_1) linked by higher energy transition states. The C_2 form is the most stable intermediate, and has the same shape as isolated (3). "b", "f" and "i" are double dsd, and "e", "j" and "k" triple dsd pathways. Thus there is only one route predicted from 1,2-$C_2B_{10}H_{12}$ to the C_2 intermediate (b+e), but two alternatives from the C_2 form to 1,7-$C_2B_{10}H_{12}$ (f+k+i or j+i).

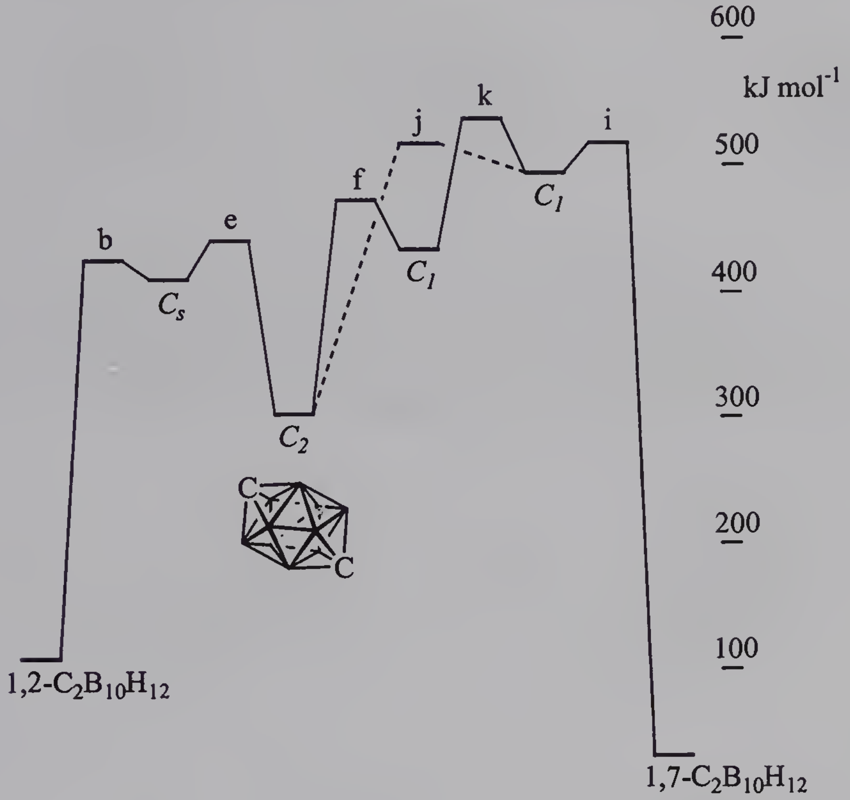


Figure 4 *Potential energy diagram for the isomerisation of 1,2-$C_2B_{10}H_{12}$ to 1,7-$C_2B_{10}H_{12}$* [11]

4 TRACKING VERTICES

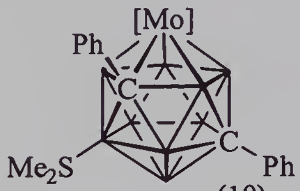
Following Wales' scheme we can track the theoretical movement of every vertex in the polyhedron as the isomerisation proceeds. By labelling vertices we can do the same thing experimentally and so compare theory with experiment.

The first and simplest labelling study is merely to have the metal fragment at vertex 3 in the (transient) overcrowded metallacarborane. Following route b+e one predicts one isomer of the "C_2" intermediate in which the heteroatoms (M and C) are in the same positions actually determined for (3). Thereafter route f+k+i predicts (one isomer of) an isomerised icosahedron (5), observed as compound (4), whilst route j+i would predict (one isomer of) an alternative icosahedron (6), not observed.

The next labelling strategy is to attach a substituent to a boron vertex of the carborane ligand and to determine the location of that vertex in the isomerised metallacarborane (and any intermediate species isolated *en route* to it). The value of this strategy depends upon the assumption of no B—substituent bond breaking (and remaking elsewhere) as the isomerisation proceeds. Given the low temperatures of these sterically-induced isomerisations, this assumption is reasonable.

(5)

(6)



(10)

We have metallated (with Mo) [7,8-Ph$_2$-10-SMe$_2$-7,8-*nido*-C$_2$B$_9$H$_8$]$^-$ and observed (Figure 5) a single intermediate (7) and from it a single isomerised icosahedron (8).[16] Whilst route b+e applied to the notional transient species (9) correctly predicts the location of the labelled boron atom in (7), route f+k+i does not predict (8), rather, species (10), in which the labelled B atom is no longer directly connected to Mo.

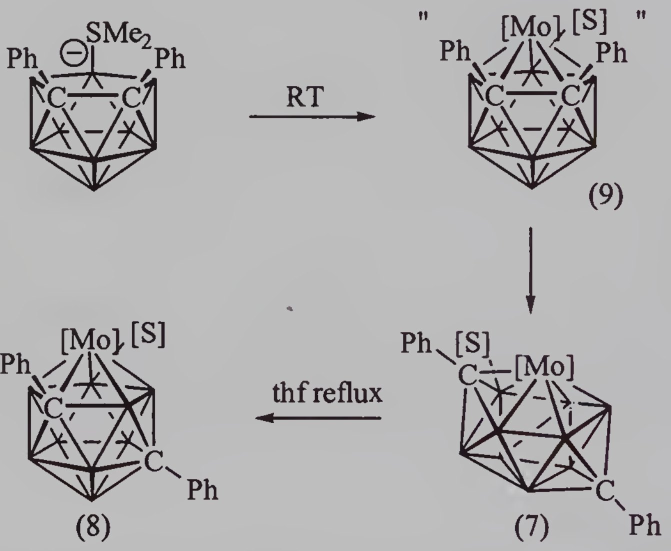


Figure 5 *Metallation of [7,8-Ph$_2$-10-SMe$_2$-7,8-nido-C$_2$B$_9$H$_8$]$^-$. [Mo] = Mo(η-C$_3$H$_5$)(CO)$_2$; [S] = SMe$_2$.*

Asymmetric labelling of the starting carborane is predicted to lead to two intermediates and thence two isomerised species (assuming equivalent groups on the cage C atoms). In keeping with this, we find[17] that metallation (with Mo) of [7,8-Ph$_2$-9-SMe$_2$-7,8-*nido*-C$_2$B$_9$H$_8$]$^-$ yields intermediates (11) and (12), and then, on gentle warming, final products (13) and (14), respectively (Figure 6). Once again, theory correctly predicts the label positions in the intermediates; but this time route f+k+i correctly predicts the location of the S-bonded B atoms in (13) and (14) as well.

Thus, overall, we find good correspondence between the theoretical predictions of Wales and our experimental results. Together these point towards the mechanism of isomerisation of icosahedral heteroboranes being *via* a series of sequential dsd steps, route b+e producing an isolatable intermediate and route f+k+i then producing the isomerised species. With one exception, compound (8), theory predicts the correct stereochemistry of the intermediates and products.

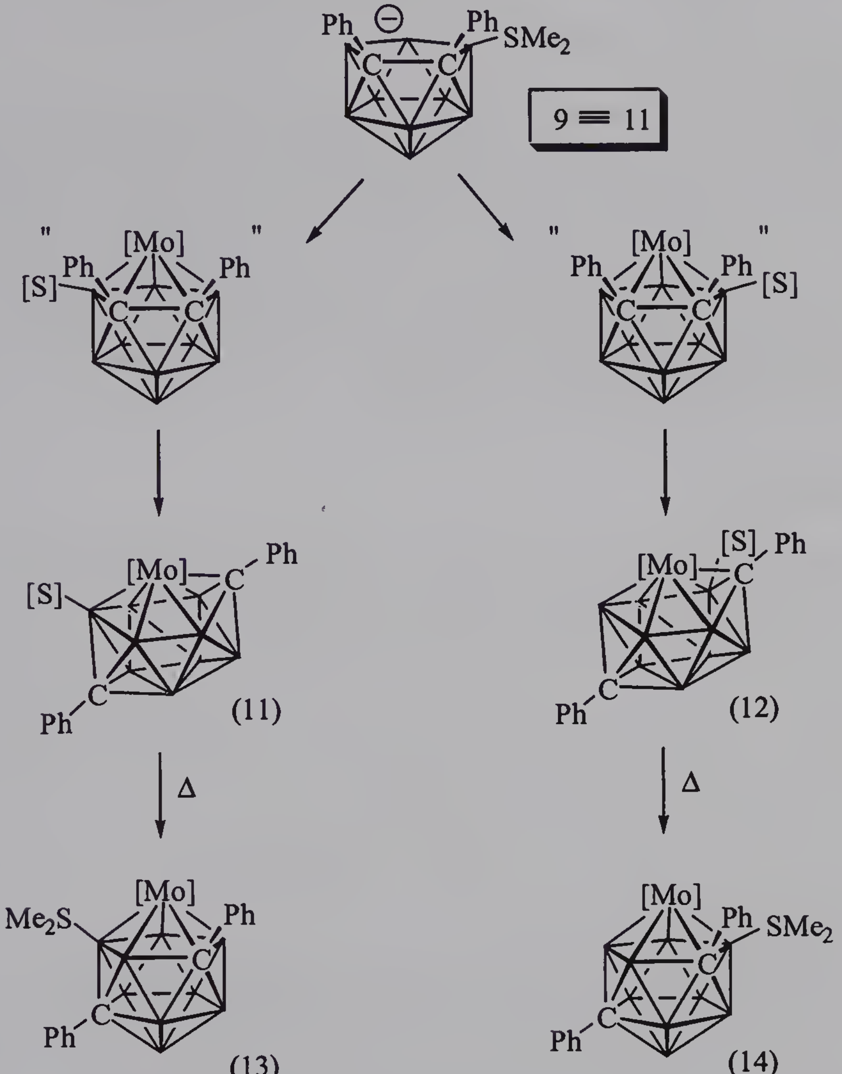


Figure 6 *Metallation of* $[7,8\text{-}Ph_2\text{-}9\text{-}SMe_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_8]^-$. *[Mo] = Mo(η-*$C_3H_5)(CO)_2$*; [S] =* SMe_2.

The importance of the isolation of intermediates in these reactions cannot be overemphasised since compounds (8), (13) and (14) could all be rationalised by single tfr transformations of the appropriate overcrowded, pre-isomerised, icosahedral species.

Future studies will include further work on the isomerisation of icosahedra derived from 10-labelled nido carboranes (since this is the only area of current disagreement between theory and experiment) and attempt to extend our present work by attaching and following appropriate labels on all other symmetry-independent boron atoms in $[7,8\text{-}Ph_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$. By these means we hope to build up a complete experimental mapping of the mechanism of the net 1,2 → 1,7 carbon atom isomerisation of icosahedral carborane, and to establish the comparability of that mechanism with current theory.

5 OTHER ISOMERISATIONS

The work described above relates only to the 3,1,2-MC_2B_9 → 2,1,8-MC_2B_9 isomerisation (net 1,2 → 1,7 C atom isomerisation) of icosahedral metallacarboranes. However, the strategy we have adopted (sterically-induced low-temperature isomerisations) to gain mechanistic insight into these isomerisations should also be amenable to 3,1,2-MC_2B_9 → 4,1,2-MC_2B_9 isomerisation [18] (net "1,2 → 1,2" C atom isomerisation) and we are currently pursuing this possibility. Finally, it is fascinating to note that Wales [11] has identified an isomerisation pathway from the C_2 intermediate form of $C_2B_{10}H_{12}$ to 1,12-$C_2B_{10}H_{12}$ without passing through 1,7-$C_2B_{10}H_{12}$. We will search for crowded metallacarboranes that will mimic this rearrangement.

Acknowledgements

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References

1. R. B. King, *Inorg. Chim. Acta,* 1981, **49**, 237.
2. D. Grafstein and J. Dvorak, *Inorg. Chem.,* 1963, **2**, 1123.
3. S. Papetti and T. L. Heying, *J. Am. Chem. Soc.,* 1964, **86**, 2295.
4. R. M. Salinger and C. L. Frye, *Inorg. Chem.,* 1965, **4**, 1815.
5. W. N. Lipscomb, *Science,* 1966, **153**, 373.
6. W. N. Lipscomb *et al, J. Am. Chem. Soc.,* 1967, **86**, 4218.
7. L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR,* 1966, **169**, 590.
8. S.-h. Wu and M. Jones, *J. Am. Chem. Soc.,* 1989, **111**, 5373.
9. H. S. Wong and W. N. Lipscomb, *Inorg. Chem.,* 1975, **14**, 1350.
10. G. M. Edvenson and D. F. Gaines, *Inorg. Chem.,* 1990, **29**, 1210.
11. D. J. Wales, *J. Am. Chem. Soc.,* 1993, **115**, 1557 and references therein.
12. M. F. Hawthorne *et al, J. Am. Chem. Soc.,* 1972, **94**, 6679.
13. M. F. Hawthorne *et al, J. Am. Chem. Soc.,* 1984, **106**, 2965.
14. A. J. Welch and A. S. Weller, J. *Chem. Soc., Dalton Trans.,* 1997, 1205.
15. S. Dunn, G. M. Rosair, Rh. Ll. Thomas, A. S. Weller and A. J. Welch, *Angew. Chem. Int. Ed. Engl.,* 1997, **36**, 645.
16. S. Dunn, R. M. Garrioch, G. M. Rosair, L. Smith and A. J. Welch, *Collect. Czech. Chem. Commun.,* 1999, **64**, 1013.
17. S. Dunn, G. M. Rosair, A. S. Weller and A. J. Welch, *J. Chem. Soc., Chem. Commun.,* 1998, 1065.
18. R. M. Garrioch, P. Kuballa, K. S. Low, G. M. Rosair and A. J. Welch, *J. Organometal. Chem.,* 1999, **575**, 57.

Metallatricarbollide Ligands – Analogues of $[\eta^5\text{-}C_5H_5]^-$

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1 INTRODUCTION

The chemistry of the eleven-vertex *nido* tricarbaboranes (tricarbollides) is, in contrast to that of the dicarbollides[1] one of the youngest areas of carborane chemistry. It was as late as in 1995 when the first representatives of this family were reported.[2] Essentially, there are two synthetic routes leading to tricarbollide compounds: cyanide and isonitrile methods.[3] The cyanide method is based on a room-temperature reaction between the dicarbaborane

$$\underset{\mathbf{1}}{5,6\text{-}C_2B_8H_{12}} + CN^- \rightarrow \underset{\mathbf{2a^-}}{[7\text{-}H_2N\text{-}7,8,9\text{-}C_3B_8H_{10}]^-} \qquad (1)$$

$$\underset{\mathbf{1^-}}{[5,6\text{-}C_2B_8H_{11}]^-} + Bu^tNC \rightarrow \underset{\mathbf{2b^-}}{[7\text{-}Bu^tNH\text{-}7,8,9\text{-}C_3B_8H_{10}]^-} \xrightarrow{\text{protonation}} \qquad (2)$$
$$\underset{\mathbf{2b}}{7\text{-}Bu^tNH_2\text{-}7,8,9\text{-}C_3B_8H_{10}}$$

nido-5,6-$C_2B_8H_{12}$ (**1**) and aqueous NaCN (Eq. 1) which produces the anion [7-H_2N-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2a**$^-$) (yield 30%), while the reaction of the [*nido*-5,6-$C_2B_8H_{11}]^-$ (**1**$^-$) anion with Bu^tNC (glyme, RT), followed by protonation (Eq. 2), gives the zwitterionic compound 7-Bu^tNH_2-*nido*-7,8,9-$C_3B_8H_{10}$. (**2b**) (yields 45-60%). Both compounds **2a**$^-$ and **2b** can be then converted into 7-Me_3N-*nido*-7,8,9-$C_3B_8H_{10}$ (**2c**) via methylation on the N-centre.[2] Subsequent reaction of **2c** with metallic sodium results in deamination to yield the parent compounds [*nido*-7,8,9-$C_3B_8H_{11}]^-$ (**3**$^-$) and *nido*-7,8,9-$C_3B_8H_{12}$ (**3**).[4] Compounds **2c** and **3**$^-$ undergo thermal rearrangement of into the isomeric species 10-Me_3N-*nido*-7,8,10-$C_3B_8H_{10}$ (**4a**) and [*nido*-7,8,10-$C_3B_8H_{11}]^-$ (**5**$^-$).[5] Anion **3**$^-$ and its aminoderivatives **2**$^-$ (derived by deprotonation of compounds **2** on the exoskeletal N atom) are ideal cluster analogues of the η^5-cyclopentadienyl (Cp) anion, and we have reported to the previous IMEBORON[6,7] siting experiments on the formation of the isomeric *closo* cyclopentadienyl ferratricarbollides, analogues of ferrocene. These were isolated from complexation reactions of the Tl^+ salts, as outlined in Eqs 3 and 4:

$$\underset{\mathbf{3^-}}{\mathrm{Tl^+[7,8,9\text{-}C_3B_8H_{11}]^-}} + \mathrm{[CpFe(CO)_2I]} \xrightarrow[\text{2. heating of the isomeric mixture at 350°C}]{\text{1.toluene, reflux}} \mathrm{TlI} + \underset{\mathbf{6}}{\mathrm{[2\text{-}Cp\text{-}2,1,7,10\text{-}FeC_3B_8H_{11}]}} \qquad (3)$$

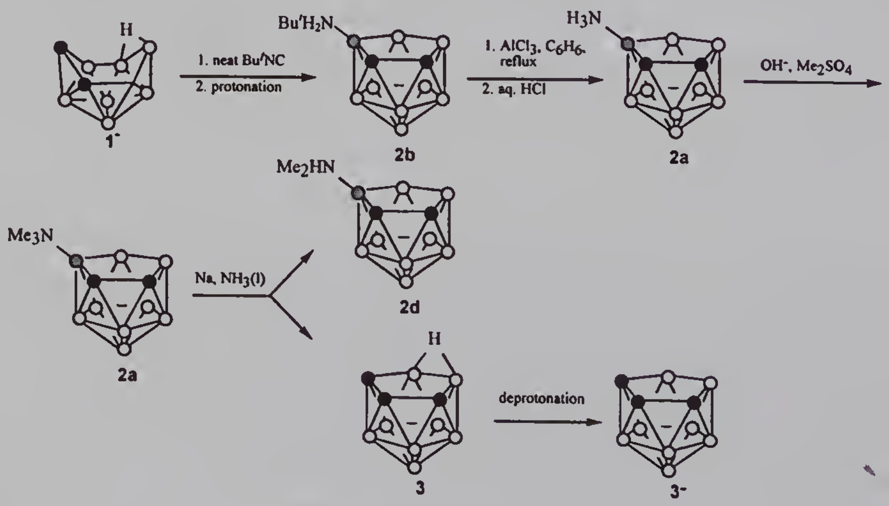
$$\underset{\mathbf{2^-}}{\mathrm{Tl^+[7\text{-}R^1R^2N\text{-}7,8,9\text{-}C_3B_8H_{10}]^-}} + \mathrm{[CpFe(CO)_2I]} \xrightarrow{\text{toluene, reflux}} \mathrm{TlI} + \underset{\mathbf{7}}{\mathrm{[2\text{-}Cp\text{-}9\text{-}R^1R^2N\text{-}2,1,7,9\text{-}FeC_3B_8H_{10}]}} \qquad (4)$$

where $R^1R^2N = H_2N$ **7a**, Bu^tHN **7b**, and Me_2N **7c**

A similar reaction of the isomeric anion **5⁻** with $[CpFe(CO)_2I]$, however, gave the 11-vertex metallatricarbaborane [1-Cp-1,2,3,4- *closo*-$FeC_3B_7H_{10}$] (**8**).[6]

2 NEW DEVELOPMENTS IN THE CHEMISTRY OF TRICARBOLLIDE LIGANDS

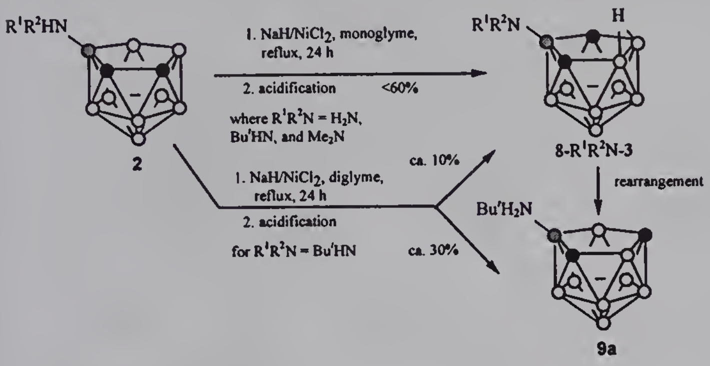
We have reported just recently an improved synthesis of Eq. 2 above (see Scheme 1).[8] Evaporation of a solution of $Na^+[5,6\text{-}C_2B_8H_{11}]^-$ (**1⁻**) in neat Bu^tNC leads to the isolation of compound **2b** in yields up to 90 %. Subsequent reaction of **2b** with $AlCl_3$ removes the Bu^t substituent to give 7-H_3N-*nido*-7,8,9-$C_3B_8H_{10}$ (**2a**) (yield 77 %) which becomes a multipurpose reagent of tricarbollide chemistry. Methylation of **2a** gives the Me_3N-derivative **2c** in quantitative yield, which substantially improves access to the parent tricarbollides **3⁻** and **3**.[2,4] A reaction of **2c** with Na in NH_3(l) results in the formation of pure compounds 7-Me_2HN-*nido*-7,8,9-$C_3B_8H_{10}$ (**2d**) (yield 71 %) and **3** (yield 19 %).



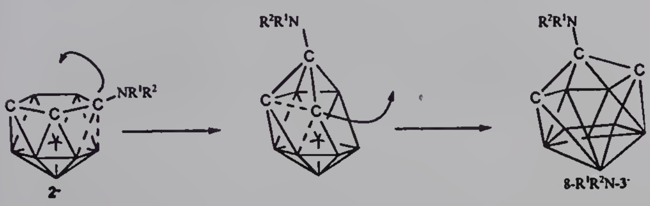
Scheme 1

As shown in Scheme 2, anions of type **2⁻** (formed by the deprotonation of the zwitterionic tricarbollides 7-R^1R^2HN-*nido*-7,8,9-$C_3B_8H_{10}$ **2** with NaH) undergo, instead of expected complexation, an interesting metal-promoted cage rearrangement upon reactions with anhydrous $NiCl_2$ (a similar reaction proceeds also with FeI_2, $FeCl_2$, $CoCl_2$, and $NiCp_2$)

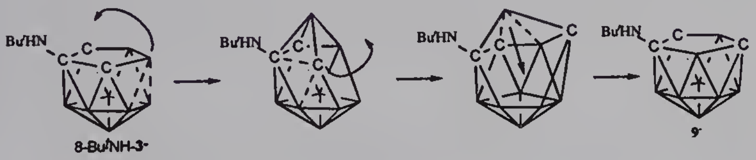
to produce a series of the *tautomeric* 8-R^1R^2N-substituted derivatives of **3** of general formulation 8-R^1R^2N-*nido*-7,8,9-$C_3B_8H_{10}$ (8-R^1R^2N-**3**), where $R^1R^2N = H_2N$, Bu^tHN, and Me_2N). As found in the case of the Bu^tNH_2-derivative **2b**, raising the reaction temperature (diglyme, reflux) causes further cluster rearrangement of the 8-Bu^tNH-**3** derivative originally formed into the zwitterionic compound 7-Bu^tNH_2-*nido*-7,8,10-$C_3B_8H_{10}$ (**9a**).[9] Schematic representation of skeletal rearrangements in the intercorversion of $\mathbf{2}^-$ to 8-R^1R^2N-$\mathbf{3}^-$, which *does not* proceed without the metal reagent, is in Scheme 3. Scheme 4 outlines one of the possible mechanisms for the 8-Bu^tNH-**3** → **9a** conversion. Methylation of **9a** gives the 7-Bu^tMeHN-*nido*-7,8,10-$C_3B_8H_{10}$ (**9b**) derivative whose structure was determined by X-ray diffraction (see Fig. 1).



Scheme 2



Scheme 3



Scheme 4

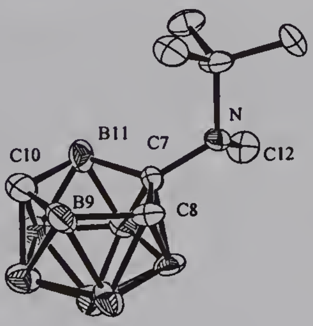


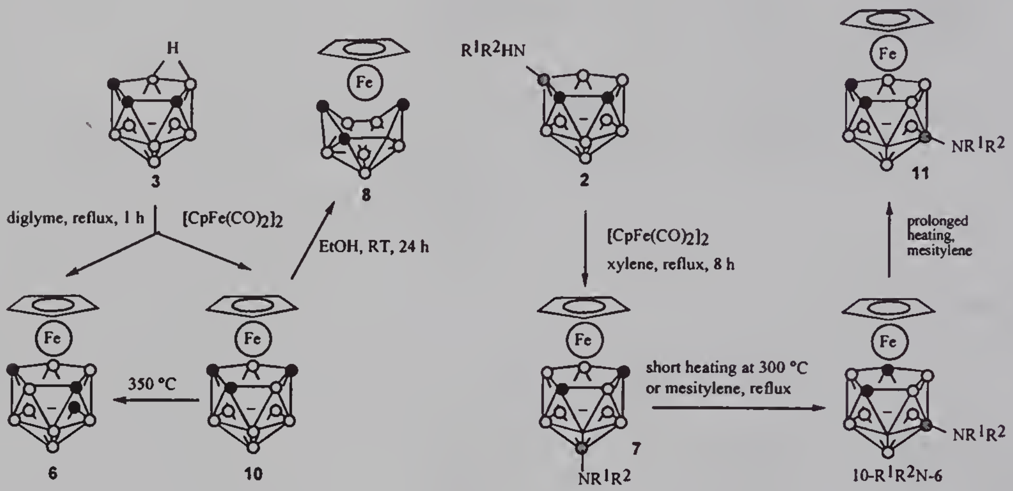
Fig. 1 Crystallographically determined structure of 7-Bu^tMeNH-*nido*-7,8,10-$C_3B_8H_{10}$ (**9b**)

3 METALLATRICARBOLLIDE COMPLEXES

We have developed new routes to various types of cyclopentadienyl ferratricacarbollides using [CpFe $(CO)_2]_2$ as iron-insertion agent. As shown in Scheme 5, this reagent and compound **3** produce two isomeric complexes **6** (yield 15%) and **10** (yield 30%):[10]

$$\underset{\mathbf{3}}{C_3B_8H_{12}} + 1/2\,[CpFe(CO)_2]_2 \rightarrow \underset{\mathbf{6}\text{ and }\mathbf{10}}{[CpFeC_3B_8H_{11}]} + 1/2\,H_2 + 2\,CO \qquad (5)$$

Compound **10** was found to undergo boron elimination upon treatment with ethanol to give the previously reported[6] 11-vertex complex **8**, while thermal rearrangement of **10** at 350 °C leads to quantitative formation of the isomer **6**.



Scheme 5

Also the zwitterionic amine tricarbollides of general formula 7-R^1R^2NH-*nido*-7,8,9-$C_3B_8H_{10}$) (**2**) (where $R^1R^2N = H_2N$, Bu^tHN; Me_2N, and Bu^tMeN) react with $[CpFe(CO)_2]_2$

$$\underset{\mathbf{2}}{R^1R^2NH\text{-}C_3B_8H_{10}} + 1/2\,[CpFe(CO)_2]_2 \rightarrow \qquad (6)$$

$$\underset{\mathbf{7}}{[Cp\text{-}R^1R^2N\text{-}FeC_3B_8H_{10}]} + 1/2\,H_2 + 2\,CO$$

in refluxing xylene with the formation of a series of the metallatricarbollides [2-Cp-9-R^1R^2N-*closo*-2,1,7,9-$FeC_3B_8H_{10}$] (**7**) (where X = H_2N **7a**, Bu^tHN **7b**, Me_2N **7c**, and Bu^tMeN **7d**) that contain amine functionalities in *p*-positions with respect to the metal centre (yields 16-54 %, see also Scheme 5 and stoichiometry as in Eq. 6). The reaction of **2e** is associated with partial loss of isobutylene and formation of the 9-MeHN-derivative **7e**.[11] Derivatives **7a** and **7b** were reported at the previous IMEBORON IX[7] (see Eq. 4 above) and the structure of **7b** was determined by an X-ray diffraction study.[7,11]

Raising the reaction temperature (refluxing mesitylene, 2-8 h, see also Scheme 5) in reaction 6 leads to a mixture of complexes of structure **7** and isomeric compounds [2-Cp-10-R^1R^2N-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (10-R^1R^2N-**6**) (where $R^1R^2N = H_2N$, Bu^tHN, Me_2N, and MeHN), the yields of the last complexes being dependent of the reaction time and the nature of the R^1R^2N-group (both the bulky substituents and increase in the reaction time promote the rearrangement). Longer reaction periods (for example, for $R^1R^2N = Bu^tHN$, 36 h-reflux) lead, apart from the formation of compounds 10-R^1R^2N-**6** (where $R^1R^2N = Bu^tHN$, yield 40 % and H_2N, yield 10 %), to the isolation of another, asymmetrical isomers of structure [3-Cp-12-R^1R^2N-*closo*-3,1,2,12-$FeC_3B_8H_{10}$] (**11**) (where

R^1R^2N = Bu^tHN, yield <5 % and H_2N, yield <4 %).[12] The structure of 10-Bu^tHN-**6** was confirmed by an X-ray diffraction study and is shown in Figure 2 (the Cp carbons are disordered). The observed 9→10 rearrangement of the substituted cluster carbon is quite unusual and it is supposed to result from higher thermodynamic stabilities of the 10-substituted isomers. Also unsuspected is the partial rearrangement of the 10-R^1R^2N-**6** derivatives into compounds **11**, in which the originally separated two cluster carbons move together. Although double-cluster metal sandwiches are quite common in metalladicarbollide chemistry,[1] we have found that the corresponding metallatricarbollide counterparts cannot be prepared easily. Nevertheless, we have succeeded in the isolation of the first representatives of double-cluster Fe(II) and Ru(II) complexes containing two tricarbollide

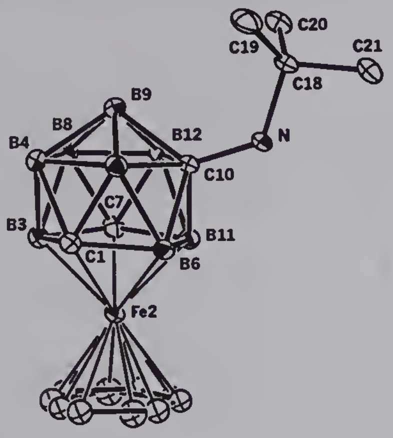
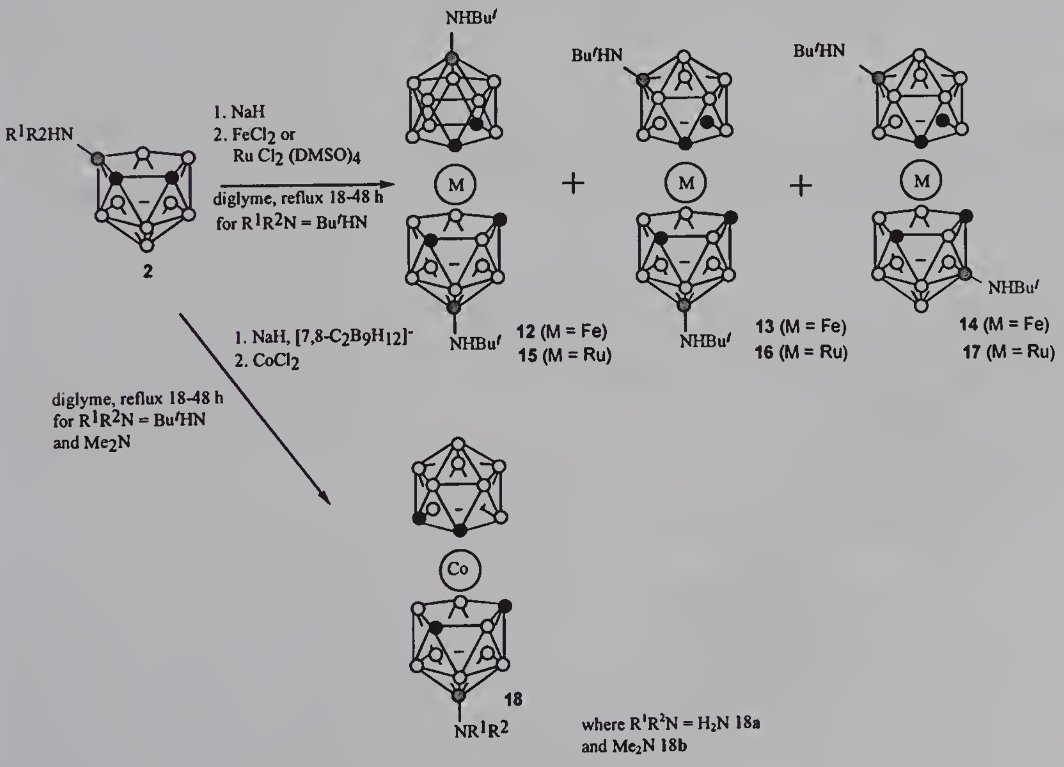


Fig. 2 Molecular structure of [2-Cp-10-Bu^tHN-*closo*-2,1,7,10-$FeC_3B_8H_{10}$] (10-Bu^tHN-**6**)



Scheme 6

ligands.[13] Inforced treatment of **2b** with excess NaH and $FeCl_2$ or $[RuCl_2(DMSO)_4]$ (Scheme 6) in refluxing diglyme leads to the isolation of complexes [9,9'-$(Bu^tHN)_2$-*commo*-2,2'-M-*closo*-(1,7,9-$C_3B_8H_{10}$)-(1',7',9'-$C_3B_8H_{10}$)] (**12** for M = Fe and **15** for M = Ru, yields 4 and 10 %, respectively), [9,10'-$(Bu^tHN)_2$-*commo*-2,2'-M-(1,7,9-$C_3B_8H_{10}$)-(1',7',10'-$C_3B_8H_{10}$)] (**13** for M = Fe and **16** for M = Ru, yields 6 and 11 %, respectively), and [10,10'-$(Bu^tHN)_2$-*commo*-2,2'-M-(1,7,9-$C_3B_8H_{10}$)-(1',7',10'-$C_3B_8H_{10}$)] (**14** for M = Fe and **17** for M = Ru, yields 2 % each). The structures of **12** and **15** were determined by X-ray diffraction analyses and are depicted in Figures 3 and 4.

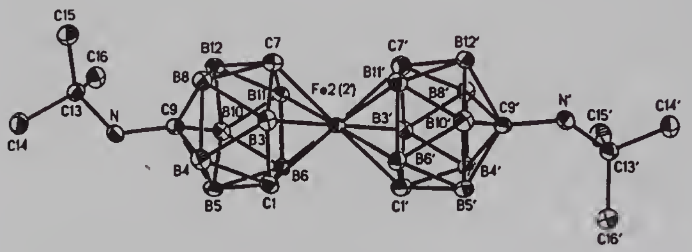


Fig. 3 Crystallographically determined structure of [9,9'-$(Bu^tHN)_2$-*commo*-2,2'-Fe-*closo*-(1,7,9-$C_3B_8H_{10}$)-(1',7',9'-$C_3B_8H_{10}$)] (**12**)

Tricarbollide analogues of the long known [*closo*-$CpCoC_2B_9H_{11}$],[14] cross-over complexes between metalladicarbollides and metallatricarbollides, were isolated as in Scheme 6. The main components of the reaction mixture were the *neutral* cobaltacarboranes [*closo*-(9-R^1R^2N-1,7,9-$C_3B_8H_{10}$)-*commo*-2,(3')-Co-(1',2'-$C_2B_9H_{11}$)] (structure **18** in Scheme 6, where $R^1R^2N = H_2N$ **18a**, yield 20 % and Me_2N **18b**, yield 10 %). Compound **18b** was also obtained from the methylation of **18a** with MeI in the presence of NaH. The structure of **18a** and was confirmed by an X-ray diffraction study and is shown in Figure5.[15]

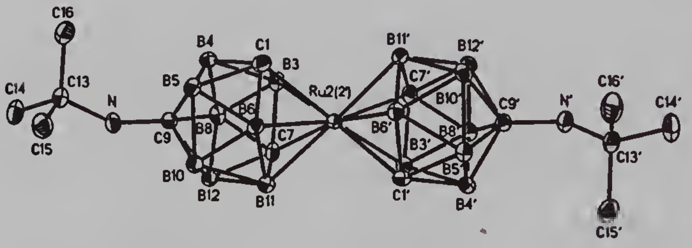


Fig. 4 Crystallographically determined structure of [9,9'-$(Bu^tHN)_2$-*commo*-2,2'-Ru-*closo*-(1,7,9-$C_3B_8H_{10}$)-(1',7',9'-$C_3B_8H_{10}$)] (**15**)

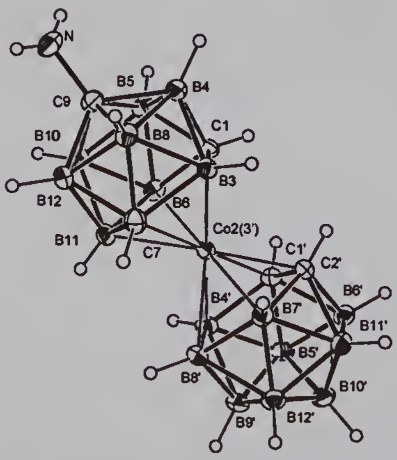


Fig. 5 Crystallographically determined structure of [*closo*-(9-H_2N-1,7,9-$C_3B_8H_{10}$)- *commo*-2,(3')-Co-(1',2'-$C_2B_9H_{11}$)] (**18a**)

4 CONCLUSIONS

The survey outlines initial studies on the formation and metal complexation of the monoanionic tricarbollide ligands. These are, in contrast to the dianionic dicarbollide anions,[1] perfect cluster analogues of Cp. It should be, however, noted that, in contrast to the smooth complexation of the

C_2B_3 open face in the dicarbollide series,[1] the tricarbollide C_3B_2 face can be complexed *only* under forcing conditions, otherwise no complexation is achieved. Moreover, the complexation is in all cases associated with an extensive rearrangement of the three cluster carbons over the cluster area to form tricarbollide complexes of extreme stability in air. Of importance is also the straightforward, one-step generation of reactive amino functionalities in *p*- or *m*- positions with respect to the metal centre in the complexation of anions of type **2**$^-$. This feature pre-destinies amino metallatricarbollides as highly stable building blocks for designed constructions of novel metallacarborane-based molecular assemblies of linear and L-shape.

Acknowledgment

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References

1. See, for example: G. B. Dunks and M. F. Hawthorne, in 'Boron Hydride Chemistry', E. Muetterties, Ed, Academic, New York, 1975, Chapter 11, pp 383-430, and refs therein; R. N. Grimes, In 'Comprehensive Organometallic Chemistry', G. Wilkinson, F. G. A. Stone and E. Abel, Eds, Pergamon, 1982, Part I, Chapter 5.5, pp 459-542.; A. K. Saxena, J. A. Maguire and N. S. Hosmane, *Chem. Rev.*, 1997, **97**, 2421.
2. J. Plešek and S. Heřmánek, *Chem. Ind. (London)*, 1971, 1267; J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun.*, 1974, **39**, 821.
3. B. Štíbr, J. Holub, F. Teixidor and C. Viñas, *J. Chem. Soc., Chem.Commun.*, 1995, 795; B. Štíbr, J. Holub, I. Císařová, F. Teixidor, C. Viñas, J. Fusek, and Z. Plzák, *Inorg. Chem.*, 1996, **35**, 3635.
4. J. Holub, B. Štíbr, D. Hnyk, J. Fusek, I. Císařová, F. Teixidor, C. Viñas, Z. Plzák and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1997, **119**, 7750-7759.
5. B. Štíbr, J. Holub, I. Císařová, F. Teixidor and C. Viñas, *Inorg.Chim. Acta.*, 1996, **245**, 129; R. Rousseau, E. Canadell, S. Lee, F. Teixidor, C. Viñas and B. Štíbr, *New J. Chem.*, 1996, **20**, 277.
6. B. Štíbr, J. Holub, F. Teixidor and C. Viñas, *Collect. Czech. Chem. Commun.* 1995, **60**, 2023-2027.
7. B. Štíbr, J. Holub, F. Teixidor In 'Advances in Boron Chemistry', W. Siebert, Ed., Royal Society: London, 1997, pp 333-340.
8. B. Štíbr, J. Holub, J. Plešek, T. Jelínek, B. Grüner, F. Teixidor and C.Viñas, *J. Organomet. Chem.*, 1999, **582**, 282-285.
9. B. Grüner, J. Holub, F. Teixidor, C. Viñas, R. Sillanpää, A. Lehtonen and B. Štíbr, Abstracts of IMEBORON X, Durham , July 11-15 1999.
10. B. Štíbr and J. Holub, manuscript in preparation.
11. J. Holub, B. Grüner, I. Císařová, J. Fusek, Z. Plzák, F. Teixidor, C. Viñas and B. Štíbr, *Inorg. Chem.*, 1999, **38**, 2775-2780.

12.B. Grüner, A. Lehtonen, R. Kivekäs, R. Sillanpää, J. Holub, F. Teixidor, C. Viñas and B. Štíbr, *Inorg. Chem.,* submitted.
13.B. Grüner, F.Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, submitted.
14.M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.
15.B. Grüner, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, J. Holub, A. Lehtonen and B. Štíbr, *Inorg. Chim. Acta.*, submitted.

Clusters from Organoboranes and Electron-poor Metal Complexes

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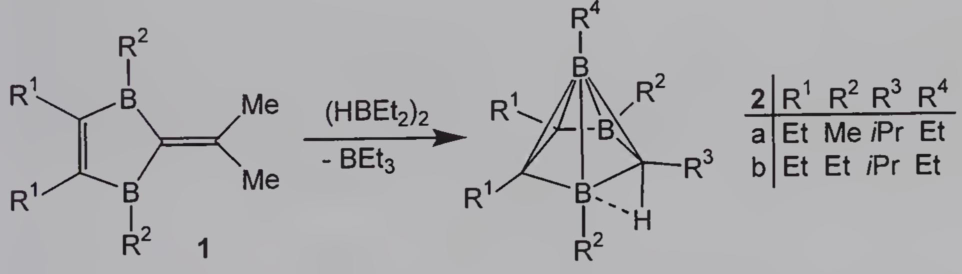
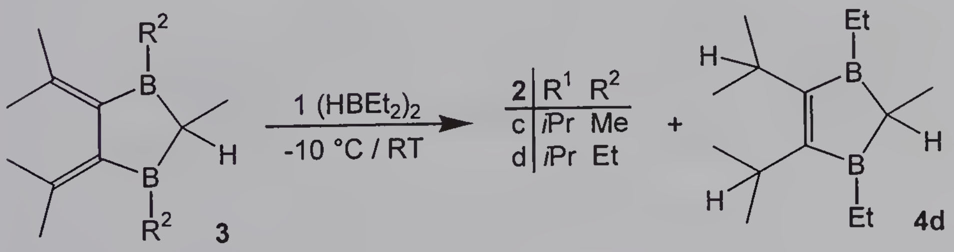
1 INTRODUCTION

Previously we have shown that nido-2,3,5-tricarbahexaboranes(7) are formed by hydroboration reactions of 1,3-dihydro-1,3-diborafulvenes **1** and of 4,5-diisopropylidene-1,3-diborolenes **3**, obtained by ring-closure of cis-diborylethenes with $(Me_3Sn)_2C{=}CMe_2$ and of 3,4-dilithio-2,5-dimethylhexa-2,4-diene-diid with diborylmethane derivatives[1,2]. The stability of the 2,3,5-tricarbahexaboranes **2** depends on the substituents in the basal positions of the carboranes.





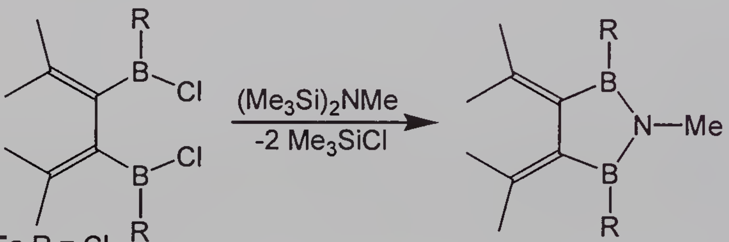
Surprisingly, the hydroboration of **3** (R^2=Et) with $(Et_2BH)_2$ leads to a mixture of **2d** and the 2,3-dihydro-3,4-diisopropyl-1,3-diborole derivative **4d** by formal 1,4-addition of hydrogen to the hexadiene part of **3**, whereby the exocyclic double bonds are transformed to an endocyclic double bond[1,3]. In **2** the axial hydrogen attached to the penta-coordinate carbon C5 has unique properties: its ^{1}H-NMR signal appears near $\delta = -1.3$, and it easily gets deprotonated to yield the *nido*-2,3,5-tricarbahexaborate anion. This carborane-id ligand functions as 6e ligand, it is isolobal with cyclopentadiene-id and allows the formation of a variety of metallacarboranes[1,4].

In the following we report in the syntheses and structures of 2,4,5-azadicarba- and 2,4,5-thiadicarbahexaboranes. Chapter 2.4 presents a new approach to *closo*-1-metalla-2,3,5-tricarbaheptaboranes by the capping of electron-poor 2,3-dihydro-1,3-diborolyl-metal complexes with the borandiyl fragment [B-H].

2 RESULTS AND DISCUSSION

2.1 nido-2,4,5-Azadicarbahexaboranes

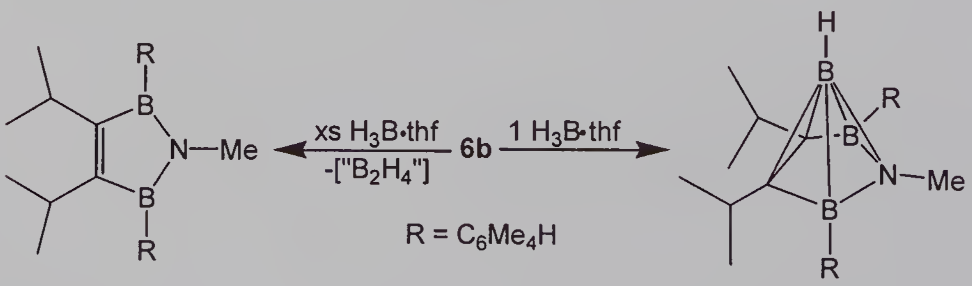
The 3,4-diborylhexadiene derivative **5b** reacts at room temperature with a stoichiometric amount of heptamethyldisilazane to give in very good yields the 1,2,5-azadiborolane **6b**, having two exocyclic double bonds in 3,4-position. Its composition follows from spectroscopic data and an X-ray structure analysis.



5a R = Cl
5b R = C_6Me_4H

6b

The reaction of **6b** with H_3B•thf yields two products depending on the amount of borane reagent used. An excess of BH_3 leads to a dihydrogenation of the hexadiene part of **6b** to give the 2,3-dihydro-1,2,5-azadiborole **7b** with two isopropyl substituents as the main product and only traces of the 2,4,5-azadicarbahexaborane **8b**. When a 1 : 1 reaction is allowed to proceed the new azacarborane **8b** is obtained[5].

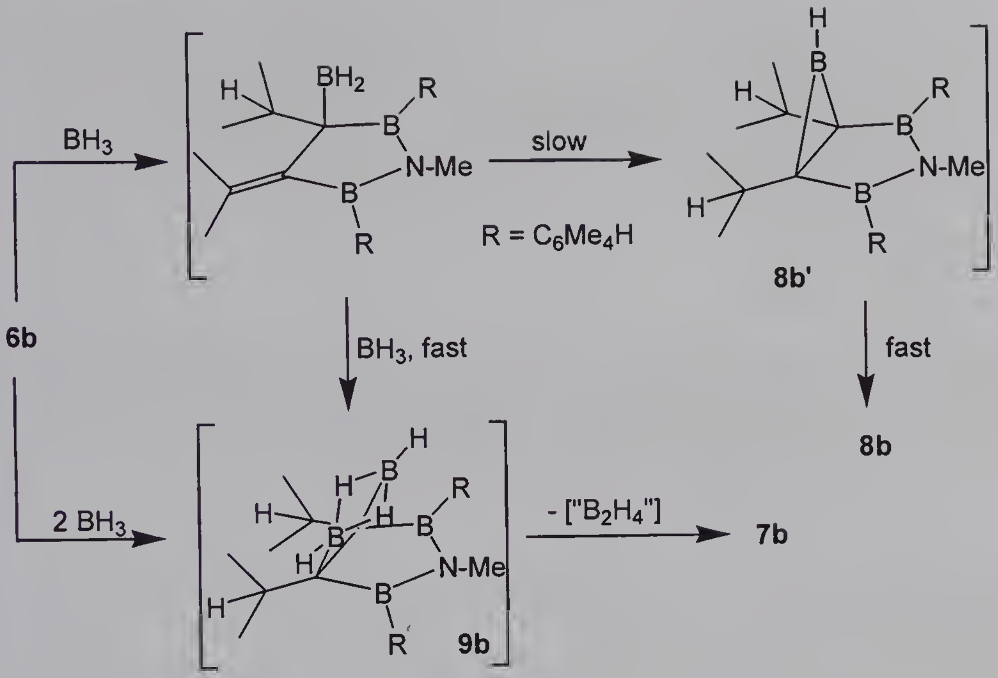


R = C_6Me_4H

7b

8b

We assume that one BH_3 molecule adds across one double bond of **6b**, which is followed by a slow intramolecular hydroboration of the remaining double bond by the adjacent BH_2 group. This may lead to the bicyclic intermediate **8b'** in which the BH group easily slips from η^2 to η^5 bonding with formation of the azacarborane **8b**.



A second BH_3 molecule attacks the monohydroborated product most likely in syn position due to the easy formation of BHB bonds with the BH_2 group to yield **9b**, which loses "B_2H_4" to give **7b**. The postulated diborane(4) is unstable and decomposes in the absence of suitable Lewis bases.

The products **7b** and **8b** are characterized spectroscopically. The X-ray structure analysis of **8b** reveals a *nido* cluster arrangement, expected on the basis of the Wade-Mingos rules[6].

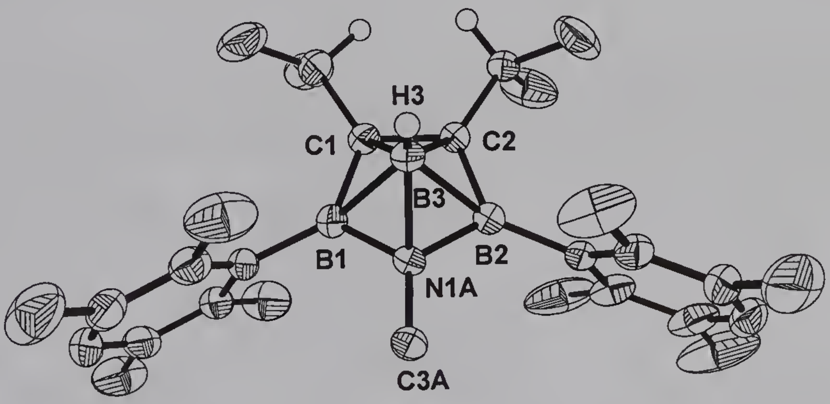
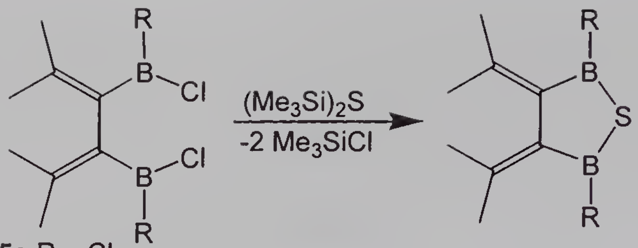


Figure 1: Molecular structure of **8b**

2.2 nido-2,4,5-Thiadicarbahexaboranes

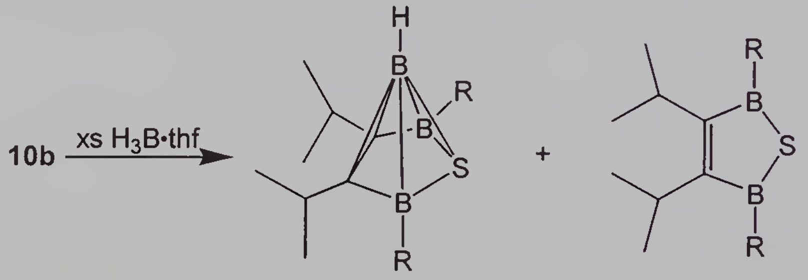
The reaction of **5a** with hexamethyldisilthiane in refluxing hexane leads to the formation of 3,4-bis(isopropylidene)-2,5-dichloro-1,2,5-thiadiborolane (**10a**) in 80% yield. The duryl derivative **10b** is obtained in high yield when **5b** and neat $(Me_3Si)_2S$ are reacted at 120°C[6].



5a R = Cl
5b R = C_6Me_4H

10a,b

The slightly yellow compounds **10a,b** are very air- and moisture-sensitive due to its B-Cl and B-S bonds. **10b** reacts with a excess of H_3B•thf to yield the *nido*-thiacarborane **11b** and traces of the 2,3-dihydro-1,2,5-thiadiborole **12b**, identified by MS.



11b R = C_6Me_4H **12b**

In contrast to the analogous hydroboration of the azadiborolane **6b**, which leads to the azadiborole **7b**, here the formation of the thiacarborane **11b** as main product is favored. This result indicates that the first hydroboration intermediate undergoes a fast intramolecular hydroboration to yield the 2,4,5-thiadicarbahexaborane **11b** presumably via the bicyclic thia analog of **8b'**. Its composition follows from spectroscopic data and an X-ray structure analysis. When **10a** is treated with lithium borates Li[RBH_3] (R = H, C_6H_5, C_6Me_4H) several products are formed of which **11a** and **13a** are identified[7].

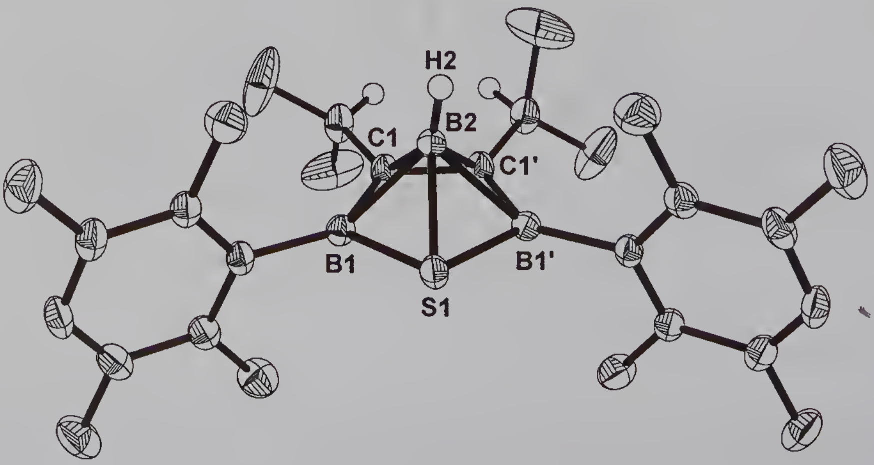
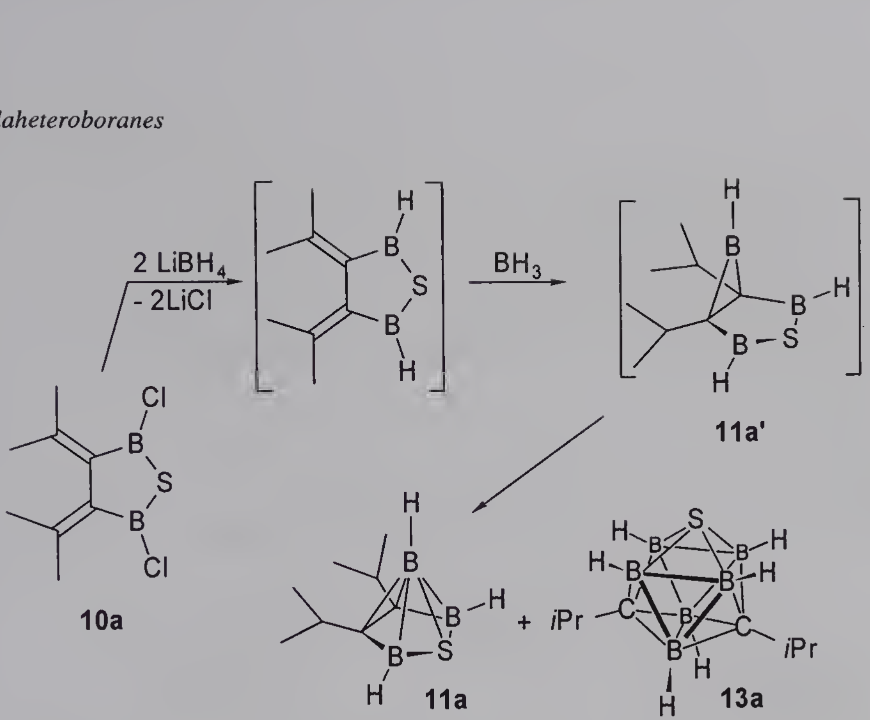


Figure 2: Molecular structure of **11b**



In the first step $LiBH_4$ substitutes the two chlorine atoms of **10a** for hydrogen, and the formed intermediate is hydroborated by BH_3 to the postulated bicyclic organothiaborane **11a'**, which then transforms into the thiacarborane **11a**. Besides **11a** other products are present in the reaction mixture as indicated by the $\{^1H\}^{11}$B-NMR spectrum (low-field signals for organthioboranes and three sets of high-field signals for thiacarboranes: δ = 1.3/2.2 (intensity ratio ca. 2:1), – 20.1/–20.7 (ca. 1:2) and –28.2/–33.8 (ca. 1:2)). The GCM-spectrum exhibits the molar peak for a $S(CiPr)_2(BH)_6$ cluster, which has 22 skeletal electrons. This suggests a nine-vertex *nido* structure. In Figure 3 the MP2(fc)/6-31G* optimized structure of **11**, **13** and **14** are shown including the computed IGLO ^{11}B-NMR chemical shifts (experimental values) for **11** and **13**.

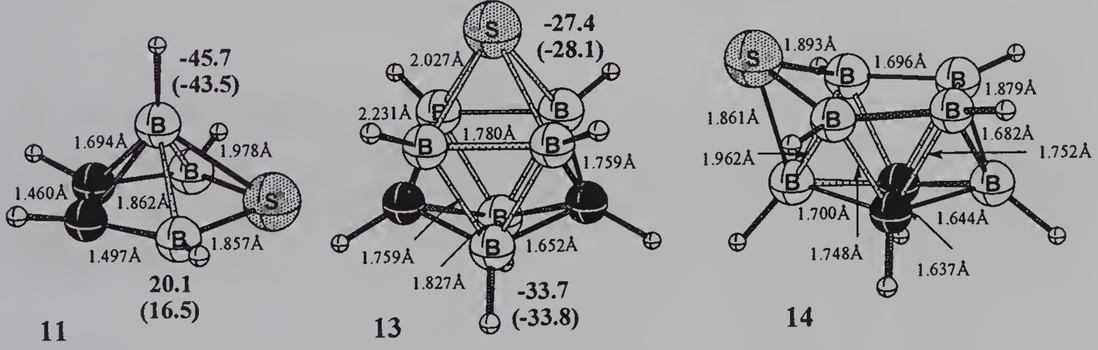
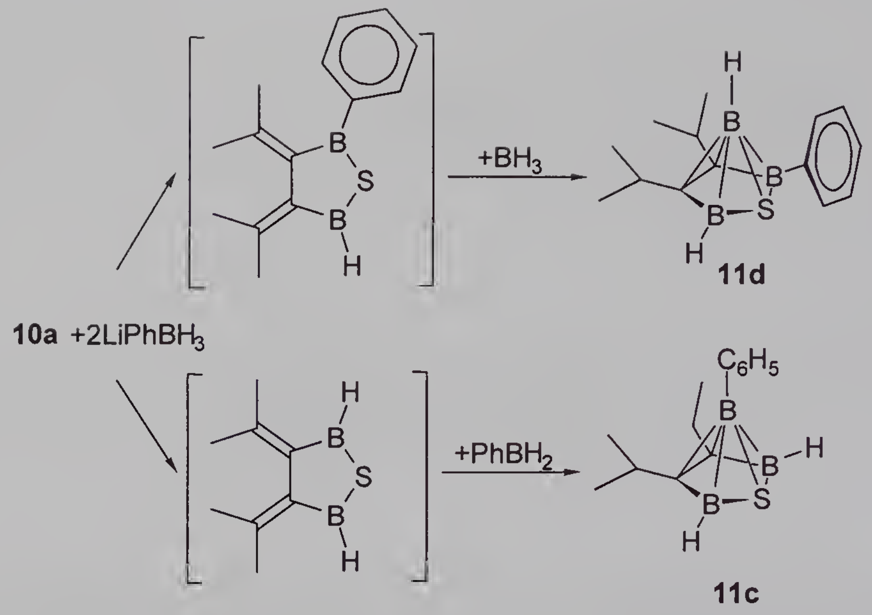


Figure 3: MP2(fc)/6-31G* optimized structures of **11**, **13** and **14**

Cluster **14** has a pentagonal open face (ni 9<V>)[8], the computed ^{11}B-NMR shifts are not in line with the experimental values (–28.1, –33.8), which agree very well with the computed shifts for **13** (–27.4, –33.7). Sulfur and the two carbon atoms occupy the capping positions of the trigonal prism of **13** (k = 4 positions). There are two large B-B distances of 2.23Å, and one short B-B interaction (1.83Å) in **13**, which suggests that the cluster has two tetragonal faces (ni–9 <IV+IV).

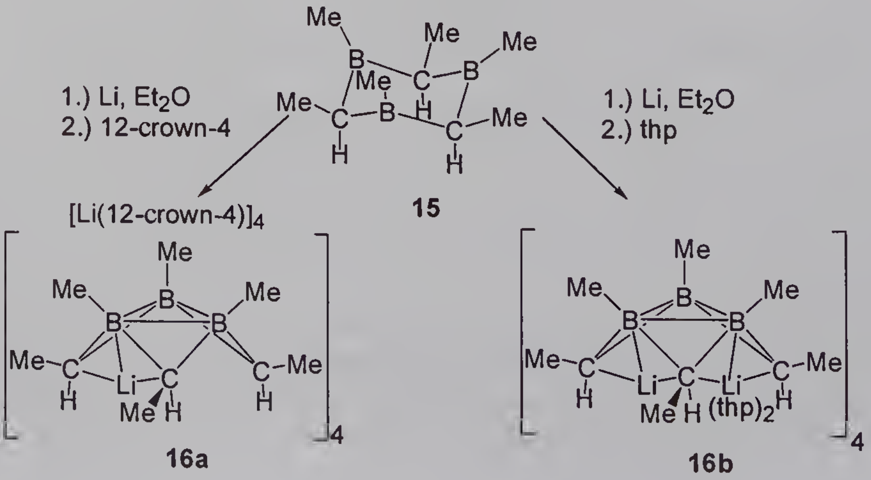
In $B_9H_9^{2-}$ the HOMO and LUMO are non-degenerate, a *nido*-electron-count (22 skeletal electrons) for a 9-vertex species would have two electrons in the LUMO. The LUMO is located along the long edges of the trigonal prism, the edges may be elongated as observed for the Si_9^{4-} cluster, having two long edges (3.09Å) and one short edge (2.63Å).



When **10a** is reacted with Li[C_6H_5-BH_3] a mixture of the isomers **11c** and **11d** (5:1 by NMR) is obtained, which could not be separated. The isomer with the phenyl group in apex position is favored, indicating that the chlorine atoms in **10a** are predominantly replaced by hydrogen and the hydroboration with C_6H_5-BH_2 leads to isomer **11c**. In contrast to this the reaction of **10a** with lithium durylborate yields to the cluster **11e** with the duryl group in basal position[7]. **11e** was studied by X-ray structure analysis which confirmed the connectivities in the molecule. However, the bad quality of the crystals did not allow a reliable refinement of the structure.

2.3 hypho-Lithiacarboranes

The hexamethyl-1,3,5-triboracyclohexane **15** reacts with lithium powder in ether or tetrahydrofurane to give a yellow-orange solution. Evaporation of the solvent leads to an amorphous product, which shows in d_8-thf a high-field ^{11}B-NMR signal at $\delta = -29.2$.
Adding tetrahydropyrane (thp) to the solution yields yellow crystals, its X-ray structure analysis proves the presence of tetrameric [$(MeCH)_3(BMe)_3Li_2(thp)_2]_4$ (**16b**), in which four monomeric units are bridged by four Li centers[9] (Figure 4).



Each unit contains one terminal lithium, stabilized by two thp ligands. Adding 12-crown-4 to the solution of reduced **16** yields crystals of $[(MeCH)_3(BMe)_3Li]_4[Li(12\text{-crown-}4)]_4$ (**16a**), the tetrameric structure of the anion (Figure 4) shows four C_3B_3 cluster units and four bridging lithium centers coordinated by two C_2B faces. The B_3 ring exhibits different bond lengths: B1-B2 1.825(2), B3-B1 1.851(5), B3-B2 1.848(5) Å, the Li-B distances are 2.239(6) and 2.251(6) Å. Each C_3B_3 unit has three axial C-H bonds orthogonal to the B_3 plane and three almost equatorial CH_3 groups.

These results indicate, that reduction of **15** leads to the trishomoaromatic compounds **16a** and **16b** as tetrameric units bridged by Li centers. Alternatively, the tetrameric units may be described as *commo*-lithiacarboranes. The (hyphothetic) monomeric unit $[(MeCH)_3(BMe)_3\,Li_3(thp)_6]^{\oplus}$ should have a *hypho* structure.

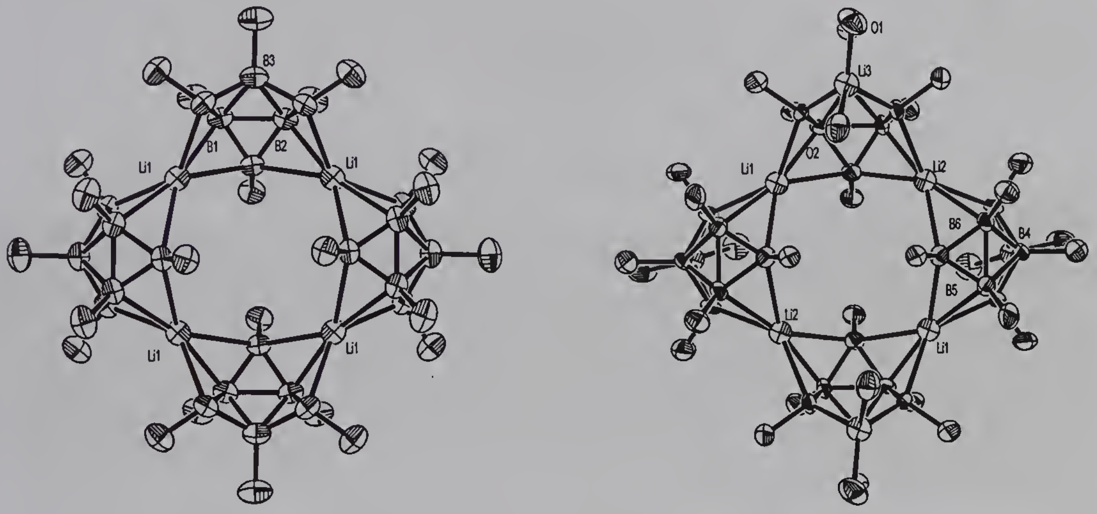
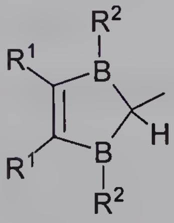


Figure 4: Molecular structures of the anions **16a** and **16b**

2.4 closo-Metallatricarbaheptaboranes

The adduct obtained from NaH and the 2,3-dihydro-1,3-diborole **4d** reacts with $[\{(C_5Me_5)FeCl\}_n]$ to give the green crystals of **17a**, in which the heterocycle is bent along the B-B vector by 41°.[3]



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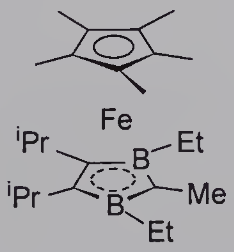
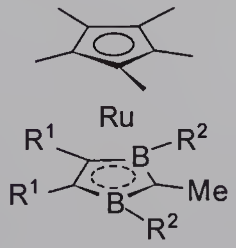


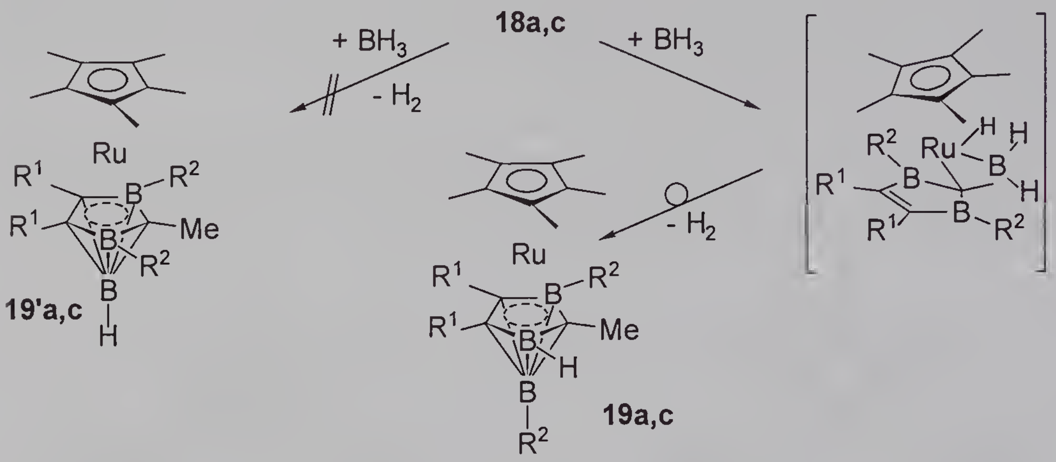
17d



18

	a	b	c	d
R^1	Et	Me	Et	*i*Pr
R^2	Et	Me	Me	Et

The reaction of 1,3-diboroles **4**, LiMe and $[\{(C_5Me_5)RuCl\}_4]$ leads to the violet, highly air-sensitive Ru sandwich complexes **18**[10]. The compounds **17** and **18** are derived from ferrocene and ruthenocene by formal replacement of two CH groups for B-R units. Therefore the complexes should have only 16 valence electrons (VE). However, the electronic structure of the iron compound **17**, studied by EH-MO theory, exhibits a unique bonding: The electron density of two B-C σ orbitals participates in the bonding by interacting with the empty d_{xz} orbital at the iron, therefore **17d** and **18** are in fact electron-poor 18 VE complexes. They easily react with 2e donor ligands (L = CO, CN*t*Bu) to give bent sandwich complexes with L bonded to the metal, e.g. [**17d**–CO], [**18a**–CN*t*Bu].



Reacting **18a,c** with H_3B•thf in hexane leads to a color change of the violet solution and the yellow compounds **19a,c** are obtained. Their structure follows from spectroscopic data, which indicate that the possible isomers **19'a,c** with BH in the apex position are not formed. Based on the results the following reaction path for the formation of the *closo*-ruthenacarboranes **19** seems likely: In the first step on oxidative addition of BH_3 to the ruthenium of **18** leads to an intermediate, which eliminates hydrogen and rearranges with migration of one B-R^2 group into the apex position yielding the *closo*-ruthenatricarbaheptaboranes **19**.

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3 REFERENCES

1 A. Feßenbecker, A. Hergel, R. Hettrich, V. Schäfer, W. Siebert, *Chem. Ber.* **1993**, *126*, 2205.
2 W. Siebert in *Current Topics in the Chemistry of Boron,* The Royal Society of Chemistry, **1994**, 275; Ed.: G. W. Kabalka.
3 R. Hettrich, M. Kaschke, H. Wadepohl, W. Weinmann, M. Stephan, H. Pritzkow, W. Siebert, I. Hyla-Kryspin, R. Gleiter, *Chem. Eur. J.* **1996**, *2*, 487.
4 W. Siebert, R. Hettrich, H. Pritzkow, *Angew. Chem.* **1994**, *106*, 215; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 203.
5 P. Greiwe, part of the planned PhD thesis, Heidelberg.
6 K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; D. M. P. Mingos, *Adv. Organomet. Chem.* **1977**, *15*, 1.
7 V. Beez, P. Greiwe, H. Pritzkow, M. Hofmann, P. v. R. Schleyer, W. Siebert, *Eur. J. Inorg. Chem.* **1998**, 1775.
8 R. E. Williams in *Adv. In Boron Chemistry* **1997**, 15-29, The Royal Society of Chemistry, Cambridge, Ed.: W. Siebert.
9 W. Lößlein, part of the planned PhD thesis, Heidelberg.
10 T. Müller, M. Kaschke, M. Strauch, A. Ginsberg, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **1999** in press.

Chemistry of Silaboranes

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1 *o*-SILABORANE IN REACTION WITH NUCLEOPHILES

In *o*-silaborane[1] (**1**) the silicon atoms are in the unique situation of being incorporated in the skeleton of a borane cluster framework. We are interested in the reactivity patterns of the icosahedral cluster and especially in the silicon centres. The nucleophilic degradation was the first reaction of *o*-silaborane which has been enlightened.[2] Removal of a silicon vertex from the icosahedral cluster results in almost quantitative isolation of the sila-*nido*-undecaborate(1-) (**2**). This eleven vertex cluster became a versatile starting material for the synthesis of transition metal complexes comprising a silicon metal interaction.[3,4,5,6]

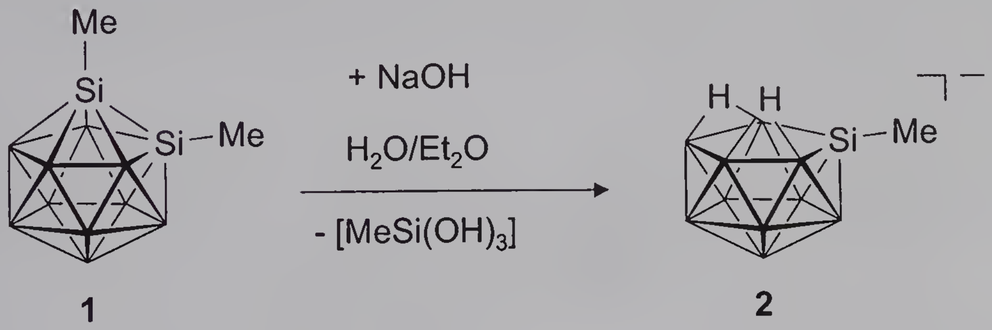


Figure 1 *Nucleophilic Degradation of o-Silaborane*

Under the attack of one equivalent OH^- in H_2O, MeO^- in MeOH, or pure NH_3 a silicon vertex was removed from the *closo*-cluster **1**.[2] A plausible mechanistic sequence for the degradation involves as the first step formation of an adduct consisting of the nucleophile and the *closo*-cluster. Afterwards this adduct should react with a protic solvent to give the isolated reaction product. In order to get indications for the expected adduct we studied the attack of nucleophiles in an aprotic solvent. Three types of nucleophiles were studied in this reaction. In the case of the dialkylamide nucleophile best results were achieved from the reaction of the *closo*-cluster with transition metal amides of zirconium and tantalum.[7,8] The anionic adduct cluster features a dialkylamide bridging both silicon centres of the silaborane cluster.

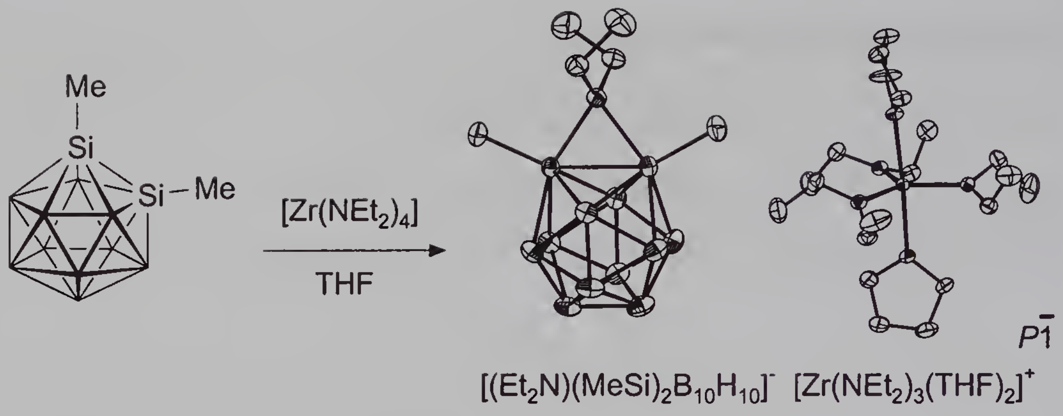


Figure 2 *Dialkyamide Adduct of o-Silaborane*

Alkoxide nucleophiles were introduced by reaction of the silaborane with water/TMPDA or methanol/TMPDA.[9] Colourless crystalline salts were isolated in both cases from the quantitatively proceeding reactions. Because of the high dynamic behaviour of the adducts in the ^{29}Si-NMR spectrum only one resonance was detected. This adduct formation is also a cluster opening reaction. The silicon atom attacked by the nucleophile is coordinated at only three boron atoms. Obviously, the connection towards the opposite boron atom in respect to the entering nucleophile was released during adduct formation. Therefore, the adduct features a quadrangle consisting of two silicon atoms and two boron atoms. Overall the coordination number of the silicon atom 1 remains six. The silicon atom not attached at the oxygen atom is embedded in the cluster framework like in the starting material. The geometry of the oxygen adducts of *o*-silaborane can be derived from the 13 vertex *closo* skeleton by removal of the four coordinate vertex. Thus, the structure in the solid state of the cluster anions of **4** and **5** is in correspondence to Williams geometrical systematics.

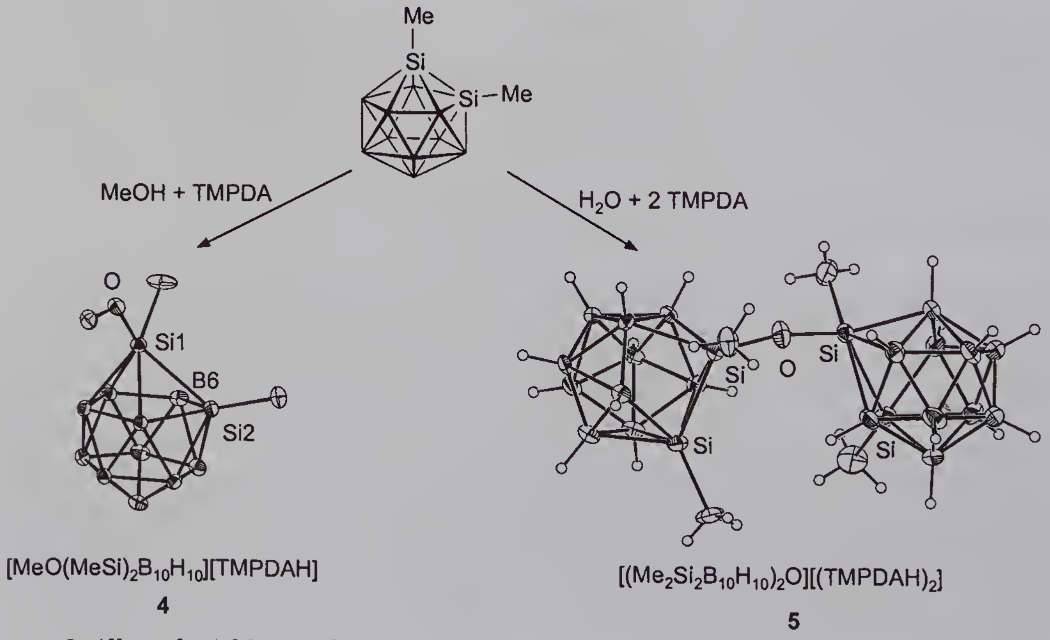
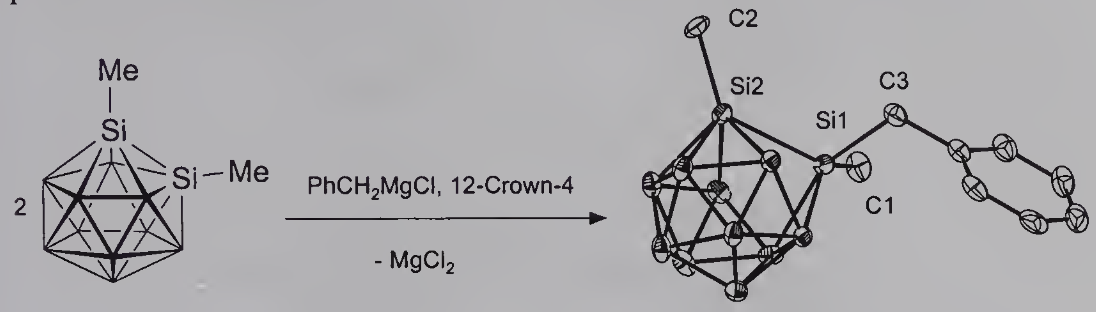


Figure 3 *Alkoxide Adducts of o-Silaborane*

Grignard reagents were proven to form carbanion adducts with *o*-silaborane in high yield.[10] These silaborates are very sensitive towards moisture resulting in the nucleophilic degradation of the cluster. In the solid state the geometry of the benzylide adduct **6** exhibits a symmetrical cluster opening in contrast to the unsymmetrically opened alkoxide adducts.

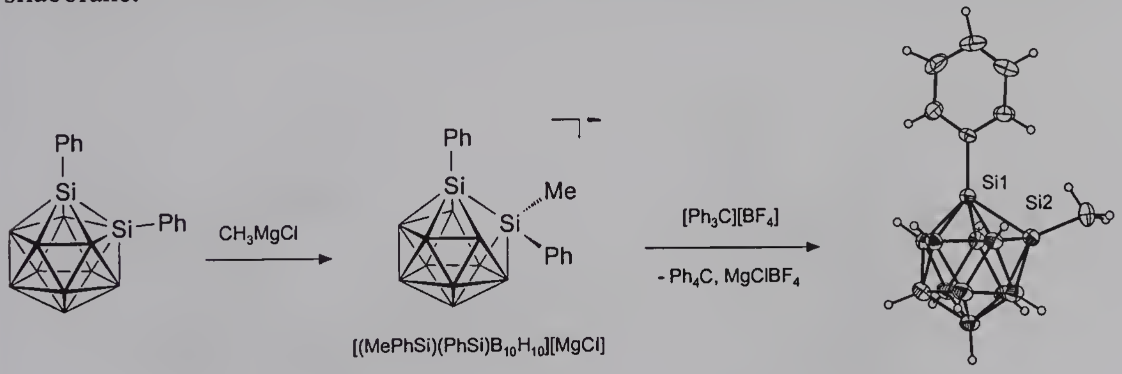


$[PhCH_2(MeSi)_2B_{10}H_{10}]_2[Mg(12\text{-Crown-}4)_2]$

6

Figure 4 *Grignard Reagents in Reaction with o-Silaborane*

So far electrophilic substitution reactions at the silicon atoms of the silaborane clusters were unsuccessful. Adduct formation as the initial step and further treatment of this anion with the electrophilic salt $[Ph_3C][BF_4]$ resulted in the isolation of methyl-phenyl-*o*-silaborane.[10]



$(MeSi)(PhSi)B_{10}H_{10}$

Figure 5 *Substitution at the Silicon Vertex*

2 COORDINATION MODES OF SILA-*nido*-UNDECABORATE(1-)

Coordination chemistry of boranes and heteroboranes is a major field of research in cluster science. By far the most extensively studied clusters are the eleven vertex carboranes dicarba-*nido*-undecaborane, carba-*nido*-undecaborane and the six vertex carborane dicarba-*nido*-hexaborane. The synthesis of the elven vertex silaborate $[MeSiB_{10}H_{12}]^-$ prompted us to study the coordination abilities of this cluster towards transition metals. In

Figure 6 the observed coordination modes of various complexes that have been characterized so far are depicted.

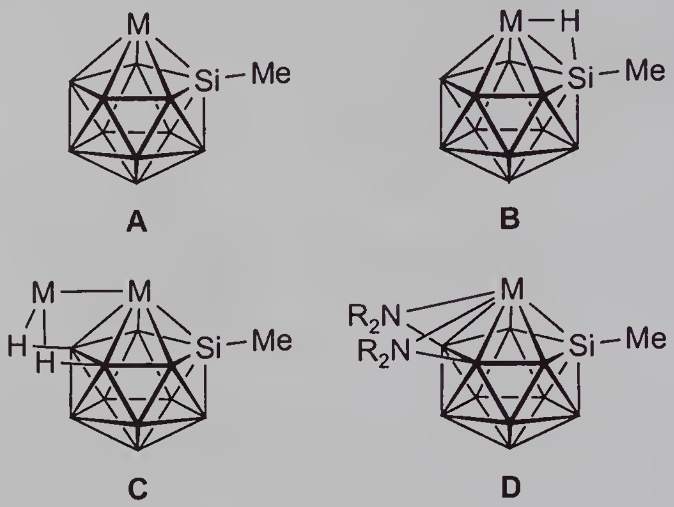


Figure 6 *Coordination Types of Sila-nido-undecaborate*

Type **A** resembles the typical η^5- coordination as it is known for many complexes of the dicarbollide (*nido*-$C_2B_9H_{13}^-$)[11,12] and carbollide (*nido*-$CB_{10}H_{13}^-$)[13,14] ligands and is found in the mixed sandwich anions $[Cp^*M(MeSiB_{10}H_{10})]^-$ (M = Co, Rh, Ir)[4] and the carbonyl complexes $[(CO)_3M(MeSiB_{10}H_{10})]^-$ (M = Ru, Fe).[5]

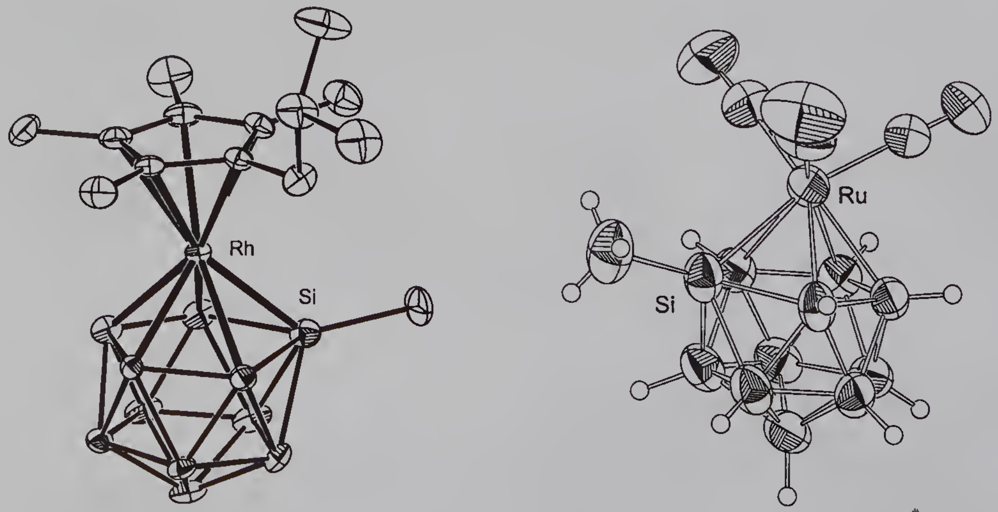


Figure 7 *$[Cp^*Rh(MeSiB_{10}H_{10})]^-$ and $[(CO)_3Ru(MeSiB_{10}H_{10})]^-$*

Both Type **B** and **C** are observed in the binuclear complex $[Bu_4N]_2[\{HFe(MeSiB_{10}H_{10})\}_2]$.[3]

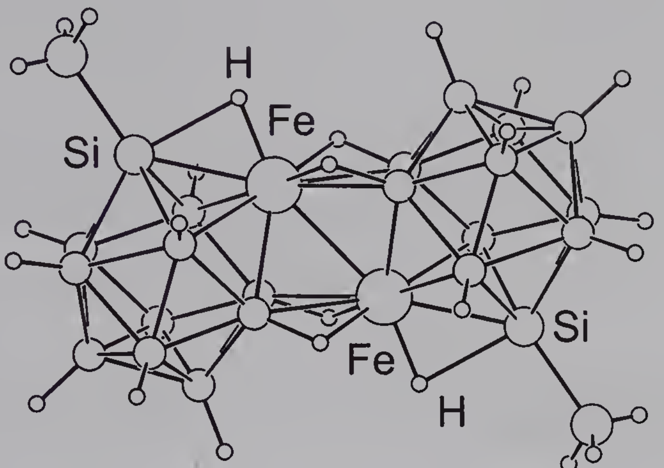


Figure 8 *$[\{HFe(MeSiB_{10}H_{10})\}_2]^{2-}$*

Compounds of Type **D** represent a hitherto unknown coordination pattern in borane and heteroborane chemistry that results from an unexpected B,H- activation.
Tantalum and niobium atoms were incorporated in the silaborate cluster by reaction of the dialkylamides with the silaborate **2**.

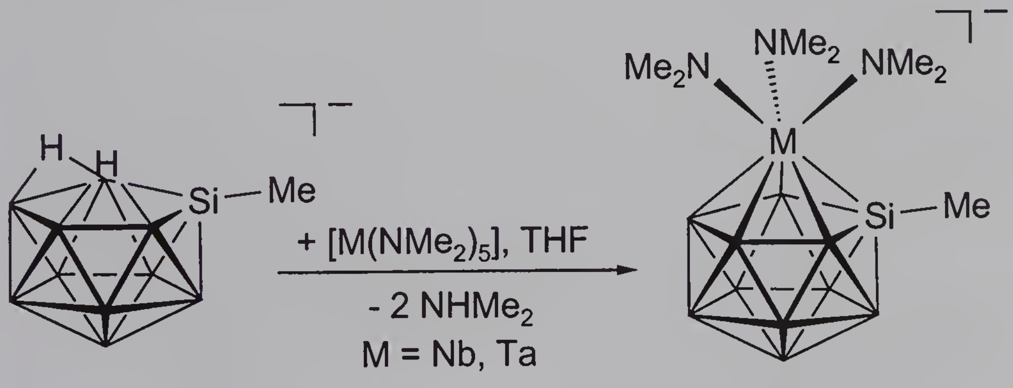


Figure 9 *Formation of Metallasilaborates*

These transition metal complexes react with any solvent able to dissolve them, making it impossible to gain crystals. Nevertheless they can be isolated from thf in good yields, characterised NMR- spectroscopically and by C,H- analysis if worked up quickly. With dichloro- and dibromomethane surprising reactions were found. Both reactions result in the quantitative formation of complexes featuring coordination mode **D**. Due to the smaller reactivity of dichloromethane this reaction could be monitored by NMR spectroscopy. Species on the way to complex of typ **D** were identified and isolated. In the first step a dialkylamide group was replaced by a chloride ligand. $[Me_2NCH_2Cl]$ was identified by mass spectrometry as the other reaction product in the first step. After two days one M-N-B bridge was formed indicated by the increasing number of signals in the ^{11}B NMR spectrum and the loss of the B-H coupling in the ^{11}B NMR spectrum for the respective boron resonance. The double bridged species was obtained after two days of reflux in dichloromethane. In the case of the more reactive dibromomethane only the end product of the reaction sequence was detected in the ^{11}B NMR spectrum. The constitution of $[NBu_4][Nb(MeSiB_{10}H_8)(\mu\text{-}NMe_2)_2Br_3]$ was verified by crystal structure analysis. Interesting structural features are the Nb-N distances [2.488(6), 2.506(6) Å] which are much longer than a single bond value in $[Nb(OAr\text{-}2,6\text{-}Ph_2)_3NMe(HNMe_2)]$ 2.326(6) Å.[15] The B-N distances [1.509(8), 1.492(8) Å] are in the middle of the range between a typical single (B-N: 1.58 Å) and a double (B=N: 1.41 Å) bond.[16]

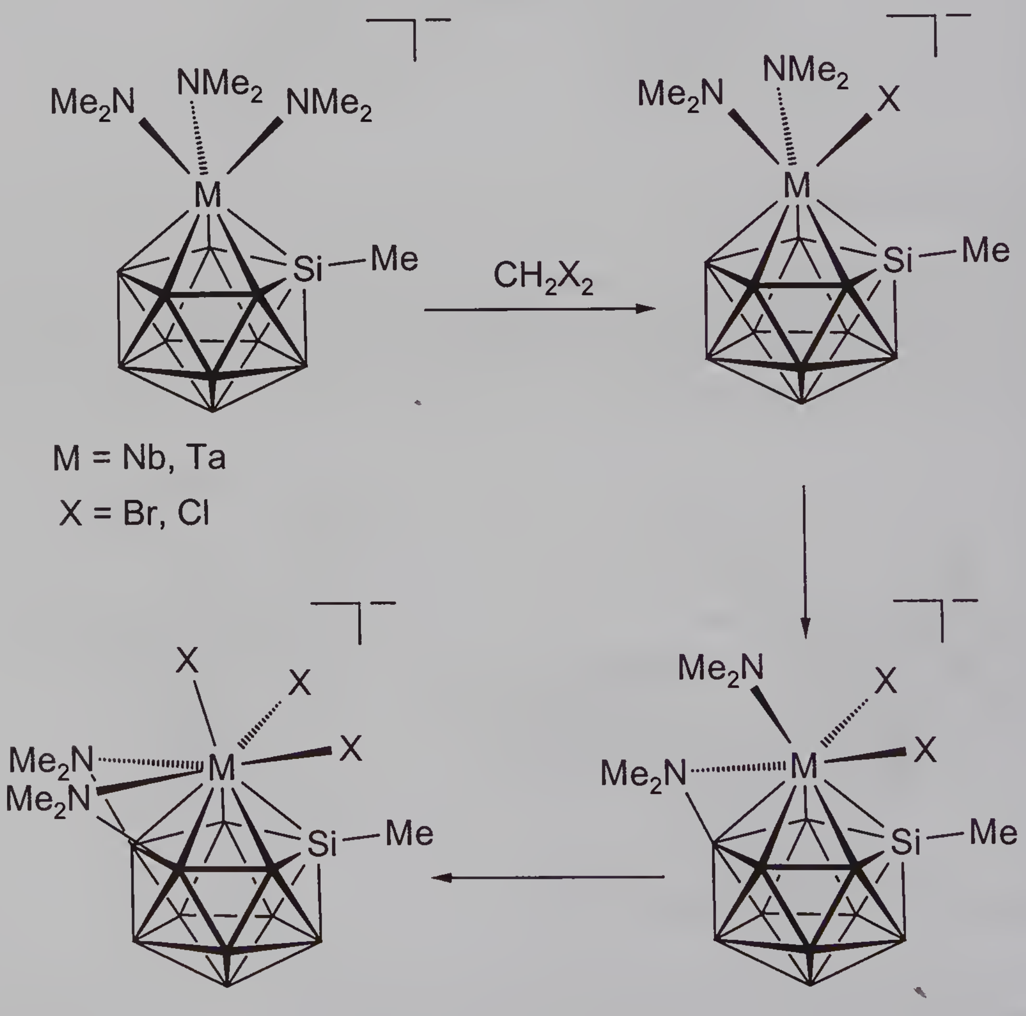


Figure 10 *Formation of the M-N-B Bridges*

Acknowledgements

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References

1. a) D. Seyferth, K. D. Büchner, W. S. Rees, Jr., W. M. Davis, *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 918. b) D. Seyferth, K. Büchner, W. S. Rees, Jr. L. Wesemann, W.M. Davis, S. S. Bukalov, L. A. Leites, H. Bock, B. Solouki, *J. Am. Chem. Soc.* 1993, **115**, 3586.
2. L. Wesemann, U. Englert, D. Seyferth, *Angew. Chem. Int. Ed. Engl.* 1995, **34**, 2236.
3. L. Wesemann, Y. Ramjoie, B. Ganter, B. Wrackmeyer, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 888.
4. L. Wesemann, Y. Ramjoie, M. Trinkaus, B. Ganter, *Inorg. Chem.* 1997, **36**, 5192.
5. L. Wesemann, Y. Ramjoie, M. Trinkaus, T. Spaniol, *Eur. J. Inorg. Chem.* 1998, 1263.
6. L. Wesemann, M. Trinkaus, M. Ruck, *Angew. Chem. Int. Ed. Engl.* 1999, in press.
7. L. Wesemann, Y. Ramjoie, M. Trinkaus, B. Ganter, J. Müller, *Angew. Chem. Int. Ed. Engl.* 1998, **37**, 1412.
8. L. Wesemann, Y. Ramjoie, M. Trinkaus, B. Ganter, *Z. anorg. allg. Chem.* 1998, **624**, 1573.
9. L. Wesemann, M. Trinkaus, Y. Ramjoie, B. Ganter, U. Englert, J. Müller, submitted for publication.
10. L. Wesemann, M. Trinkaus, U. Englert, J. Müller, *Organometallics* accepted for publication.
11. M. F. Hawthorne, *Acc. Chem. Res.* 1968, **1**, 281.
12. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., P. A. Wegner, *J. Am. Chem. Soc.* 1968, **90**, 879.
13. D. J. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, L. J. Todd, *J. Am. Chem. Soc.* 1967, **89**, 3342.
14. W. H. Knoth, *J. Am. Chem. Soc.* 1967, **89**, 3342.
15. R. W. Chesnut, P. E. Fanwick, I. P. Rothwell, *Inorg. Chem.* 1988, **27**, 752.
16. P. Paetzold, *Adv. Inorg. Chem.* 1987, **31**, 123.

Synthesis, Structures and Coordination Chemistry of New Phosphamonocarbaboranes

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1 INTRODUCTION

We recently reported high yield routes for heteroatom-cage insertions that allowed the systematic syntheses of a range of isoelectronic and isostructural *nido*-11-vertex thia- and phospha-boranes, thia- and phospha-dicarbaboranes and the first thiaphosphaborane cluster.[1] We describe here the synthesis and structural characterizations of the first 10-vertex phosphamonocarbaboranes, *exo*-6-R-*arachno*-6,7-PCB_8H_{12} and 6-R-*nido*-6,9-$PCB_8H_9{}^{1-}$, which have also been prepared using these methods. In addition, we report preliminary studies of the coordination chemistry of these clusters which have now demonstrated that they are a versatile new class of transition metal ligands capable of forming a variety of π, as well as *endo*- and *exo*-sigma complexes containing the formal R-*arachno*-$PCB_8H_{11}{}^{1-}$, R-*arachno*-$PCB_8H_{10}{}^{2-}$, R-*arachno*-$PCB_8H_9{}^{3-}$ or R-*nido*-$PCB_8H_9{}^{1-}$ anions.

2 RESULTS AND DISCUSSION

2.1 Synthesis and Structures of *exo*-6-R-*arachno*-6,7-PCB_8H_{12} and 6-R-*nido*-6,9-$PCB_8H_9{}^{1-}$

The reaction (**Eq. 1**) of *arachno*-4-CB_8H_{14} with $RPCl_2$ (R = Ph or Me) in the presence of proton sponge (PS) was found to give 90-95% yields of the new phosphamonocarbaboranes *exo*-6-R-*arachno*-6,7-PCB_8H_{12} (**1a** or **1b**), along with smaller amounts (5-10%) of the 6-R-*nido*-6,9-$PCB_8H_9{}^{1-}$ anions (**2a**⁻ and **2b**⁻).

$$\textit{arachno}\text{-4-}CB_8H_{14} + \text{exs PS} + RPCl_2 \longrightarrow$$

$$1\text{-x } \textit{exo}\text{-6-R-}\textit{arachno}\text{-6,7-}PCB_8H_{12} + \text{x } 6\text{-R-}\textit{nido}\text{-6,9-}PCB_8H_9{}^{-}PSH^{+} + 2\,PSH^{+}Cl^{-} \quad \textbf{(1)}$$

1a, R = Ph　　**2a**⁻, R = Ph

1b, R = Me　　**2b**⁻, R = Me

These new 10-vertex phosphamonocarbaboranes are isoelectronic with the known thiamonocarbaboranes, *arachno*-6,9-SCB_8H_{12} and *nido*-6,9-$SCB_8H_9{}^{1-}$, respectively,[2,3] and would normally be expected to show similar structures. The 6-Ph-*nido*-6,9-$PCB_8H_9{}^{1-}$

structure of **2a⁻** was, in fact, crystallographically established (**Figure 1**) to be similar to that proposed for *nido*-6,9-$SCB_8H_9{}^{1-}$ where the phosphorus and carbon atoms adopt the low-coordinate 6,9-vertices on the puckered 6-membered open-face of the 10-vertex *nido*-framework.

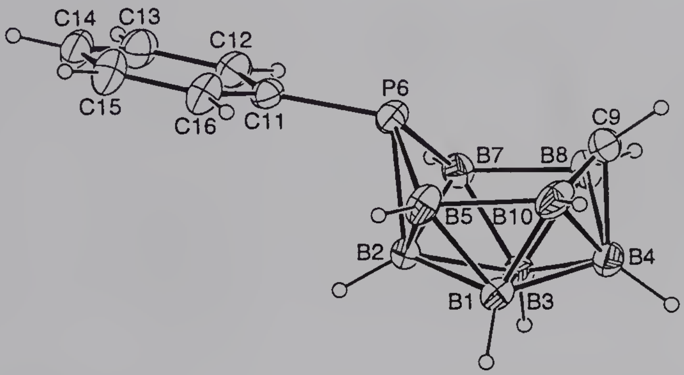


Figure 1. Crystallographically determined structure of **2a⁻**

However, in contrast to the above, the spectroscopic data for **1a** and **1b** clearly indicate a structure that is different than that found for the isoelectronic *arachno*-6,9-SCB_8H_{12}. Thus, the ^{11}B NMR spectra of **1a** and **1b** each showed eight separate resonances, indicating C_1 symmetry rather than the C_s symmetry of *arachno*-6,9-SCB_8H_{12}. Their ^{13}C NMR spectra at -83 °C, each show a broad doublet resonance with additional fine coupling (J_{CP} = 27 Hz) indicating a CH group adjacent to a phosphorus atom. As shown in **Figure 2**, their ^1H NMR spectra also support C_1 symmetry, each showing two different bridge hydrogen resonances, as well as only a single CH resonance rather than the CH_2 resonance found for *arachno*-6,9-SCB_8H_{12}. Most significantly, both the ^1H and ^{31}P NMR spectra of **1a** and **1b** contain a doublet resonance characteristic of a P-H group (**1a**, J_{PH} = 425; **1b**, J_{PH} = 415).

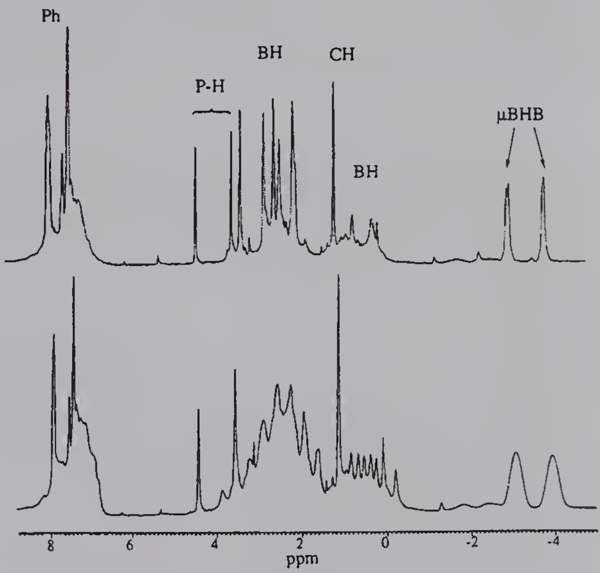
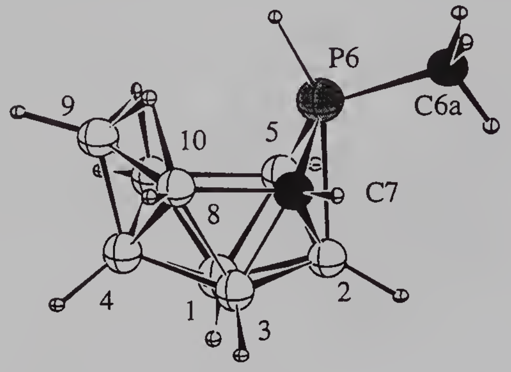


Figure 2. 500 MHz ^1H NMR spectra of **1a**: top, ^{11}B-decoupled; bottom, ^{11}B-coupled

It was not possible to crystallographically characterize **1a** or **1b**, so DFT/GIAO calculations (B3LYP/6-311G*) were employed to confirm their structures.[4] Numerous isomeric structures having C_1 symmetry, as well as the symmetric C_s isomer were examined. The spectroscopic data and DFT/GIAO computational results for **1b** are in excellent agreement for the structure shown in **Figure 3** containing the unique P-H unit. In agreement with a 26 skeletal-electron count, the cage geometry is based on an icosahedron missing two vertices with the phosphorus and carbon atoms in adjacent positions on the puckered 6-membered open face. The phosphorus has both *exo* (methyl) and *endo* (hydrogen) substituents. Additionally, bridge protons span the B8-B9 and B9-B10 edges.



^{11}B NMR

exp	calc
3.0 (B2)	3.0 (B2)
-4.8 (B8,10)	-4.1 (B10)
	-7.3 (B8)
-19.0 (B1)	-18.3 (B1)
-23.0 (B3)	-24.5 (B3)
-25.0 (B9)	-25.4 (B9)
-43.1 (B4)	-45.9 (B4)
-43.9 (B5)	-45.8 (B5)

^{13}C NMR

exp	calc
3.45 (CH)	7.18 (C7)
7.67 (CH_3)	14.82 (C6a)

^{31}P NMR

exp	calc
-46.8 (P6)	-45.6 (P6)

Figure 3. DFT-optimized geometry (B3LYP/6-311G*) for *exo*-6-Me-*arachno*-6,7-PCB_8H_{12} (**1b**) and comparisons of its experimentally-determined and GIAO-calculated (B3LYP/6-311G*) ^{11}B, ^{13}C, and ^{31}P NMR shifts and assignments

Reaction of *exo*-6-R-*arachno*-6,7-PCB_8H_{12} with NaH gives the monoanion resulting from P-H deprotonation. Reprotonation of this anion with $HCl{\cdot}OEt_2$ regenerates *exo*-6-R-*arachno*-6,7-PCB_8H_{12}. In contrast, the reaction of 6-Ph-*nido*-6,9-$PCB_8H_9{}^{1-}$ with acid results in cage degradation rather than producing the neutral 6-Ph-*nido*-6,9-PCB_8H_{10}.

The mechanism of formation of **1** and **2**$^-$ has yet to be determined; however, the simple scheme shown in **Figure 4** can be used to rationalize the formation of both species in the reaction. Thus, the initially formed 4-$CB_8H_{13}{}^-$ can react with $PhPCl_2$ to form a bridge-substituted species which can then undergo dehydrohalogenation with loss of PSH^+Cl^- to yield the RP inserted species.

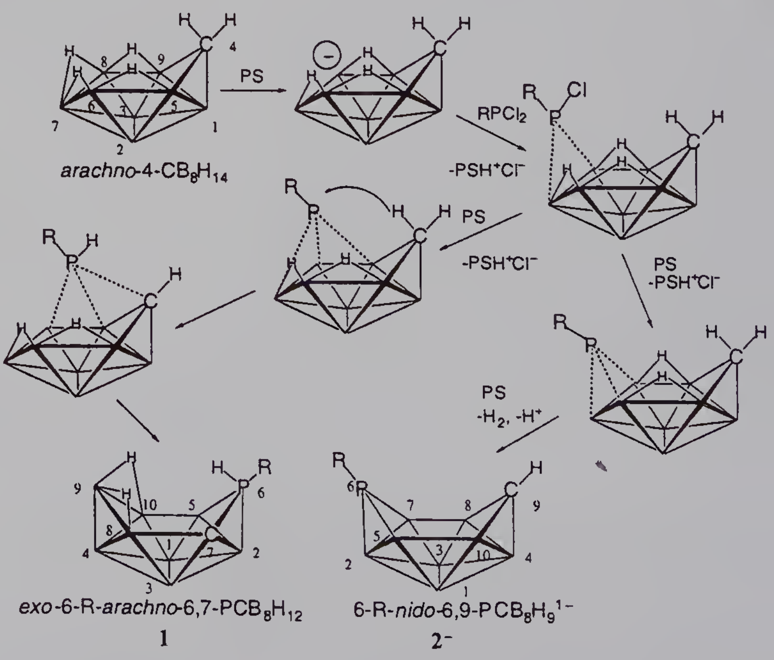


Figure 4. Possible reaction sequence leading to **1** and **2**$^-$

If the insertion takes place along the 7-8-9 edge and is accompanied by hydrogen-transfer to the phosphorus, then **1** will result. If, on the other hand, the insertion takes place along the 6-7-8 edges with subsequent loss of H_2 and deprotonation, then **2**$^-$ would be produced.

2.2 Coordination Chemistry of *exo*-6-R-*arachno*-6,7-PCB_8H_{12}

As shown in **Figure 5**, a number of anionic species could potentially be generated from *exo*-6-R-*arachno*-6,7-PCB_8H_{12}. Thus, deprotonation of the two bridge hydrogens and the *endo*-PH would generate a 6-R-*arachno*-6,7-$PCB_8H_9{}^{3-}$ trianion, while removal of only one or two protons would form the 6-R-*arachno*-6,7-$PCB_8H_{11}{}^{1-}$ and 6-R-*arachno*-6,7-$PCB_8H_{10}{}^{2-}$ anions, respectively. Alternatively, single deprotonation and loss of molecular hydrogen would generate the 6-R-*nido*-6,7-$PCB_8H_9{}^{1-}$ anion (an isomer of **2**$^-$).

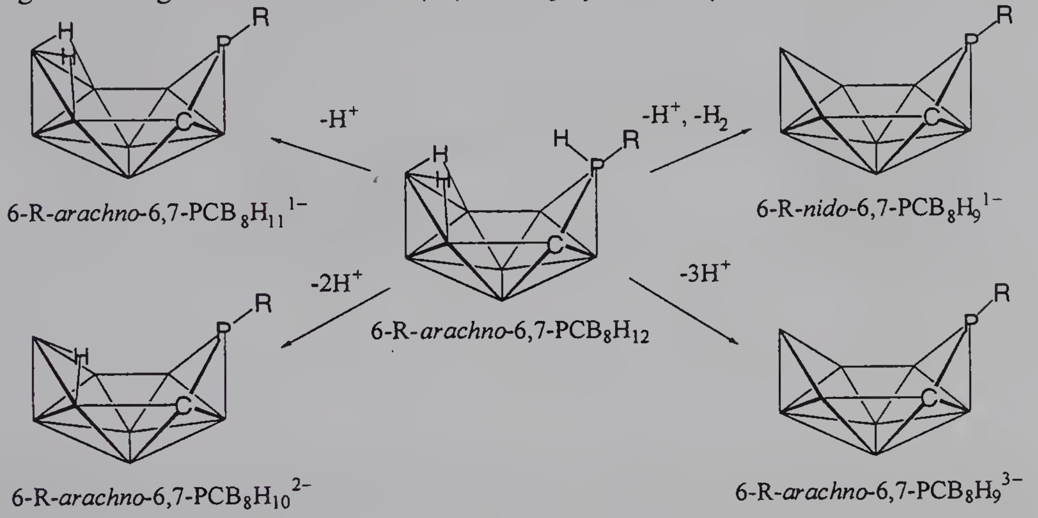


Figure 5. Possible anions that can be derived from *exo*-6-R-*arachno*-6,7-PCB_8H_{12}

As outlined in the examples given in **Figure 6**, because of the range of their accessible formal charges (-1 to -3) and possible coordination geometries (η^1, η^4, η^5 and η^6), these anions could potentially serve as a versatile new class of transition metal ligands. Our preliminary studies have now, in fact, demonstrated each of the coordination modes illustrated in the figure. For example, as given in **Eqs. 2** and **3**, the reactions of $CpFe(CO)_2I$ and $BrMn(CO)_5$ with the 6-Ph-*arachno*-6,7-$PCB_8H_{11}{}^{1-}$ anion (**1a**$^-$) gave excellent yields of the η^1-complexes **3** and **4**, respectively. X-ray crystallographic studies of these compounds established the structures shown in **Figure 7**.

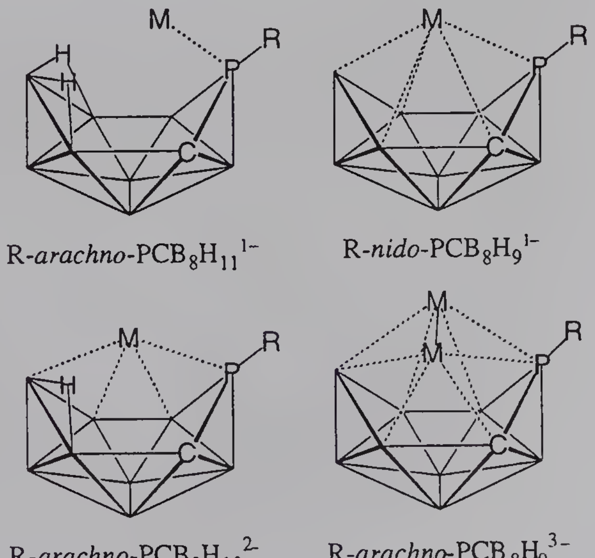


Figure 6. Possible coordination compounds derived from *exo*-6-R-*arachno*-6,7-PCB_8H_{12}

$$\underset{\mathbf{1a}^-}{\mathrm{Na^+\ 6\text{-}Ph\text{-}}\textit{arachno}\text{-}6,7\text{-}\mathrm{PCB_8H_{11}}^{1-}} + (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2I} \xrightarrow{\text{-NaI}} \underset{\mathbf{3}}{\textit{endo}\text{-}6\text{-}[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]\text{-}\textit{exo}\text{-}6\text{-}\mathrm{Ph}\text{-}\textit{arachno}\text{-}6,7\text{-}\mathrm{PCB_8H_{11}}} \quad (2)$$

$$\underset{\mathbf{1a}^-}{\mathrm{Na^+\ 6\text{-}Ph\text{-}}\textit{arachno}\text{-}6,7\text{-}\mathrm{PCB_8H_{11}}^{1-}} + \mathrm{BrMn(CO)_5} \xrightarrow{\text{-NaBr}} \underset{\mathbf{4}}{\textit{exo}\text{-}6\text{-}[\mathrm{(CO)_5Mn}]\text{-}\textit{endo}\text{-}6\text{-}\mathrm{Ph}\text{-}\textit{arachno}\text{-}6,7\text{-}\mathrm{PCB_8H_{11}}} \quad (3)$$

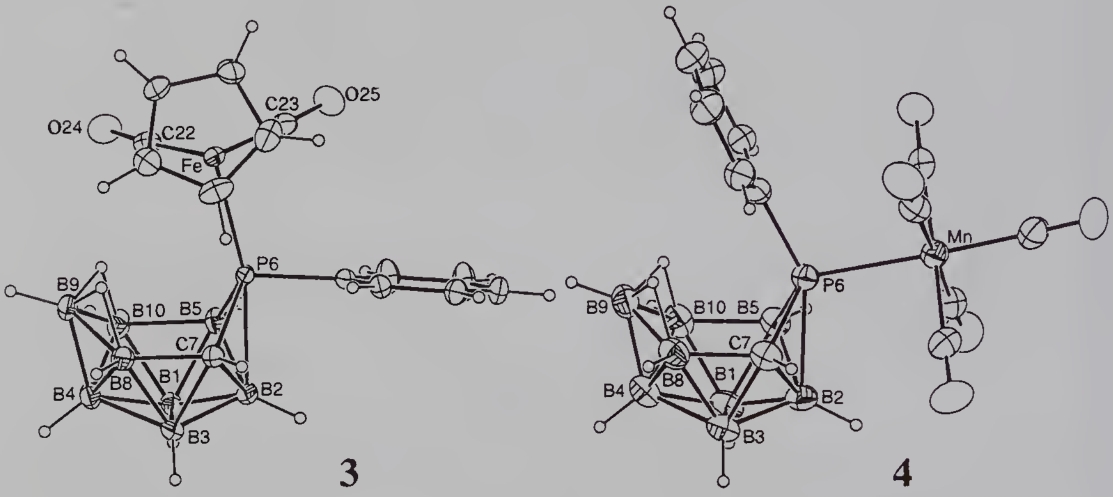


Figure 7. Crystallographically established structures of **3** and **4**

In both **3** and **4** the formal 6-Ph-*arachno*-6,7-$\mathrm{PCB_8H_{11}}^{1-}$ anion is coordinated in an η^1-fashion to the metal atom by means of a single metal-phosphorus bond. The CO stretching frequencies in **3** (2030 and 1987 $\mathrm{cm^{-1}}$) are higher than those found for either $\mathrm{CpFe(CO)_2(PPh_2)}$ (2015, 1966 $\mathrm{cm^{-1}}$)[5] or $\mathrm{CpFe(CO)_2(PPh_2(BC_5H_5))}$ (2024, 1982 $\mathrm{cm^{-1}}$)[6], indicating that 6-Ph-*arachno*-6,7-$\mathrm{PCB_8H_{11}}^{1-}$ is less electron donating than either the $\mathrm{PPh_2}^-$ or $\mathrm{(PPh_2(BC_5H_5))^-}$ anions.

It is perhaps surprising that in **3** the $\mathrm{CpFe(CO)_2}$ fragment is at the *endo*-position, while in **4** the $\mathrm{Mn(CO)_5}$ unit adopts the *exo*-position. However, as illustrated in **Figure 8**, DFT calculations have shown that the *endo*-6-Me-*arachno*-6,7-$\mathrm{PCB_8H_{12}}$ and *exo*-6-Me-*arachno*-6,7-$\mathrm{PCB_8H_{12}}$ configurations are close in energy with the *exo*-configuration being favored by only 2.5 kcal/mol.

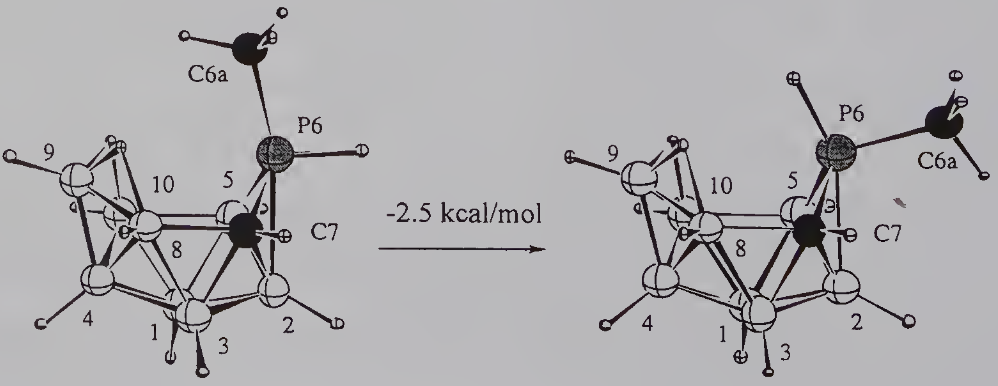


Figure 8. Energy comparison of the DFT-optimized (B3LYP/6-311G*) structures of *endo*-6-Me-*arachno*-6,7-$\mathrm{PCB_8H_{12}}$ and *exo*-6-Me-*arachno*-6,7-$\mathrm{PCB_8H_{12}}$

Based on steric interactions alone, it would be expected that the *exo*-coordination would be even more stable for metal coordination. In agreement with these expectations, it was found (**Eq. 4**) that photolysis of **3** results in its quantitative conversion to a new isomer **5**. While **5** has not yet been crystallographically characterized, its ^{11}B NMR spectrum is nearly identical to that of **4** thus providing strong evidence that isomerization of the *endo*-$CpFe(CO)_2$ unit to the *exo*-position has occurred.

$$\underset{\mathbf{3}}{endo\text{-}6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]\text{-}exo\text{-}6\text{-}Ph\text{-}arachno\text{-}6,7\text{-}PCB_8H_{11}} \xrightarrow{h\nu} \underset{\mathbf{5}}{exo\text{-}6\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]\text{-}endo\text{-}6\text{-}Ph\text{-}arachno\text{-}6,7\text{-}PCB_8H_{11}} \quad (4)$$

The reaction of **1a**$^-$ with *cis*-$(Ph_3P)_2PtCl_2$ in the presence of proton sponge results in the formation of both the η^1-complex **6**, which is similar to **3**, containing an *endo*-$(Ph_3P)_2PtCl$-group, and the 11-vertex platinaphosphacarbaborane **7** resulting from platinum insertion into the cage framework (**Eq. 5**). Both **6** and **7** were crystallographically characterized as shown in **Figure 9**.

$$\underset{\mathbf{1a^-}}{Na^+ exo\text{-}6\text{-}Ph\text{-}arachno\text{-}6,7\text{-}PCB_8H_{11}^-} + cis\text{-}(Ph_3P)_2PtCl_2 + PS \xrightarrow{\text{-NaCl, -PSH}^+\text{Cl}^-} \underset{\mathbf{6}}{endo\text{-}6\text{-}[cis\text{-}(Ph_3P)_2PtCl]\text{-}exo\text{-}6\text{-}Ph\text{-}arachno\text{-}6,7\text{-}PCB_8H_{11}} + \underset{\mathbf{7}}{7\text{-}(Ph_3P)_2\text{-}8\text{-}Ph\text{-}nido\text{-}7,8,9\text{-}PtPCB_8H_{10}} \quad (5)$$

In contrast to the η^1-coordination observed in complexes **3-6**, the platinum in **7** is η^4-coordinated to the formal R-*arachno*-$PCB_8H_{10}^{2-}$ ligand. In agreement with a 26 skeletal electron count, the resulting cluster has a *nido*-framework based on an icosahedron missing one vertex. One bridge hydrogen spans the boron-boron edge on the five-membered open face of the cluster.

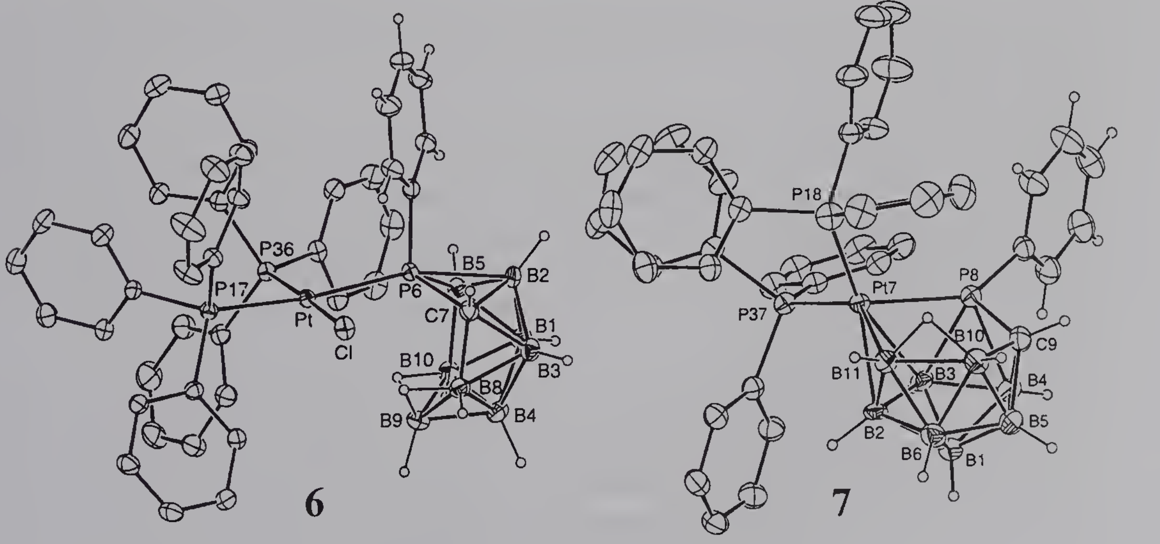
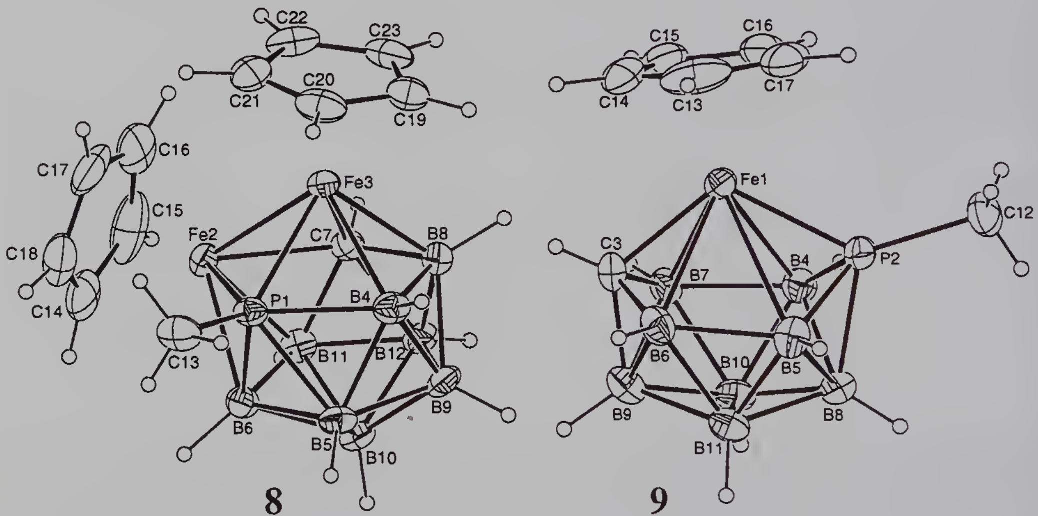


Figure 9. Crystallographically established structures of 6 and 7

Further metal insertions into the phosphamonocarbaborane framework to yield η^5- and η^6-coordinated metals were observed in the reaction (**Eq. 6**) of $FeCl_2$ with Na^+Cp^- and **1b⁻** which gave the two new metalla-phosphacarbaborane complexes, 1-Me-2,3-(η^5-$C_5H_5Fe)_2$-1,7-PCB_8H_9 (**8**) and 2-Me-*closo*-1-(η^5-C_5H_5)Fe-2,3-PCB_8H_9 (**9**) in an overall 87% yield. The structures of both compounds were crystallographically characterized as shown in **Figure 10**.

$$Na^+\ \text{Me-}arachno\text{-}PCB_8H_{11}{}^{1-} + NaCp + FeCl_2 \xrightarrow{-H_2\ -2NaCl}$$
$$\mathbf{1b^-}$$

$$\text{1-Me-2,3-}(\eta^5\text{-}C_5H_5Fe)_2\text{-1,7-}PCB_8H_9 + \text{2-Me-}closo\text{-1-}(\eta^5\text{-}C_5H_5)Fe\text{-2,3-}PCB_8H_9 \quad (6)$$
$$\mathbf{8} \qquad\qquad\qquad\qquad \mathbf{9}$$



8 **9**

Figure 10. Crystallographically established structures of **8** and **9**

The icosahedral structure of the paramagnetic diferraphosphacarbaboranyl complex **8** can be viewed as derived from the insertion of two (η^5-C_5H_5)Fe units into the formal R-*arachno*-$PCB_8H_9{}^{3-}$ fragment. Since **8** is neutral, this requires that the two iron atoms have formal Fe^{II} and Fe^{III} oxidation states, but the x-ray structural data show no apparent differences in the bonding configurations of the two iron atoms suggesting averaged oxidation states. Likewise, even though the cluster has only a 25 skeletal-electron count, rather than the 26 electrons normally expected for a *closo*-icosahedral structure, there are no obvious cage distortions. The carbon and phosphorus atoms in **8** have migrated from their adjacent positions in **1a** to the non-adjacent positions that are connected to both Fe atoms.

Complexes **3-8** are each based upon metal coordination to an *arachno*-phosphamonocarbaborane framework, i.e. R-*arachno*-$PCB_8H_{11}{}^{1-}$ (**3-6**), R-*arachno*-$PCB_8H_{10}{}^{2-}$ (**7**), or R-*arachno*-$PCB_8H_9{}^{3-}$ (**8**); however, complex **9**, 2-Me-*closo*-1-(η^5-C_5H_5)Fe-2,3-PCB_8H_9, is best formulated as based on iron coordination to a R-*nido*-$PCB_8H_9{}^{1-}$ fragment. Such a *nido* cage-fragment could be formed from *exo*-6-R-*arachno*-6,7-PCB_8H_{12} by a process similar to that shown in **Figure 5**, in which deprotonation and loss of molecular H_2 occurs. Consistent with its predicted 24 skeletal electron count, **9** has an 11-vertex *closo*-octadecahedral framework, in which the iron is η^6-coordinated at the 6-membered puckered face. As in **8**, the phosphorus and carbon atoms have migrated away from their adjacent positions in **1a** and are now in the low-coordinate positions adjacent to the iron atom. Thus, **9** is actually a derivative of **2a**$^-$, 6-Ph-*nido*-6,9-$PCB_8H_9{}^{1-}$.

9 is isoelectronic and isostructural with the ferratricarbadecaboranyl complex 2-Me-*closo*-1-(η^5-C_5H_5)Fe-2,3,5-$C_3B_7H_9$,[7] and both **9** and 2-Me-*closo*-1-(η^5-C_5H_5)Fe-2,3,5-$C_3B_7H_9$ can be considered ferrocene analogs in which an Fe(II) is sandwiched between one Cp^{1-} and the 6-Me-*nido*-6,9-$PCB_8H_9{}^{1-}$ or *nido*-6-Me-5,6,9-$C_3B_7H_9{}^{1-}$ anions, respectively. We have found, however, that even though the 6-R-*nido*-6,9-$PCB_8H_9{}^{1-}$ and *nido*-6-Me-5,6,9-$C_3B_7H_9{}^{1-}$ anions have the same charge and ability to function as a 6-π electron donor as the Cp^{1-} anion, their resulting metallatricarbadecaboranyl and metallaphosphacarbadecaboranyl complexes have many properties that are significantly different than their metallocene counterparts. For example, as a result of the strong electron withdrawing properties of the coordinated 6-Me-*nido*-6,9-$PCB_8H_9{}^{1-}$ and *nido*-6-Me-5,6,9-$C_3B_7H_9{}^{1-}$ ligands, both 2-Me-*closo*-1-(η^5-C_5H_5)Fe-2,3,5-$C_3B_7H_9$ and **9** have greatly increased oxidative stabilities (>0.4 V) compared to ferrocene. Such differences suggest a number of potential applications for metallatricarbadecaboranyl and metallaphosphacarbadecaboranyl complexes where the use of traditional metallocenes has been limited by their instability. For example, we are now exploiting the stabilizing influence of these new ligands to design and synthesize new metallatricarbadecaboranyl and metallaphosphacarbadecaboranyl analogs of the known metallocene anti-tumor agents which, because of their increased oxidative and chemical stabilities, may show better delivery to the tumor site and increased bioactivities.[8]

In conclusion, because of their ease of synthesis and unusual ranges of readily accessible oxidation states and coordination modes, the 10-vertex phosphamonocarbaboranes offer unique opportunities as potential ligands that can stabilize transition metals in a variety of environments. We are currently investigating the synthesis of a wider range of phosphamonocarbaboranes and related isoelectronic heteroatomcarbaborane clusters, as well as exploiting the unusual coordinating properties of these clusters.

3 ACKNOWLEDGEMENTS

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References

1. A. M. Shedlow and L. G. Sneddon, *Inorg. Chem.*, 1998, **37**, 5269-5277.
2. J. Holub, J. D. Kennedy, T. Jelinek, and B. Stíbr, *J. Chem. Soc., Chem. Commun.*, 1991, 1389-1390.
3. J. Holub, J. D. Kennedy, T. Jelinek, and B. Stíbr, *J. Chem. Soc., Dalton Trans.*, 1994, 1317-1323.
4. For a description of the computational procedures and methods employed see ref. 1.
5. J. C. T. R. Burckett-St. Laurent, R. J. Haines, C. R. Nolte and N. D. C. T. Steen, *Inorg. Chem.*, 1980, **19**, 577-587.
6. D. A. Hoic, W. D. Davis, and G. C. Fu, *J. Am. Chem. Soc.*, 1996, **118**, 8176-8177.
7. (a) C. A. Plumb, P. J. Carroll, and L. G. Sneddon, *Organometallics*, 1992, **11**, 1665-1671. (b) C. A. Plumb, P. J. Carroll, and L. G. Sneddon, *Organometallics*, 1992, **11**, 1672-1680.
8. (a) M. D. Wasczcak, I. H. Hall, P. J. Carroll and L. G. Sneddon, *Angew. Chem., Int. Ed. Eng.*, 1997, **36**, 2227-2228. (b) I. H. Hall, A. E. Warren, C. C. Lee, M. D. Wasczcak and L. G. Sneddon, *Anticancer Research*, 1998, **18**, 951-962.

Organic and Inorganic Chemistry of Mono- and Di-boron Systems

Transition Metal Complexes of Boron

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1 INTRODUCTION

In contrast to other transition metal compounds of boron such as borides or metallaboranes, the class of transition metal complexes of boron, e.g. borane (**I**), boryl (**II**), and borylene (**IIIa**, **b**) complexes (Figure 1),[1] are characterized by two-center-two-electron bonds between the metal center and boron.

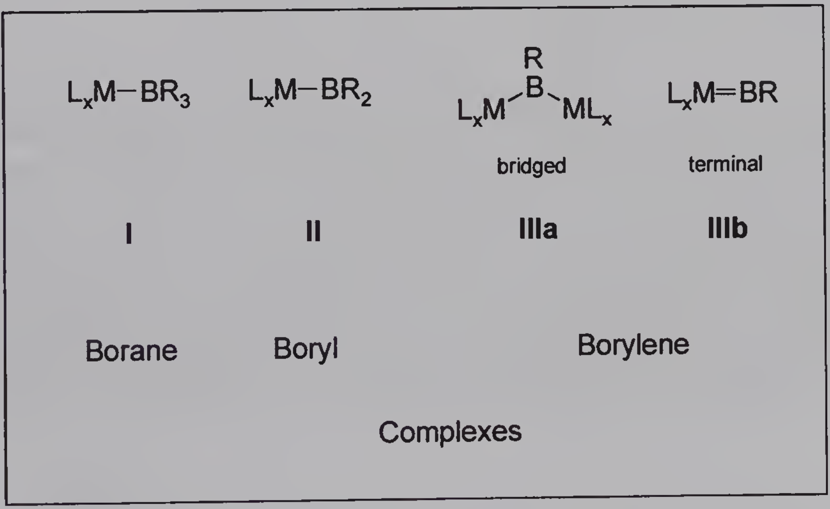


Figure 1 *Classification of transition metal complexes of boron*

Numerous reports on such compounds date back to the 1960´s [3], but all conclusions concerning constitution and bonding situation of the proposed complexes were solely drawn on the basis of spectroscopic data. The existence of boryl and borylene complexes was proven as late as in the 1990´s (Figure 2), thus demonstrating the difficulties being associated with their synthesis and structural characterization. In the course of recent investigations the earlier findings were disproved to a great extent.

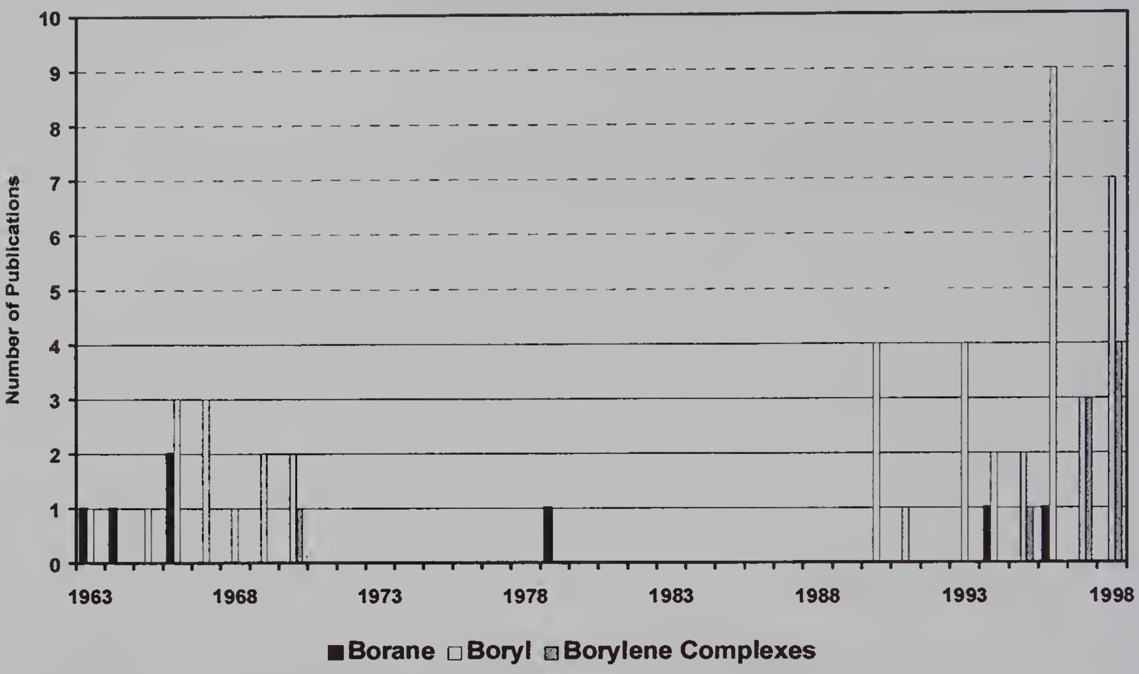
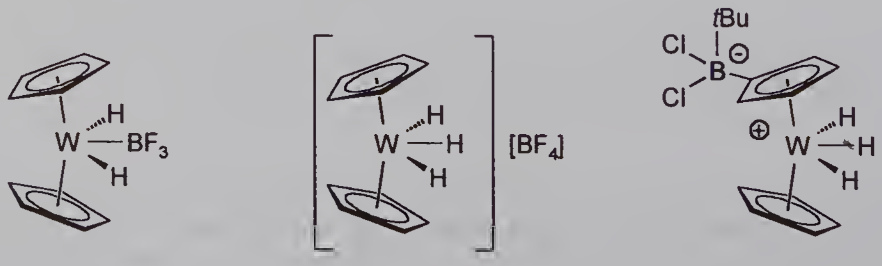


Figure 2 *Publications on transition metal complexes of boron from 1963 to 1998*

2 BORANE COMPLEXES

Upon reaction with basic transition metal complexes the general tendency of electronically unsaturated boranes to form Lewis acid-base adducts should result in the formation of borane complexes (I). $[Cp_2WH_2(BF_3)]$ (**1**), which is known from many textbooks represents the best known example for such a compound [4]. Recently, however, the proposed constitution of **1** was disproved, and it was shown that reactions of $[Cp_2WH_2]$ with boranes yield salt like compounds **2** and zwitterionic species **3**, respectively. [5,6] For the formation of **2** one equivalent of HF is required, and in this reaction the borane acts as a fluoride source, while the WH_2 moiety supplies a proton (Figure 3). [7] Until now no structurally authentic borane complex was reported.

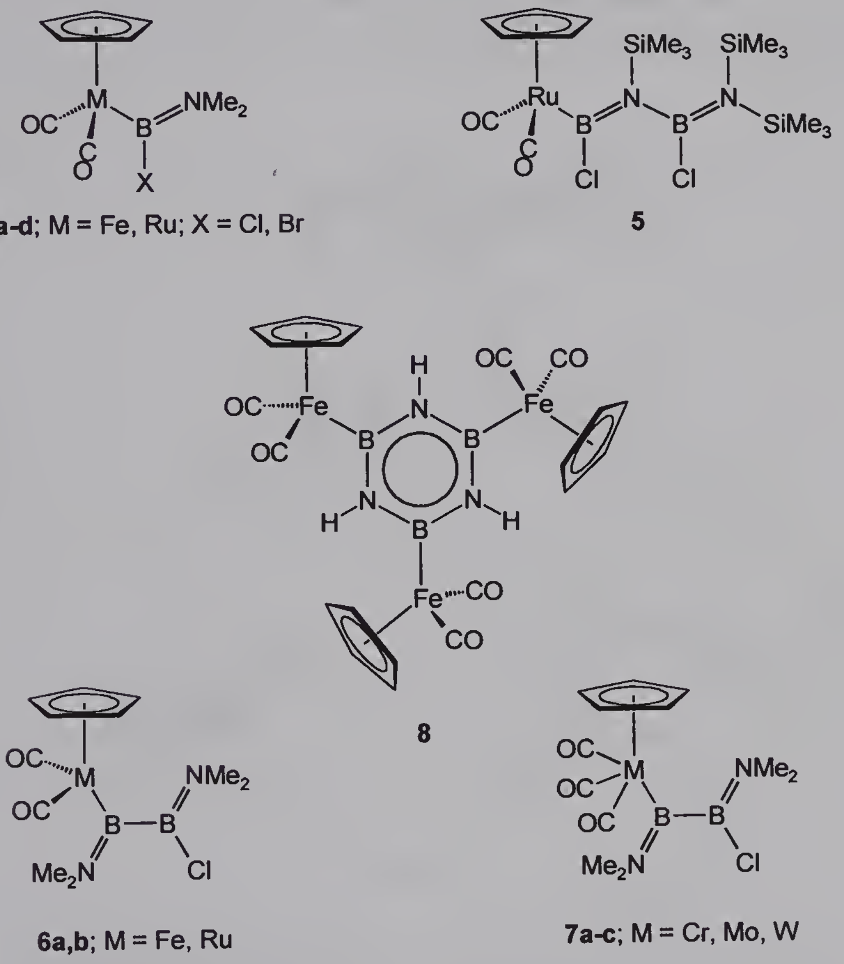


1 **2** **3**

Figure 3 *Reactions of $[Cp_2WH_2]$ with boranes: Proposed (1) and authentic (2) constitution of the product obtained from $[Cp_2WH_2]$ and BF_3; zwitterionic complex (3) obtained from $[Cp_2WH_2]$ and $tBuBCl_2$*

3 BORYL COMPLEXES

Catecholborane and its derivatives had a pivotal role in establishing the class of boryl complexes, since they proved to be the most versatile starting materials for the synthesis of such compounds. This was demonstrated in many works especially by Baker, Hartwig, Marder, Norman, and Smith.[1,2] In the course of our investigations we aimed at boryl complexes with different substituents attached to boron, and we could show that boranes with B-N bonds are also very well suited for the synthesis of boryl complexes. Over the last three years a wide variety of products was obtained by salt elimination reactions between anionic transition metal complexes and haloboranes. Examples include aminoboryl- **4**, **5**,[8,9] diborane(4)yl- **6**, **7**,[10,11] and η^1-borazine complexes **8**[12] (Figure 4).



4a-d; M = Fe, Ru; X = Cl, Br

5

8

6a,b; M = Fe, Ru

7a-c; M = Cr, Mo, W

Figure 4 *Boryl complexes derived from N-substituted boranes: aminoboryl complexes* **4** *and* **5**, *diborane(4)yl complexes* **6** *and* **7**, η^1*-borazine complexes* **8**

All of these compounds are characterized in solution by their ^{11}B-NMR signals ranging from $\delta = 50$ to $\delta = 70$ which are distinctly lowfield shifted with respect to the signals of the starting boranes. The iron compound **4a** shall serve as a typical example for all structurally characterized compounds **4** - **8** to discuss the nature of the metal boron bond (Figure 5). The molecule adopts C_1 symmetry in the crystal which is due to an almost perpendicular (87.4°) orientation of the N-B-Cl plane with respect to the Cp(centroid)-Fe-B plane. This orientation allows no Fe-B π-interaction between the metallike a''-symmetrical HOMO with the free p orbital on boron. The description of the Fe-B linkage as a pure σ-bond is corroborated by the Fe-B distance (202.7(5) pm), which is significantly longer than the sum of the covalent radii of iron and boron. The CO stretching frequencies in the IR spectrum of **4a** (ν = 1988, 1928 cm^{-1}) are red shifted with respect to those of corresponding iron alkyl complexes, thus proving the same bonding situation in solution. Similar structural and spectroscopic results are known for the complexes **4b** – **8**, so obviously all boryl complexes with B-N bonds display metal-boron linkages without significant π-interaction. That this is not generally true for all boryl complexes was for example shown by Hartwig and coworkers, who structurally characterized the catecholanalogue [CpFe(CO)$_2$Bcat] of **4a** already in 1993[13]. In this case all structural and spectroscopic data give evidence for the presence of an albeit weak Fe-B backbonding.

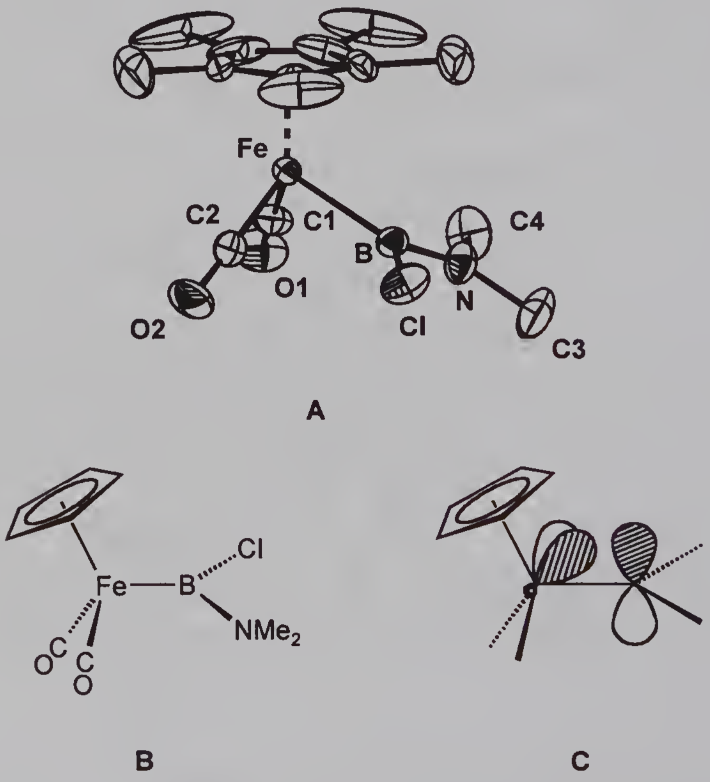
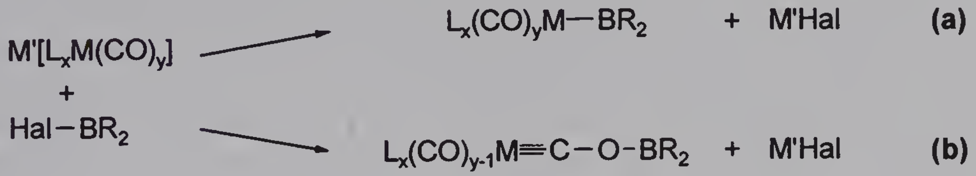
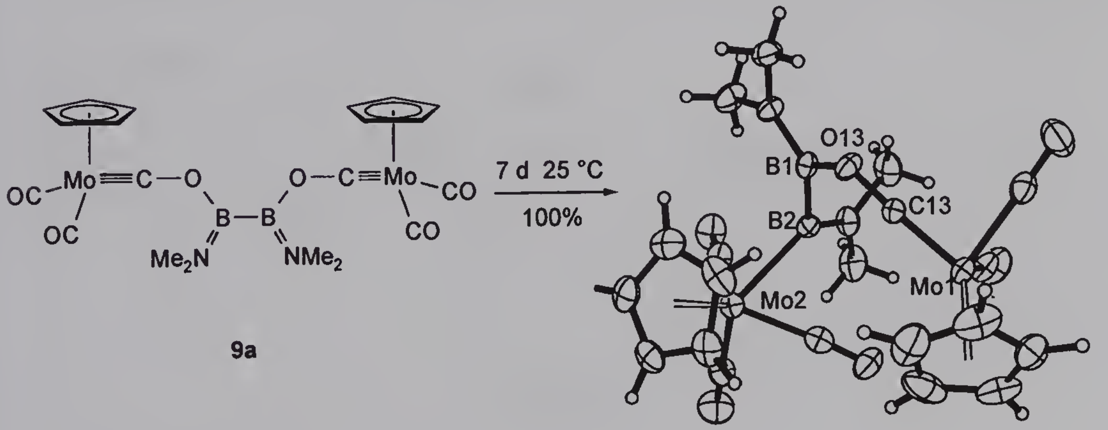


Figure 5 *Ortepplot (A) and schematic structure (B) of **4a**; orientation of the metallike HOMO and the p orbital at boron (C)*

The formation of boryl complexes from anionic transition metal complexes and haloboranes according to Equation 1a implies that the metal generally acts as the nucleophilic center in such salt elimination reactions. There is, however, evidence from one other system,[14] that the CO oxygen atom also displays some nucleophilic character, which in the case of haloboranes would lead to the formation of (boryloxy)carbyne complexes according to Equation 1b. Very recently we found an example for this alternative pathway to the common formation of M-B bonds: $B_2(NMe_2)_2I_2$ and two equivalents of Na[CpM(CO)$_3$] react with elimination of two NaI yielding the dinuclear oxycarbyne complexes **9a, b** (M = Mo, W).[15] In this case the R_2B-O-C≡M moiety was formed by nucleophilic attack of one CO oxygen to each boron center. Characteristic for the formation of B-O instead of B-M bonds are the highfield shifted ^{11}B-NMR signals at $\delta \sim 31$. Interestingly **9a, b** do not represent the thermodynamically stable products of this reaction, since they proved to rearrange quantitatively in solution within 7d at ambient temperature yielding the complexes **10a, b**. This unique rearrangement occurs with 1,3-shift of one borylgroup from the carbyne oxygen atom to the metal center and restoration of the former CO ligand according to Equation 2; for steric reasons a corresponding rearrangement of the second R_2B-O-C≡M moiety is not observed.



Equation 1



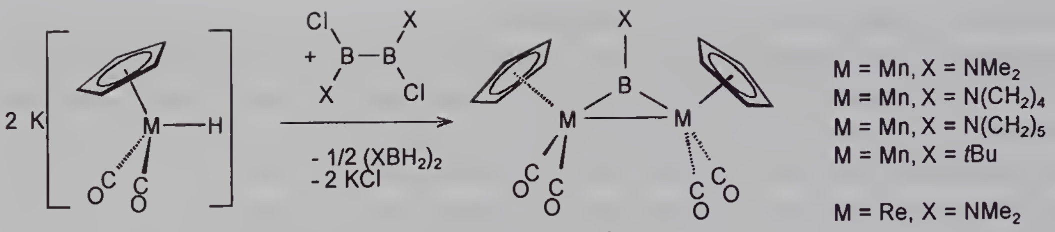
9a

10a

Equation 2

4 BORYLENE COMPLEXES

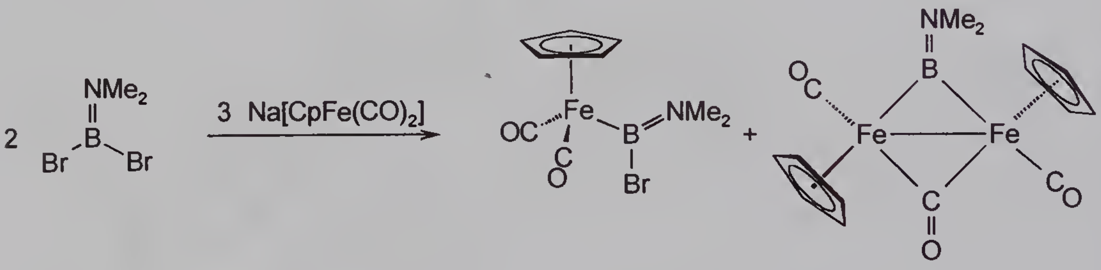
Already in 1995 we obtained the first bridged borylene complexes **11a, d** from the unusual reaction of 1,2-dihalodiboranes(4) with K[CpMn(CO)$_2$H] (Equation 3).[16,17] Although this synthesis was recently extended to further examples **11b, c**[18] and also to the rhenium analogue **11e** we aimed at a more general access to this interesting class of compounds.



11a - e

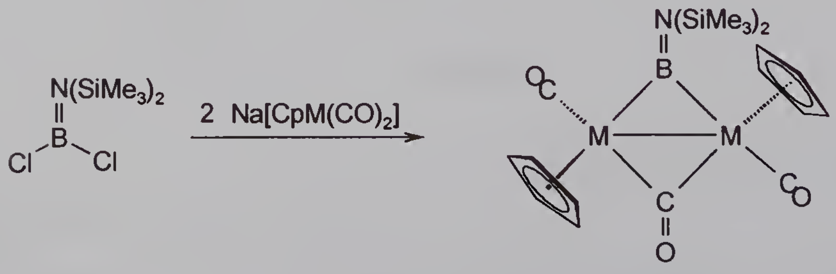
Equation 3

Hence, we investigated the reactions of aminodihaloboranes with anionic transition metal complexes, and expected Me_2NBCl_2 to react with two equivalents of $Na[CpFe(CO)_2]$ yielding a bridged borylene complex of the general formula $L_nM\text{-}B(R)\text{-}ML_n$ (**IIIa**). All attempts, however, led to $[CpFe(CO)_2(BClNMe_2)]$ (**4a**) without substitution of the second chloride ligand. The more reactive bromoderivative Me_2NBBr_2 already yielded a mixture of the boryl complex $[CpFe(CO)_2(BBrNMe_2)]$ (**12**) and the desired borylene complex **13** according to Equation 4. Although both products could not be seperated by crystallization, it was possible to isolate **13** in pure form after treating the mixture with air and water, thus selectively hydrolyzing the boryl complex **12**.[9] Finally, corresponding reactions of the sterically crowded albeit more electrophilic $(Me_3Si)_2NBCl_2$ provided good access to the bridged borylene complexes **14, 15** (Equation 5).[8,9]



12 **13**

Equation 4



14; M = Fe
15; M = Ru

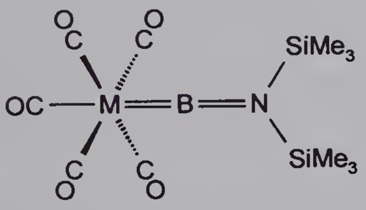
Equation 5

As expected for complexes with two metal-boron bonds **11a** – **15** show lowfield shifted ^{11}B-NMR signals ranging from $\delta = 90$ to 170; their structure in the crystal resembles that of corresponding bridged carbene complexes with M-B distances indicating σ-bonds. The manganese complex **11a** proved to be stable towards air and water and served as starting material for substitution reactions yielding further borylene complexes [μ-BX{CpMn(CO)$_2$}$_2$] (**16a-d**, X = Cl, NR$_2$, OR, OH).[19]

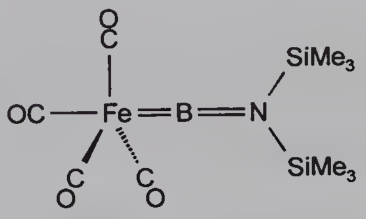
The missing link in this series of compounds, terminal borylene complexes **17** - **19** (Figure 6) with twofold coordinated boron atoms, were obtained very recently again by salt elimination reactions from dianionic transition metal complexes and dihaloboranes according to Equation 6.[20]

$$\mathrm{M'_2[M(CO)_n]} + \mathrm{R{-}BHal_2} \longrightarrow \mathrm{(OC)_nM{=}B{-}R} + 2\,\mathrm{M'Hal}$$

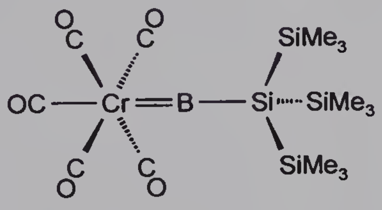
Equation 6



17a-c; M = Cr, Mo, W



18



19

Figure 6 *Terminal borylene complexes 17 – 19*

These complexes show again lowfield shifted ^{11}B-NMR signals at about $\delta = 90$ and the results of the crystal structure analyses for **17a, c** reveal that the central M-B-N moiety adopts the expected linear arrangement. The M-B distances resemble those of corresponding Fischer type carbene complexes, thus indicating the presence of M-B double bonds (Figure 7). Results of an ab initio study on such compounds showed that strong metal-boron π-bonds are present in amino- and flouroborylene complexes, and that the M-B bond dissociation energy exceeds the corresponding value for a M-C bond cleavage in carbonyl complexes by some 30 Kcal/mol.[21] The synthesis of the silylborylene complex **19** shows, that such compounds are not restricted to the use of aminoboranes. Due to the electron sextett at boron, **19** shows an extreme ^{11}B-NMR resonance at $\delta = 204.7$.

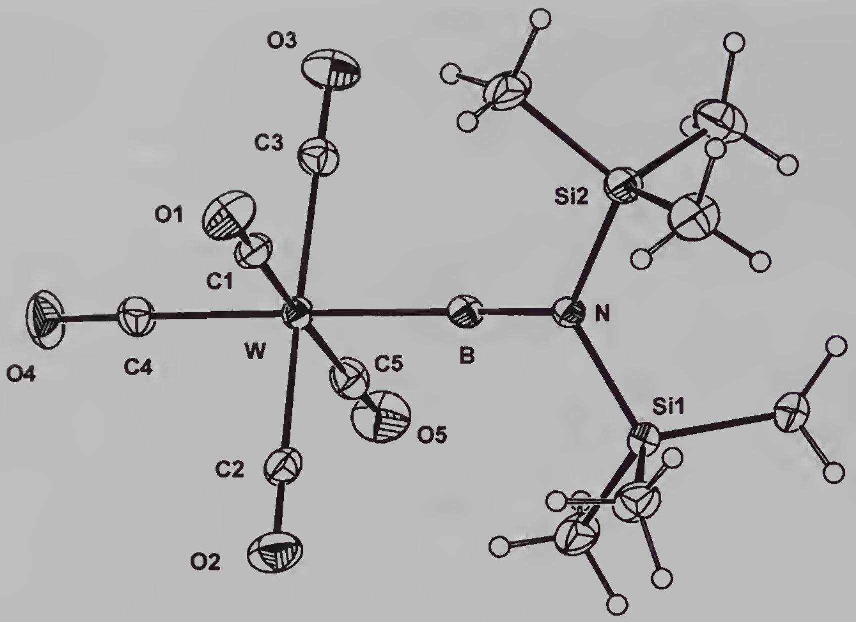


Figure 7 *Structure of 17c in the crystal*

References

1. H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882, *Angew. Chem. Int. Ed. Engl. 37*, **1998**, 1786.
2. G. I. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685.
3. G. Schmid, *Angew. Chem.* **1970**, *82*, 920, *Angew. Chem. Int. Ed. Engl. 9*, **1970**, 819.
4. M. P. Johnson, D. F. Shriver, *J. Am. Chem. Soc.* **1966**, *88*, 301.
5. H. Braunschweig, T. Wagner, *Chem. Ber.* **1994**, *127*, 1613.
6. H. Braunschweig, T. Wagner, *Z. Naturforsch.* **1996**, *51b*, 1618.
7. H. Braunschweig, C. Kollann, *Z. Naturforsch.* **1999**, *54b*, in press.
8. H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465.
9. H. Braunschweig, C. Kollann, K. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, in press.
10. H. Braunschweig, B. Ganter, M. Koster, T. Wagner, *Chem. Ber.* **1996**, *129*, 1099.
11. H. Braunschweig, M. Koster, R. Wang, *Inorg. Chem.* **1999**, *38*, 415.
12. H. Braunschweig, C. Kollann, M. Müller, *Eur. J. Inorg. Chem.* **1998**, 291.
13. J. F. Hartwig, S. Huber, *J. Am. Chem. Soc.* **1993**, *115*, 4908.
14. R. N. Vrtis, C. P. Rao, S. Warner, S. J. Lippard, *J. Am. Chem. Soc.* **1988**, *110*, 2669.
15. H. Braunschweig, M. Koster, K. W. Klinkhammer, *Angew. Chem.* **1999**, *111*, in press.
16. H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825.
17. H. Braunschweig, B. Ganter, *J. Organomet. Chem.* **1997**, *545*, 163.
18. H. Braunschweig, M. Koster, *J. Organomet. Chem.* **1999.**
19. H. Braunschweig, M. Müller, *Chem. Ber.* **1997**, *130*, 1295.
20. H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3179.
21. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U.Radius, *Chem. Eur. J.* **1998**, *14*, 210.

Boryl Complexes of Ruthenium and Osmium

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1 INTRODUCTION

Compounds with transition metal-boron, 2c-2e bonds ($L_nM\text{-}BR_2$) have been widely studied in the past decade primarily because of the recognition that these compounds are key intermediates in the metal-catalysed syntheses of boron-functionalised organics. Several reviews[1-3] have covered developments in this area. Bcat derivatives of palladium, platinum, rhodium, and iridium have figured prominently in these studies. On the other hand, boryl derivatives of ruthenium and osmium have attracted less attention, partly because there are fewer catalytic applications. However, from our own studies there is now a substantial number of these compounds known, with a range of differently substituted boryl ligands. Systematic structural studies reveal trends in M-B bond distances as changes are made to the heteroatoms present on boron, or to the accompanying ligands especially those ligands trans to the boryl ligand. The observed trends can be accommodated by attributing not only good σ-bonding capability to boryl ligands, but also, at least in some cases, good π-acceptor capability. Moreover, complexes which are good models for postulated intermediates in either metal-catalysed hydroboration processes or the metal-catalysed borylation of arenes have been characterised and substitution reactions at the boron centre, without cleavage of M-B bonds, have been explored. These developments are the subject of this article.

2 SYNTHESES THROUGH B-H AND B-B OXIDATIVE ADDITION REACTIONS

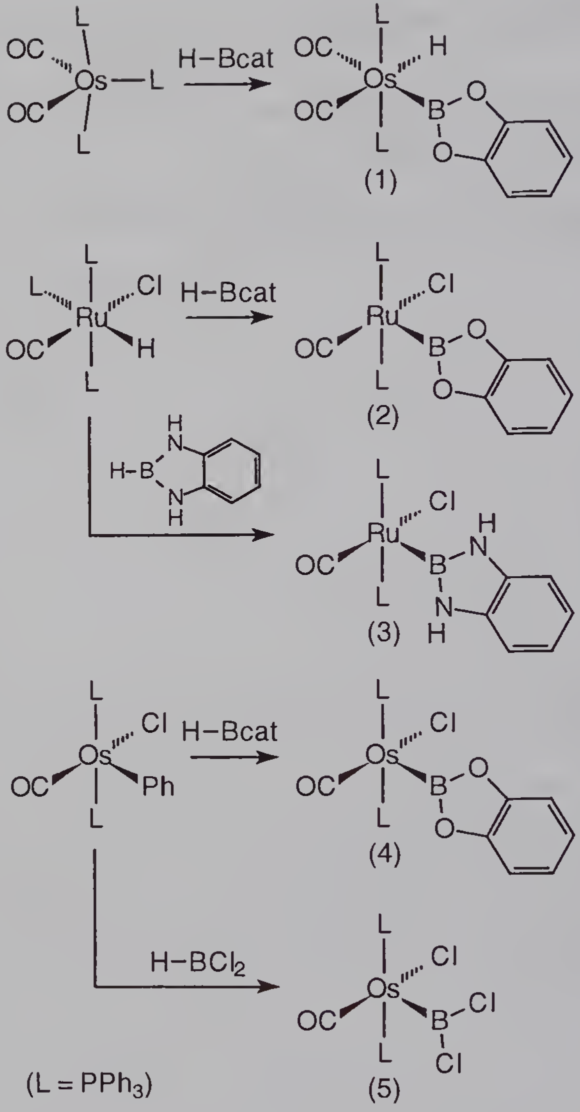
2.1 B-H Additions

A simple example of this reaction is provided by the addition of H-Bcat to the zero oxidation state complex, $Os(CO)_2(PPh_3)_3$, to form (1)[4] (see Scheme 1). (1) has mutually *trans* phosphine ligands and is coordinatively saturated. In contrast, H-Bcat addition to $RuHCl(CO)(PPh_3)_3$, which presumably reacts via the five-coordinate hydride, $RuHCl(CO)(PPh_3)_2$, and is accompanied by dihydrogen loss, yields the coordinatively unsaturated Bcat complex, $Ru(Bcat)Cl(CO)(PPh_3)_2$ (2).[5] A variety of related boranes react in the same manner and an example is provided by compound (3). To access the corresponding osmium complexes it is necessary to use the five-coordinate osmium phenyl complex $OsPhCl(CO)(PPh_3)_2$. In an interesting extension of this synthesis use of $H-BCl_2$ leads to the highly reactive five coordinate dichloroboryl complex, $Os(BCl_2)\ Cl(CO)(PPh_3)_2$ (5).[4] This compound has two very easily displaceable substituents on boron and the extensive substitution chemistry which (5) undergoes is discussed below.

2.2 B-B Additions

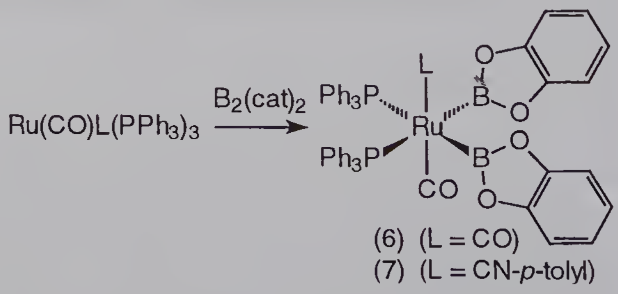
$B_2(cat)_2$ adds readily to the ruthenium zero oxidation state compounds, $Ru(CO)L(PPh_3)_3$ (L = CO, CN-*p*-tolyl), to give six coordinate bis(boryl)-complexes in which both the two phosphine ligands, and the two boryl ligands, are mutually *cis* (see Scheme 2).[6] This reaction is not general since the corresponding osmium complexes do not react directly with $B_2(cat)_2$, however, bis(boryl)-osmium complexes have been prepared in another way (see below).

2.3 Derivatisation of Boryl Complexes through Ligand Exchange at the Metal Centre



Scheme 1

The five coordinate Bcat complex (4) has both a vacant coordination site and a labile chloride ligand. As shown in Scheme 3 addition of a simple Lewis acid ligand affords the saturated complexes (8) or (9) where the introduced ligand is *trans* to Bcat.[4] Halide removal from (4) with $AgSbF_6$/MeCN gives the cation (10) in which the two acetonitrile ligands can be easily replaced as exemplified in the reaction with sodium formate to give (11).[7] The bidentate formate ligand in (11) thermally decarboxylates in the presence of PPh_3 to give hydride, Bcat-complex (12). It is noteworthy that the Os-B bond remains intact through these various transformations



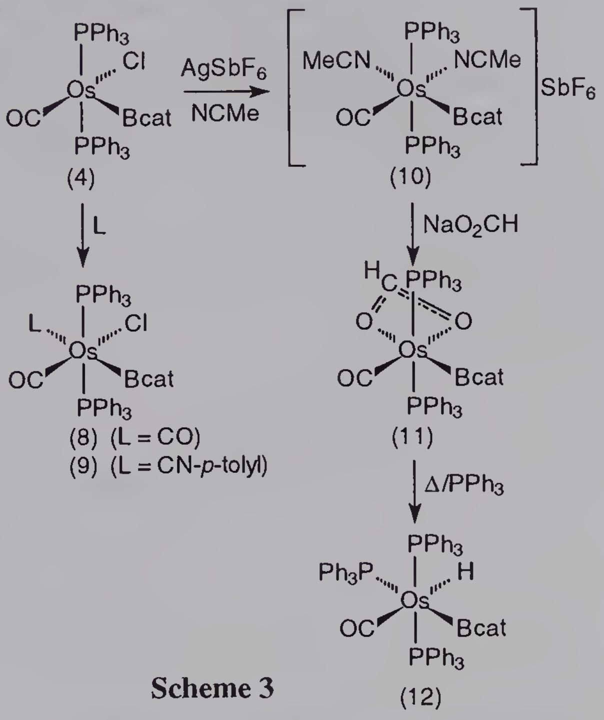
(6) (L = CO)
(7) (L = CN-*p*-tolyl)

Scheme 2

and these ligand substitution processes greatly extend the range of readily available osmium boryl complexes.

3 STRUCTURAL STUDIES

3.1 Transition Metal-Boron Bonds

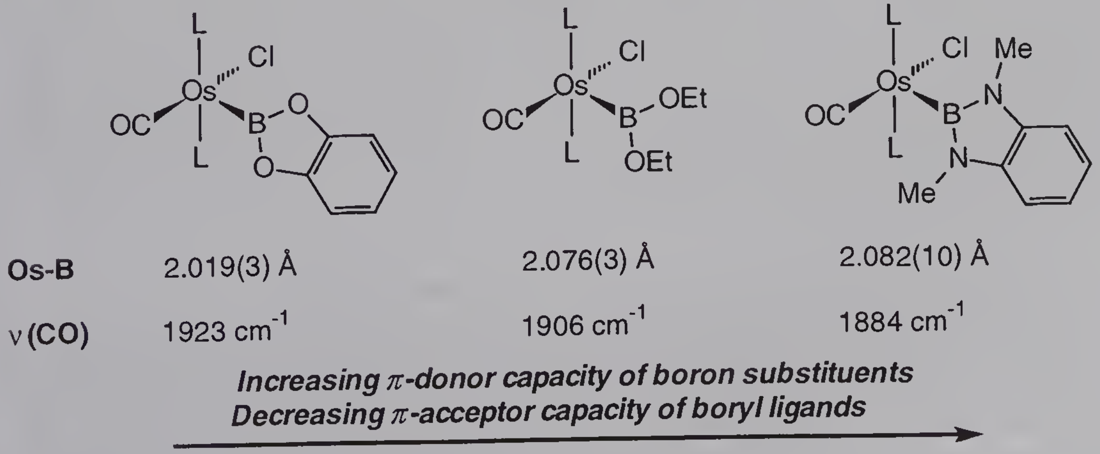


Scheme 3

The M-BX$_2$ bond involves two interactions, the first is a sigma donation from a boron sp^2 orbital to an unoccupied metal orbital and the second is back-donation from a filled metal d$_\pi$ orbital to the unoccupied p$_\pi$ orbital on boron. The relative importance of these two interactions will depend upon the nature of the metal and the accompanying ligands as well as the substituents on boron.[8] The resulting bond is strong, comparable to an M-H interaction, and stronger than a M-C interaction.[9] The π-interaction will be less important when the boryl ligand is in competition with other good π-acceptor ligands, such as CO, on the metal. Similarly, good π-donor substituents on boron will reduce the π-contribution in the M-B bond. The wide range of ruthenium and osmium boryl complexes now available makes possible a systematic evaluation of factors influencing Ru-B and Os-B distances.

3.2 Os-B Bond Length Variation

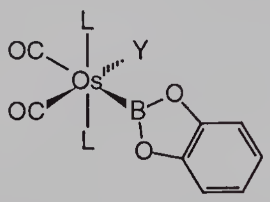
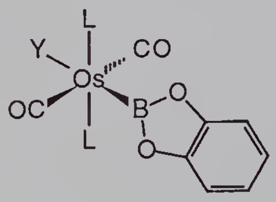
In Scheme 4 can be seen the trend in Os-B distances in a set of closely related complexes as the heteroatom on boron is changed.[4,7] It is clear that the shortest Os-B distance is found in the complex which has the least effective π-donor substituents on the boron (the catecholate O atoms). Likewise the longest Os-B distance is found in the



Scheme 4

complex with the strongest π-donors of this set (the N atoms). This suggests that the π-acceptor capability of the boryl ligands falls in the order Bcat > $B(OEt)_2$ > $B(NMe)_2C_6H_4$ and it is noteworthy that the ν(CO) values reflect exactly the same order.

Particularly revealing structural information follows from the examination of two pairs of *cis/trans* osmium-boryl isomers.[6,10] The data is presented in Scheme 5. It can be seen that the Os-B distance is constant (within esd's) when Bcat is *trans* to either CO or *o*-tolyl but shorter when *trans* to I. Furthermore, the Os-CO distances are significantly longer when *trans* to Bcat than when *trans* to I, *o*-tolyl, or even another CO. The clear implication is that the Bcat ligand, in these compounds, is functioning as a strong π-acceptor. In addition, an indication of a strong σ-donor component in the Os-B bond is given by the Os-I and Os-*o*-tolyl distances which are both greater when *trans* to Bcat than when *trans* to CO.

				
	Y = I	Y = *o*-tolyl	Y = I	Y = *o*-tolyl
Os-B	2.145(5) Å	2.154(7)	2.090(3)	2.132(7)
Os-CO$_{trans\ to\ B}$	1.968(5) Å	1.964(7)	-	-
Os-CO$_{cis\ to\ B}$	1.867(4) Å	1.903(6)	1.941(2) (av.)	1.941(4) (av.)
Os-C$_{o\text{-}tolyl}$	-	2.202(6)	-	2.277(5)
Os-I	2.7883(3) Å	-	2.8346(2)	-

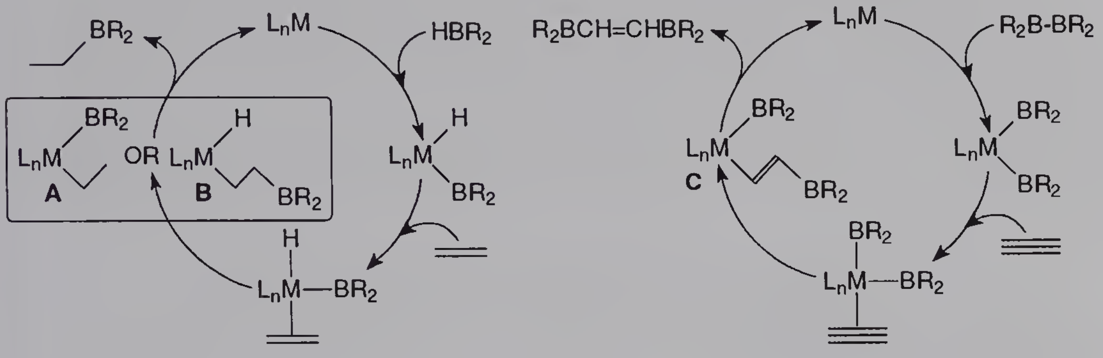
Scheme 5

4 MODELS FOR CATALYTIC INTERMEDIATES

Part of the intense interest in M-B compounds derives from the participation of these species in various catalytic processes.[1,2] Scheme 6 depicts proposed catalytic cycles for metal-catalysed alkene hydroboration and alkyne diborylation. Key steps involve the insertion of unsaturated organic substrates into M-B bonds and a key intermediate involved in the formation of product is molecule **A** in which there are adjacent M-C and M-B bonds. The ruthenium and osmium boryl complexes described in this section provide models for these steps and intermediates.

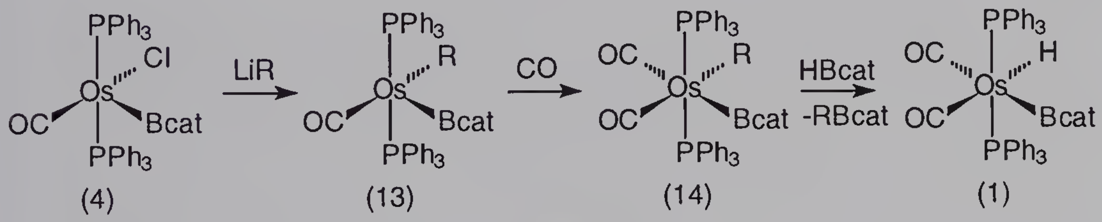
4.1 Osmium Complexes with *cis*- and *trans*-*o*-tolyl, Bcat Ligands

Treatment of (4) with *o*-tolyl lithium (see Scheme 7) produces the five-coordinate *o*-tolyl, Bcat complex, $Os(o\text{-tolyl})(Bcat)(CO)(PPh_3)_2$ (13).[10] This adds CO giving the *cis*-dicarbonyl complex, $Os(o\text{-tolyl})(Bcat)(CO)_2(PPh_3)_2$ (14). Both these fully characterised compounds model the intermediate **A** in Scheme 6. Furthermore, $Os(o\text{-tolyl})(Bcat)(CO)_2(PPh_3)_2$ readily eliminates *o*-tolylBcat, thus modelling the product-forming step in the catalytic cycle. In the presence of HBcat the Os-B bond is re-established through a simple oxidative addition reaction (Scheme 7). In the presence of $B_2(cat)_2$ $Os(Bcat)_2(CO)_2(PPh_3)_2$ is produced. Treatment of $Os(Bcat)Cl(CO)_2(PPh_3)_2$ with *o*-tolyl lithium gives an isomer of $Os(o\text{-tolyl})(Bcat)(CO)_2(PPh_3)_2$ in which the *o*-tolyl and Bcat ligands are mutually *trans*. This isomer is stable towards *o*-tolylBcat elimination.[10]



Proposed mechanisms of transition metal catalysed hydroboration of alkenes and diboration of alkynes

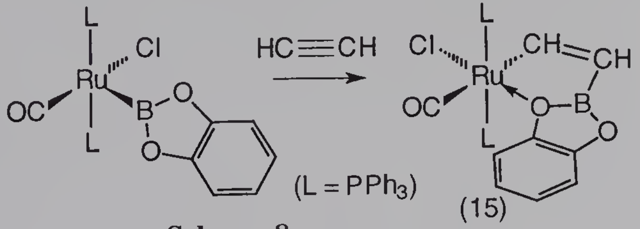
Scheme 6



Scheme 7

4.2 Ethyne Insertion into a Ru-B Bond

The five-coordinate Ru-boryl complex, $Ru(Bcat)Cl(CO)(PPh_3)_2$, inserts ethyne into the Ru-B bond forming the borylvinyl-compound (13) (Scheme 8).[11] This reaction and product models the acetylene insertion step to give intermediate **C** in the metal-catalysed diboryl-ation reaction shown in Scheme 6. Furthermore, treatment of (13) with HBcat returns $Ru(Bcat)Cl(CO)(PPh_3)_2$, a reaction which models the proposed regeneration of catalyst in alkene hydroboration.



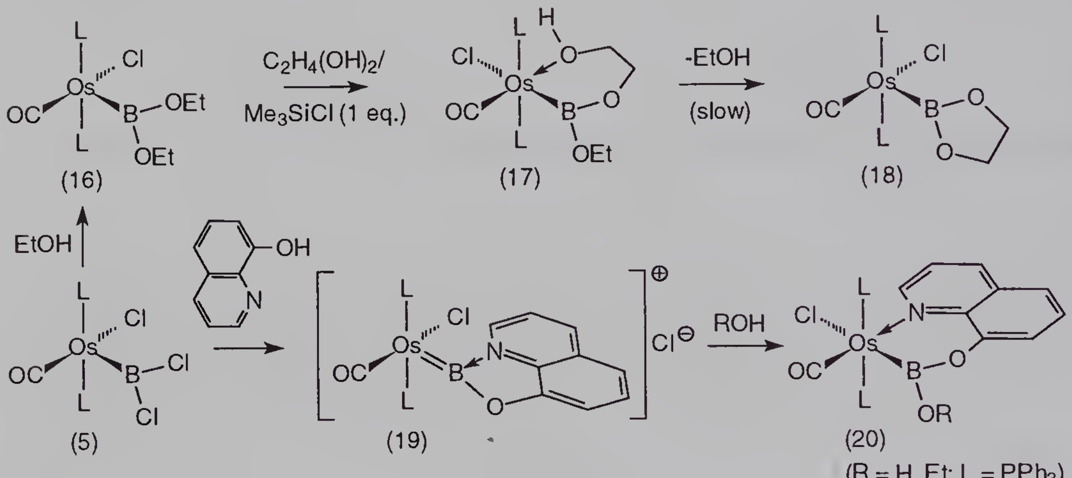
Scheme 8

5 REACTIONS AT THE BORON CENTRE

An unusual feature of the Bcat ligand in metal-Bcat complexes is the resistance of the the B-O(catecholate) bonds to exchange with other alcohols. For example, whereas $Ru(Bcat)Cl(CO)(PPh_3)_2$ may be recovered unchanged from EtOH solutions, compound (15), where the Bcat function is no longer directly attached to the metal, undergoes rapid ethanolysis.[11] The observation of substitution reactions at the boron centre therefore requires the presence of exceptionally good leaving-groups on boron (e.g., chloride) or a suitable catalyst for this reaction.

5.1 Reactions of the $B(OEt)_2$ Ligand

$Os(B[OEt]_2)Cl(CO)(PPh_3)_2$ is readily formed from treatment of compound (5) with ethanol (see Scheme 9). This compound does not react with ethanediol under neutral conditions, but in the presence of one equivalent of Me_3SiCl, *one* of the ethoxy-groups is replaced to give the chelated boryl ligand in complex (17), as depicted in Scheme 9.[6] Compound (17), the structure of which has been confirmed by X-ray crystallography, slowly loses ethanol in solution forming the cyclic ethanediolate-boryl ligand in the five coordinate compound (18).



Scheme 9

5.2 Reactions of the BCl_2 Ligand

Compound (5) has both reactive B-Cl bonds and is coordinatively unsaturated at osmium. Therefore, reaction with compounds having O-H or N-H functions together with a suitably positioned donor group should give rise to stable, octahedral complexes where the boryl ligand is tethered to osmium. This is exemplified by the reaction between (5) and 8-hydroxyquinoline depicted in Scheme 9. Here it can be seen that the ultimate product is the expected coordinatively saturated product (20) where one chloride on boron has been replaced by an 8-hydroxyquinolinate group and the second chloride by either OH or OEt. There is an isolable intermediate in this reaction, compound (19), which has salt-like character and could be considered as a base-stabilised borylene complex. This has a highly electrophilic boron centre and reacts rapidly with either water, to give (20) (R = H), or ethanol to give (20) (R = Et), where the quinoline nitrogen has shifted from boron to osmium.

The transformations detailed in this section involving the versatile BCl_2 ligand indicate that extensive elaboration of boryl ligands will be possible.

Acknowledgement

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References

1. H. Wadepohl, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2441.
2. H. Braunschweig, *Angew. Chem. Int. Ed. Engl.*, 1998, **37**, 1786.
3. G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685.
4. G. J. Irvine, PhD Thesis, The University of Auckland, 1996.
5. G. J. Irvine, W. R. Roper, and L. J. Wright, *Organometallics*, 1997, **16**, 2291.
6. C. E. F. Rickard, W. R. Roper, A. Williamson, and L. J. Wright, unpublished work, 1998-1999.
7. C. E. F. Rickard, W. R. Roper, A. Williamson, and L. J. Wright, *Organometallics*, 1998, **17**, 4869.
8. S. Sakaki and T. Kikuno, *Inorg. Chem.*, 1997, **36**, 226.
9. P. R. Rablen, J. F. Hartwig, and S. P. Nolan, *J. Amer. Chem. Soc.*, 1994, **116**, 4121.
10. C. E. F. Rickard, W. R. Roper, A. Williamson, and L. J. Wright, *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 1110.
11. G. R. Clark, G. J. Irvine, W. R. Roper, and L. J. Wright, *Organometallics*, 1997, **16**, 5499.

Organoboron Compounds of the Heavier Group 14 Elements

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While the quest for boron compounds featuring B$\equiv$N triple bonds [1], B=P or B=As double bonds [2], and BC multiple bonds [3] with dicoordinated boron atoms has been successful and opened up new aspects in boron chemistry, no attempt has as yet been reported (to our knowledge) for boron compounds having multiple bonds to the heavier elements of group 14. (Si to Pb). Even our knowledge regarding silylboranes $R_3Si\text{-}BR_2$ or cyclic silylboranes $(R_2Si\text{-}BR)_n$ is only scanty and becomes even less so as we move down the elements of this group [4],

Taking this aspect into account we performed MO calculations (using the 6-311G* basis sets and MP2+ZPE level calculations) for a fairly large number of isomers and conformers of composition $Si_3B_2H_8$ with the aim to get some insight into the relative stabilities of structures that can be described either as electron precise or electron deficient systems. Included were compounds having a formal B=B double bond (such as $H_3Si\text{-}SiH_2\text{-}B\text{=}B\text{-}SiH_3$), or a B=Si bond [such as $(H_3Si)_2Si\text{=}BH_2$ or $H_3Si(H)Si\text{=}B\text{-}B(H)SiH_3)$], as well as three, four, and five membered rings, and finally nido-polyhedral species.

Figure 1 gives an overview of some calculational results which clearly shows that silylboranes with a B=B double bond are less stable than those with a B=Si double bond. The most stable species is a nido-pentaborane. Consequently, the quest for a silyleneborane needs a strategy in which electronic as well as a steric effects must play a decisive factor.

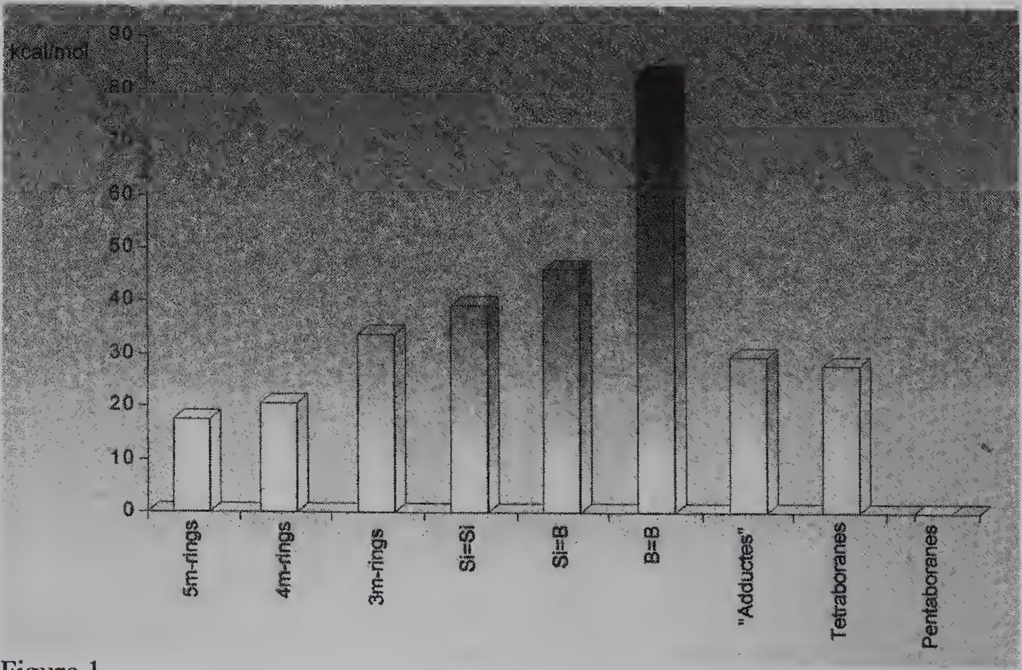


Figure 1

Possible precursors for silyleneboranes might be amino(silyl)boranes with sterically bulky amino and silyl groups. For this reason silylboranes of types $R_3Si\text{-}B(tmp)X$ and tmpB-

$(SiR_3)_2$ (tmp = 2,2,6,6-tetramethylpiperidino group) have been prepared by the route shown in eq. (1).

$$\text{tmp-BCl}_2 + 2\,\text{LiSiR}_3 \rightarrow \text{tmp-B(SiR}_3)_2 + 2\,\text{LiCl} \qquad \text{Eq. (1)}$$

Attempts to prepare $B(SiPh_3)_3$ from $LiSiPh_3$ and BX_3 (X = Cl, Br) have not been successful most likely for steric reasons. $B(SiMe_3)_3$ should however be accessible (v. i.). None of these compounds is, however, a good precursor for a compound with a B=Si double bond. A functional group on the silicon atom is also needed. Chlorosilyl aminochloroboranes can, however, be obtained by the route described in Figure 2 in a two step reaction.

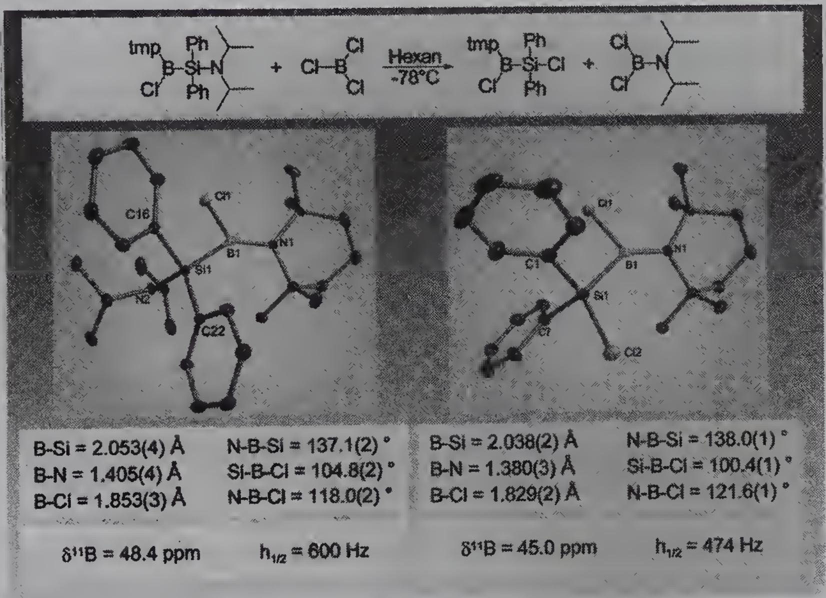
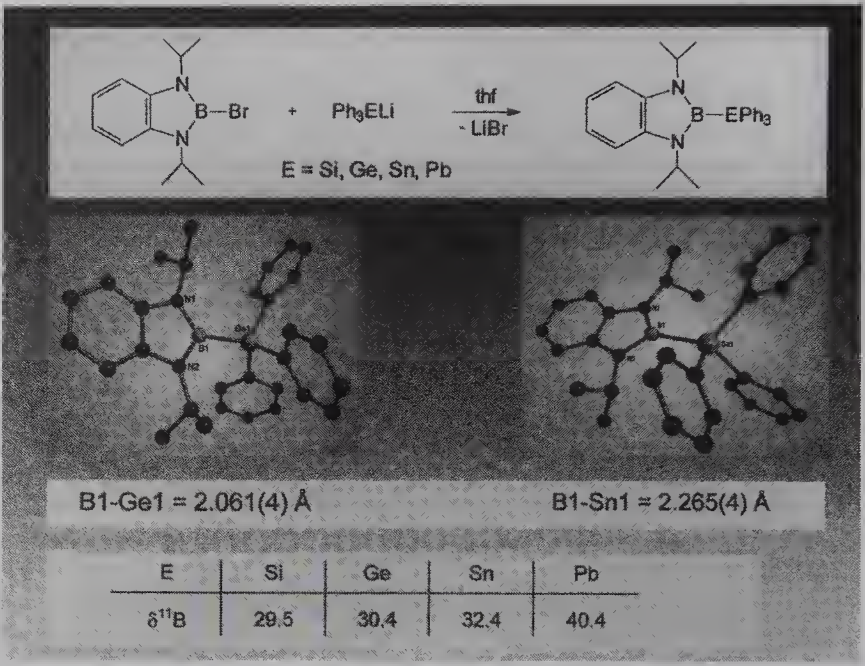


Figure 2

The determination of the crystal structures of a series of silyl(amino)boranes shows that the B-Si bond is significantly shortened by the introduction of chlorine substituent at boron and is even shorter in the presence of a Cl atom at the silyl group. This definitely shows that the Cl atoms have a noticeable *inductive* effect on the length (and strength) of the B-Si single bond.

So far, our attempts to dehalogenate compounds of type **4** by alkali metals and sodium potassium alloy to silyleneboranes failed even in the presence of catalysts.

In analogy to silylboranes a series of triphenylgermyl, triphenylstannyl-, trimethylstannyl- and trimethylplumbyl boranes were obtained in moderate to good yield, the thermal stability decreasing from the Si to the Pb compounds. ^{11}B chemical shifts of a series these boranes having the same aminoborane moiety shows that the best shielded boron nucleus is present in the lead compound. We attribute this to the paramagnetic shift of the lead atom. Successive introduction of a triphenylgermyl and triphenylstannyl groups allows the synthesis of $tmpB(GePh_3)(SnPh_3)$ whose B-Sn and B-Ge bond lengths comply nicely with those found for all other germyl and stannylboranes.

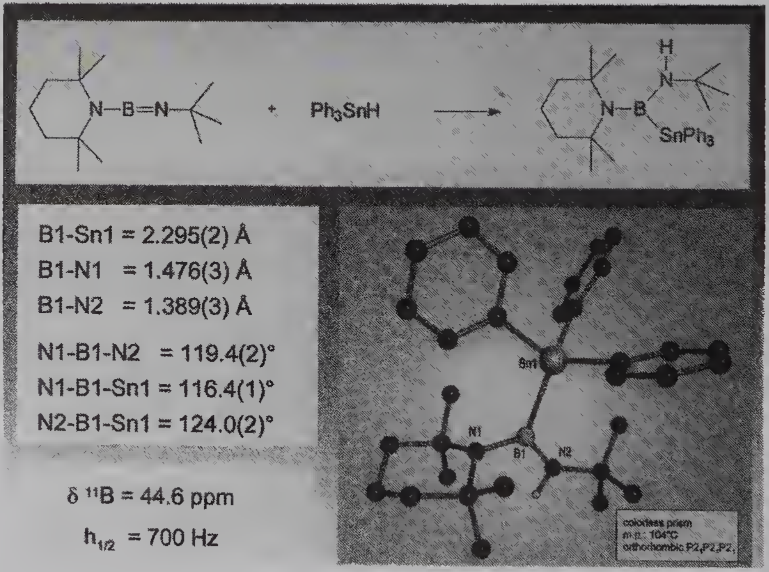


B1-Ge1 = 2.061(4) Å

B1-Sn1 = 2.265(4) Å

E	Si	Ge	Sn	Pb
$\delta^{11}B$	29.5	30.4	32.4	40.4

Figure 3



B1-Sn1 = 2.295(2) Å
B1-N1 = 1.476(3) Å
B1-N2 = 1.389(3) Å

N1-B1-N2 = 119.4(2)°
N1-B1-Sn1 = 116.4(1)°
N2-B1-Sn1 = 124.0(2)°

$\delta\ ^{11}B$ = 44.6 ppm
$h_{1/2}$ = 700 Hz

Figure 4

Interestingly we found that stannylboranes are also accessible by hydrostannylation of the amino imino borane tmp-B≡NCMe$_3$ as shown in Figure 4.

In the context with our studies on silylboranes we also investigated silylborates having a tetracoordinated boron atom. The crystal structure determination of the previously reported LiB(SiMe$_3$)$_4$ [5] (see Figure 5) revealed a most interesting result: the B-Si bond lengths are *shorter* than in the silylboranes . This unusual feature is also observed in the silylborate Li(Ph$_3$SiBH$_3$) . A typical example is shown in fig. 6.

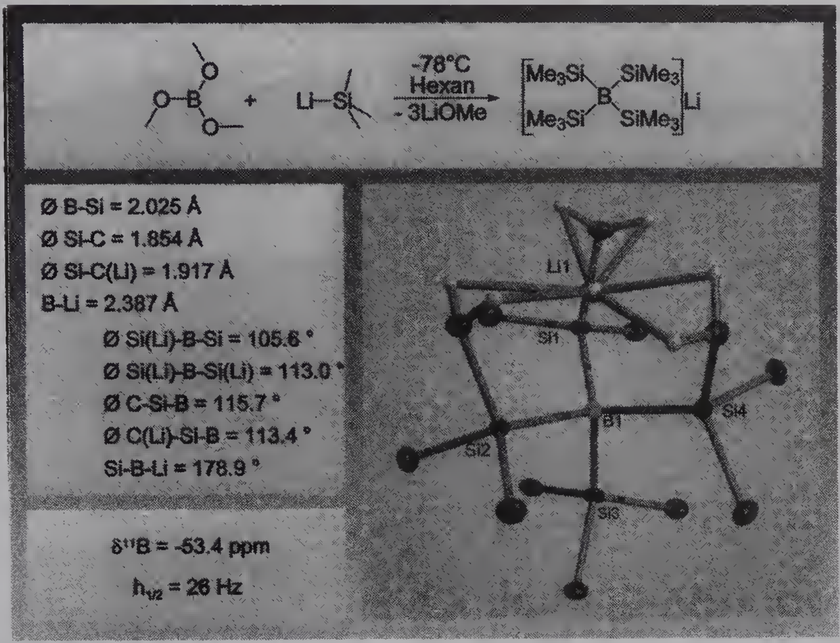


Figure 5

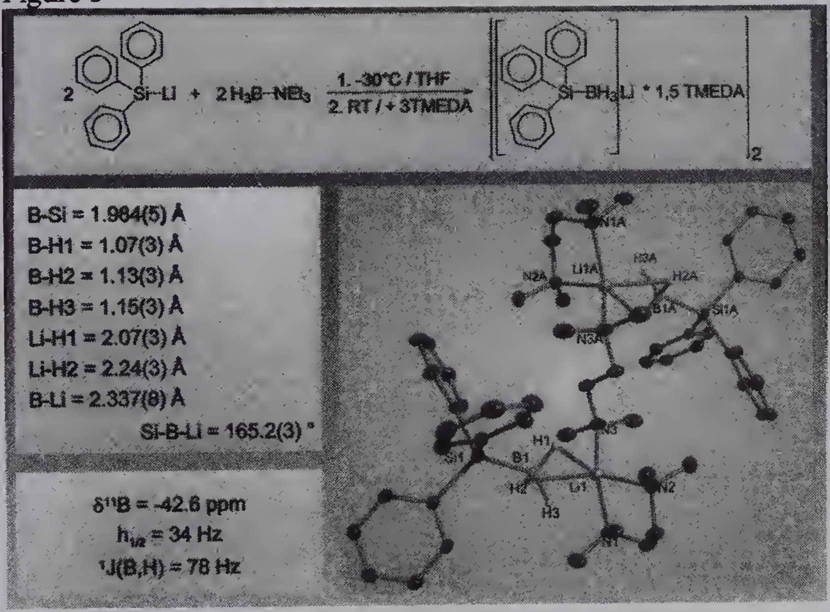
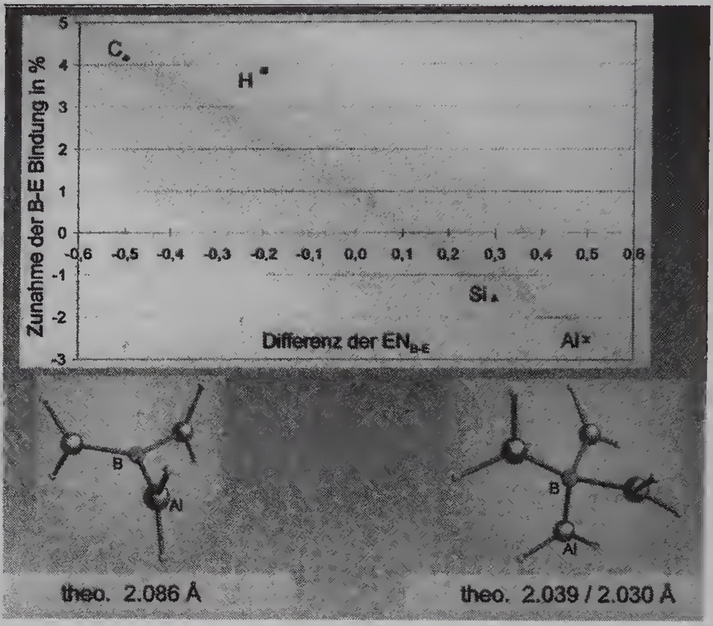


Figure 6

This bond length shortening even holds for a comparison of the B-Sn bond in stannylboranes and the stannyltrihydridoborate $[Li(H_3BSnPh_3)]_2TMEDA$ (Fig. 6).although the difference in bond lengths is less pronounced than in the silyl analogues.

In order to explain these results we have performed MO calculations (G-311G* basis set, MP2-ZPE level) on the following pair of compounds: BH_3/BH_4^-; BMe_3/BMe_4^-, $B(SiH_3)_3$ $/B(SiH_3)_4^-$, and $B(AlH_2)_3/$ $B(AlH_2)_4^-$. Figure 7 shows a correlation of the bond lengths difference vs. the electronegativity difference between boron an its substituent atom. H and C are more electronegative than boron while silicon and aluminum are more electropositive. Obviously this change in polarity is the reason why the B-Si bond in silylborates is shorter than in silylboranes - and this is even more drastic for the unknown alanylborates. No doubt, to verify this is a challenge to be solved in the future.



<u>References</u>

1. H. Nöth, Angew. Chem. Int. Ed. **1986**, *27*, 1603; - P. Paetzold, Advanc. Inorg. Radiochem. **1987**, *33*, 123.

2. A. Berndt, Angew. Chem. Int. Ed. **1993**, *32*, 985. - H. Nöth, Proceed. 6th IME-BORON, World Scientic, Singapore, Editor: S. Hermanek, **1987**, 438. R. Boese, P. Paetzold, A. Tapper, Chem. Ber. **1987**, *120*, 1069.

3. R. A. Bartlett, X. Feng, P.P.Power, J. Amer. Chem. Soc. **1986**, *108*, 6817; P.P.Power, Angew. Chem. Int. Ed. **1990**, *29*, 449; M. A. Petrie, S. C. Shoner, H. V. R. Dias, ibid. **1990**, *29*, 1033; H. G. von Schnering, M. Somer, M. Hartweg, K. Peters, ibid, **1990**, *29*, 65; - G. Linti, H. Nöth, ibid.

4. E. P. Mayer, H. Nöth, W. Rattay, U. Wietelmann, Chem. Ber. **1992**, *125*, 401; - S. Onazawa, T. Hatanake, S. Sakakura, T. Hayashi, M. Tanaka, Organometallics, **1996**, *15*, 5450; - J. D. Kennedy, W. McFarlane, B. Wrackmeyer, Inorg. Chem. **1976**, *15*, 1299.

5. W. Biffar, H. Nöth, Chem Ber. **1982**, *115*, 934.

6. W. Lippert, PhD Thesis, University of Munich, 1999. W. Lippert, H. Nöth, W. Ponikwar, T. Seifert, Eur. J. Inorg. Chem. **1999**, 817.

Recent Advances in Diborane(4) Chemistry

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1 INTRODUCTION

Diborane(4) compounds contain unsupported two-centre, two-electron B–B bonds examples of which, such as the diboron tetrahalides, have been known for many years.[1] However, due in large part to the recent work of many groups in the field of transition metal catalysed diboration reactions,[2] there has been a resurgence of interest in their synthesis and reactivity. Herein, we describe some of our own work in this area.

2 SYNTHESIS

The standard entry into diborane(4) chemistry is *via* the tetradimethylamido species $B_2(NMe_2)_4$ (**1**) prepared according to Eqn. (1) details of which are described in refs. 3. Whilst **1** is a convenient, moderately air-stable distillable liquid, other suitable starting compounds are the dichloro species 1,2-$B_2Cl_2(NMe_2)_2$ (**2**) (also a liquid)[3c,4] and the crystalline amine adduct of B_2Cl_4 namely $[B_2Cl_4(NHMe_2)_2]$ (**3**)[3b,5] prepared according to Eqns. (2) and (3) respectively.

$$BCl_3 + 2\ B(NMe_2)_3 \rightarrow 3\ BCl(NMe_2)_2$$

$$2\ BCl(NMe_2)_2 + 2\ Na \rightarrow B_2(NMe_2)_4 + 2\ NaCl \tag{1}$$

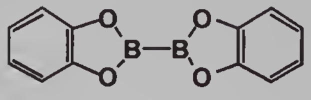
$$B_2(NMe_2)_4 + 2\ HCl \rightarrow 1,2\text{-}B_2Cl_2(NMe_2)_2 + 2\ NHMe_2 \tag{2}$$

$$B_2(NMe_2)_4 + 4\ HCl \rightarrow [B_2Cl_4(NHMe_2)_2] + 2\ NHMe_2 \tag{3}$$

Much of the recent chemistry of diborane(4) compounds has been associated with the diolate species $B_2(cat)_2$ (**4**) (cat = 1,2-$O_2C_6H_4$)[3b,6] and $B_2(pin)_2$ (**5**) (pin = $OCMe_2CMe_2O$)[7] both of which exist as 1,1-isomers with unbridged B–B bonds and prepared according to Eqn. (4).

$$B_2(NMe_2)_4 + 2\ catH_2/pinH_2 + 4\ HCl \rightarrow B_2(cat/pin)_2 + 4\ [NH_2Me_2]Cl \tag{4}$$

Treatment of **2** with the disodium salt of catechol afforded one of the first structurally characterised examples of a diborane(4) compound with a bridging diolate, namely 1,2-$B_2(NMe_2)_2(cat)$ (**6**). In contrast, the reaction between **2** and the dilithium salt of thiocatechol afforded the 1,1-isomer, 1,1-$B_2(NMe_2)_2(thiocat)$ (**7**) as the major product based on the disparate ^{11}B NMR chemical shifts of the two inequivalent borons (the borons would be equivalent in a structure analogous to **6**). Reactions between **6** or **7** and diols afforded mixtures of the symmetrical compounds as 1,1-isomers together with mixed 1,1-species, for example 1,1-B_2(cat)(pin) from the reaction between **6** and pinacol, indicating that 1,1-isomers are the favoured forms and that intermolecular exchange of diolate groups is likely at least in the initial stages of the reactions. It has not proved possible to prepare the 1,2-isomer of **4**.



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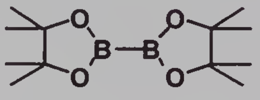

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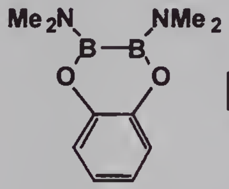

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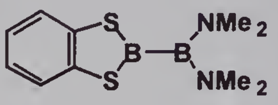

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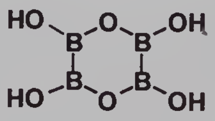
Another novel diborane(4) compound has previously been obtained by adventitious hydrolysis of **1**, namely the cyclic reduced boric acid species $B_4O_2(OH)_4$ (**8**).[8] Compound **8** is produced in much higher yield from a more controlled hydrolysis of either **1** or **2** but can be prepared almost quantitatively from the reaction between **3** and aqueous ethanol as a material with co-crystallised [NH_2Me_2]Cl.[8] Electrospray mass spectrometry revealed that the more highly condensed species **9** can also be formed indicating that a large family of condensed, reduced boric acids/borates derived from $B_2(OH)_4$ may be synthetically accessible.



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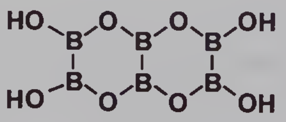

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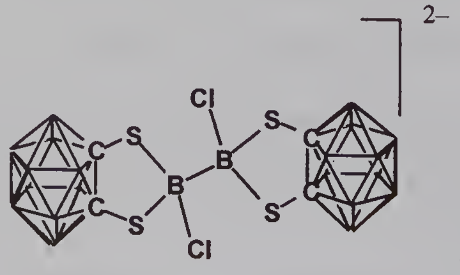
More recently, some carboranyl diborane(4) derivatives have been prepared from the reaction between **1**, 1,2-$(HE)_2C_2B_{10}H_{10}$ (E = S, Se) (generated in situ from $Li_2C_2B_{10}H_{10}$ followed by addition of elemental S or Se and acidification) and HCl. Two crystallographically characterised examples are the dianionic species **10** and **11**, the latter representing the first example of a diborane(4) compound with B–Se bonds.



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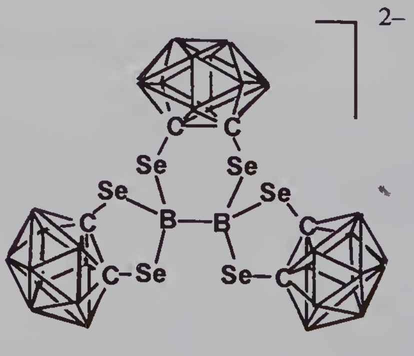

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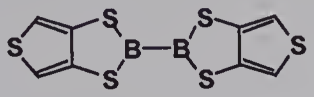
Finally, some electron rich, sulphur-containing species have been prepared as part of a study of potential molecular electronic materials containing diborane(4) compounds. In a recent study,[9] several crystal structures of 1:1 adducts of **4**, and the thiocatecholate analogue $B_2(1,2\text{-}S_2C_6H_4)_2$, with the electron acceptors TCNE (tetracyanoethene) and TCNQ (7,7,8,8-Tetracyano-*p*-quinodimethane) were described. The fact that co-crystals with TCNE and TCNQ formed indicates that co-crystals with more electron-rich species are also possible. Such materials may have interesting electronic properties. Preliminary work has resulted in the synthesis of compounds **12** and **13**.[10]



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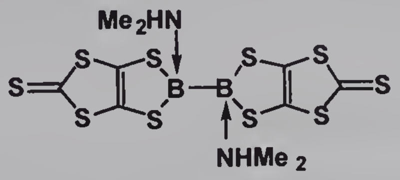

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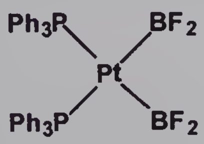
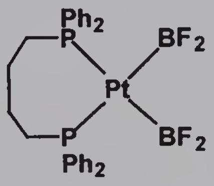
3 REACTIVITY

Recent examples of reactivity studies have focussed on several areas. Exploration of the chemistry of B_2F_4 has led to the isolation and characterisation of the first example of a transition metal complex containing a BF_2 ligand, namely *cis*-$[Pt(PPh_3)_2(BF_2)_2]$[11] followed by the synthesis and structural characterisation of *cis*-$[Pt(dppb)(BF_2)_2]$ (**14**) (dppb = 1,4-bis-diphenylphosphino butane) and *fac*-$[Ir(CO)(PPh_3)_2(BF_2)_3]$ (**15**), the latter from the reaction of Vaska's compound with two equivalents of B_2F_4.





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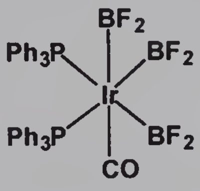

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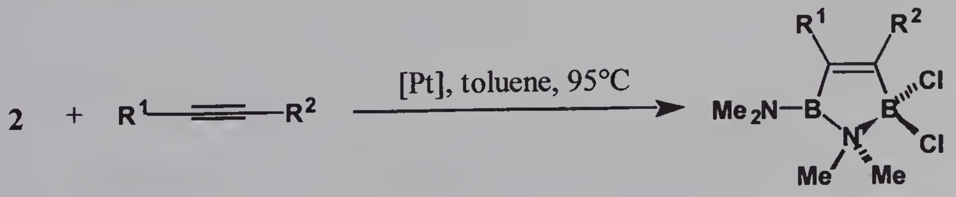
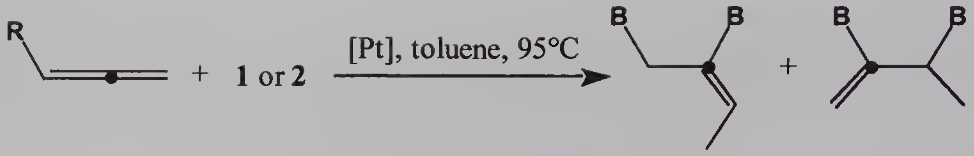
The platinum catalysed diboration of alkynes with **2** resulted in cyclic boron species of the type **16** as shown in Scheme 1 in which a redistribution of Cl and NMe_2 groups has occurred, the driving force for which is possibly the formation of an extra B–N bond. Also studied was the diboration of allenes[12] which, for unsymmetrical species, resulted in both 1,2- and 2,3-addition products (Scheme 2), the ratio of the two regioisomers formed varying slightly with temperature. Complex product mixtures were found from allenes containing hydroxo or carboxylate functional groups but in no case were any products observed consistent with prior rearrangement of an allene to an alkyne.



$R^1 = Ph$, $R^2 = Me$; $R^1 = R^2 = Ph$, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$

16

Scheme 1



R = *n*-octyl, Ph; B = B(cat), B(pin)

Scheme 2

ACKNOWLEDGEMENTS

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4 REFERENCES

1. A. G. Massey, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 1; T. D. Coyle and J. J. Ritter, *Adv. Organometal. Chem.*, 1972, **10**, 237; G. Lesley, T. B. Marder, N. C. Norman and C. R. Rice, *Main Group Chemistry News*, 1997, **5**, 4.
2. G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, E. G. Robins, W. Roper, C. R. Rice, G. R. Whittell, J. Wright, *Chem. Rev.*, 1998, **98**, 2685; T. B. Marder and N. C. Norman, *Topics in Catal.*, Ed. W. Leitner and D. G. Blackmond, Baltzer Science Publishers, Amsterdam, 1998, **5**, 63.
3. (a) R. J. Brotherton, J. L. McCloskey, L. L. Petterson and H. Steinberg, *J. Am. Chem. Soc.*, 1960, **82**, 6242; (b) F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore and J. C. Green, *Inorg. Chem.*, 1998, **37**, 5282; (c) M. J. G. Lesley, N. C. Norman and Craig R. Rice, *Inorg. Synth.*, submitted.
4. H. Nöth and W. Meister, *Z. Naturforsch., Teil B*, 1962, **17**, 714.
5. S. C. Malrotra, *Inorg, Chem.*, 1964, **3**, 862.
6. W. Clegg, M. R. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor and T. B. Marder, *Inorg.Chem.*, 1998, **37**, 5289.
7. H. Nöth, *Z. Naturforsch., Teil B*, 1984, **39**, 1463.
8. C. J. Carmalt, W. Clegg, A. H. Cowley, F. J. Lawlor, T. B. Marder, N. C. Norman, C. R. Rice, O. J. Sandoval and A. J. Scott, *Polyhedron*, 1997, **16**, 2325.
9. T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle and C. R. Rice, *J. Chem. Soc., Dalton Trans.*, 1999, 2127.
10. N. C. Norman, A. G. Orpen, M. J. Quayle and C. R. Rice, *Acta Crystallogr., Sect. C*, submitted.
11. A. Kerr, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, P. L. Timms and G. R. Whittell, *Chem. Commun.*, 1998, 319.
12. T. Ishiyama, T. Kitano and N. Miyaura, *Tetrahedron Lett.*, 1998, **39**, 2357.

H–D Exchange Reaction of Borane–Lewis Base Adducts by Rhenium Polyhydride Complexes

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1 INTRODUCTION

Borane-Lewis base adducts, $BH_3 \cdot L$ are isoelectronic and isostructural with alkanes. We previously reported complexes of $BH_3 \cdot L$, $[M(CO)_5(\eta^1\text{-}BH_3 \cdot L)]$ (M = Cr, W; L = PMe_3, PPh_3, NMe_3), in which the borane coordinates to the central metal through a M-H-B single bridge.[1] These complexes show fluxional behavior due to rapid scrambling between the bridging and terminal hydrogen atoms. Photochemical reaction of $[Cp^*M(CO)_3CH_3]$ in the presence of $BH_3 \cdot PMe_3$ gave trimethylphosphineboryl complex, $[Cp^*M(CO)_3(BH_2 \cdot PMe_3)]$ (M = Mo, W).[2]

Transition metal polyhydride complexes attracted our attention for their easiness to liberate H_2 giving coordinatively unsaturated species under mild conditions.[3] The resulting intermediates are highly reactive and interact with various substrates to produce new complexes. In many cases, polyhydride complexes are fluxional, where the hydrogen atoms in the coordination sphere rapidly exchange their positions.

Thus we examined the reactions of borane-Lewis base adducts with rhenium polyhydride complexes to synthesize highly fluxional polyhydride(borane) complexes. However, treatment of several boranes with the rhenium complexes in deuterated solvents resulted in an unexpected reaction: H-D exchange between the boranes and solvents. This is the first example of H-D exchange between sp^2 carbon and sp^3 boron, and closely associated with metal-catalyzed deuteration of alkanes.[4]

2 RESULTS AND DISCUSSION

A benzene-d_6 solution of $BH_3 \cdot PMe_3$ and $[ReH_7(PPh_3)_2]$ (1) in 1 : 2 ratio was heated at 47 °C, and the progress of the reaction was monitored by NMR spectroscopy. The $^{11}B\{^1H\}$ NMR spectral change during the reaction is shown in Figure 1. Before heating, $BH_3 \cdot PMe_3$ displays a doublet coupled with a ^{31}P nuclei at -37.0 ppm. This signal

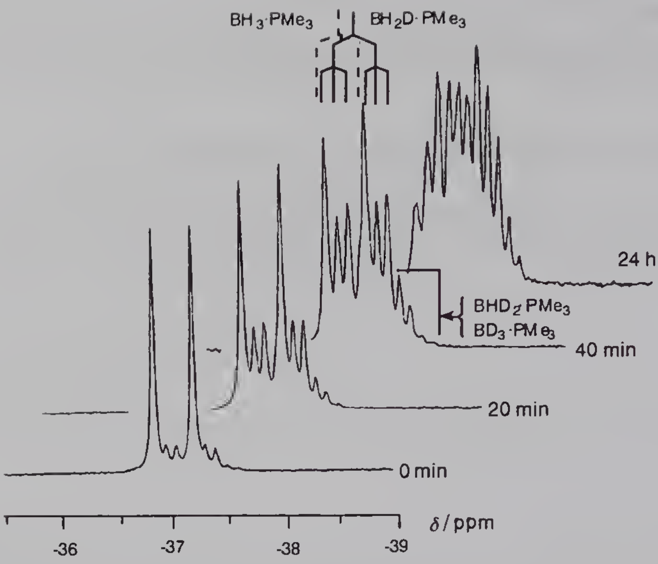
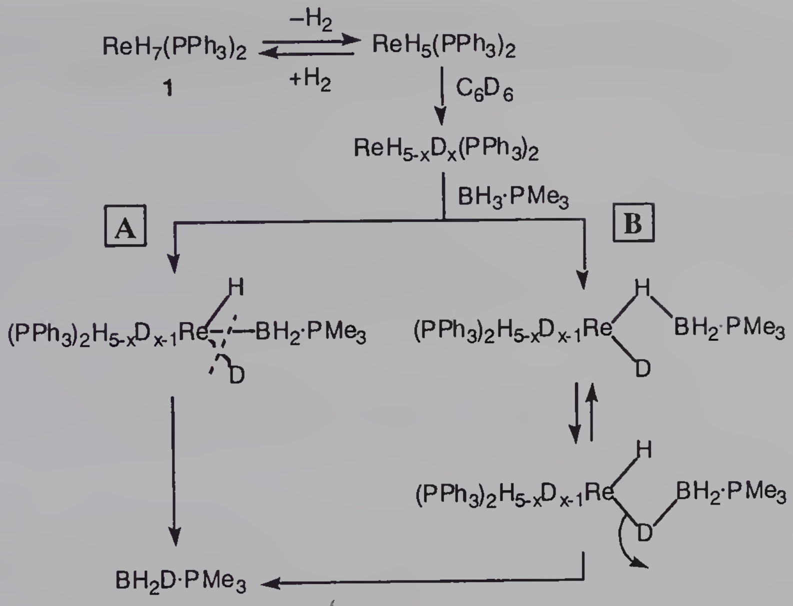


Figure 1. ^{11}B NMR spectral change (160.4 MHz, reference: $BF_3{\cdot}OEt_2$) during the reaction of $BH_3{\cdot}PMe_3$ with **1** in C_6D_6 at 47 °C.

changed to the overlapping multiplets upon heating. The spectrum after 40 min of heating essentially consists of a doublet of triplet. This is attributed to the coupling with a ^{31}P (I = 1/2) and a ^{2}H (I = 1) nuclei, and assigned to the mono-dueterated isotopomer, $BH_2D{\cdot}PMe_3$. This signal is shifted by 0.13 ppm to the higher field relative to that of starting $BH_3{\cdot}PMe_3$ due to an isotope effect. Owing to the overlap with the doublet of $BH_3{\cdot}PMe_3$, two peaks in the signal are observed strongly. At the base of the signal, toward the higher field, the weak peaks of the di- and tri-deuterated isotopomers, $BHD_2{\cdot}PMe_3$ and $BD_3{\cdot}PMe_3$ are also found. Apparent change of the ^{11}B NMR spectra ceased after 24 h of heating. The final spectrum was consistent with that of independently prepared $BD_3{\cdot}PMe_3$ in the chemical shift and the splitting pattern. The ratio of deuteration of $BH_3{\cdot}PMe_3$ was ca. 80% as estimated by ^{11}B NMR. At this stage, the signal of **1** completely disappeared in the ^{31}P NMR. Thus, the H-D exchange in $BH_3{\cdot}PMe_3$ is terminated with the decomposition of complex **1**. Similarly, $BH_3{\cdot}NMe_3$ underwent H-D exchange in the reaction with **1** in benzene-d_6. The final percentage of the deuteration was also ca. 80%. On the other hand, no reaction was observed when $BH_3{\cdot}PMe_3$ was treated with **1** in cyclohexane-d_{12}.

Possible mechanism for the H-D exchange of $BH_3{\cdot}L$ are shown in Scheme 1. First, a polydeuteride intermediate $[ReH_{5-x}D_x(PPh_3)_2]$ is formed by repeated oxidative addition / reductive elimination of C_6D_6 to the coordinatively unsaturated rhenium center, which was generated by elimination of H_2.[5] In path A, oxidative addition of $BH_3{\cdot}L$ to the polydeuteride intermediate gives a boryl complex. Reductive elimination of the boryl group with a deuterido ligand affords the deuterated boranes. In path B, $BH_3{\cdot}L$ coordinates to the polydeuteride intermediate through a 3c2e bond as found in $[M(CO)_5(\eta^1\text{-}BH_3{\cdot}L)]$.[2] The H-D exchange of the boranes is achieved by rapid scrambling of hydrido



Scheme 1.

or deuterido ligands on rhenium, the hydrogen atom bridging rhenium and boron, and terminal hydrogen on boron followed by the elimination of the borane. Although no intermediates have been detected spectroscopically, we prefer path B as the mechanism of deuteration of the boranes due to the following reasons. An MO calculation for $BH_3 \cdot PH_3$ indicates that the antibonding orbitals of BH are energetically so high that oxidative addition of the BH bond would be quite difficult.[1] Moreover, rapid interchange between terminal and bridging BH's is observed in many polyboranes.[6] For zirconium and osmium tetrahydroborate complexes $[Cp_2ZrH(\eta^2\text{-}BH_4)]^-$ and $[OsH_3(\eta^2\text{-}BH_4)(PR_3)^2]$,[8] scrambling of the terminal and bridging BH atoms as well as the hydrido ligands on metal has been found. The fact that the H-D exchange does not occur in cyclohexane-d_{12} indicates that C_6D_{12} is not activated by **1**. This contrasts with the report of Baudry et al., where cyclohexane undergoes dehydrogenation by **1** in the presence of a hydrogen acceptor neohexene, to give cyclohexene.[9]

Deuteration of boranes by the use of pentahydride complexes $[ReH_5L_3]$ (**2**: L = PPh_3, **3**: L = $PPhMe_2$) required photo-irradiation using a medium-pressure Hg lamp. Photochemical liberation of a phosphine ligand rather than H_2 from $[ReH_5L_3]$ has been reported.[10,11] Thus, thermolysis of **1** and photolysis of **2** give the identical intermediate, and it mediates the H-D exchange of boranes. In the **3**-$BH_3 \cdot PMe_3$ system, formation of $BH_{3-n}D_n \cdot PPhMe_2$ by ligand exchange on borane was also observed. The photolysis and following measurement of ^{11}B NMR of a toluene-d_8 solution of $BH_3 \cdot PMe_3$ and **3** at -64 °C was carried out for the purpose of direct observation of the intermediate. Even under such a condition, however, no complex with a borane–rhenium interaction was detected. The reactions with use of $BH_2Cl \cdot PMe_3$ and $B_2H_4 \cdot 2PMe_3$ lead to B-Cl and B-B bond cleavage to produce $BH_{3-n}D_n \cdot PMe_3$. Treatment of boranes with $[CpReH_2(PPh_3)_2]$ (**4**) under photo-irradiation yielded only a trace amount of $BH_2D{\cdot}PMe_3$. This indicates that the boranes scarcely interact with the intermediate derived from **4**, as opposed to the alkane–C_6D_6 H-D exchange catalyzed by **4**.[4]

References and Notes

1. a) Shimoi, K. Katoh, M. Uruichi, S. Nagai, and H. Ogino, 'Current Topics in the Chemisty of Boron', The Royal Society of Chemistry, London, 1994. p. 293. b) M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, and H. Ogino, submitted for publication.
2. Y. Kawano and M. Shimoi, 'Advances in Boron Chemistry,' The Royal Society of Chemistry, London, 1997. p. 393.
3. a) R. H. Crabtree, *Angew. Chem., Int. Ed. Engl.*,1993, **32**, 789. b) G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120. c) D. M. Heinekey and W. J. Oldham, Jr., *Chem. Rev.*, 1993, **93**, 913.
4. For example, W. D. Jones, G. P. Rosini, and J. A. Maguire, *Organometallics*, 1999, **18**, 1754, and references cited therein.
5. Progressive decrease of the hydrido signal of **1** in CD_2Cl_2 has been reported, suggesting the incorporation of deuteron onto the rhenium: D. Baudry, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 1982, **224**, 363.
6. H. Beall and C. H. Bushweller, *Chem. Rev.*, 1973, **73**, 465.
7. T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 3397.
8. a) P. W. Frost, J. A. K. Howard, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1984, 1362. b) I. Dewachy, M. A. Esteruelas, Y. Jean, A. Lledds, F. Maseras, L. A. Oro, C. Valero, and F. Volatron, *J. Am. Chem. Soc.*, 1996, **118**, 8388.
9. a) D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1982, 606. b) D. Baudry, M. Ephritikhine, and H. Felkin, *J. Chem. Soc., Chem. Commun.*, 1980, 1243. c) D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.*, 1980, 249.
10. M. A. Green, J. C. Huffman, K. G. Caulton, W. K. Rybak, and J. Ziolkowski, *J. Organomet. Chem.*, 1981, **218**, C39.
11. Free PPh_3 was actually observed in ^{31}P NMR during the reaction.

Rhodium-catalyzed Addition Reactions of Organoboronic Acids

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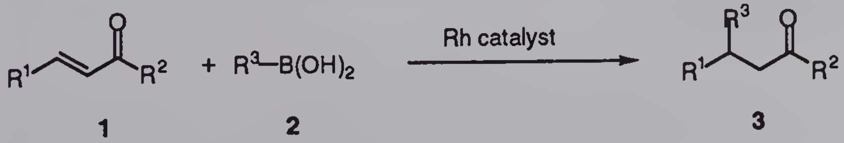
1. Introduction

Organoboron compounds are highly electrophilic, but the organic groups on boron are weakly nucleophilic, thus limiting the use of organoboron reagents for the ionic reactions. However, organoboron compounds, even organoboronic acids and esters, have sufficiently enough reactivity for the transmetallation to other metals. The cross-coupling reaction of organoboron compounds, which involves the transmetallation to palladium(II) halides as a key-step, have been proved to be a quite general tecknique for a wide range of selective carbon-carbon bond formation.[1] Many organometallic reagents undergo similar cross-coupling reactions, but much attention has recently been focused on the use of organoboronic acids in laboratories and industries since they are convenient reagents, generally thermally stable and inert to water and oxygen, thus allowing the handling without special precautions.

The metal-catalyzed addition reaction of organoboron compounds have not yet been well developed, but the reaction of $NaBPh_4$ or arylboronic acids with enones in the presence of $Pd(OAc)_2$ and NaOAc or $SbCl_3$ was recently reported by Uemura and his co-workers.[2] The reaction was proposed to proceed through the oxidative addition of the C-B bond to the Pd(0) species; however, another probable process, the transmetalation to transition metals, may allow a similar catalytic transformation by the use of organoboronic acids. We report here the 1,4-addition reaction of organoboronic acids to α,β-unsaturated ketones or esters and 1,2-addition to aldehydes or imines catalyzed by a $(acac)Rh(CH_2{=}CH_2)_2$/phosphine complex, which may involve the B–Rh transmetalation as the key step.

2. Rhodium-Catalyzed 1,4-Addition to Enones[3]



(1)

R = aryl, 1-alkenyl; R2= alkyl, aryl

Various phosphine ligands gave good results for methyl vinyl ketone (MVK), giving a quantitative yield of 4-phenyl-2-butanone as the sole product, but the reaction with less reactive 2-octen-4-one revealed the order of dppb > dppp > TFP > dppe, PPh_3 and $AsPh_3$ suggesting that the reaction is accelerated upon the increase of the P-Rh-P angles. Other rhodium(I) complexes such as $[Rh(cod)_2]BF_4$/dppb (99%), $[Rh(CO)(PPh_3)_2]ClO_4$ (95%), (acac)Rh(cod)/dppb (99%), $RhCl(PPh_3)_3$ (16%), and $RhCl(CO)(PPh_3)_2$ (35%) were also effective for MVK. The solvent also affects the rate of addition. Aqueous DMF can be used for methyl vinyl ketone, but less polar solvents such as aqueous alcohols, DME, and dioxane afforded a high yield for 2-octen-4-one. The yields significantly decreased in the absence of water. The addition of a base such as NaOH, NaOAc, and Et_3N, or the addition of $SbCl_3$ retarded the reaction, which is in sharp contrast to the palladium-catalyzed cross-coupling reaction of organoboronic acids and the conjugate addition of Ph_4BNa with palladium(II) acetate.[1,2]

The representative results obtained by the procedure using $Rh(acac)(CO)_2$/dppb in aqueous solvents at 50 °C are shown in Table 1.

Table 1. 1,4-Addition to Enones[a]

entry	$RB(OH)_2$	enone	yield/%[b]
1	$4\text{-}MeOC_6H_4B(OH)_2$	$CH_2{=}CHCOCH_3$	84
2	$4\text{-}BrC_6H_4B(OH)_2$		90
3	$4\text{-}MeCOC_6H_4B(OH)_2$		94
4	$2\text{-}MeOC_6H_4B(OH)_2$		84
5	$2,4,6\text{-}Me_3C_6H_2B(OH)_2$		80
6	$PhB(OH)_2$	$CH_3CH{=}CHCOC_4H_9$	96
7		$PhCH{=}CHCOCH_3$	99
8		$PhCH{=}CHCOPh$	86
9		$CH_2{=}C(Me)COPh$	84
10		β-ionone	93[c]
11		2-cyclohexenone	92
12		2-cyclopentenone	72
13	$(E)\text{-}C_4H_9CH{=}CHB(OH)_2$	$CH_2{=}CHCOCH_3$	74
14		$PhCH{=}CHCOC_4H_9$	75
15		2-cyclohexenone	68

[a] A mixture of $RB(OH)_2$ (1.3~2 mmol), enone (1 mmol), $[(acac)Rh(CO)_2]$ (3 mol%) and dppp or dppb (3 mol%) in DMF/H_2O (entries 1-5), MeOH/H_2O or DME/H_2O (entries 6-15) was stirred at 50 °C for 16 h.

[b] Isolated yields by chromatography over silica gel.

[c] The reactions were carried out at 100 °C in dioxane/H_2O (6/1) in the presence of $[Rh(cod)(CH_3CN)_2]BF_4$ (3 mol%).

Various arylboronic acids having *ortho-* and *para-* substituents smoothly underwent the addition to methyl vinyl ketone (MVK) (entries 1-5). There is no appreciable difference in the yields between electron-withdrawing and -donating groups, but the *ortho*-substituents strongly retarded the addition (entries 4 and 5). For such reaction of sterically hindered arylboronic acids, the use of excess (2 equivs) of arylboronic acids was advantageous to achieve high yields. (*E*)-1-Hexenylboronic acids similarly participated in the rhodium-catalyzed conjugate addition, but alkylboronic acids or trialkylboranes having β-hydrogen failed to add to enones (entries 13-15).

Work on mechanistic details is in progress, but the present transformation may result from a catalytic cycle that involves the transmetalation between the hydroxorhodium(I) **4** and arylboronic acid to give the arylrhodium(I) species **5**, and the insertion of enone to the Ar-Rh bond. The hydrolysis of the rhodium(I) enolate with water reproduces the hydroxorhodium species, as shown in Figure 1. The arylrhodium(I) complexes are unstable such as to preclude isolation in pure form, but they have been reasonably speculated to be the key intermediates carrying out various coupling reactions with organic halides and the addition to alkenes and alkynes.

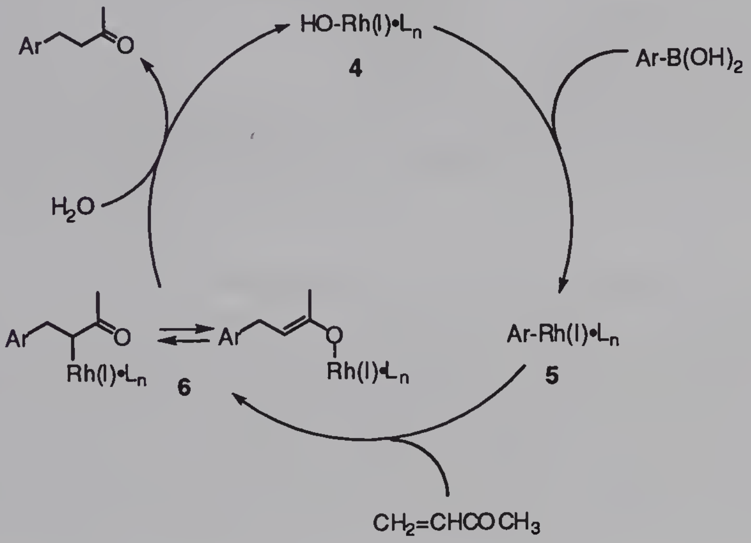


Figure 1. Catalytic Cycle

3. Asymmetric 1,4-Addition to Enones[4]

The reaction is catalyzed by transition metal complexes coordinated with phosphine ligands. Since chiral phosphine ligands are the chiral auxiliaries most extensively studied for transition metalcatalyzed asymmetric reactions, one can use the accumulated knowledge of the chiral phosphine ligands for the asymmetric reaction. The asymmetric 1,4-addition of aryl- and 1-alkenylboronic acids to enones proceeded with high enantioselectivity in the presence of a chiral phosphine-rhodium catalyst (Table 2).

The reaction was efficiently catalyzed by a rhodium complex generated *in situ* by mixing Rh(acac)($CH_2=CH_2$)$_2$ with 1 equiv of (S)-binap in an aqueous solvent at 100 ℃. It was interesting that the enantioselectivity was kept constant at the reaction temperature ranging between 40-120 ℃ in the addition to 2-cyclohexenone. High enantioselectivity exceeding 90%ee were readily achieved for both cyclic and acyclic α,β-unsaturated ketones with variety of aryl- and alkenylboronic acids.

Table 2. Asymmetric 1,4-Addition to Enones[a]

entry	enone	$RB(OH)_2$	yield/%	%ee
1	2-cyclohexenone	$PhB(OH)_2$	93	97
2		$4\text{-}MeC_6H_4B(OH)_2$	97	97
3		$4\text{-}CF_3C_6H_4B(OH)_2$	70	99
4		$3\text{-}MeOC_6H_4B(OH)_2$	97	96
5		$3\text{-}ClC_6H_4B(OH)_2$	96	96
6		$C_5H_{11}CH{=}CHB(OH)_2$	88	94
7		$t\text{-}BuCH{=}CHB(OH)_2$	76	91
8	2-cyclopentenone	$PhB(OH)_2$	93	97
9		$C_5H_{11}CH{=}CHB(OH)_2$	64	96
10	2-cycloheptenone	$PhB(OH)_2$	51	93
11	$i\text{-}PrCH{=}CHCOCH_3$	$PhB(OH)_2$	82	97
12	$C_5H_{11}CH{=}CHCOCH_3$	$PhB(OH)_2$	88	92

[a] A mixture of $ArB(OH)_2$ (2~4 mmol), enone (1 mmol), $[(acac)Rh(CH_2{=}CH_2)_2]$ (3 mol%) and (S)-binap (3 mol%) in dioxane/H_2O or DME/H_2O was stirred at 100 °C.

The addition of phenylboronic acid to cyclohexenone with Rh/(S)-binap gave (S)-3-phenylcyclohexanone. The figure 2 shows the stereochemical pathway forming the products of (S) configuration for 2-cyclohexenone. The (S)-binap/rhodium intermediate should have an open space at the lower part of the vacant coordination site, the upper part being blocked by one of the phenyl rings of the binap ligand. The olefinic double bond of 2-cyclohexenone coordinates to rhodium with its 2Si, which undergoes migratory insertion to form a stereogenic carbon center whose absolute configuration is (S).

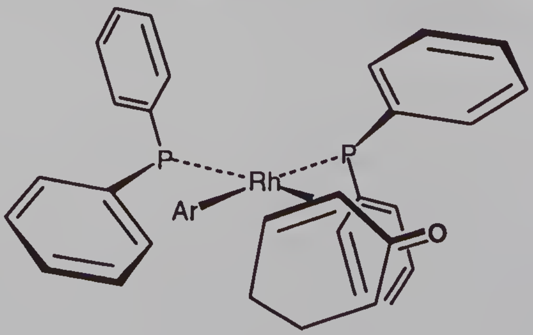
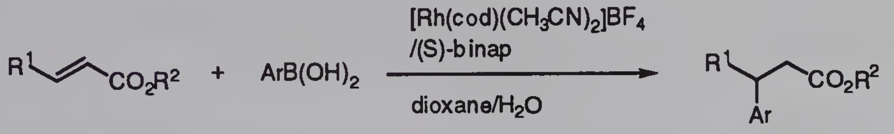


Figure 2. Transition State

4. Asymmetric 1,4-Addition to α,β-Unsaturated Esters[5]

Various rhodium complexes such as $Rh(acac)(CH_2{=}CH_2)_2$, $Rh(acac)(CO)_2$ and $[Rh(cod)(CH_3CN)_2]BF_4$ plus a phosphine ligand efficiently catalyzed the addition to α,β-unsaturated esters. The reaction rates were highly dependent on the substituent (R^1) which may affect the rate of insertion of **7** to the rhodium-carbon bond. Thus, the addition to **7f** smoothly proceeded at 50 °C whereas **7a** and **7b-e** required heating to 80 °C and 100 °C, respectively. Similarly to the addition to enones, aqueous solvents combining water and a weak donor solvent such as methanol, dimethoxyethane, or dioxane gave good results. Under the conditions, the saponification of esters was in a very minor amount during 16 h, even at 100 °C. The addition of phenylboronic acid to **7a** involved some β-hydride elimination to give **7f** since the reaction was accompanied with ethyl 3,3-diphenylpropanoate (8%) which was derived from a sequence of β-elimination and addition of phenylboronic acid to **7f**, but such by-product was not observed in the addition to **7b-g**.



(3)

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7a: R^1=H, R^2=Me
7b: R^1=Me, R^2=*i*-Pr
7c: R^1=Me, R^2=cyclohexyl
7d: R^1=Me, R^2=*t*-Bu
7e: R^1=Me, R^2=CH_2Ph
7f: R^1=Ph, R^2=Me
7g: R^1=Ph, R^2=CH_2Ph

The results obtained for the asymmetric 1,4-addition of arylboronic acids to crotonates or cinnamates in the presence of a $Rh(acac)(C_2H_4)_2$-(S)-binap catalyst are summarized in Table 3. The ester group (R^2) significantly affects the %ee. Thus, the *i*-propyl, cyclohexyl, *t*-butyl, benzyl esters achieved a high %ee whereas the methyl and ethyl esters (entries 1-4) resulted in low asymmetric induction. The absolute configuration of benzyl 3-phenylbutanoate ($[\alpha]_D$ -14.5 (c 1.02, $CHCl_3$) obtained from (S)-binap was established to be (R) by the specific rotation reported for (R)-3-phenylbutanoic acid ($[\alpha]_D$ -45.8 (c 0.77, benzene).

Various arylboronic acids having *o*-, *m*-, and *p*-substituents smoothly underwent the addition to benzyl crotonate (**7e**) with high yields and high %ee (entries 5-11). There is no appreciable difference in yields and %ee between *m*- and *p*-functionalized arylboronic acids. The presence of *o*-substituent slightly retarded the addition due to its steric hindrance (entries 10 and 11) and the methoxy group again diminished the %ee (entry 11). The addition of 4-methylphenylboronic acid and 1-naphthylboronic acid to **7g** resulted in 48 and 11%ee, respectively (entries 12 and 13).

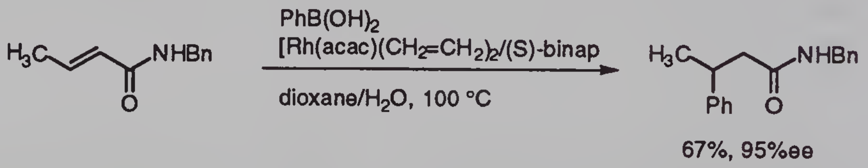
Table 3. Asymmetric 1,4-Addition to α,β-Unsaturated Esters[a]

entry	7	$ArB(OH)_2$	yield/%[b]	%ee
1	**7a**	$PhB(OH)_2$	82	37 (R)
2	**7b**	$3\text{-}MeOC_6H_4B(OH)_2$	91	91
3	**7c**	$3\text{-}MeOC_6H_4B(OH)_2$	97	91
4	**7d**	$3\text{-}MeOC_6H_4B(OH)_2$	54	92

5	**7e**	$3\text{-MeOC}_6H_4B(OH)_2$	97	87
5	**7e**	$4\text{-CF}_3C_6H_4B(OH)_2$	98	86
6	**7e**	$4\text{-MeC}_6H_4B(OH)_2$	92	87
7	**7e**	$4\text{-MeOC}_6H_4B(OH)_2$	78	85
8	**7e**	$3\text{-ClC}_6H_4B(OH)_2$	99	88
10	**7e**	$2\text{-MeC}_6H_4B(OH)_2$	34	92
11	**7e**	$2\text{-MeOC}_6H_4B(OH)_2$	51	97
12	**7f**	$4\text{-MeC}_6H_4B(OH)_2$	65	48
13	**7g**	1-naphthylB(OH)_2	16	11

[a] A mixture of $[Rh(cod)(CH_3CN)_2]BF_4$ (0.03 mmol), (S)-binap (0.045 mmol), arylboronic acid (2.0 mmol) and α,β-unsaturated ester (1.0 mmol) in dioxane (6 ml) and H_2O (1 ml), was stirred for 16 h at 100 °C. Isolated yields by chromatography over silica gel.

Preliminary results for the addition to α,β-unsaturated amides are shown in Eq. 3. The %ee thus obtained were higher than the corresponding addition to α,β-unsaturated esters.



(3)

5. Rhodium-Catalyzed 1,2-Addition to Aldehydes[6] and Imines[5]

The efficiency of transmetalation from boron to palladium in the catalytic 1,4-addition of aryl or 1-alkenylboronic acids to enones encouraged us to extend the protocol to the addition of aryl- and 1-alkenylboronic acids to aldehydes in an aqueous solution (Eq. 4). The insertion of carbonyl groups into transition metal-carbon bonds has not received much attention, but the catalytic use of transition metals may allow such addition of various organometallics which are inert without a catalyst, the asymmetric addition using a chiral phosphine complex, or the reaction in an aqueous phase.

(4)

R^1 = alkyl, aryl; R^2= aryl, 1-alkenyl

The reaction was induced by the phosphine complexes having a large P-Rh-P angle which may affect the rate of carbonyl insertion into the Rh-C bond. Thus, monodentate phosphines and dppe were totally ineffective, but the complexes derived from dppp, diop, dppf and biap exhibited high catalytic activity.

The reaction was rather sensitive to electronic effects both in aldehydes and arylboronic acids, suggesting the mechanism proceeds through the nucleophilic attack of the aryl group to the carbonyl (Table 4). Thus, the reaction was facilitated in the presence of an electron-withdrawing group in aromatic aldehydes (entries 1-7) and a donating group in arylboronic acids (entries 8-11). On the other hand, the addition to electron-rich aldehydes (entry 7) and the arylation with electron-deficient arylboronic acids (entries 10 and 11) were slow at 80 °C. However, 4-nitrobenzaldehyde exceptionally remained intact during the reaction (entry 5).

Table 4. 1,2-Addition to Aldehydes[a]

entry	$ArB(OH)_2$	aldehyde	yield/%[b]	
1	$PhB(OH)_2$	PhCHO	92	
2		$4\text{-}CF_3C_6H_4CHO$	97	
3		$4\text{-}NCC_6H_4CHO$	97	
4		$4\text{-}MeCOC_6H_4CHO$	93	
5		$4\text{-}NO_2C_6H_4CHO$	< 1[c]	
6		$4\text{-}BrC_6H_4CHO$	88	
7		$4\text{-}MeC_6H_4CHO$	48	(76)[d]
8	$4\text{-}MeOC_6H_4B(OH)_2$	$4\text{-}NCC_6H_4CHO$	84	
9	$4\text{-}MeC_6H_4B(OH)_2$	$4\text{-}NCC_6H_4CHO$	99	
10	$4\text{-}FC_6H_4B(OH)_2$	$4\text{-}NCC_6H_4CHO$	52	
11	$4\text{-}MeCOC_6H_4B(OH)_2$	$4\text{-}NCC_6H_4CHO$	< 1[c]	
12	$2\text{-}MeC_6H_4B(OH)_2$	$4\text{-}MeOC_6H_4CHO$	80	(86)[d]
13	$2,4,6\text{-}Me_3C_6H_2B(OH)_2$	$4\text{-}MeOC_6H_4CHO$	31	(43)[d]
14	$PhB(OH)_2$	2-furaldehyde	78	
15		1-naphthaldehyde	91	
16		$C_5H_{11}CHO$	69	
17		$C_6H_{11}CHO$	45	(95)[d]
18	(*E*)-$C_4H_9CH{=}CHB(OH)_2$	$4\text{-}NCC_6H_4CHO$	76	

[a] A mixture of $ArB(OH)_2$ (2 mmol), aldehyde (1 mmol), $[(acac)Rh(CO)_2]$ (3 mol%) and dppf (3 mol%) in DME/H_2O (1/1, 6 ml) was stirred at 80 °C for 16 h.

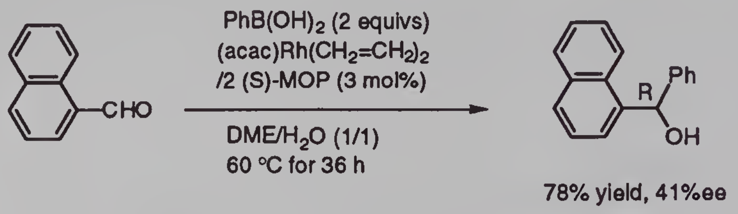
[b] Isolated yields by chromatography over silica gel.

[c] The aldehyde were recovered unchanged.

[d] The reactions were carried out at 95 °C for 16 h in dioxane/H_2O (1/1, 6 ml).

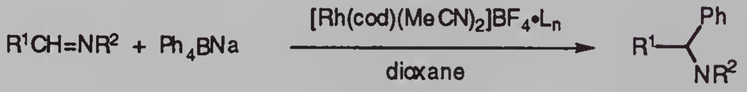
The reaction is specific for aldehydes. Aromatic ketones, esters, nitriles, halides (Cl, Br) were unreactive as evidenced by the recovery of these substrates. The steric hindrance around the boron atom retarded the reaction (entry 13), but those reactions of *ortho*-monosubstituted arylboronic acids proceeded smoothly at 80 °C (entry 12). The additions to aliphatic aldehydes such as hexanal and cyclohexanecarbaldehyde were very slow at 80 °C due to their lower electrophilicity than that of aromatic aldehydes, but the reaction at 95 °C in dioxane/H_2O achieved high yields of the carbinols (entries 16 and 17). (*E*)-1-Hexenylboronic acid also participated in the catalytic reaction, retaining its stereochemistry (entry 18).

The facile addition of arylboronic acids to aldehydes encouraged us to examine the asymmetric version of this protocol (Eq. 5). A monodentate ligand of (*S*)-MeO-MOP revealed a moderate asymmetric induction with the (*R*)-(+)-1-naphthylphenylmethanol being preferentially formed (41%ee), though the chiral bidentate ligands such as DIOP and BINAP unfortunately resulted in the formation of racemic alcohols.



(5)

The addition of arylboronic acids to imines in an aqueous solvent gave a mixture of amine (Eq. 6) and alcohol (Eq. 4) because the imines were partially hydrolyzed to the aldehyde during the reaction. The use of Ph_4BNa in place of phenylboronic acid allowed the catalytic addition to various N-sulfonyl imines in the absence of water (Eq. 6). The representative results are summarized in Table 5. The cationic rhodium complexes such as $[Rh(cod)(MeCN)_2]BF_4$ was found to be the most efficient catalyst for both aromatic and aliphatic N-sulfonyl imines whereas no reactions were observed for N-alkyl and N-aryl imine derivatives.



(6)

R^1 = alkyl, aryl; R^2= SO_2Ph

Table 5. 1,2-Addition to Imines[a]

entry	**9**	time/h	yield/%
1	$PhCH{=}NCH_2Ph$	3	trace
2	$PhCH{=}NPh$	3	8
3	$PhCH{=}NSO_2Ph$	3	89
4	$4\text{-}MeOC_6H_4CH{=}NSO_2Ph$	3	94
5	$4\text{-}FC_6H_4CH{=}NSO_2Ph$	3	91
5	$2\text{-}MeC_6H_4CH{=}NSO_2Ph$	16	90
6	$cyclohexylCH{=}NSO_2Ph$	3	60
7	$C_5H_{11}CH{=}NSO_2Ph$	3	59

[a] Amixture of Ph_4BNa (1.3 mmol), imine (1 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.03 mmol) and dppb (0.03 mmol) in dioxane was stirred at 90 °C. Isolated yields are shown in Table.

References

1) Miyaura, N.; Suzuki, A. *Chem. Rev*, **1995**, *95*, 2457.
2) Cho, C. S.; Motofusa, S.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 883.
3) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics*, **1997**, *16*, 4229.
4) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580.
5) Ueda, M.; Miyaura, N. unpublised results.
6) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem. Int. Ed. Engl.*, **1998**, *37*, 3279.

Metal-catalyzed Routes to Alpha-Heteroatom-substituted Boronic Acids and Boronate Esters

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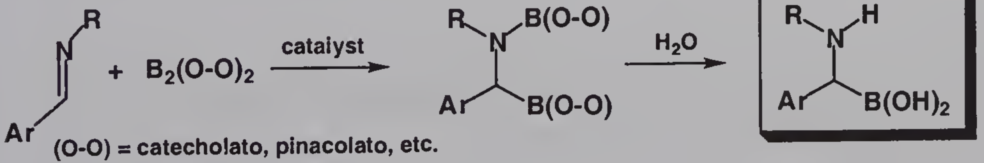
1 INTRODUCTION

1.1 Why Make Boronic Acids and Boronate Esters?

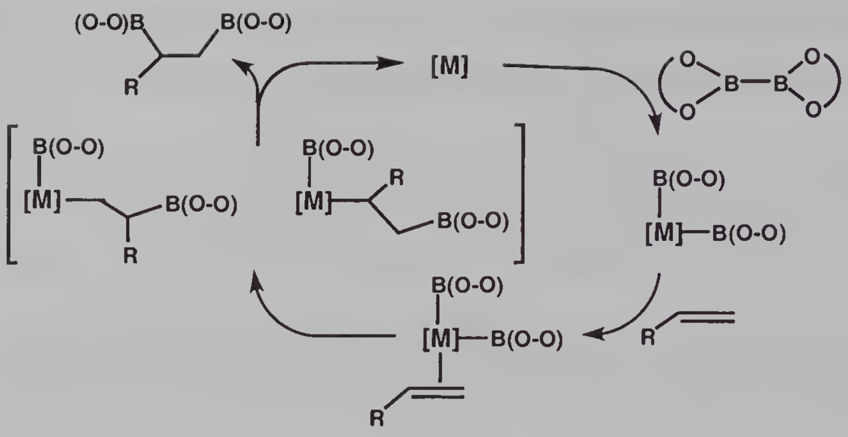
Boronate esters have proven to be very useful intermediates in organic synthesis, particularly as substrates for Pd-catalyzed carbon-carbon bond formation using the Suzuki-Miyaura coupling method.[1] Boronic acids are multifunctional molecules that have found a number of molecular recognition applications such as amine and sugar sensors,[2,3] saccharide transport,[4-6] and as enzyme inhibitors.[7] For instance, several groups have shown that alpha-aminoboronic acids [RR'NCHR"B(OH)$_2$] are particularly selective enzyme inhibitors for serine proteases[8-10] and recent work has shown that alpha-phosphonylboronate esters [(OH)$_2$P(O)CHRB(OR')$_2$] also exhibit bioactivity.[11,12] Although some excellent chemistry has been developed for the preparation of alpha-haloboronic acids and the alpha-heteroatom substituted compounds referred to above,[13,14] we envisioned a more direct route to these compounds using the metal-catalyzed addition of diboron reagents to heteroatom-containing unsaturated organics as shown for aldimines in Equation 1.



1)

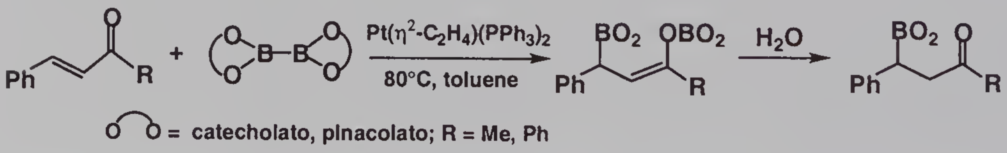
1.2 Catalyzed Addition of Diboron Reagents to Unsaturated Organics

We and others recently reported the metal-catalyzed addition of diboron compounds to alkenes and alkynes.[15,16] Subsequent work has improved the catalysts and extended the scope of the substrate to include disubstituted alkenes, enynes, and dienes.[17] Stoichiometric reactivity studies support a mechanism which involves oxidative addition of the B-B bond to the metal center, followed by insertion of the substrate into the M-B bond, and product-forming B-C reductive elimination (Scheme 1).[18]



Scheme 1

One particular advantage of diboration over hydroboration involves addition to heteroatom-containing unsaturated organics. While elegant asymmetric hydroborations of imines and carbonyl compounds have been reported using chiral auxiliaries,[19,20] after hydrolysis the result is equivalent to an asymmetric hydrogenation which can sometimes be carried out more efficiently and without the need for recovery of the chiral auxiliary. In the diboration reaction, however, a boron-carbon bond is formed which can either remain intact or be coupled with a variety of C-X bonds to form more complex, multifunctional products. Another synthetic strategy to alpha-substituted boronate esters involves metal-catalyzed hydroboration or diboration of functionalized alkenes. The sole example reported to date involves the Pt-catalyzed diboration of α-β-unsaturated carbonyl compounds to give allylboronate and β-acylboronate ester products (Equation 2).[21]

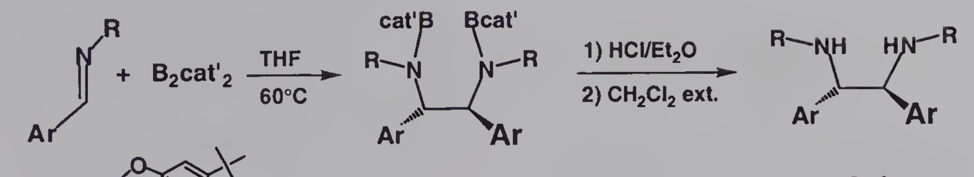


2)

2 RESULTS

2.1 Uncatalyzed Addition of Diboron Reagents to Aldimines: Stereospecific Formation of C_2-symmetric *N*-boryldiamines

Treatment of relatively electron-rich, sterically compact *C*-arylaldimines with $B_2cat'_2$ (cat' = 4-*t*-Bu-catecholato) in refluxing THF affords both enantiomers of *racemo-N*-boryldiamines, **1a-f**; the *meso* diastereomers are not observed (Equation 3). Although alternative aqueous work-up procedures would likely give higher yields of the C_2-symmetric diamine products, **2a-f**, we have employed a rapid protonolysis work-up, followed by extraction into CH_2Cl_2 which gives the products in high purity without chromatography. We propose that the coupling reaction proceeds via the bis(imine) adduct of the diboron reagent[22] and that the *trans* disposition of the N-substituents fixes the stereochemistry of the C-C bond via the pseudo-chair transition state (Scheme 2).

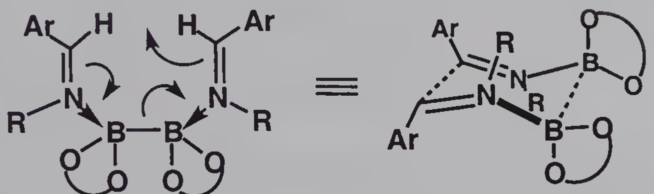


3)

Ar = Ph; R = Me, CH_2Ph, *i*-Bu, Ph, *p*-OMe-Ph; **1a-e**

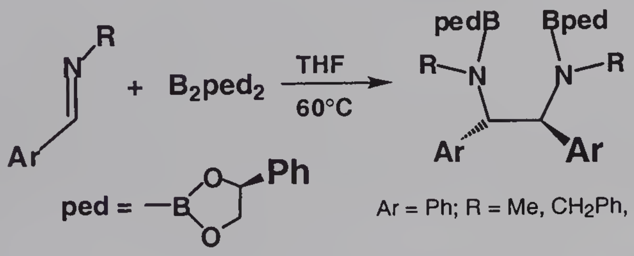
Ar = *p*-OMe-Ph; R = Ph; **1f**

2a-f



Scheme 2

For reactive N-alkylaldimines, higher yields of the *N*-boryldiamines, **3a-c**, are obtained using the less Lewis acidic B_2ped_2 reagent (ped = phenylethanediolato, Equation 4), but attempts to achieve enantioselection from either the *R,R*- or *S,S*-ped-derived diboron reagents were unsuccessful. Similar attempts with chiral 1,2-diphenylethanediol- and pinenediol-derived reagents gave no reaction (even with MeN=CHPh).



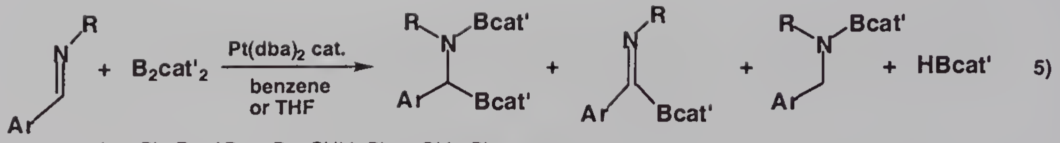
4)

Ar = Ph; R = Me, CH_2Ph, i-Bu; **3a-c**

2.2 Metal-catalyzed Addition of Diboron Reagents to Aldimines: Formation of Alpha-aminoboronate Esters

Addition of a catalytic amount of $Pt(dba)_2$ (dba = dibenzylidene acetone) to reactions with a variety of *C*-arylaldimines and $B_2cat'_2$ in benzene or THF at 25°C yielded HBcat' and a mixture of diboration, **4a-j**, boration, **5a-j**, and hydroboration products, **6a-j** (Equation 5). Addition of one equivalent of a phosphine such as PPh_3 or PCy_3 to the Pt catalyst severely reduced activity, while Wilkinson's catalyst, $RhCl(PPh_3)_3$, gave much less of the diboration product. Both cationic and neutral rhodium complexes with chelating phosphines were also inactive.

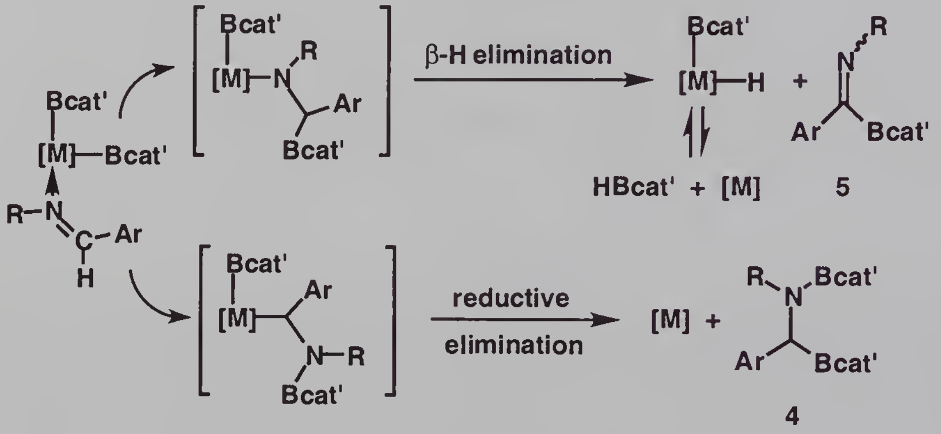
Based on previous observations in alkene diboration, we presume that the observed reaction mixtures result from poor regiocontrol of insertion of the imine into the Pt-B bond (Scheme 3). Initial formation of Pt-C and B-N bonds leads to diboration, while forming Pt-N and B-C bonds leads to β-hydrogen elimination which gives HBcat' and *C*-borylimine **5**. Further reaction of HBcat' with the starting imine then affords hydroboration product **6**.



5)

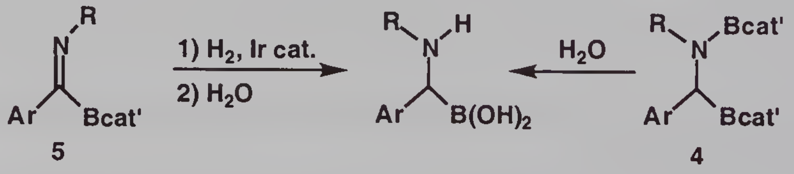
Ar = Ph; R = *i*-Bu, *t*-Bu, CHMePh, *o*-OMe-Ph, *p*-OMe-Ph, xylyl, 2,4-Me$_2$-Ph, 2,6-(*i*-Pr)$_2$-Ph; **4a-h**
Ar = *o*-OMe-Ph; R = *i*-Bu, Ph; **4i,j**

5a-j **6a-j**



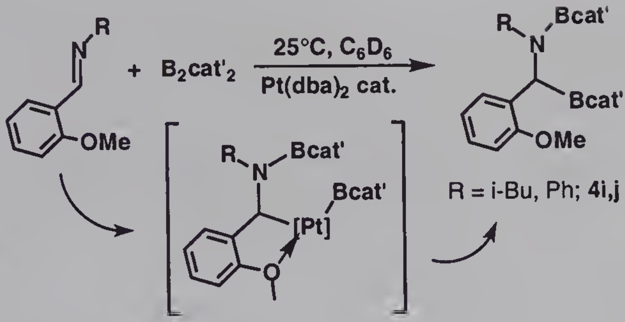
Scheme 3

Given the apparently high steric demands of catalyzed imine diboration and our difficulty in finding a better catalyst, how could we increase the yield of diboration product? Our first thought was to hydrogenate the *C*-borylimine **5** *in situ* using a cationic iridium catalyst.[23] Upon aqueous work-up, both product **4** and hydrogenated **5** would then afford the alpha-aminoboronic acid (Equation 6). Unfortunately, ^{11}B NMR monitoring of the catalyzed diboron additions showed that, for some substrates, **5** reacts further to give a much less reactive four-coordinate B-containing product which we propose is the cyclic dimer. A second strategy was to use a substrate with a large *N*-substituent so the imine would have to insert with the desired regiochemistry.



6)

This worked well {[(2,6-(*i*-Pr)$_2$-Ph]N=CHPh and (2,6-Me$_2$-Ph)N=CHPh gave 94 and 79% diboration, respectively}, but significantly limited the 'molecular diversity' of the resulting alpha-aminoboronate esters. Our third strategy arose from an observation that an *ortho*-methoxyphenyl substituent on the imine nitrogen yielded *no* diboration product. We presumed this was due to a substrate directing effect, and use of this substituent on the imine *carbon* then allowed us to diborate a number of *N*-alkylaldimines in good yield (Equation 7).

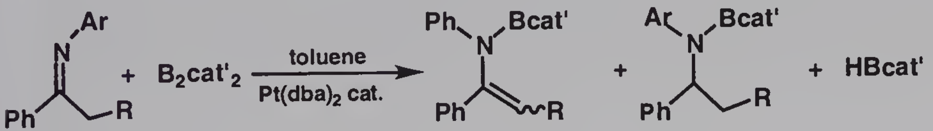


R = i-Bu, Ph; **4i,j**

7)

2.3 Metal-Catalyzed Multiple Boration of Ketimines

Pt-catalyzed reaction of several ketimines with $B_2cat'_2$ in toluene afforded HBcat' and *N*-borylenamines, **7a-e**, along with a small amount of hydroborated ketimine, **8a-e** (Equation 8). Again, $RhCl(PPh_3)_3$ gave almost equal amounts of **7** and **8**.

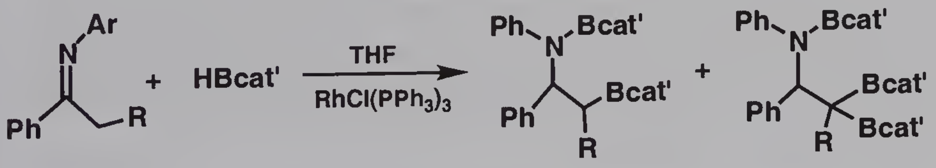


8)

R = H; Ar = Ph, *p*-CF_3-Ph, *o*-OMe-Ph; **7a-c**
R = Ph; Ar = *p*-OMe-Ph; **7d**
R =Me; Ar = *p*-CF_3-Ph; **7e**

8a-e

Stoichiometric reactivity studies suggested that HBcat' could be used in the place of $B_2cat'_2$, and by using the $RhCl(PPh_3)_3$ catalyst in THF, we obtained multiply borated products, **9a-d** and **10a-c** (Equation 9) from Rh-catalyzed ketimine boration and subsequent Rh-catalyzed *N*-borylenamine hydroboration.[24] Formation of **9** vs. **10** presumably reflects the competitive insertion of the imine into the Rh-H vs. Rh-B bond (Scheme 4). Compounds **9** and **10** are interesting intermediates for Suzuki-Miyaura coupling, but conditions will have to be chosen carefully to avoid elimination to give alkene and alkenylboronate ester, respectively.



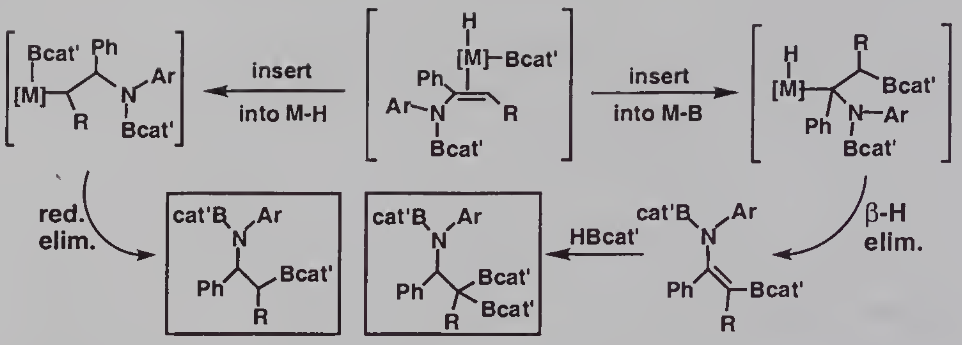
9)

R = H; Ar = Ph, *p*-CF_3-Ph, *o*-OMe-Ph; **9a-c**
R = Ph; Ar = *p*-OMe-Ph; **9d**

10a-c

2.4 Preparation of Alpha-Thioboronate Esters

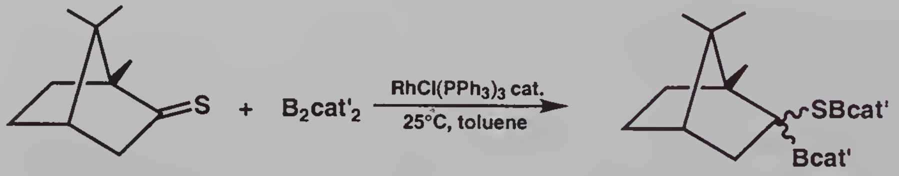
Addition of $B_2cat'_2$ to thiocamphor in toluene with 2 mol% Wilkinson's catalyst afforded the diborated product **13** stereospecifically in high yield (Equation 10). Rapid



9 10

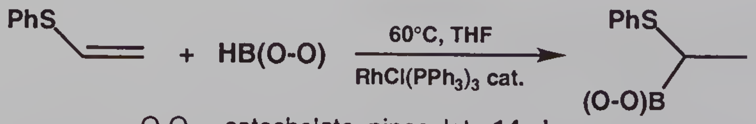
Scheme 4

acidic aqueous work-up gave the S-H thiol-substituted boronate ester, while extended aqueous treatment (hours) gave the S-H-substituted boronic acid. Only one isomer was obtained, but neither NOE NMR studies or molecular modeling have yet ascertained whether the addition is *exo* or *endo* with respect to the bridgehead.



(1R)-(-)-thiocamphor 13 10)

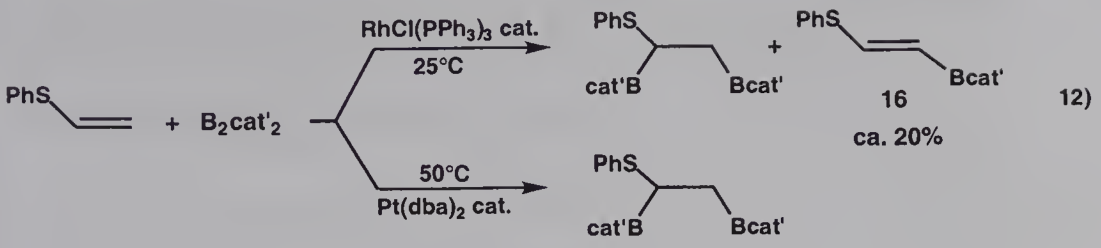
A second metal-catalyzed route to alpha-thioboronate esters consists of the regiospecific, Markovnikov hydroboration of phenyl vinylsulfide which proceeds in high yield to give **14a,b** (Equation 11). We are in the process of extending this unique reaction to other alkenyl sulfides and to alkenyl phosphines in order to determin whether the observed regiochemistry of addition is due to a directing effect of the soft heteroatom donor towards the catalyst center.



11)

O-O = catecholato, pinacolato;**14a,b**

Diboration of phenyl vinylsulfide to give **15** is best performed with a phosphine-free Pt catalyst, as Wilkinson's catalyst affords the *Z*-(phenylthio)-vinylboronate ester side product, **16**, presumably due to β-hydrogen elimination being competitive with B-C reductive elimination (Equation 12).



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3 CONCLUSIONS

Reactions of diboron reagents with heteroatom-containing, unsaturated organics give a wide variety of products formed by an array of chemical processes. While the uncatalyzed aldimine coupling has ample precedent with more common reducing agents,[25] the unique mechanism adopted by the diboron reagents leads to a stereospecific coupling which affords only C_2-symmetric diamines. Extension of this coupling method to carbonyl compounds and related cross-couplings are complicated by elimination of catBOBcat.[26] The synthetic utility of metal-catalyzed addition of diboron reagents to aldimines is limited by poor regiocontrol of substrate insertion into the M-B bond. This problem is alleviated to some extent for aldimines with sterically bulky *N*-aryl substituents, and for those which have an ortho-directing group on the *C*-aryl substituent. Metal-catalyzed addition of diboron reagents to ketimines is dominated by β-hydrogen elimination to give N-borylenamines. The resulting Rh-catalyzed hydroboration of N-borylenamines is remarkably solvent dependent for reasons which are not yet clear.[24] Metal-catalyzed diboration of the C=S bond in thiocamphor is very efficient, and we are currently examining the scope of the substrate for these reactions. Metal-catalyzed Markovnikov hydroboration of alkenyl sulfides also appears to be a promising route to alpha-thioboronate esters and –boronic acids and we are currently investigating the asymmetric variant of this reaction using rhodium catalysts containing chiral phosphine ligands. The corresponding metal-catalyzed diboration of alkenyl sulfides (and alkynyl sulfides) may also be useful for further elaboration of the products through metal-catalyzed C-C coupling methods.[1,27,28]

References

1. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
2. M. T. Reetz, C. M. Niemeyer, and K. Harms, *Angew. Chem., Intl. Ed. Eng.*, 1991, **30**, 1474.
3. T. D. James, K. R. A. Sandanayake Samankumara, and S. Shinkai, *Angew. Chem., Intl. Ed. Eng.*, 1996, **35**, 1911.
4. S. Shinkai, *NATO ASI Ser., Ser. C*, 1997, **492**, 37.
5. P. R. Westmark, S. J. Gardiner, and B. D. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 11093.
6. B. D. Smith, *Supramolec. Chem.*, 1996, **7**, 55.
7. G. E. Lienhard, *Science*, 1973, **180**, 149.
8. E. Tsilikounas, C. A. Kettner, and W. W. Bachovchin, *Biochemistry*, 1992, **31**, 12839.

9. E. Skordalakes, R. Tyrell, S. Elgendy, C. A. Goodwin, D. Green, G. Dodson, M. F. Scully, J.-M. H. Freyssinet, V. V. Kakkar, and J. J. Deadman, *J. Am. Chem. Soc.*, 1997, **119**, 9935.
10. S. J. Coutts, T. A. Kelly, R. J. Snow, C. A. Kennedy, R. W. Barton, J. Adams, D. A. Krolikowski, D. M. Freeman, S. J. Campbell, J. F. Ksiazek, and W. W. Bachovchin, *J. Med. Chem.*, 1996, **39**, 2087.
11. I. Pergament and M. Srebnik, *Tetrahedron Lett.*, 1999, **40**, 3895.
12. M. Srebnik, I. Pergament, and A. Al Aziz Quntar, Abstract INOR 287, 218th ACS National Meeting, New Orleans, USA, 1999.
13. D. S. Matteson, *Chemtech*, 1999, **29**, 6.
14. S. Elgendy, G. Claeson, V. K. Kakkar, D. Green, G. Patel, C. A. Goodwin, J. A. Baban, M. F. Scully, and J. Deadman, *Tetrahedron*, 1994, **50**, 3803.
15. R. T. Baker, P. Nguyen, T. B. Marder, and S. A. Westcott, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1336.
16. T. Ishiyama, N. Matsuda, N. Miyaura, and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11018.
17. T. B. Marder and N. C. Norman, *Top. Catal.*, 1998, **5**, 63.
18. R. T. Baker, J. C. Calabrese, S. A. Westcott, P. Nguyen, and T. B. Marder, *J. Am. Chem. Soc.*, 1993, **115**, 4367.
19. E. J. Corey, R. K. Bakshi, S. Shibata, C. P. Chen, and V. K. Singh, *J. Am. Chem. Soc.*, 1987, **109**, 7525.
20. S. Hashiguchi, N. Uematsu, and R. Noyori, *Yuki Gosei Kagaku Kyokaishi,* 1997, **55**, 99.
21. Y. G. Lawson, M. J. G. Lesley, N. C. Norman, C. R. Rice, and T. B. Marder, *Chem. Commun.*, 1997, 2051.
22. C. Dai, S. M. Johnson, F. J. Lawlor, P. Lightfoot, T. B. Marder, N. C. Norman, A. G. Orpen, N. L. Pickett, M. J. Quayle, and C. R. Rice, *Polyhedron*, 1998, **17**, 4139.
23. F. Spindler, B. Pugin, H.-P. Jalett, H.-P. Buser, W. Pittelkow, and H.-U. Blaser, in 'Catalysis of Organic Reactions' (Ed.: R. E. Malz), Marcel Dekker, New York, 1996, p. 153.
24. T. M. Cameron, R. T. Baker, and S. A. Westcott, *Chem. Commun.*, 1998, 2395.
25. T. Wirth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 61.
26. R. L. Broene, J. M. Boncella, and R. T. Baker, unpublished results.
27. D. M. T. Chan, K. L. Monaco, R.-P. Wang, and M. P. Winters, *Tetrahedron Lett.*, 1998, **39**, 2933.
28. D. E. Evans, J. L. Katz, and T. R. West, *Tetrahedron Lett.*, 1998, **39**, 2937.

Organoborane Dienophiles as 1-Alkene Equivalents, Terpenylboranes, and Catalytic Hydroboration of Conjugated Dienes and Enynes

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1 INTRODUCTION

The Diels-Alder reaction and catalytic processes are powerful methods of modern organic synthesis. In both these areas organoboranes play an important role being used as dienophiles,[1] and hydroborating agents.[2]

Among a variety of dienophiles the simplest one ethylene, and 1-alkenes react sluggishly.[3] Consequently, their equivalents are highly desirable and a few such compounds have been introduced.[4] Vinylic organoboranes are good candidates for that purpose, provided they would be sufficiently reactive and the carbon-boron bond of the adduct could be transformed into the carbon-hydrogen bond without isomerization of the double bond. Here, our studies in this direction are described.[5]

Catalytic hydroboration is a new methodology of great synthetic potential. The reaction is usually carried out with catecholborane in the presence of rhodium, palladium, iridium and ruthenium compounds.[2] In contrast to olefins, very little is known on catalytic hydroboration of conjugated dienes and enynes. Our earlier studies on the uncatalyzed monohydroboration of conjugated dienes,[6] reports on the hydroboration of 1-decene with catecholborane catalyzed by lanthanide iodides,[7] and monohydroboration of 1,3-enynes in the presence of palladium compounds,[8] prompted us to search for other transition metal catalysts for monohydroboration of conjugated dienes and enynes.[9,10]

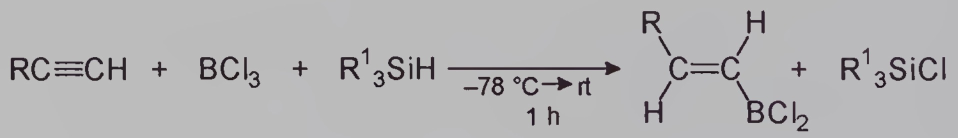
In the course of our earlier studies on terpenylboranes we developed a simple transformation of α- into β-pinene,[11] and a stereoselective synthesis of allylic alcohols by the reduction of vinylic epoxides.[12] An extension of these studies to contrathermodynamic isomerization of α-thujene, 2- and 3-carene,[13] and kinetic resolution of vinylic epoxides by the reduction with terpenylboranes,[14] is described.

2 ORGANOBORANE DIENOPHILES AS ETHYLENE AND 1-ALKENE EQUIVALENTS

Recently, it has been shown that in contrast to vinylic boronates, vinylic dialkyl- and dihalogenoboranes are considerably more reactive dienophiles.[15-17] Protonolysis of their adducts with 1,3-dienes could lead to products equivalent to adducts of alkenes. Protonolysis of trialkylboranes can be achieved by heating with carboxylic acids, however, little is known on the reaction course of homoallylic alkenylboranes which are produced in the Diels-Alder reaction of vinylic organoboranes. Racemization due to the double bond shift observed in protonolysis of the monohydroboration product of (+)-limonene,[18] indicates the possibility of isomerization of alkenes with isolated double bond under these conditions.

In our study,[5] dibromovinylborane (**1**), dichlorovinylborane (**2**), di-(*n*-butyl)vinylborane (**3**), and B-vinyl-3,6-dimethylborepane (**4**), were used as dienophiles, equivalents of ethylene. Their reactivity was tested for the reaction with 2,3-dimethyl-1,3-butadiene. The following reactivity order was observed **1** > **2** > **3**,**4**. Dibromovinylborane is highly reactive and the additions proceed below room temperature. The less reactive dichlorovinylborane gives adducts at room temperature. Additions of **3** and **4** required warming for several hours at 80 °C. Other dienes used for the study were 2,4-hexadiene, isoprene, 2,4-dimethyl-1,3-pentadiene, 1,3-cyclopentadiene, and 1,3-cyclohexadiene. The addition reactions of these dienes with dibromovinylborane were difficult to control, oligomerization of the dienes was observed, and the yields of adducts varied. The reactions with dichlorovinylborane were free from these inconveniences, proceeding at temperatures not exceeding 60 °C to give the corresponding adducts (Table 1). The addition of dichlorovinylborane to 1,3-cyclohexadiene is highly stereoselective. Oxidation of the adduct afforded *endo*-bicyclo[2.2.2]oct-5-en-2-ol. The reaction is a convenient one-pot synthesis of this alcohol which can be readily converted to the corresponding ketone. The addition of dichlorovinylborane to 1,3-cyclopentadiene is less selective, producing a mixture of *endo* and *exo* adducts (84 : 16). The additions to 2,4-dimethyl-1,3-pentadiene were examined carefully, since the adducts containing a quaternary carbon atom might be expected. Unfortunately, the reactions with **1** and **2** resulted in oligomerization of of the diene, and heating the diene with B-vinyl-3,5-dimethylborepane resulted in dehydroboration of the reagent and monohydroboration of the diene. Apparently, steric hinderance at the quaternary carbon center is a limiting factor in these additions.

Based on the additions described above, alkenyldichloroboranes were used as dienophiles, equivalents of 1-alkenes. The organoboranes were conveniently prepared by monohydroboration of 1-alkynes with dichloroborane, generated *in situ*.[19]



(1)

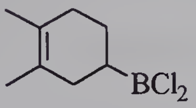
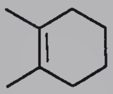
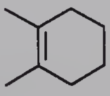
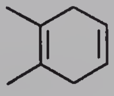
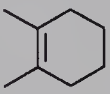
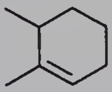
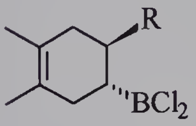
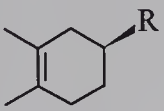
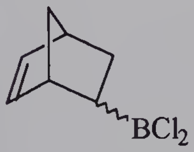
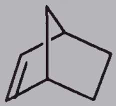
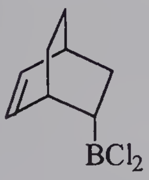
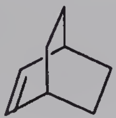
(**5**) R = *n*-Bu; R^1 = Me
(**6**) R = *n*-C_6H_{13}; R^1 = Et
(**7**) R = Ph; R^1 = Et

The reactivity of alkenyldichloroboranes thus obtained was lower compared with dichlorovinylborane, and the addition of **5** to 2,3-dimethyl-1,3-butadiene required heating at 100 °C for 12 h. Oxidation of the adduct gave *trans*-6-butyl-3,4-dimethylcyclohex-3-enol. No isomeric alcohols were detected in the oxidation products, indicating no thermal isomerization of the adduct.

Initially, protonolysis of the organoborane adducts was carried out with propionic acid. The adducts prepared from dichlorovinylborane were treated with two equivalents of sodium methoxide to avoid the formation of hydrogen chloride, and then refluxed with propionic acid. The expected olefins, obtained in low to moderate yields, were contaminated with isomers.

Clearly, direct protonolysis with propionic acid is limited to adducts producing olefins stable in acidic medium. To circumvent these difficulties an indirect conversion of carbon-boron bond to carbon-hydrogen bond was used. Thus, the adducts were oxidized to the corresponding alcohols which were transformed into mesylates, reduced in turn with lithium aluminum hydride. This route worked better than direct protonolysis producing olefins in 40-60 % yield. However, 1,2-dimethylcyclohexene obtained in this way was contaminated with 1,2-dimethyl-1,4-cyclohexadiene, regardless of the reaction conditions. Fortunately, the undesidered side elimination reaction, leading to the diene, could be avoided by using lithium triethylborohydride instead of lithium aluminum hydride. The reaction sequence oxidation-mesylation-reduction with lithium triethylborohydride worked well with the adducts shown in Table 1, producing the corresponding olefins in ~80 % yields and excellent purity. Consequently, dichlorovinylborane and (E)-1-alken-1-yldichloroboranes can serve as convenient ethylene and 1-alkene equivalents for the Diels-Alder reaction.

Table 1 *Olefins Prepared from Adducts of Alkenyldichloroboranes and 2,3-Dimethyl-1,3-butadiene, 1,3-Cyclopentadiene and 1,3-Cyclohexadiene*

Adduct	*Reagents*	*Product Olefin Composition, %*	*Yield, %*
	1. H_2O_2, NaOH 2. MsCl, pyridine 3. $LiBEt_3H$, THF		81
	1. H_2O_2, NaOH 2. MsCl, pyridine 3. $LiAlH_4$, Et_2O	 75  25	60
	1. NaOMe 2. EtCOOH	 82  18	20
	1. H_2O_2, NaOH 2. MsCl, pyridine 3. $LiBEt_3H$, THF	 R = *n*-Bu R = *n*-C_6H_{13} R = Ph	80 82 83
	1. H_2O_2, NaOH 2. MsCl, pyridine 3. $LiBEt_3H$, THF		85
	1. H_2O_2, NaOH 2. MsCl, pyridine 3. $LiBEt_3H$, THF		83
	1. NaOMe 2. EtCOOH		50

3 CATALYTIC MONOHYDROBORATION OF CONJUGATED DIENES AND ENYNES

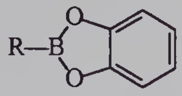
In contrast to olefins, little is known on catalytic hydroboration of conjugated dienes. Suzuki and Miyaura[20] described a 1,4-addition of catecholborane to acyclic 1,3-dienes, catalyzed with tetrakis(triphenylphosphine)palladium(0). An interesting Markovnikov type regioselectivity was observed in the enantioselective dihydroboration of (E)-1-phenyl-1,3-butadiene with catecholborane, catalyzed by chiral rhodium complexes.[21] However, the scope of these reactions is not well known, and the choice of catalysts is very limited.

In a search for a suitable catalyst we started with lanthanide iodides, monitoring by ^{11}B NMR analysis the stability of 1 *M* catecholborane solutions in tetrahydrofuran containing 10 molar % of SmI_3, *t*-$BuOSmI_2$, and LaI_3. Unfortunately, in the presence of these iodides a signal corresponding to borane-tetrahydrofuran, and other signals, appeared in less than 1 h. In contrast, catecholborane in tetrahydrofuran was stable in the presence of nickel(II), cobalt(II) and iron(II) chloride complexes with dppe.

Hydroboration of isoprene with catecholborane at 1 : 1 molar ratio in tetrahydrofuran in the presence of 1 molar % of $NiCl_2$(dppe) at room temperature was completed in 6 h. An interesting observation is a lower reactivity of 1-decene compared with isoprene under these conditions. It is the first case of higher reactivity of 1,3-diene than 1-alkene in the hydroboration reaction. It is also an indirect indication that borane is not involved in the reaction, since acyclic conjugated dienes are less reactive than 1-alkenes toward borane. Hydroboration of representative conjugated dienes in the presence of $NiCl_2$(dppe) was carried out on a preparative scale and the results are shown in Table 2.[9] The monohydroboration products were isolated by distillation and oxidized to the corresponding unsaturated alcohols.

Table 2 *Monohydroboration Products of Conjugated Dienes and Enynes with Catecholborane Catalyzed by $NiCl_2$(dppe) in THF at 20 °C*

Diene, Enyne	*Time*	*Hydroboration Product R–Bc*[a]	
	h	*R*	*Yield,*[b] *%*
1,3-Butadiene	6	But-3-en-1-yl	79
2-Methyl-1,3-butadiene	6	2-Methylbut-3-en-1-yl, 77 % 3-Methylbut-3-en-1-yl, 23 %	80
2,3-Dimethyl-1,3-butadiene	6	2,3-Dimethylbut-en-1-yl	76
(E)-1,3-Pentadiene	6	(E)-Pent-3-en-1-yl	82
1,3-Cyclopentadiene	24	Cyclopent-3-en-1-yl	[c]
1,3-Cyclohexadiene	48	Cyclohex-2-en-1-yl, 50 % Cyclohex-3-en-1-yl, 50 %	54
But-1-en-3-yne	10	But-1,3-dien-1-yl	54
2-Methylbut-1-en-3-yne	8	3-Methylbut-1,3-dien-1-yl	59
Hex-1-en-3-yne	8	Hex-1,3-dien-3-yl Hex-1,3-dien-4-yl	78
4-Methyl-1-phenylpent-3-en-1-yne	24	(Z)-1-Phenyl-4,4-dimethylbut-1,3-dien-1-yl	[c]
1-Ethynylcyclohexene	8	(E)-2-(Cyclohex-1-en-1-yl)	87

[a] R–Bc =  ; [b] Isolated by distillation; [c] Not isolated

In contrast to palladium and rhodium catalyzed monohydroboration of 1,3-dienes,[20] no 1,4-addition and only 1,2-addition products were obtained with *anti*-Markovnikov regioselectivity. Acyclic dienes were more reactive than cyclic dienes, and styrene was unreactive. Among iron(II) and cobalt(II) chloride complexes with dppe, dppp and dppb only $CoCl_2$(dppp) showed catalytic activity albeit lower than $NiCl_2$(dppe).

Recently, Hayashi[8] described the reaction of 2-substituted but-1-en-3-ynes with catecholborane in the presence of palladium(0) complexes with monodentate and bidentate phosphine ligands. The formation of 1,2- and 1,4-addition products, depending on the ligand structure and the molar ratio of palladium to ligand, was observed. Encouraged by our results with dienes, we examined the monohydroboration of representative conjugated enynes with catecholborane in the presence of $NiCl_2$(dppe).[10] The reactions produced 1,3-dien-1-yl catecholborane derivatives in 53-87 % yield (Table 2). Mild reaction conditions enable the synthesis of labile products, e. g., but-1,3-diene-1-yl derivative, not readily available by other methods. The 1,2-addition products were obtained exclusively, regardless of the substitution of the enyne system. High regioselectivity of the addition to enynes with terminal triple bonds was observed, whereas for internal triple bonds the reactivity and direction of addition depend on the substitution of the enyne.

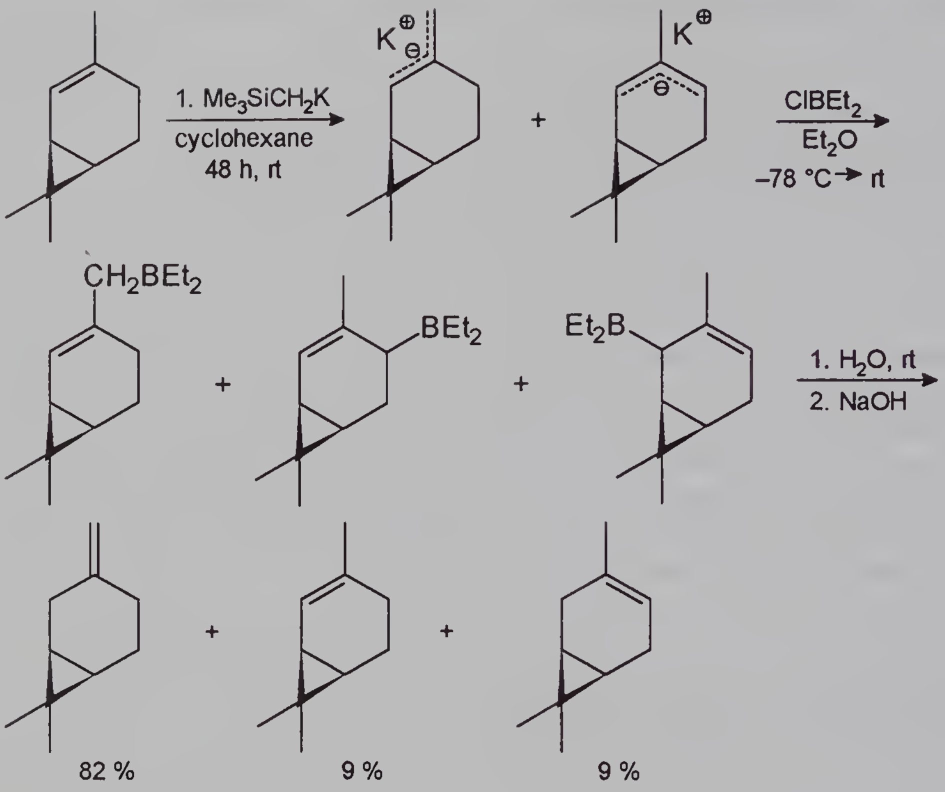
4 SYNTHESIS OF (+)-3(10)-CARENE, (+)-SABINENE, AND KINETIC RESOLUTION OF VINYLIC EPOXIDES

Several years ago, we developed a contrathermodynamic isomerization of α- to β-pinene via diethylmyrtenylborane obtained from α-pinene by metalation-transmetalation.[11] Later, (+)-β-pinene of > 99 % ee was prepared by this method.[22] Extending this work to other bicyclic monoterpenes, the isomerization of (+)-2-, (+)-3-carene, and (–)-α-thujene, was studied.[13] Among bicyclic monoterpene olefins with an exocyclic double bond, 3(10)-carene is a rare compound reported only a few times in the long history of terpene chemistry, and its rotation is still controversial.[23,24] Sabinene is isolated from the oil of savin, and no convenient synthesis of an optically active sabinene is known.

Initially, the metalation of (+)-2-carene was carried out with *n*-butyllithium and potassium *tert*-butoxide. The metalation product was treated with trimethyl borate and the intermediate ate complex was hydrolyzed with dilute hydrochloric acid. Although the procedure worked well for the transformation of α- into β-pinene, only a small amount of (+)-3(10)-carene in a mixture with (+)-2- and (+)-3-carene was obtained. Metalation-transmetalation under these conditions leads to organoborane intermediates which are hydrolyzed without isolation. Consequently, a substantial amount of unreacted (+)-2-carene is present, rendering difficult the isolation of (+)-3(10)-carene.

Metalation with trimethylsilylmethylpotassium is free from these inconveniences. The unreacted (+)-2-carene is readily separated from the solid metalation product which is transformed into the corresponding allylic diethylorganoborane intermediate isolated by distillation. The intermediate upon hydrolysis at room temperature affords (+)-3(10)-carene containing only small amounts of (+)-2- and (+)-3-carene (eq. 2).

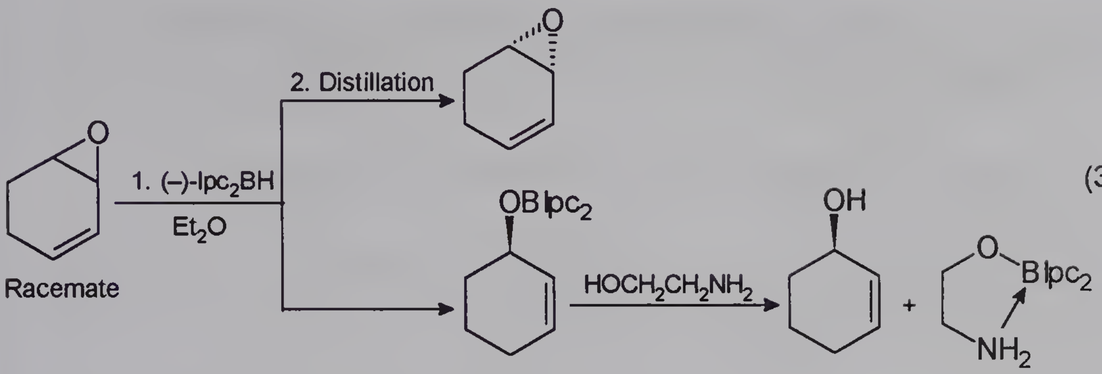
(+)-Sabinene was obtained from (–)-α-thujene using *n*-butyllithium-potassium *tert*-butoxide for the metalation. The unreacted (–)-α-thujene can be easily separated from (+)-sabinene.



(2)

Recently, Jacobsen[25] reported an enantioselective monoepoxidation of cyclic 1,3-dienes catalyzed by chiral manganese complexes affording products of 52-71 ee % in 33-73 % yield. Several years ago, we described a stereoselective reduction of vinylic epoxides with borane to allylic alcohols.[12] A ready access to terpenyl dialkylboranes of high optical purity prompted us to apply this reaction for kinetic resolution of racemic vinylic epoxides.[14] 2-Vinyloxirane and monoepoxides of 1,3-cycloalkadienes with 5-8 membered rings were used as representative epoxides. The reductions were carried out with diisopinocampheylborane (Ipc_2BH) di-(2-isocaranyl)borane (2-$^{d}Icr_2BH$) and di-(4-isocaranyl)borane (4-$^{d}Icr_2BH$) of > 99 % ee, in 2 : 1 epoxide / dialkylborane molar ratio, in diethyl ether. The dialkylboranes are only slightly soluble and progress of the reaction can be easily controlled by observing the amount of solid reagent present. The reaction is complete when a clear solution is obtained. Enantiomerically enriched epoxides were readily isolated by distillation directly from the reaction mixture in 40-49 % yields. The reduction of vinylic epoxides with borane proceeds with the double bond shift and the epoxide ring opening.[12] The allylic alcohol produced retains the configuration of epoxide. Consequently, the enantiomerically enriched unreacted epoxide has the opposite configuration as shown in eq. 3 for 1,3-cyclohexadiene monoepoxide.

The reactivity of the dialkylboranes toward vinylic epoxides decreases in the following order Ipc_2BH > 2-$^{d}Icr_2BH$ > 4-$^{d}Icr_2BH$. 2-$^{d}Icr_2BH$ gave products of the highest enantiomeric excess (40-54 % ee).



(3)

Kinetic resolution of vinylic epoxides by the reduction with terpenyl dialkylboranes of high optical purity is a simple and direct method for the preparation of enantiomerically enriched epoxides. It allows for convenient configurational assignment of epoxides if the configuration of the corresponding allylic alcohol is known. Both enantiomers can be prepared using readily available enantiomeric diisopinocampheylboranes.

References

1. M. Voultier and B. Carboni, in 'Comprehensive Organometallic Chemistry II', Pergamon, Vol. 11, A. McKillop Ed., Oxford, 1995, p. 211.
2. I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, ***53***, 4958.
3. M. B. Smith, 'Organic Synthesis', McGraw-Hill, New York, 1994, p.1115.
4. C. V. R. Carr, R. V. Williams, and L. A. Paquette, *J. Org. Chem.*, 1983, **48**, 4976.
5. M. Zaidlewicz, J. R. Binkul, and W. Sokół, *J. Organometal. Chem.*, 1999, **580**, 354.
6. M. Zaidlewicz and Z. Walasek, *Polish J. Chem.*, 1994, **68**, 2489.
7. D. A. Evans, A. R. Muci, and R. Stürmer, *J. Org. Chem.*, 1993, **58**, 5307.
8. Y. Matsumoto, M. Naito, and T. Hayashi, *Organometallics*, 1992, **11**, 2732.
9. M. Zaidlewicz and J. Meller, *Tetrahedron Lett.*, 1997, **38**, 7279.
10. M. Zaidlewicz and J. Meller, *Collection Czech. Chem. Commun.*, 1999, **64**, 1049.
11. M. Zaidlewicz, *J. Organometal. Chem.*, 1985, **239**, 139.
12. M. Zaidlewicz, A. Uzarewicz, and R. Sarnowski, *Synthesis*, 1979, 62.
13. M. Zaidlewicz and M. Gimińska, *Tetrahedron: Asymmetry*, 1997, **8**, 3847.
14. M. Zaidlewicz and M. Krzemiński, *Tetrahedron Lett.*, 1996, **37**, 7131.
15. D. A. Singleton, J. P. Martinez, J. V. Watson, and G. M. Ndip, *Tetrahedron*, 1992, 48, 5831.
16. D. A. Singleton, J. P. Martinez, and G. M. Ndip, *J. Org. Chem.*, 1992, **57**, 5768.
17. N. Noriet, A. Youssofi, B. Carboni, and M. Voultier, *J. Chem. Soc. Chem. Commun.*, 1992, 1105.
18. H. C. Brown and K. J. Murray, *Tetrahedron*, 1986, **42**, 5497.
19. R. Soundarajan and D. S. Matteson, *Organometallics*, 1995, **14**, 4157.
20. M. Satoh, Y. Miyaura, and A. Suzuki, *Tetrahedron Lett.*, 1989, **30**, 3789.
21. Y. Matsumoto and T. Hayashi, *Tetrahedron Lett.*, 1991, **32**, 3387.
22. H. C. Brown, M. Zaidlewicz, and K. S. Bhat, *J. Org. Chem.*, 1989, **54**, 1764.
23. K. Gollnick and G. Schade, *Tetrahedron*, 1966, 22, 133.
24. L. A. Paquette, R. J. Ross, and Y-I. Shi, *J. Org. Chem.*, 1990, **55**, 1589.
25. S. Chang, R. M. Heid, and E. N. Jacobsen, *Tetrahedron Lett.*, 1994, **35**, 669.

Boron Derivatives of Aminopyridines (B, Si and P N-substituted)

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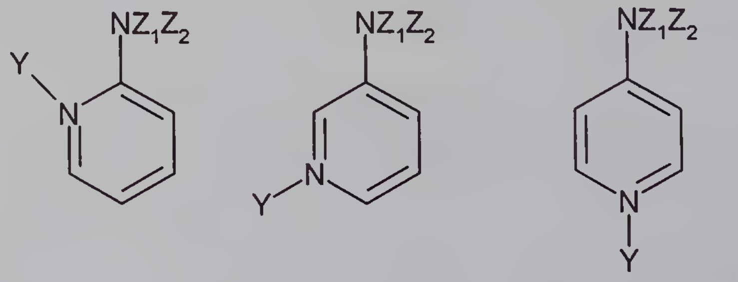
We are interested in the study of the structure and reactivity of biological molecules and their active sites through their boron derivatives. In particular, we investigate the coordination of aromatic amines[1-9] towards tricoordinated boron molecules and boronium groups [BY_2^+ Y = halogen or aromatic groups],[10,11] which are diamagnetic compounds which can mimic the structure of paramagnetic metallic complexes. It is well known that the NMR data of borane adducts of amines give useful information about the basic sites and the steric hindrance in organic molecules. The acidic aromatic N-H protons can be substituted by main group elements, which become also acidic atoms that easily accept the coordination of a Lewis base.

We are investigating a series of reactions of aminopyridines and aminopyrimidines and main group compounds. These heterocycles can form adducts with both kinds of nitrogen atoms: pyridinic or anilinic. Bonding of several aminopyridines to heteroatoms such as boron, silicon, or phosphorus gives polyfunctional molecules rich in lone pairs and therefore candidates to be used as ligands.

The equimolar reactions of 2-, 3-, and 4-aminopyridines with $BH_3{\cdot}THF$ or $BF_3{\cdot}OEt_2$ at low temperature give the corresponding pyridinic adducts (Figure 1).



Y= lone pair, or BH_3 or Y= BF_3 Z = H and/or heteroatom

Figure 1 Studied aminopyridines and their BH_3 or BF_3 adducts

The BH_3 and BF_3 aniline and pyridine adducts present systematic shifts in the ^{13}C NMR spectra, especially in *ortho* and *para* carbon atoms[12-14] (Figure 2), this information can be used to determine the coordination sites in aminopyridines.

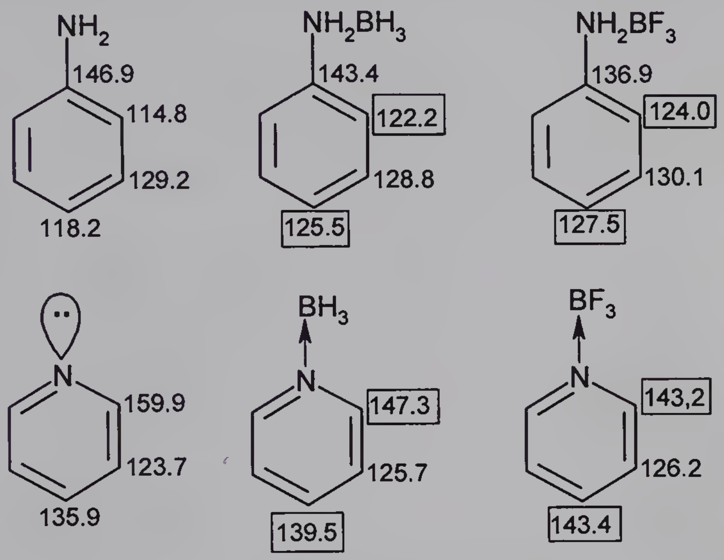


Figure 2 ^{13}C NMR data of aniline and pyridine and their BH_3 and BF_3 adducts

Herein, we would like to discuss some of our results related to 2-aminopyridine. The IR and UV investigation showed that it has strong hydrogen bonds[15], by MM calculations it has been found that the hydrogen bonds form a stable eight membered ring dimer (Figure 3).

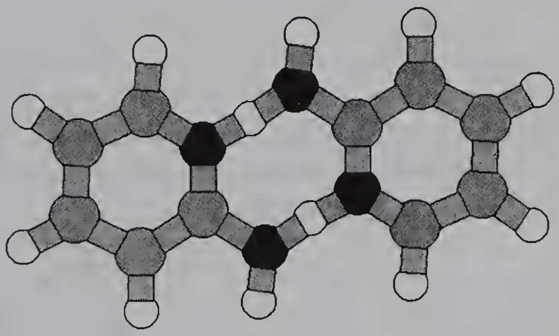


Figure 3 Molecular mechanics structure of the 2-aminopyridine dimer

NMR data of 2-aminopyridine adducts are shown in Figure 4. The ^{1}H, ^{13}C, ^{11}B, and ^{19}F show that the boron is coordinated to the pyridinic nitrogen and not to the exocyclic nitrogen atom.

The BH_3 adduct of 2-aminopyridine seems to be very stable to internal hydroboration and polymerisation compared to borane pyridine. We attribute the extra stability to hydride-proton interactions; these together with those of fluorine-proton were reported for other amine borane compounds[16] (Figure 5). The MM models for the two boron complexes shown in Figure 6, present atomic distances

BH····HC and BH·····HN of ~ 2.02 Å and BF·····HC and BF·····HN ~ 2.2 Å, in both cases these are shorter distances than the corresponding van der Waals radius[16] (r_{vdw} of proton 1.2 Å + r_{vdw} of hydride 1.45 = 2.65 Å and r_{vdw} of proton 1.2 Å + r_{vdw} of fluoride 1.55 Å = 2.75 Å).

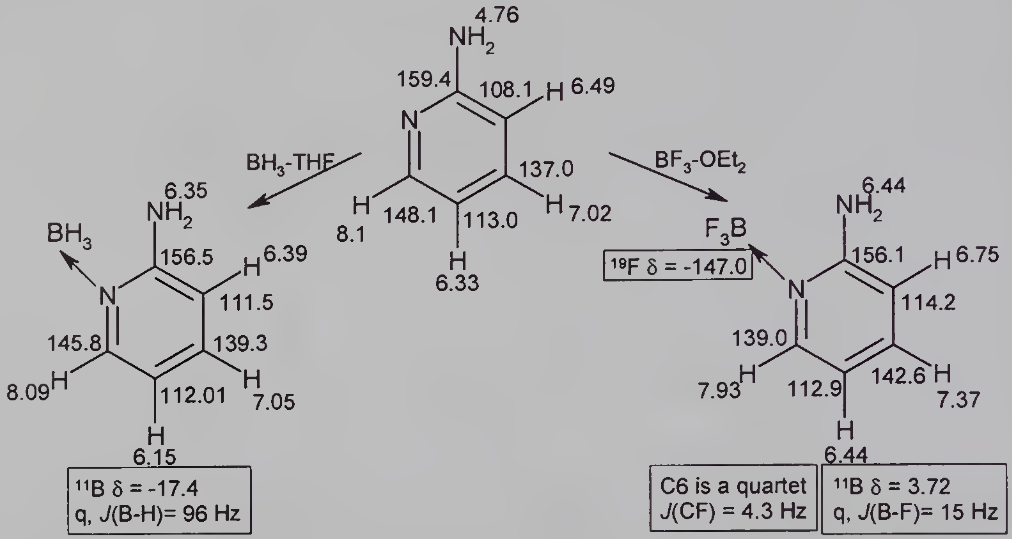


Figure 4 NMR data of 2-aminopyridine adducts

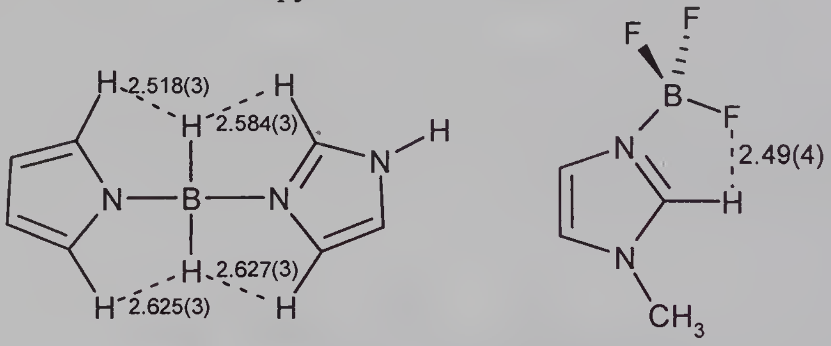


Figure 5 Atomic distances Å between hydrides-protons or fluorine-proton in amine boranes where weak bonding interactions are proposed[16]

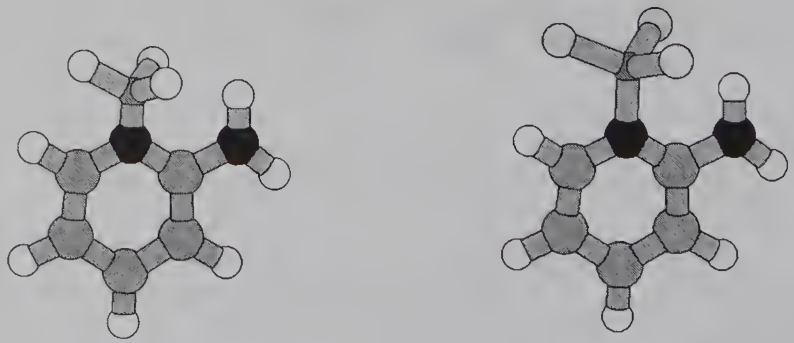


Figure 6 Molecular mechanics model of BH_3 and BF_3 adducts of 2-aminopyridine

The formation of BH_3 adduct of 2-aminopyridine from its reaction with $NaBH_4$ and $CoCl_2$ in water, as well as the lack of reaction of the N-methyl-2-aminopyridine under the same conditions are known.[17] This fact motivated us to investigate if the substitution at nitrogen by trimethylsilyl groups could affect the borane addition. It was also of interest to look for the formation of B-N covalent bonds by reducing the N-Si bond. Therefore, we have prepared the mono- and disilylated derivatives of aminopyridines and investigated their reactions with BH_3 and BF_3.

The structure and conformation of the silylated compounds were established from NMR data and MM calculations. The 2-aminopyridine monosilylated is planar with the silicon atom on the same side of the pyridine nitrogen atom as is shown in structure B of Figure 7.

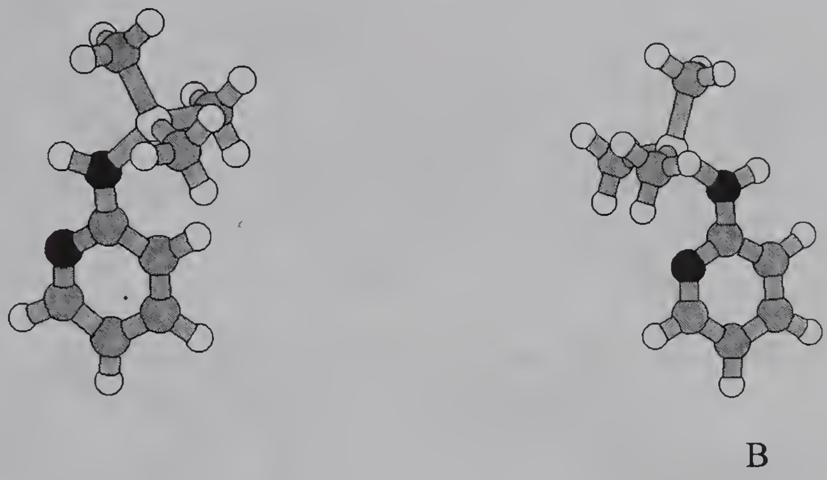


Figure 7 MM models of the conformers of N-trimethylsilyl-2-aminopyridine

Reactions of mono- and disilylated derivatives of aminopyridines with $BH_3 \cdot THF$ and $BF_3 \cdot OEt_2$ give stable pyridinic adducts in spite of the steric effects (Figure 8). The ^{13}C δ of C-5 shows that both adducts (BH_3 and BF_3) of the monosilylated 2-aminopyridine were planar, in consequence two preferred conformers could be expected for each one. In BH_3 and BF_3 adducts interactions proton-hydride or proton fluoride are possible as is shown in the MM models for BH_3 (Figure 9).

Examination of ^{11}B NMR data showed that in the monosilylated derivatives the boron is on the same side of the N-H as is deduced by comparison with the non-silylated compounds (Figure 8). In the other hand, in spite of the bulkiness of the disilylated compound, it gives stable adducts. Deshielding of the ^{13}C δ of C5 is evidence that the N-silyl groups are not anymore in the plane of the aromatic ring, and thus the anilinic nitrogen atom is not giving electronic density to the ring. The new conformation avoids the steric interaction between the boron and the N-groups, as it has been confirmed by the MM in Figure 10.

Borane addition shifted the ^{29}Si signal at higher frequencies. At this point the question of a hydride or fluoride spatial interaction with silicon can be answered by the ^{29}Si δ of 2-aminopyridine derivative (+6.48) compared with those of 4-aminopyridine (+6.70). In the latter, only electronic effects through the ring can be detected, and therefore similar chemical shifts suggest that such spatial interaction is not present.

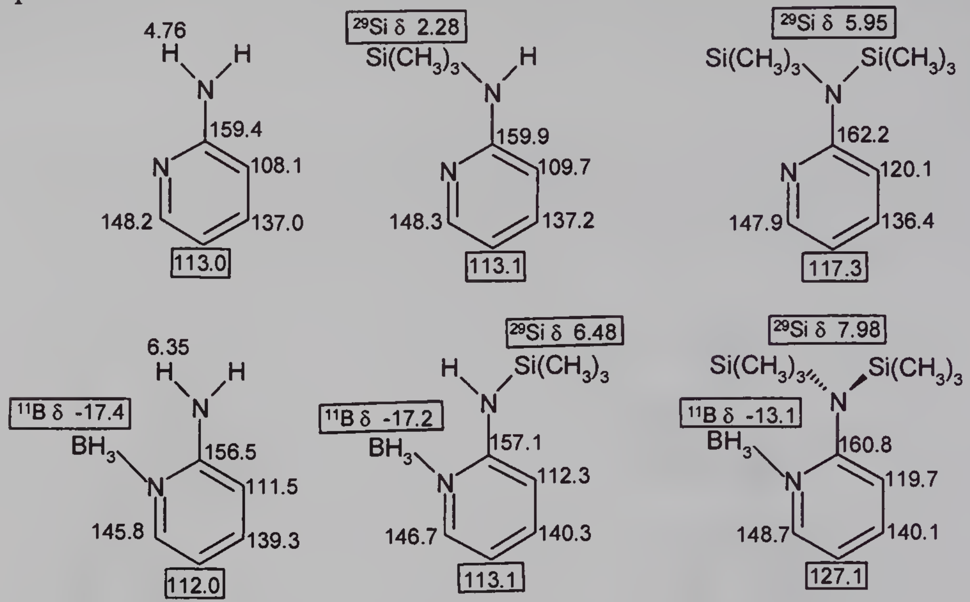


Figure 8 NMR data of BH_3 adducts of 2-aminopyridine derivatives

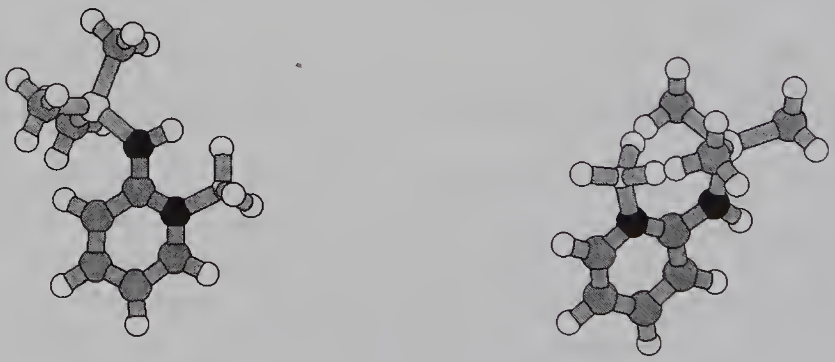


Figure 9 MM models of the two conformers for N-BH_3 adduct of the 2-aminopyridine N-silylated showing hydride-proton interactions

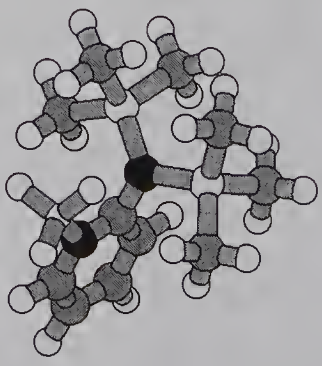


Figure 10 MM model of the BH_3 adduct of the bis(trimethylsilyl)-2-aminopyridine

The reaction of N-BH_3 adducts of 2-aminopyridine or its monosilylated derivative with an excess of borane afforded a new product, its ^{11}B NMR spectrum shows a triplet assigned to an NBH_2 group N-coordinated, which could be explained by the formation of a dimer, such structure was supported by calculations (Figures 11-12), similar dimer has been reported[17-18] (Figure 13).

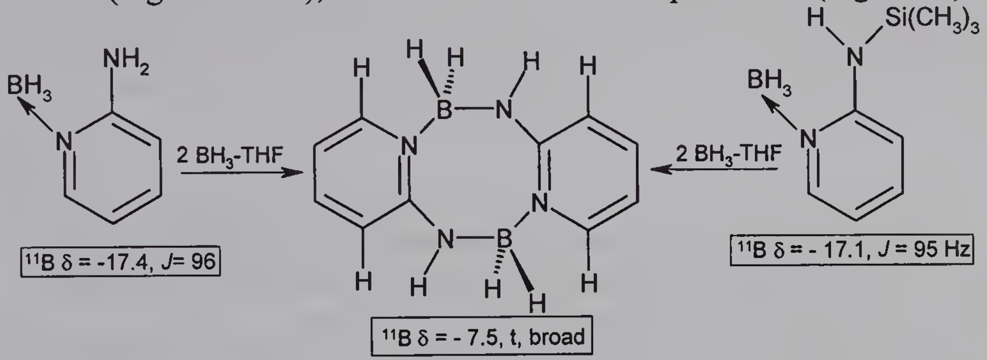


Figure 11 Syntheses of the N-BH_2 dimer derived from 2-aminopyridine

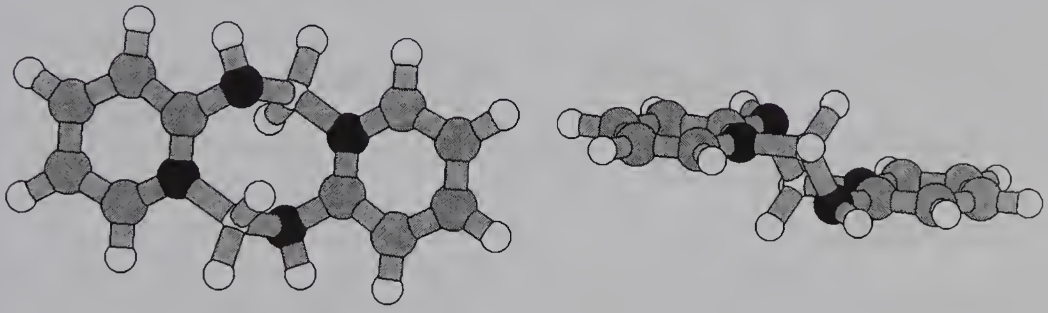


Figure 12 MM structure of the dimer of NBH_2 derivative of 2-aminopyridine

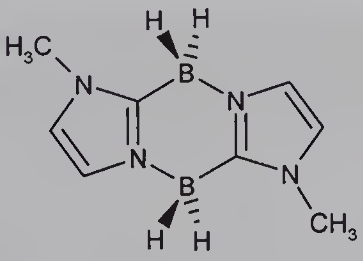


Figure 13 Stable dimer of a BH_2 group stabilised by N-coordination[17-18]

We have prepared aminoborane derivatives by reaction of 2-aminopyridine with $B[N(CH_3)_2]_3$ in C_6H_6. The ^{11}B NMR spectrum shows a broad signal ($\delta = 23.6$) characteristic of a trisaminoborane, ^{13}C and ^{1}H are also in agreement with the structure depicted in Figure 14. The same product can be obtained through the reaction of the lithium amide of 2-aminopyridine and $BF_3{\cdot}OEt_2$. A model of the trisaminoborane shows that intramolecular hydrogen bonds are possible.

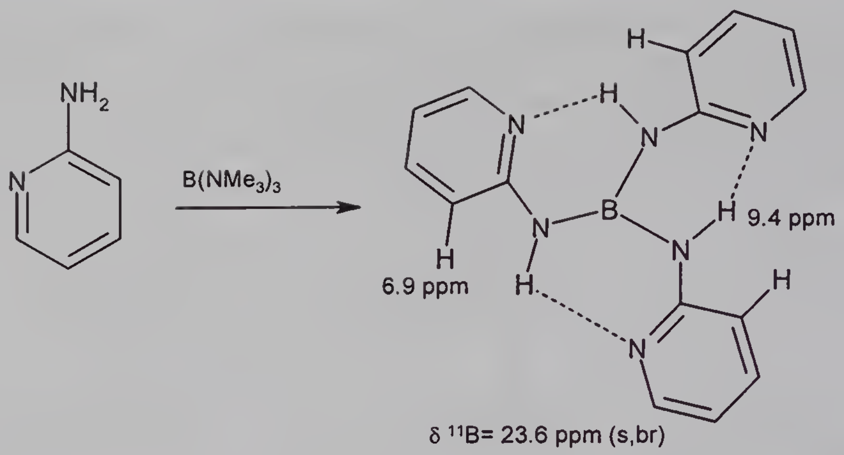


Figure 14 Synthesis of the trisaminoborane derived from 2-aminopyridine

A similar reaction performed with $P(NMe_2)_3$ and 2-aminopyridine gives trisaminophosphorus compound. Borane addition gives the corresponding phosphorus and pyridinic adducts (Figure 15).

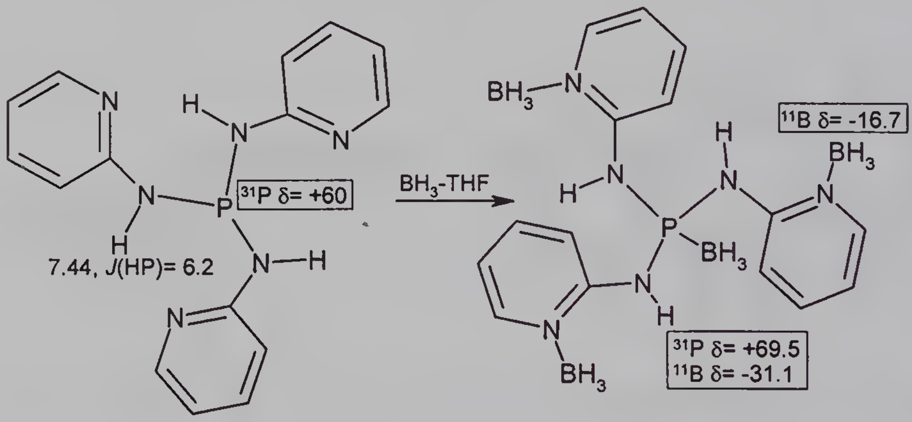


Figure 15 Trisaminophosphorus derivative of 2-aminopyridine and its tetraborane adduct

Both trisaminoborane and trisaminophosphorus compounds could function as ligands for organometallic species which are currently investigated in our laboratory. A model of their coordinating ability to a metallic atom is shown in Figure 16.

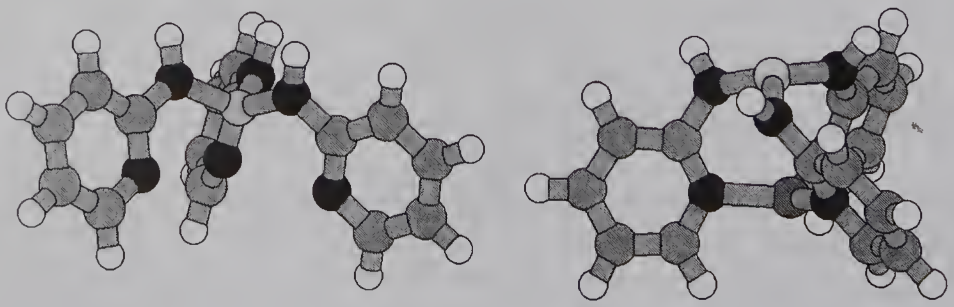


Figure 16 MM model of the trisaminophosphorus derivative of 2-aminopyridine (left) and its complex with a metallic atom (right)

Now, we are actively investigating the adducts of several aminopyridines and aminopyrimidines in order to know the reactivity of the different isomers and how the substitution of the NH by a heteroatom affects the coordinating behaviour. We are also interested in collecting multinuclear NMR data of these systems that could be used to study more complex molecules.

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References

1. A. Flores-Parra and R. Contreras, *Coord. Chem. Rev.* In the press 1999.
2. M. Anez, G. Uribe, L. Mendoza and R. Contreras. *Synthesis,* 1981, 214.
3. C. Camacho, G. Uribe and R. Contreras. *Synthesis,* 1982, 1027.
4. H. R. Morales, H. Tlahuext, F. Santiesteban and R. Contreras. *Spectrochim. Acta*, 1984, **A 40**, 855.
5. N. Farfán and R. Contreras. *Heterocycles*, 1985, **23**, 2989.
6. N. Farfán and R. Contreras. *J. Chem. Soc. Perkin Trans. II.* 1988, 1787.
7. M. A. Paz-Sandoval, C. Fernández-Vincent, G. Uribe, R. Contreras and A. Klaébé. *Polyhedron,* 1988, **7**, 679.
8. N. Farfán, P. Joseph-Nathan, L. M. Chiquete and R. Contreras. *J. Organometal. Chem.*, 1988, **348**, 149.
9. I. I. Padilla-Martínez, A. Ariza-Castolo and R. Contreras. *Magn. Reson. Chem.,* 1993, **31**, 189.
10. N. Andrade-López, R. Cartas-Rosado, E. García-Baéz and R. Contreras. *Heteroatom Chem.*, 1988, **9**, 399.
11. M. P. Fialon, E. García-Baéz, N. Andrade-López, G. Osorio-Monreal, G. Canseco-Melchor, I. Velázquez-Montes, N. Barba-Behrens and R. Contreras. *Heteroatom Chem.*, 1999 in the press.
12. C. Camacho, M. APaz-Sandoval and R. Contreras. *Polyhedron*, 1986, **5**, 1723.
13. N. Farfán and R. Contreras. *J. Chem. Soc. Perkin Trans. II*, 1987, 771.
14. M.A. Paz-Sandoval, C. Camacho, R. Contreras and B. Wrackmeyer. *Spectrochim. Acta,* 1987, **A 43**, 1331.
15. J. Hinem, J. Hwang, V. Balasubramanian, *J. Org. Chem.*,1988, **53**, 5145.
16. I. I. Padilla-Martínez, M. J. Rosales-Hoz, H. Tlahuext, C. Camacho-Camacho and R. Contreras, *Chem. Ber.*,1996, **129**, 441.
17. Y. Okamoto, T. Osawa, T. Kinoshita, *Synthesis*, 1982, 462.
18. I. I. Padilla-Martínez, M. J. Rosales-Hoz, R. Contreras, S. Kerschi and B. Wrackmeyer. *Chem. Ber*. 1994, **127**, 343.
19. I. I. Padilla-Martínez F. J. Martínez-Martínez, A. López-Sandoval, K. I. Girón-Castillo, M.A. Brito, R. Contreras. *Eur. J. Inorg. Chem.* 1998, **10**, 1547.

Evaluation of an Organocyanoborane as Chiral Auxiliary in the Stereoselective Synthesis of Phosphines

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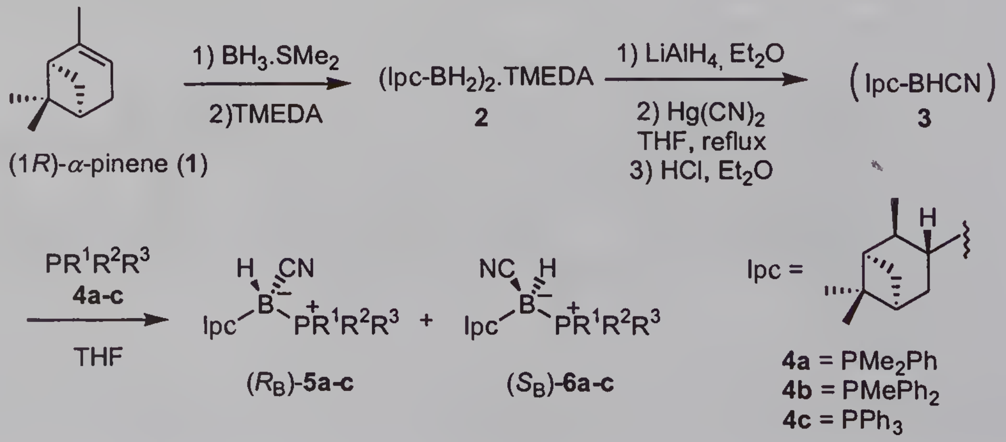
1 INTRODUCTION

Enantiomerically pure phosphines are frequently employed as ligands in transition-metal-catalyzed asymmetric reactions. For this reason, various methods have been designed for their preparation.[1] Many of them involve the use of borane adducts of trivalent phosphorus compounds,[2] in which the borane moiety mainly acts as a protecting group. These Lewis adducts are easily prepared and stable to air, and several methods have been designed to cleave them.

A chiral, enantiomerically pure organoborane bound to an achiral phosphine could not only serve as a protecting group, but could also, in principle, deliver an asymmetric induction in stereoselective processes, thus playing the role of a chiral auxiliary.

2 SYNTHESIS OF PHOSPHINE-MONOISOPINOCAMPHEYLCYANOBORANE ADDUCTS

To test this strategy, we have prepared several phosphine adducts of an organocyanoborane derived from (1*R*)-(+)-α-pinene (**1**), as described in Scheme 1.[3]



Scheme 1

Hydroboration of **1** followed by treatment with tetramethylethylenediamine (TMEDA), as described by Brown,[4] afforded enantiomerically pure complex **2**, which was then converted in three steps to monoisopinocampheylcyanoborane (**3**). This compound was directly reacted with phosphines **4**, leading to the corresponding adducts **5** and **6** (Table 1). The yields reported are from the TMEDA adduct **2**.

Table 1 *Complexation of Monoisopinocampheylcyanoborane with Phosphines*

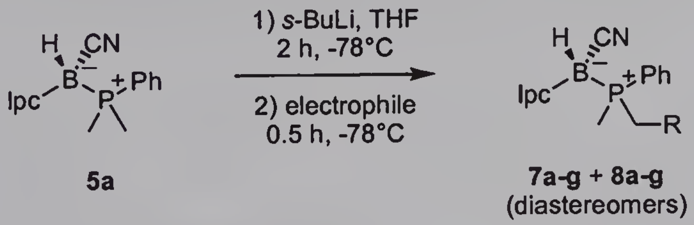
Phosphine	*Time* (days)	*Yield* (%)	*5 / 6 Ratio*
PMe_2Ph (**4a**)	3	70	50 /50
$PMePh_2$ (**4b**)	3	62	65 /35
PPh_3 (**4c**)	5	39	> 98 /2

The yield of the complexation depended upon the substitution pattern of the phosphine. The less nucleophilic and more sterically demanding triphenylphosphine led with only 30% yield to adduct **5c**, obtained as a single diastereomer according to ^1H NMR and ^{13}C NMR spectra. On the contrary, complexation of phosphines **4a** and **4b** led to mixtures of diastereomers. Pure **5a** was then isolated by recrystallization and pure **5b** was obtained by stirring the mixture of **5b** and **6b** in THF at room temperature for 10 days.

The structures of these compounds were ascertained by single-crystal X-ray analyses or chemical correlation.

3 STEREOSELECTIVE ALKYLATION OF ADDUCT 5a

The alkylation of dimethylphenylphosphine adduct **5a** with various electrophiles was then studied. The conditions used were as follows: after treatment of a THF solution of **5a** with *sec*-butyllithium at -78°C for two hours, the electrophile was added and stirring was continued for 30 minutes at -78°C (Scheme 2).



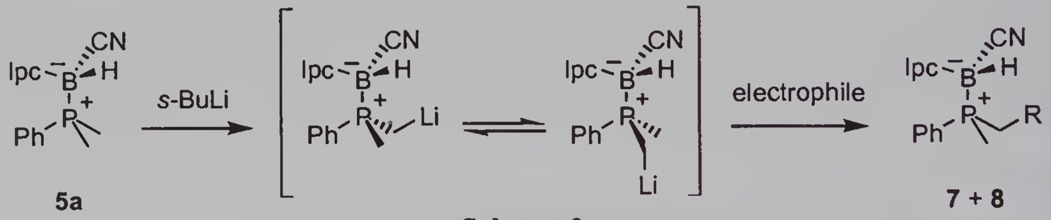
Scheme 2

The results are summarized in Table 2. With the exception of methyl iodide, alkyl halides did not react, but alkyl trifluoromethanesulfonates could be employed instead. After hydrolysis and work-up, the corresponding diastereomeric adducts **7** and **8** were isolated by column chromatography. In several cases, the diastereomers were separated. The diastereomeric excesses were determined using ^1H NMR, or by H.P.L.C., or by weighing the isomers after separation.

Table 2 *Alkylation of Dimethylphenylphosphine Adduct* ***5a***

Electrophile	*R*	*Major adduct*	*Yield of 7 + 8 (%)*	*De (%)*
CH_3I	CH_3	**7a**	85	49
$CH_3(CH_2)_2I$	$CH_3(CH_2)_2$		0	-
$CH_3(CH_2)_4OTf$	$CH_3(CH_2)_4$	**7b**	78	5
$PhCH_2Br$	$PhCH_2$	**7c**	77	60
2,5-(MeO)$PhCH_2I$	2,5-(MeO)$PhCH_2$	**7d**	92	51
Ph_2CO	$Ph_2(HO)C$	**7e**	84	74
n-Bu_3SnCl	*n*-Bu_3Sn	**7f**	88	30

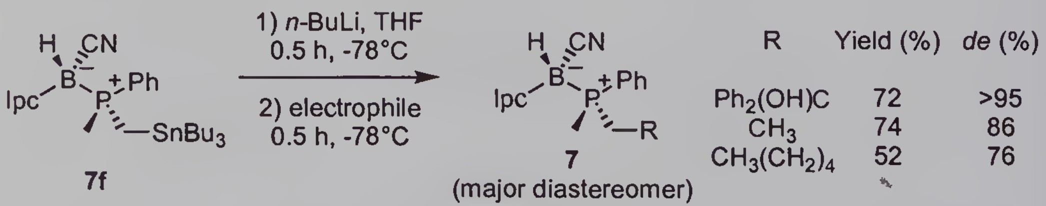
The selectivity of the alkylation depended strongly upon the electrophile: from 5% *de* with pentyl triflate to 74% *de* with benzophenone. This suggested that two lithiated species were generated following the addition of *sec*-butyllithium to **5a** (Scheme 3).



Scheme 3

However, it was possible to obtain the adduct of pentyl triflate with 60% *de* (83% yield) when the electrophile was added to the reaction mixture 24 hours after *sec*-butyllithium. The same *de* was measured when the electrophile was added after 72 h. Thus, the ratio of the two organolithium compounds is close to 80 / 20 at equilibrium.

Several reactions were also carried out from the major stannyl derivative **7f** (Scheme 4). The major adducts were the same as in the direct alkylation of **5a**.



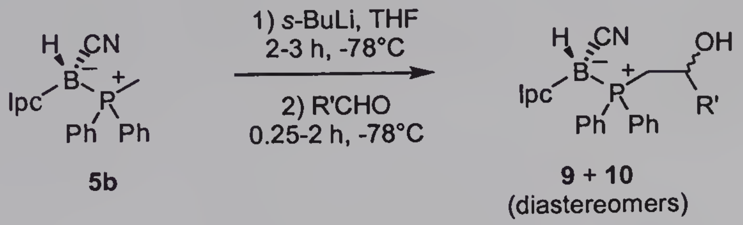
R	Yield (%)	*de* (%)
$Ph_2(OH)C$	72	>95
CH_3	74	86
$CH_3(CH_2)_4$	52	76

Scheme 4

The absolute configuration of the major adduct **7a** obtained from methyl iodide was shown to be *S* after removal of the organocyanoborane moiety by treatment with DABCO, oxidation of the phosphine obtained and then, comparison with the known (*R*)-ethylmethylphenylphosphine oxide.

4 REACTION OF THE LITHIATED DERIVATIVE OF ADDUCT **5b** WITH ALDEHYDES

Since only one methyl group is present in the phosphine part of adduct **5b**, treatment of this compound with *sec*-butyllithium generates a single lithium derivative. Its reaction with selected aldehydes was tested as described in Scheme 5.



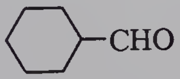
5b

9 + 10
(diastereomers)

Scheme 5

The corresponding diastereomeric adducts of *β*-hydroxyphosphines **9** and **10** were obtained, as unseparable mixtures (Table 3). The diastereomeric excesses observed in this transformation ranged from 20 to 56%.

Table 3 *Reaction of Diphenylmethylphosphine Adduct **5b** with Aldehydes*

Aldehyde	*Yield of **9** + **10** (%)*	*De (%)*
PhCHO	89	40
	70	20
$(CH_3)_3CCHO$	77	50
$(CH_3)_2CHCHO$	70	56

5 CONCLUSION

This work represents a first attempt to employ an organocyanoborane as chiral auxiliary, in the context of the enantioselective synthesis of phosphines. However, improvement of the selectivity is needed for this strategy to be of more general use. Investigation of adducts of boron compounds containing a heteroatom able to chelate the lithium cation, which might lead to more structured intermediates, is under way.

References

1. Reviews: K. M. Pietrusiewicz and M. Zablocka, *Chem. Rev.*, 1994, **94**, 1375; O. I. Kolodiazhnyi, *Tetrahedron: Asymmetry*, 1998, **9**, 1279.
2. Reviews: M. Ohff, J. Holz, M. Quirmbach and A. Börner, *Synthesis*, 1998, 1391; B. Carboni and L. Monnier, *Tetrahedron*, 1999, **55**, 1197.
3. P. Vedrenne, V. Le Guen, L. Toupet, T. Le Gall and C. Mioskowski, *J. Am. Chem. Soc.*, 1999, **121**, 1090.
4. H. C. Brown, A. K. Mandal, N. M. Yoon, B. Singaram, J. R. Schwier, P. K. Jadhav, *J. Org. Chem.* 1982, **47**, 5069.

Combination of 1,1- and 1,2-Allylboration of Acetylenic Derivatives of Silicon and Tin – A Route to New Heterocycles

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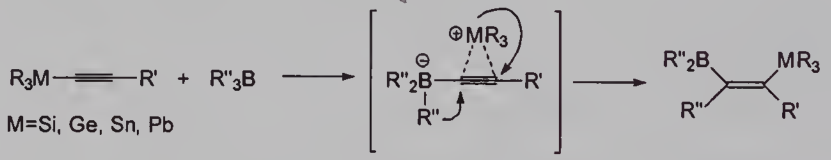
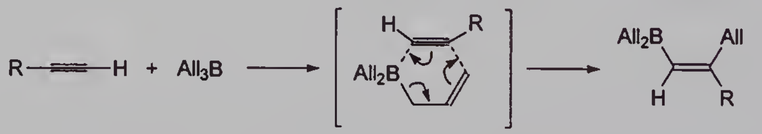
INTRODUCTION

Reaction of acetylenic derivatives of the elements of group 14 with triorganoboranes gives products of 1,1-organoboration [eq. (1)].[1] At the same time, allylic boranes react with triple bonds by 1,2-addition mechanism through a six-membered transition state [eq. (2)].[2] Therefore two different reaction pathways may be expected for interaction of All_3B with Si-, Ge- and Sn-containing acetylenes.



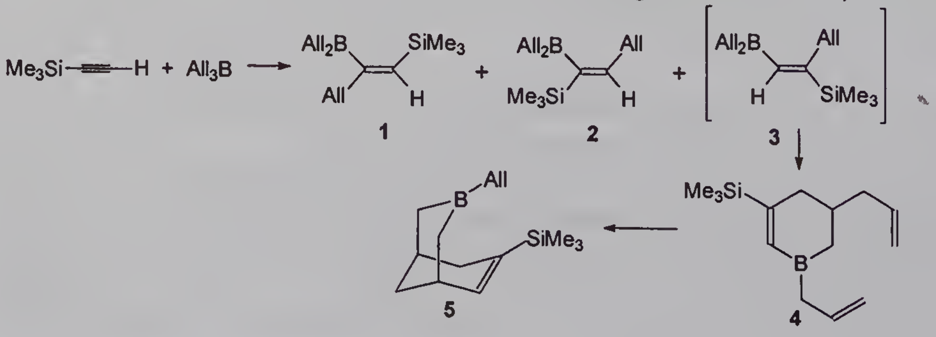
(1)



(2)

1 REACTION WITH MONOACETYLENIC DERIVATIVES[3]

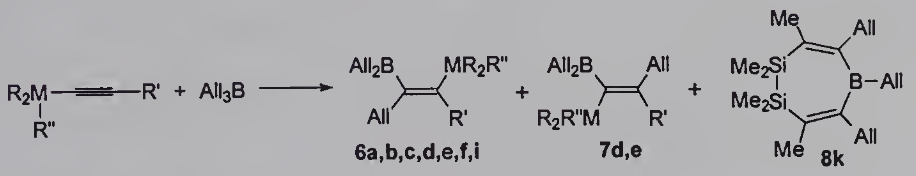
Trimethylsilylacetylene gave in reaction with All_3B a complicated mixture of products [eq. (3)]. Only compound **1** is produced by 1,1-organoboration. 1,2-Addition of



(3)

triallylborane gives isomeric olefins **2** and **3**. The latter compound is unstable and was not found in the final mixture. Instead compounds **4** and **5** formed by intramolecular cyclization of **3** were observed.

The reaction of All_3B with all other studied acetylenes proceeds mainly by the 1,1-organoboration mechanism. However, in the case of acetylenes with bulky substituents (such as *t*-Bu or Me_3Si) only the exchange reaction was observed. Phenylacetylenes gave mixtures of the products of 1,1- and 1,2-allylboration. It should be noted that in all cases the reaction began on carbon atom adjacent to the heteroatom in the starting acetylenes.



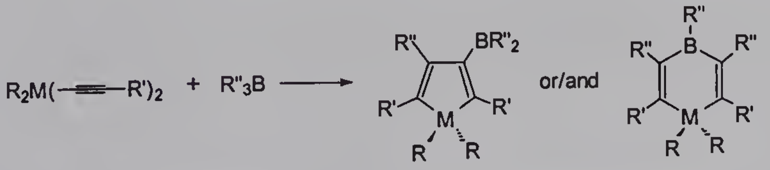
(4)

a, R=R'=R"=Me, M=Si;
b, R=R'=R"=Me, M=Sn;
c, R=R"=Me, R'=—≡—SiMe$_3$, M=Si;
d, R=R"=Me, R'=Ph, M=Si;
e, R=R"=Me, R'=Ph, M=Ge;
f, R=R"=Me, R'=Ph, M=Sn;
g, R=R"=Me, R'=t-Bu, M=Sn;
h, R=R'=R"=Ph, M=Si;
i, R=Me, R'=Ph, R"=Cl, M=Si;
k, R=R'=Me, R"=Me$_2$Si—≡—Me

Dipropyl(but-2-en-1-yl)borane gave the 1,1-allylboration products without rearrangement of allylic substituent likewise 1,2-allylboration.[2] The final olefin contains predominantly the allylic substituent that means that 1,1-allylboration is much faster than 1,1-organoboration with nonallylic boranes. It can be explained by the higher Lewis acidity of allylboranes compared to trialkylboranes.

2 REACTION WITH DI- AND POLYACETYLENIC DERIVATIVES

It is known that the reaction of trialkylboranes with polyacetylenic derivatives of group 14 elements affords five- or six-membered heterocycles depending on the nature of substituents [eq. (5)].[1]

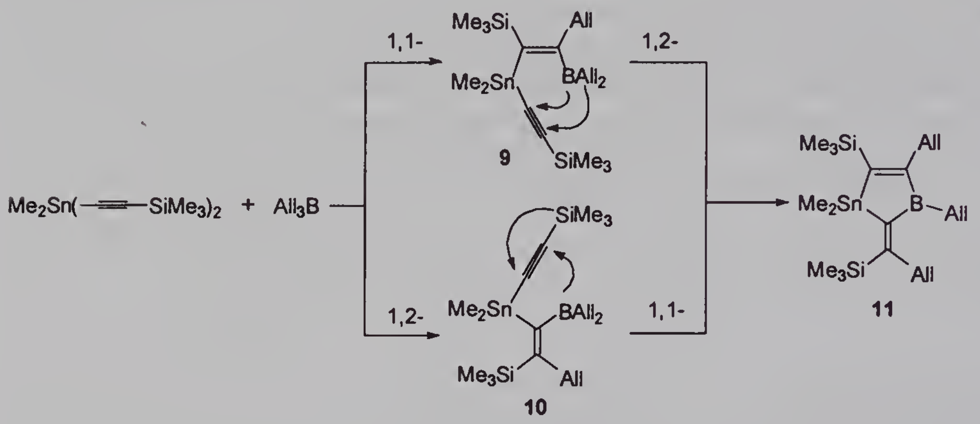


(5)

Similarly, on treatment of bis(trimethylsilylethynyl)dimethylsilane with All_3B the quantitative formation of a silole was observed. At the same time, changing the central silicon atom in the starting compound for tin leads to a completely different product. NMR data suggest that the compound obtained contains three different allyl groups. The Me_3Si-groups are also non-equivalent and have different couplings with tin atom (99 and 72 Hz). The boron resonance (64.4 ppm) is unusual for triorganoboranes.

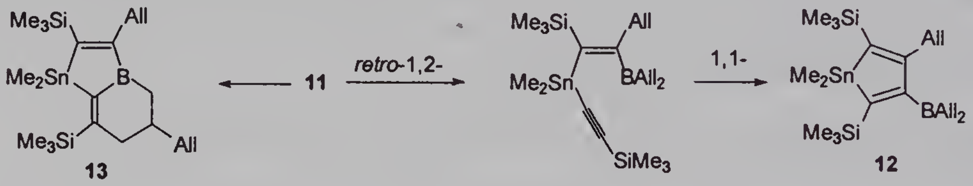
That data allowed to suggest structure **11** for the product. We assume that initially the olefins **9** and **10** are obtained due to 1,1- or 1,2-organoboration respectively. In **9** the following 1,2-organoboration seems more preferable both due to steric reasons and to the

Sn-C-bond being more reactive than the Si-C-bond. In contrast, in olefin **10** the next 1,1-organoboration is favourable (since hindered four-membered transition state is necessary for 1,2-organoboration). Both sequences afford heterocycle **11**.



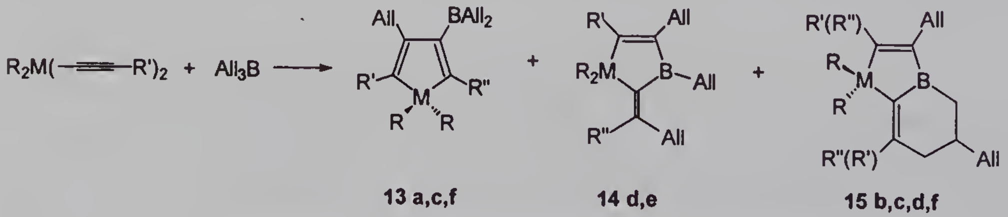
(6)

When heated compound **11** undergoes further rearrangements resulting in the stannole **12** and bicycle **13**. The former compound is formed via retro-1,2-allylboration followed by 1,1-allylboration, while the latter is a result of an intramolecular addition of allylboron moiety to the terminal double bond like it occurs in the allylboron-acetylenic condensation.[2]



(7)

Eq. (8) gives the overall outline of the allylboration of di- and polyacetylenic derivatives of 14 group elements.



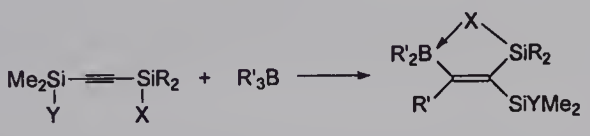
(8)

a, R=Me, R'=Ph, M=Si;
b, R=Me, R'=t-Bu, M=Si;
c, R=Me, R'=Me_3Si, M=Si;
d, R=R'=Me, M=Sn;
e, R=$(Me_3Si)_2N$, R'=Me, M=Sn;
f, R=$Me_3Si{-}{\equiv}{-}$, R'=Me_3Si, M=Si

3 REACTION WITH ACETYLENIC DERIVATIVES OF SILICON HYDRIDES[4]

As has been noted above, the 1,1-allylboration is a much faster reaction when compared with “normal” 1,1-organoboration. However the reaction rate still increases when acetylenes containing silicon hydrides are used as starting materials. Thus, the reaction of All_3B with bis(dimethylsilyl)acetylene was complete after several hours at room temperature. The proton NMR spectrum of the product **16** contains two separate resonances of Me_2SiH-groups. Chemical shifts ^1H, as well as ^1H-^{29}Si couplings are dramatically different for these two signals. One of the silicon resonances has an exceptionally downfield position (3.2 ppm). The value of the boron chemical shift (64.3 ppm) is also unusual for triorganoboranes. The Si-H band in the IR spectrum of **16** is moved to low frequency area.

These data suggest that a specific interaction between boron atom and hydrogen atom of Me_2SiH-group exists in **16**. The same spectra were observed for compounds **17-20** (Table 1).



16, R=Me, R'=All, X=Y=H
17, R=Y= Me, R'= All, X=H;
18, R=Pr, R'= All, X=H, Y=Me;
19, R=Y= Me, R'= Et, X=H;
20, R=Y=Me, R'=All, X=D

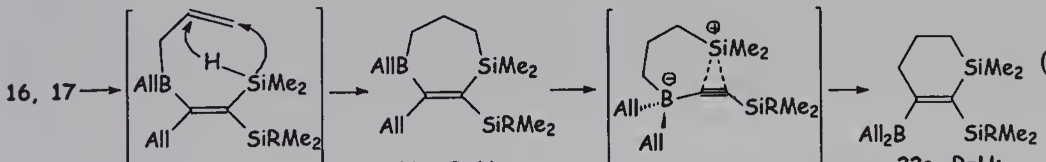
(9)

Table 1. IR and NMR data of olefins **17-20**.

Compound	$\delta^{29}Si$, ppm	$^1J_{X\text{-}Si}$, Hz	$\delta^{11}B$, ppm	$\nu_{Si\text{-}H}$, cm^{-1}
16	3.2	146.5	63.4	--
17	12.6	145.0	51.6	1905
18	31.1	133.6	55.8	--
19	-1.1	150.9	69.4	2055
20	12.9	19.7*	50.5	--

* - In starting acetylene $^1J_{D\text{-}Si}$=69.0 Hz

Reactivity of the compounds **16, 17** is also unusual. They easily (at room temperature) undergo intramolecular hydrosilylation affording seven-membered heterocycles **21a, b**, which in turn rearrange when stored to silacyclohexenes **22a, b** [eq. (10)]. It should be noted, that hydrosilylation usually requires the high temperature or/and the catalyst. Facility of intramolecular hydrosilylation of **16** and **17** is in accord with the existence of the new type of the three-center-two-electron Si-H-B bond in these molecules.



(10)

21a, R=H;
21b, R=Me

22a, R=H;
22b, R=Me

Acknowledgments. This work was supported by the Volkswagen-Stiftung.

References

1. B. Wrackmeyer, *Coord. Chem. Rev.*, 1995, **145**, 125.
2. Yu. N. Bubnov, *Pure Appl. Chem.*, 1988, **59**, 895.
3. B. Wrackmeyer, O. L. Tok, Yu. N. Bubnov, *J. Organomet. Chem.*, 1999, **580**, 234.
4. B. Wrackmeyer, O. L. Tok, Yu. N. Bubnov, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 124

Cyclic Polyunsaturated Triorganoboranes. Dynamic Behaviour and Chemical Properties

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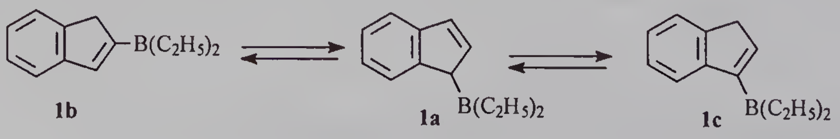
The electron-accepting character of the boron atom is responsible for many of the unusual chemical properties of unsaturated organoboranes. For instance, π-conjugation of the unoccupied boron 2 *p*-AO with the double bond in vinylboranes strengthens the B—C bond. In allylic triorganoboranes the boryl group is spatially separated from the double bond and such conjugation is largely reduced. However, some residual interaction must be present leading to low activation barriers for otherwise orbital-forbidden [1,3] sigmatropic boron shifts.

The present paper deals with the properties of cyclic polyunsaturated triorganoboranes where the cyclic structures provide numerous possibilities for through-space orbital interactions of the unoccupied boron p-AO with the extended π-system.

1. Synthesis and Dynamic Behaviour of 1-Indenyl(diethyl)borane

1-Indenyl(diethyl)borane **1** was prepared in 83% yield from indenyl lithium and diethylchloroborane.[1] Immediate analysis of the reaction mixture showed clean formation of **1a**; however, the equilibrium between allylic isomer **1a** and both possible vinylic isomers **1b,c** is rapidly established at elevated temperatures (Eq. 1). Compound **1a** is fluxional, ^{1}H EXSY data indicate a [1,3]-B shift mechanism ($E_A = 17.7 \pm 0.2$ kcal mol^{-1}, $\ln A = 28.6 \pm 0.5$).[3] At least three different rearrangements are observed: a [1,3]-B shift in **1a**, a [1,5]-H shift interconverting **1a** and **1b**, a combination of these two, or two subsequent [1,3]-B shifts as well as [1,5]-H migrations.

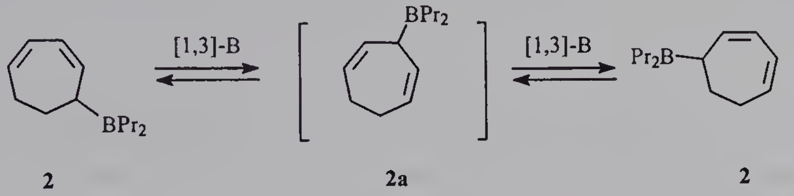


1a : **1b** : **1c** = 1.0 : 2.2 : 0.2

(1)

2. Synthesis and Dynamic Behaviour of Cycloheptadienyl(dipropyl)borane

Cycloheptadienyl(dipropyl)borane **2** was prepared from the lithium derivative in 40% yield.[2] Two-dimensional ^{1}H and ^{13}C EXSY experiments show that the dipropylboryl group in **2** migrates reversibly between positions 1 and 5; $E_A = 23.6 \pm 0.8$ kJ mol^{-1}, $\ln A = 39.3 \pm 1.4$, $\Delta G^{\neq}_{298} = 28.3$ kJ mol^{-1}. This dynamic behavior can be explained either by a direct [1,5]-B shift or by a combination of two [1,3]-B shifts involving the thermodynamically unstable isomer **2a** (Eq. 2).[2] The latter explanation seems to be more probable, since the [1,3]-B shift is a general reaction[3] whereas no [1,5]-B shift had been reliably documented so far. Besides, the high activation barrier of the borotropic migration is close to that in pentadienyl(dipropyl)borane, *i.e.*, the acyclic analogue of **2** where the stepwise mechanism had been proven experimentally.[4]

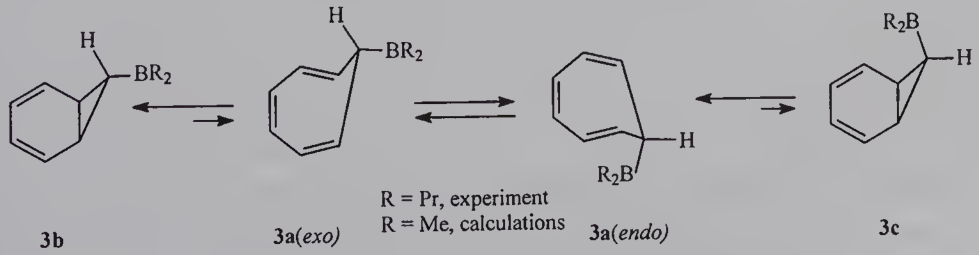


(2)

3. Cycloheptatrienyl(dipropyl)borane–Dipropylborylnorcaradiene Equilibrium

Cycloheptatrienyl(dipropyl)borane **3a** is a spectacular example for the importance of orbital interactions between the dipropylboryl group and the cyclic π-system. Compound **3a** equilibrates readily with its valence tautomer 7-*exo*-dipropylborylnorcaradiene **3b** (Eq. 3).[5] Experimentally determined thermodynamic parameters for the equilibrium ($\Delta H = 2.4 \pm 0.1$ kcal mol^{-1}; $\Delta S = -5.5 \pm 0.3$ cal mol^{-1} K^{-1}) and the activation barriers at 228 K ($\Delta G^{\neq}_{228}$(**3a**→**3b**) = 8.2 ± 0.1 kcal mol^{-1}, $\Delta G^{\neq}_{228}$(**3b**→**3a**) = 9.4 ± 0.1 kcal mol^{-1}) are in good agreement with the results computed by *ab initio* DFT-calculations for cycloheptatrienyl(dimethyl)borane *3* (ΔH = 2.0 kcal mol^{-1}, ΔS = −3.7 cal mol^{-1} K^{-1}; $\Delta G^{\neq}_{228}$(*3a*→*3b*) = 4.1 kcal mol^{-1} and $\Delta G^{?}_{228}$(*3b*→*3a*) = 6.8 kcal mol^{-1}). The computations also indicate that 7-*endo*-dimethylborylnorcaradiene *3c* is 7.6 kcal mol^{-1} less stable than the *exo*-isomer *3b* due to a more favorable overlap of the unoccupied boron 2p-AO with the Walsh orbital of the three-membered ring moiety in *3b*.

Lineshape analyses together with 2D ^{1}H EXSY data for the equilibrating system of **3a** and **3b** allowed the detection of a [1,7] sigmatropic shift in **3a** at temperatures above 293 K. This is also confirmed by the computations identifying the [1,7] B shift as the one with the lowest activation energy (*3a*, E_A = 18.4 kcal mol^{-1}), whereas other conceivable rearrangements have much higher activation barriers (25.7 kcal mol^{-1} and 27.4 kcal mol^{-1} for [1,5] and [1,3] B shifts respectively).

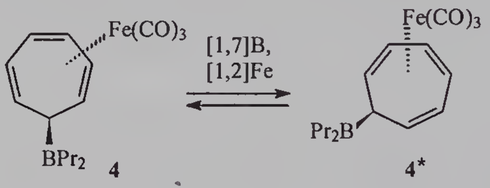


(3)

The decisive influence of unoccupied 2p-AO of boron on the molecular properties of **3** is well illustrated by its reaction with pyridine. In the unsymmetrical deuteropyridine complex the empty boron 2p-AO interacts strongly with the nitrogen lone pair. This reduces the stabilization of the *exo*-norcaradiene skeleton yielding only the “pure“ cycloheptatrienyl form in the NMR spectra.[5]

4. Fluxionality in Irontricarbonyl Complex of Cycloheptatrienylborane

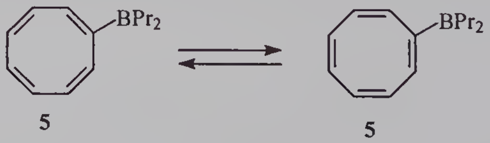
In the irontricarbonyl complex of cycloheptatrienyl(dipropyl)borane **4** no norcaradienyl isomer was detected.[6] Naturally, the electronic properties of the cycloheptatrienyl cycle are dramatically changed in **4** compared with **3** due to the complexation of two double bonds with iron. However, the main reason of relative instability of a norcaradienyl isomer of **4** is the axial orientation of the dipropylboryl group, which cannot be changed by simple rotations due to the *exo*-configuration of the complex. It prevents effective orbital interactions of the empty boron 2p-AO with the Walsh orbital of the cyclopropane moiety in the norcaradienyl isomer. Nevertheless, complex **4** exhibits very rich dynamic behavior: together with sigmatropic [1,3]-B and haptotropic [1,3]-Fe shifts, a new diatropic rearrangement occurs in this compound, *viz.* [1,7] migration of dipropylboryl group accompanied by simultaneous [1,2]-Fe shift (Eq. 4).[6] Interestingly, this rearrangement proceeds faster ($E_A = 17.0 \pm 0.5$ kcal mol^{-1}, $\ln A = 32 \pm 1$) than simple [1,7]-B shift in **3a** or [1,3]-B shift in **4**. The reasons for this are obscure.



(4)

5. Synthesis and Dynamic Behaviour of Cyclooctatetraenyl(dipropyl)borane

In cyclooctatetraenyl(dipropyl)borane **5** the dipropylboryl group occupies a vinylic position, and its orbital interaction with the adjacent double bond is very strong. This is one of the reasons why no borotropic rearrangements for **5** were found. The only dynamic process taking place in **5** is the reversible fluctuation of the double bonds ($\Delta H = 14.0 \pm 0.2$ kcal mol^{-1}; $\Delta S = -7.6 \pm 1.2$ cal mol^{-1} K^{-1}) common to all monosubstituted cyclooctatetraenes (Eq. 5).[7]

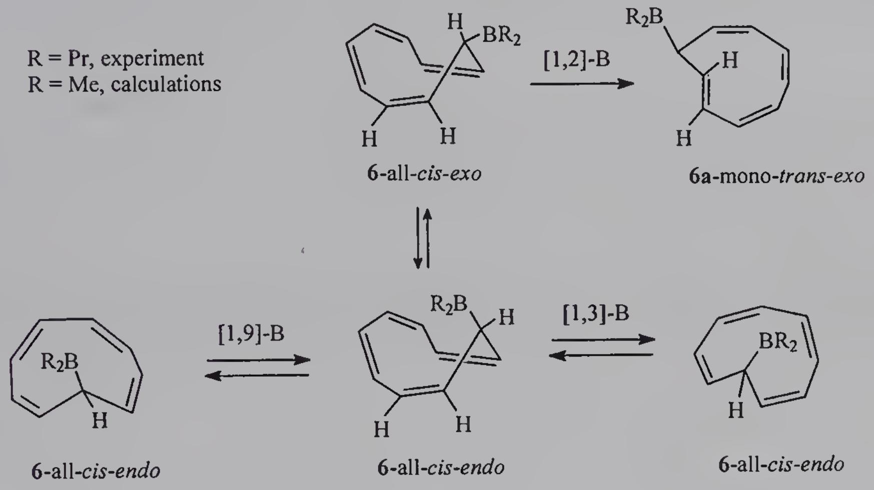


(5)

6. Chemistry of Compounds Derived from Cyclononatetraenylborane

In cyclononatetraenyl(dipropyl)borane **6** the extended system of conjugated double bonds together with flexibility of the cycle lead to plethora of intramolecular rearrangements, many of which do in fact take place.

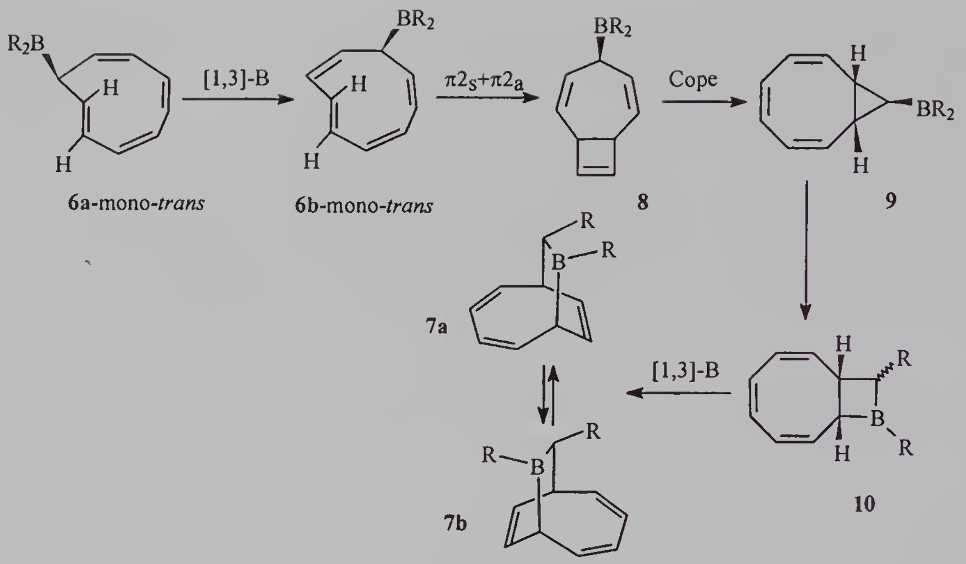
6.1. Sigmatropic migrations of dialkylboryl group in cyclononatetraenylborane. Analysis of the EXSY spectra of **6** at –100°C showed that the [1,3]-B shift (Eq. 6) is the fastest rearrangement taking place in **6**-all-*cis-endo* ($E_A = 6.2 \pm 0.5$ kcal mol^{-1}).[8] Accompanying density functional theory (DFT) calculations at the B3LYP/6-311+G*//B3LYP/6-31G* level of theory[9,10] confirmed this conclusion (the computed E_A is 6.6 kcal mol^{-1}) but also revealed the possibility of an almost equally facile (E_A = 6.9 kcal mol^{-1}) [1,9]-B shift in **6**-all-*cis-endo*.[11] Moreover, calculations showed the possibility of a non-degenerate [1,2]-B shift in **6**-all-*cis-exo* leading to **6a**-mono-*trans*.[11] The latter compound is a key intermediate in further thermal rearrangements of **6** (Eq. 7).



(6)

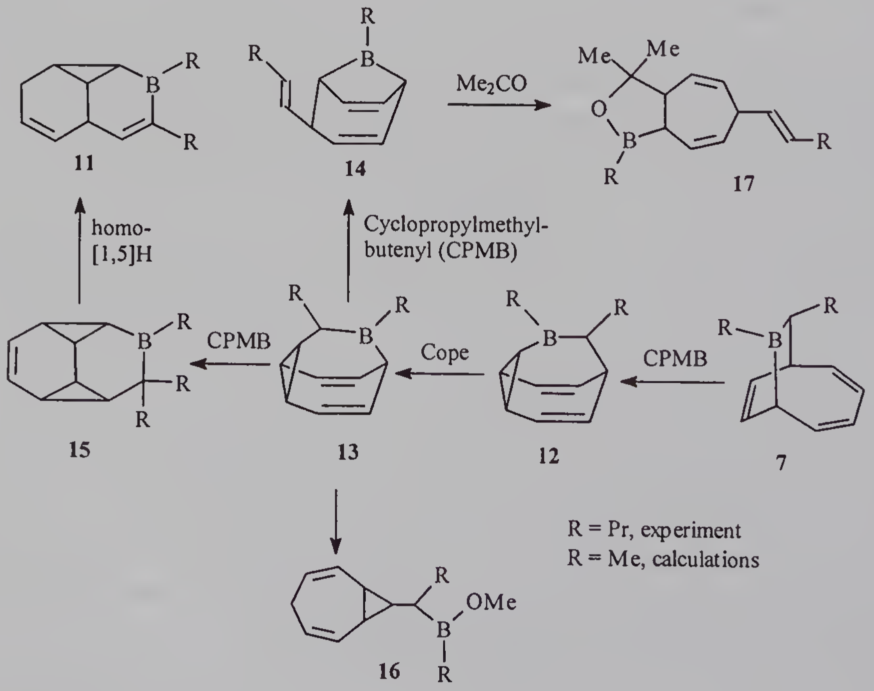
6.2. Thermal rearrangements starting from cyclononatetraenylborane. All known cyclooctatetraenes above 0°C rearrange quantitatiively to corresponding dihydroindenes. This reaction pathway also takes place in the case of borane **6**, but only as a side process.[8,11,12] The main product of rearrangement of **6** at 0°C is bicyclic borane **7**. The most probable reaction pathway is outlined by Eq. 7. *Cis-exo*-dipropylboryl **9** was characterized by NMR as a metastable intermediate.[12]

Direct $\pi 4_s + \pi 2_s$ cyclization of **6**-all-*cis* is known to give the corresponding dihydroindenes (a side process in the thermal rearrangement of **6**), whereas other modes of intramolecular cyclizations are orbitally prohibited in this compound. On the other hand, allowed $\pi 6_s + \pi 2_a$ cyclization in **6a**-mono-*trans* hypothetically could produce a borane with a bicyclo[6.1.0]octane skeleton but it would have a *trans*-configuration. Therefore **6a**-mono-*trans* is more likely to transform to **6b**-mono-*trans via* a [1,3]-B shift. The latter compound rearranges to **9** by subsequent $\pi 2_s + \pi 2_a$ cyclization and Cope rearrangement.[13] Thus, the reason for the unique chemical behavior of the borylated cyclononatetraene is apparently the possibility of fast and reversible interconversion of **6**-all-*cis*, **6a**-mono-*trans* and **6b**-mono-*trans*. Simultaneous migration of two alkyls converting **9** to **10** is unusual for organoboron chemistry, however examples of such transformations are known for structurally similar phosphirenes.[14]



(7)

6.3. Dynamic behaviour and chemical properties of 9,10-dipropyl-9-borabicyclo[4.2.2]deca-triene. In 9,10-dipropyl-9-borabicyclo[4.2.2]deca-triene **7** the unoccupied boron 2p-AO effectively overlaps with the diene system of the cyclooctatriene moiety. This is reflected in an unusually low value of $\delta^{11}B = 70.2$; however, the fast [1,3]-B shift interconverting the two isomers of **7** ($E_A = 11.6$ kcal mol^{-1}) is not supressed.[15] Moreover, chemical transformations of **7** show that other intramolecular rearrangements may be very fast in this bicyclic borane (Eq. 8).[16]



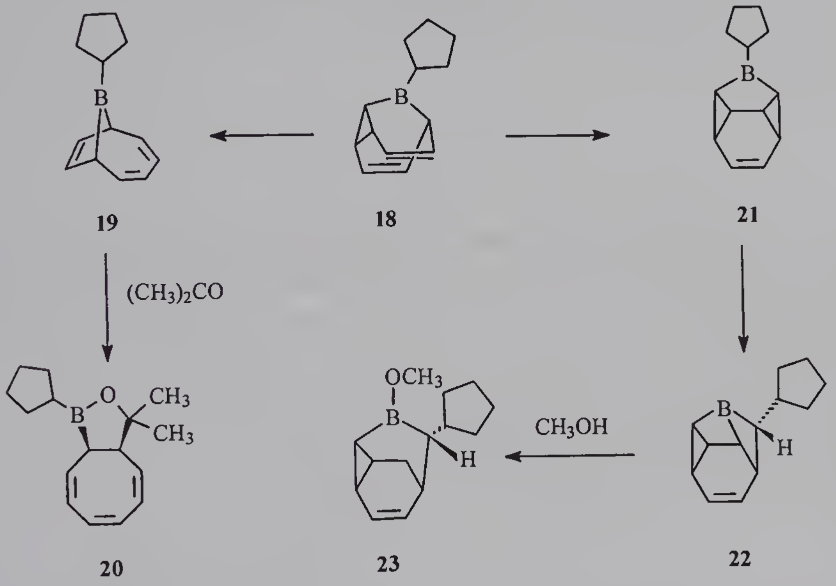
(8)

Heating **7** for 1 h at 130°C affords an equilibrium mixture of **7** and tricyclic borane **11** in a 5 : 95 ratio. The greater thermodynamic stability of **11** is due to the vinylic position of the boron atom. Calculations show that **11** is 1.8 kcal mol^{-1} more stable than **7**. The pathway depicted in Equation 8 requires a series of two butenyl-cyclopropylmethyl rearrangements, a Cope rearrangement, and a homo-[1,5]-H shift. Borabullvalene **13** has been intercepted as an unstable valence tautomer by treatment of **7** with methanol affording **16** selectively. The butenyl-cyclopropylmethyl rearrangement in **13** is well illustrated by the reaction of **7** with acetone yielding **17** as the single product.[16]

7. Dynamic Behaviour and Chemical Properties of 9-Cyclopentyl-9-borabarbaralane

Equilibria very similar to those of **7**, **12**, **13** and **15** were found for 9-cyclopentyl-9-borabarbaralane **18**, which can be regarded as alkylated homologue of either **12** or **13** (Eq. 9).[17]

Due to a more rigid geometry of **18** the overlap of the boron 2p-AO with the π-system is less effective compared to **7**. This can be concluded from the chemical shift of boron ($\delta^{11}B = 80.5$) which is an almost "normal" value for a triorganoborane. Like all known barbaralanes, borane **18**[15] and other 9-alkyl-9-borabarbaralanes[16] undergo fast degenerate Cope rearrangement (in **18** $\Delta G^{\neq}(208) = 12.0\pm0.1$ kJ mol^{-1}). However, chemical transformations of **18** show convincingly that the dynamic behavior of **18** is much more complex than can be deduced from its NMR spectra only.[17]



(9)

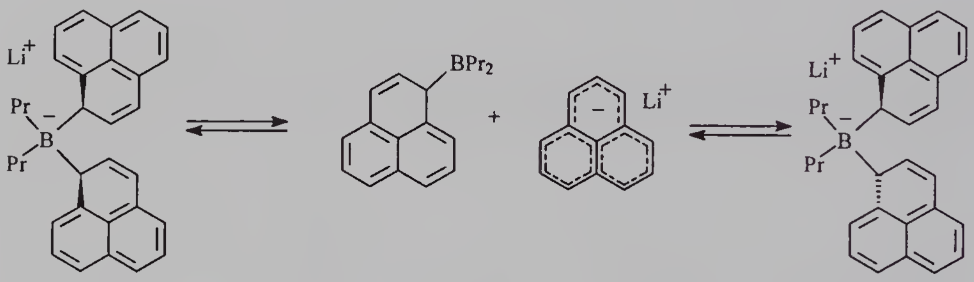
When **18** is treated with acetone, boronic ester **20** with a cyclooctatriene structure is cleanly obtained indicating the valence tautomerism between **18** and **19**. In fact, **19** appears to be the kinetic product in the borylation of lithium or potassium cyclononatetraenide with alkylboron dihalides which rearranges quickly to **18** due to the comparatively high thermodynamic stability of the latter.[18,19] Acetaldehyde, ethoxyacetylene, acetonitrile, and acetic acid react with **18** in the same fashion yielding only the products with a cyclooctatriene structure.[17]

The occurrence of the butenyl-cyclopropylmethyl rearrangement in **18** is supported by its reaction with methanol affording tricyclic borane **23** as the single product. Apparently, this transformation occurs *via* intermediate formation of **21** which rearranges further to **22** by the same diatropic rearrangement responsible for the conversion of **9** to **10** (Eq. 7).

Thus, the properties of two structurally related bicyclic boranes **7** and **18** show that incorporation of a boron atom with an empty 2p-AO into a bicyclic unsaturated framework results in structurally very labile molecules with complex dynamic behaviour and unusual chemical properties.

8. Synthesis of Phenalenyl(dipropyl)borane 24. Two different degenerate [1,3]-B shifts

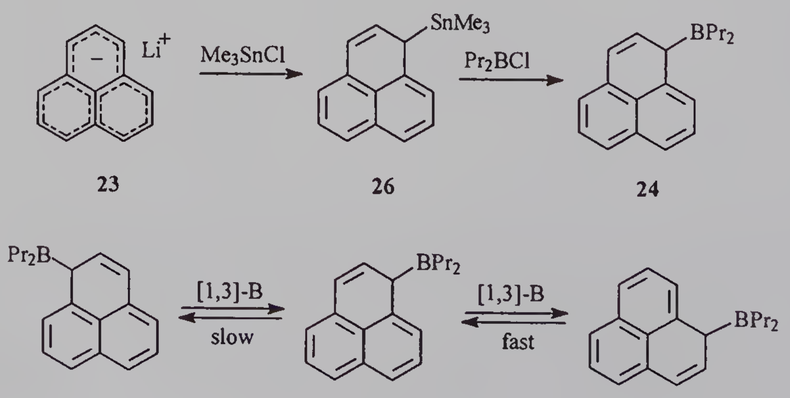
The phenalenyl derivative of boron seemed to be an intersting target molecule in our studies of cyclic polyunsaturated triorganoboranes. However, the attempted direct borylation of phenalenyllithium **23** did not give the desired borane **24** but the "ate"-complex **25** instead, independent of the reagents ratio. Examination of the EXSY spectra of **25** showed that its two diastereomers are in a fast equilibrium (Eq. 10). Interconversion of **25a** and **25b** apparently proceeds *via* a dissociation-association mechanism with intermediate formation of **23** and **24**.



25a **24** **23** **25b**

(10)

Synthesis of pure borane **24** was acomplished by transmetallation of the tin derivative **26** (Eq. 11). In borane **24** both possible [1,3]-B shifts are observed; however, the migration of the dipropylboryl group to position 9 proceeds much faster than the similar rearrangement to position 3.



23 **26** **24**

24 **24** **24**

(11)

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References.

1. I. D. Gridnev, A. Meller, *Main Group Metal Chemistry* 1998, **21**, 121.
2. I. D. Gridnev, M. E. Gurskii, A. V. Geiderikh, Y. N. Bubnov, *Mendel. Commun.* 1996, 176.
3. I. D. Gridnev, M.E.Gurskii, Yu.N.Bubnov, in: *Current Topics in the Chemistry of Boron,* Kabalka, G. ed., Cambridge: R. Soc. Chem. Spec. Publ. 1994, **143**, 56.
4. M. E. Gurskii, , I. D. Gridnev, A. V. Geiderikh, A. V. Ignatenko, Y. N. Bubnov, V. I. Mstislavsky, Y. A. Ustynyuk; *Organometallics* 1992, **11**, 4056.
5. I. D. Gridnev, O. L. Tok, N. A. Gridneva, Y. N. Bubnov, P. R. Schreiner, *J. Am. Chem. Soc.,* 1998, **120**, 1034.
6. I. D. Gridnev, O. L. Tok, M. E. Gurskii, Y. N. Bubnov; *Chem. Eur. J.,* 1996, **2**, 1483.
7. M. E. Gurskii, I. D. Gridnev, A. V. Buevich, T. V. Potapova, A. O. Krasavin, V. I. Mstislavsky, Y. N. Bubnov, *Mendel. Commun.,* 1994, 221.
8. M.E.Gurskii, I. D. Gridnev, A. B. Buevich, Y. N. Bubnov, *Organometallics,* 1994, **13**, 4658.
9. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
10. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
11. I. D. Gridnev, P. R. Schreiner, M.E.Gurskii, Y. N. Bubnov, A. O. Krasavin, V. I. Mstislavski, *J. Chem. Soc. Chem. Commun.*, 1998, 2507.
12. I. D. Gridnev, M. E. Gurskii, A. V. Buevich, Y. N. Bubnov, *Russ Chem Bull* 1996, **45**, 107.
13. G. Boche, M. Bernheim, D. Lawaldt, B. Ruisinger, *TetrahedronLett* **1979**, 4285.
14. S. Haber, M. Schmitz, U. Bergsträsser, J. Hoffmann, M. Regitz, *Chem. Eur. J.*, 1999, **5**, 1581.
15. I. D. Gridnev, M. E. Gurskii, A. V. Buevich, Y. N. Bubnov, *Russ Chem Bull* 1996, **45**, 2243.
16. I. D. Gridnev, M. E. Gurskii, A. V. Buevich, T. V. Potapova; Y. N. Bubnov; *J. Org. Chem.* 1996, **61**, 3514.
17. I. D. Gridnev, A. Meller, *J. Org. Chem.*, 1998, **63**, 3085.
18. G. E. Herberich, , H.-W. Marx., S. Moss, P. v. R. Schleyer, T. Wagner, *Chem. Eur. J.* 1996, **2**, 458.
19. W. Maringgele, D. Stalke, A. Heine, A. Meller, G. M. Sheldrick, *Chem. Ber.* 1990, **123**, 489.

Allylboration of Nitrogen Heterocycles

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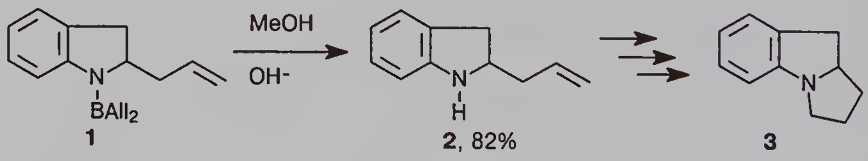
1 REDUCTIVE α-ALLYLATION OF INDOLES WITH ALLYLBORANES

Pyridines and isoquinoline undergo reductive *trans*-α,α'-allylation on consequent treatment with triallylborane and alcohol[1]. Similar reaction of pyrrole leads to a mixture of 2-allyl-3-pyrroline (20%) and *trans*-2,5-diallylpyrrolidine (60%)[1]. Certain allylated nitrogen heterocycles thus obtained were used for preparation of alkaloids and related compounds[2,3].

In this presentation, reductive α-allylation of indoles and reductive diallylation of lactams with allylic boranes as well as a new way to isoquinuclidine structures are described.

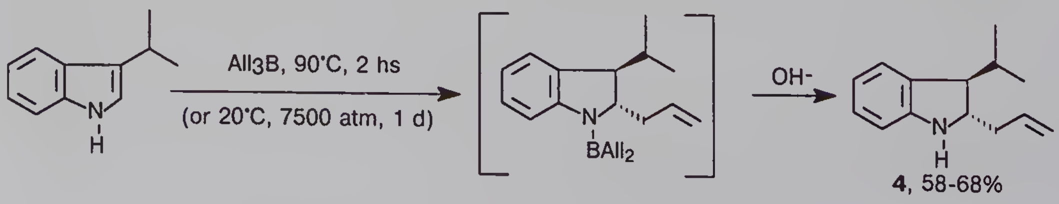
We have recently found that indole undergoes reductive allylboration upon heating with triallylborane (1:1) in ether for 3 hs to give aminoborane **1** (80%, δ ^{11}B 46.0 ppm)[4].



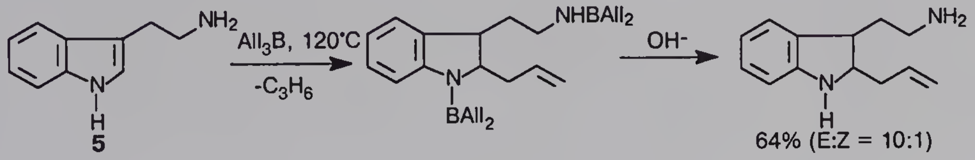
Deboronation of **1** with methanol and/or aqueous NaOH gave 2-allylindoline 2 (82%). The latter was transformed into benzo[f]pyrrolizidine **3** via hydroboration-oxidation-cyclization sequence[2,5].

3-R-Indolines also undergo α-allylboration under the action of All_3B. However, the reactions at r.t. proceed slowly (20-30 days), and heating at 80-130°C or high pressure is required.

The reaction between All_3B and isopropylindole proceeds stereoselectively to afford, after deboronation, *trans*-2-allyl-3-isopropylindoline **4** as a sole product.

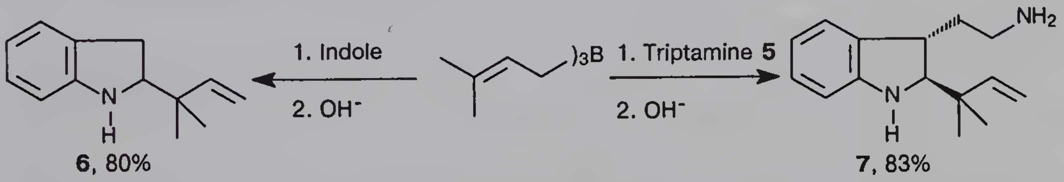


trans-Allylboration is also the main process in the reaction of All_3B with 3-(2-hydroxyethyl)indole, 3-(4-hydroxybutyl)indole and triptamine **5**. However, the minor amounts of corresponding *cis*-isomers (9-14%) are formed in these reactions (NMR).



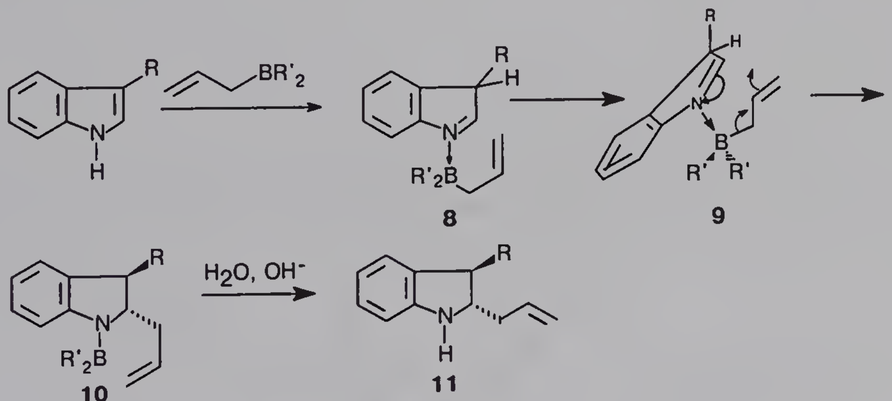
Therefore CH_2-R groups are not bulky enough to provide selective *trans*-addition of the boron-allylic fragment to heterocycle.

Indolines **6** and **7** with reversed prenyl group were obtained by prenylboration of indole (90°C, 2 hs) and triptamine **5** (125°C, 8 hs) respectively.



These results show unambiguously, that reductive α-allylboration of indoles proceeds with allylic rearrangement. From the reaction of 1-deuteroindole and All_3B (1:1, ether, 36°C, 7 hs), a 1:1 mixture of *cis*- and *trans*-2-allylindoline (78%) was isolated.

Data obtained allow us to propose the following mechanism of the reductive α-allylation of indoles by allylboranes:

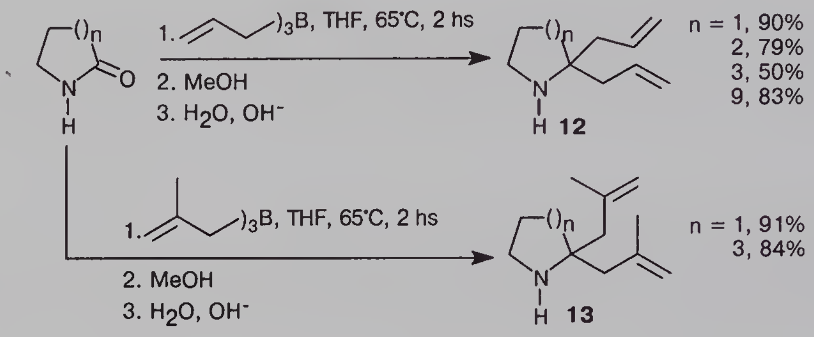


Upon treatment of indoles with allylic borane, [1,3]hydrogen shift from the nitrogen atom to C-3 proceeds, producing the imine complex **8**. Further allylboration of the C=N bond formed occurs with rearrangement through the chair-like six-membered transition state **9** allylic group being added mainly or quantitatively in *trans*-fashion relative to the 3-R. Hydrolysis of iminoborane **10** formed leads to the 2-allylated indoline **11**.

Prenylboration of generated *in situ* 3-chloroindolenine derivatives was used in synthesis of gypsetin and triptostatin B[6].

2 REDUCTIVE DIALLYLATION OF LACTAMS

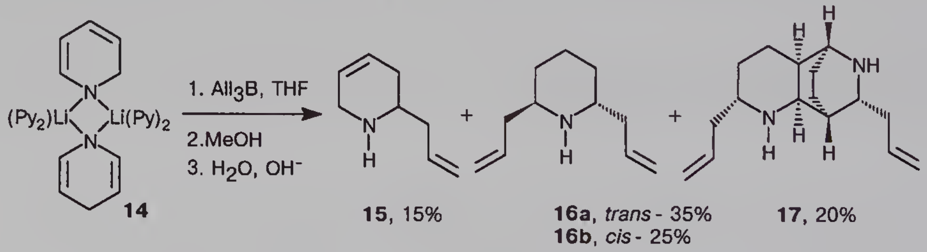
Lactams containing N-H bond are smoothly transformed into the corresponding 2,2-diallylated nitrogen heterocycles **12** and **13** on heating with trialyl- or trimethallylborane, followed by treatment with methanol and alkali solution.



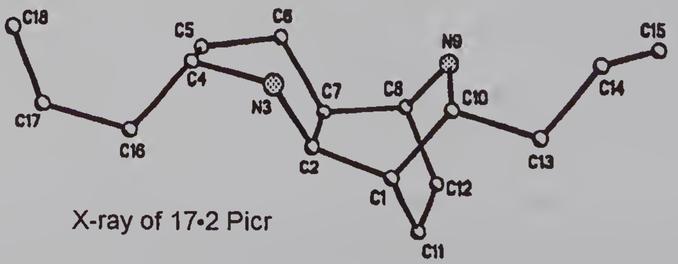
The reaction seem to process via N-H borylation - allylboration - β-elimination - allylboration sequence.

3 ALLYLATION OF 1,2- AND 1,4-DIHYDROPYRIDINE DERIVATIVES WITH TRIALLYLBORANE

The reaction of BuLi with pyridine (1:7) leads to the air-stable dimeric complex **14**[7]. We have found that consequent treatment of the adduct **14** with All_3B, methanol and alkali affords mono- (**15**) and diallylated (**16**) heterocycles along with unexpected tricyclic compounds **17** (20%).

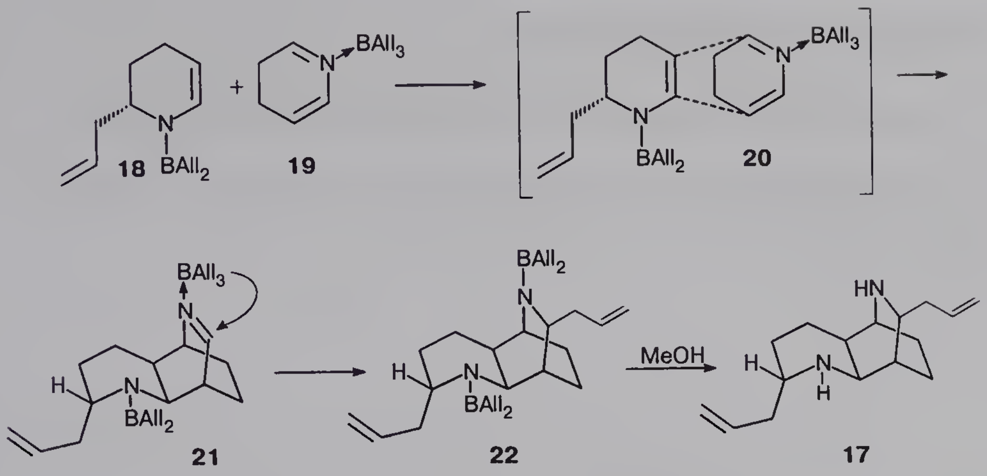


All the four compounds (**15**, **16a**, **16b**, and **17**) were isolated in pure state by chromatography and their structures were established by NMR. The structure of **17**•2 Picr was also determined by X-ray analysis.



X-ray of 17•2 Picr

The key step to the tricyclic compound **17** seems to be the stereoselective aza Diels-Alder reaction (**20**) of the intermediate enamine dienophile **18** with azadiene adduct **19** to produce the imine complex **21**. Allylboration of C=N bond in the latter proceeds also stereoselectively (**21**, arrow) furnishing the diborylated compound **22**.



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References

1. a) Yu. N. Bubnov, *Pure Appl. Chem.*, 1994, **66**, 235. b) Yu. N. Bubnov, *Izv. Acad. Nauk, Ser. Khim.*,**1995**, 1203 [*Russ. Chem. Bull.*, 1995, **44**, 1156 (Engl. Transl.)].
2. Yu. N. Bubnov, in "Adv. in Boron Chemistry", Ed. W. Siebert, Royal Society of Chemistry, Thomas Graham House, Cambridge, 1997, pp 123-138.
3. Yu. N. Bubnov, E. V. Klimkina, A. V. Ignatenko, *Izv. Acad. Nauk, Ser. Khim.*,**1998**, 971 [*Russ. Chem. Bull.*, 1998, **47**, 941 (Engl. Transl.)].
4. Yu. N. Bubnov, A. Yu. Zykov, L. I. Lavrinovich, A. V. Ignatenko, *Izv. Acad. Nauk, Ser. Khim.*,**1993**, 1329 [*Russ. Chem. Bull.*, 1993, **42**, 1271 (Engl. Transl.)].
5. Yu. N. Bubnov, M. E. Gurskii, T. V. Potapova, *Izv. Acad. Nauk, Ser. Khim.*,**1996**, *2807 [Russ. Chem. Bull.*, 1996, **45**, 2665 (Engl. Transl.)].
6. a) J. M. Schkeryantz, J. C. G. Woo, S. J. Danishefsky, *J. Am. Chem. Soc.*, **117**, 7035 (1995). b) K. M. Depew, S. J. Danishefsky, N. Rosen, L, Sepp-Lorenzino, *J. Am. Chem. Soc.*, **118**, 12463 (1996).
7. W. Clegg, L. Dunbar, L. Horsburgh, R. E. Mulvay, Angew. Chem. Int. Ed. (Engl.), 1996, **35**, 753.

Allylboration of Nitroarenes

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1 INTRODUCTION

β,γ-Unsaturated (allylic) boron derivatives (not alkyl-, aryl- and vinylboranes) readily react with organic compounds containing multiple bonds to form novel carbon-carbon bonds (**Scheme 1**). In the last 30 years, allylboration reactions have been widely used in organic synthesis.[1]

Scheme 1

The N=O bond is not included in **Scheme 1** because the allylboration of nitro compounds has not been studied yet. We decided to investigate this reaction.

To our knowledge, reactions of organometallic compounds with nitroarenes lead, as a rule, to mixtures of reduction and alkylation (or arylation) products.[2-11] Only few examples have been described where the reactions proceed with the formation of *N,N*-disubstituted hydroxylamine and/or secondary amines.[4-6,9]

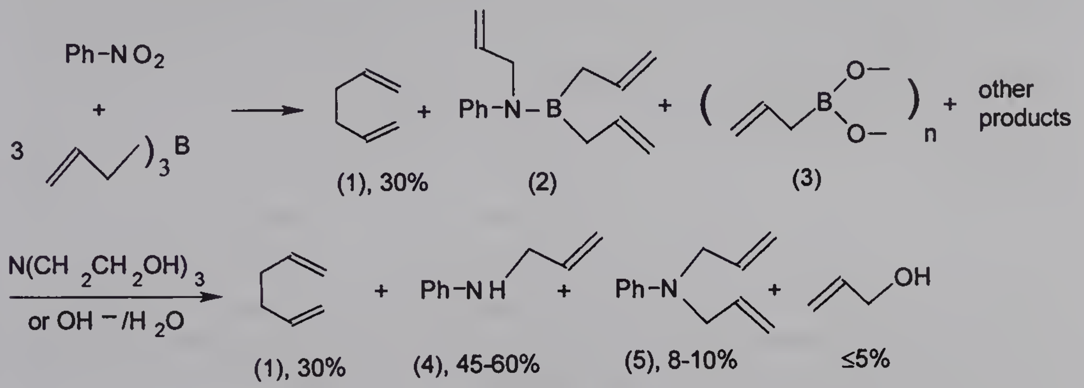
There are no publications concerning the reaction of nitroarenes with organoboranes. The only known reaction, is the electrolysis of trialkylboranes in nitromethane in the presence of R_4'NX salts, which leads to higher nitroalkanes.[12] The reaction of R_3B with NO, which proceeds by a radical mechanism, has been used for the preparation of hydroxylamine derivatives (R_2NOH), heterocyclic boron derivatives or alkylamines (see ref.[1], p. 283.)

The purpose of our investigation was the study of the reaction of allylboranes with nitroaromatic compounds.

2 RESULTS AND DISCUSSION

The optimal procedure for carrying out the reaction consists of a gradual addition of one equivalent of nitroarene to three equivalents of triallylborane at 80 - 100°C (with or without a solvent). The mixture is then stirred at the same temperature for 1 - 1.5 hrs to complete the reaction.

Three compounds, diallyl (1), (*N*-allyl-*N*-phenylamino)-diallylborane (2), (δ ^{11}B 44 ppm) and an allylboronic acid derivative (3) (δ ^{11}B 32 ppm) were identified by NMR as the products of the reaction of All_3B with $PhNO_2$ (**Scheme 2**).



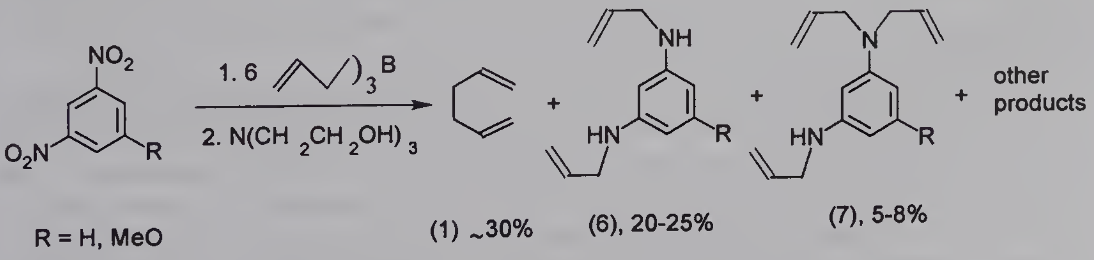
Scheme 2

Diallyl (1) (~30%) was distilled off and *N*-allylaniline (4) (45—60%), *N,N*-diallylaniline (5) (8—10%) and allylalcohol (~5%) were isolated after deboronation of the residue (**Table 1**). Negligible amounts of aniline as well as the products of allylation of *N*-allylaniline in aromatic ring and in α-position of the allylic group were also detected. Trimethallylborane reacts in the same way to produce dimethallyl (33%), *N*-methallylaniline (57%), *N,N*-dimethallylaniline (8.5%) and negligible co-products. Similar products were isolated from the allylboration of *p*-chloronitrobenzene, and *o*- and *p*-nitrobiphenyl (**Table 1**).

Table 1. *Reductive allylboration of nitroarenes*

Ar in ArNO₂	*Products (%)*		
	diallyl	*ArNHAll*	*ArNAll₂*
C_6H_5—	30	60	8
p-Cl-C_6H_4—	34	63	5.5
o-Ph-C_6H_4—	30	46	15
p-Ph-C_6H_4—	32	60.5	9.5

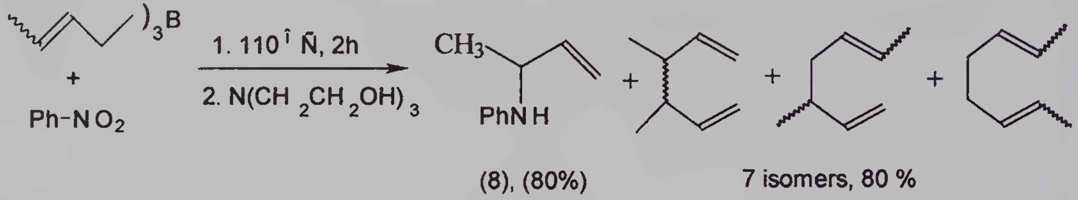
N,N'-Diallyl- (6) and *N,N,N'*-triallylphenylenediamines (7) were identified as the main products of the reaction of 1,3-dinitrobenzene and 1-methoxy-3,5-dinitrobenzene with triallylborane (**Scheme 3**).



Scheme 3

The data show that allylboration of aromatic nitro compounds is a complicated process. *N*-Monoallylated and *N,N*-diallylated arylamines are the products of reductive allylboration of the nitro group and diallyl is apparently formed by the recombination of allyl radicals. Surprisingly, allyl alcohol is produced only in a negligible amount (<5%).

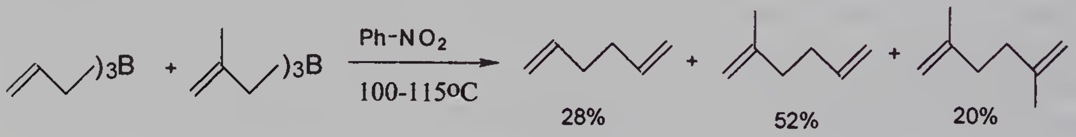
To clarify the reaction mechanism, the reaction of tricrotylborane with nitrobenzene was performed (**Scheme 4**). Amine (8) (80%) proved to be the sole product of crotylboration of $PhNO_2$. A mixture of dimethyl-1,5-hexadienes (7 isomers, 80%) was also obtained.



Scheme 4

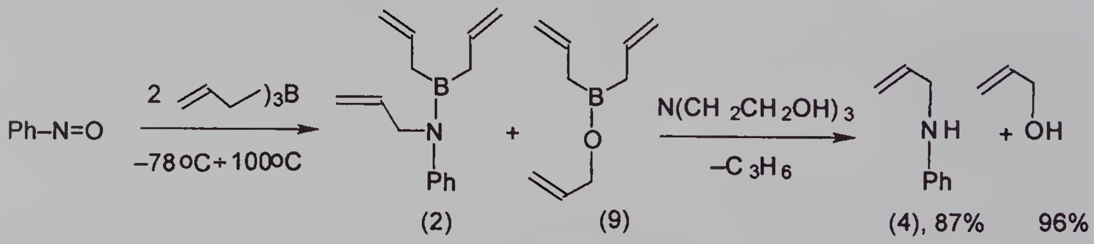
This result indicates that reductive allylboration of the nitro-group occurs with transposition of the double bond in the allylic group and the reaction seems to proceed via a six-membered transition state (see **Scheme 1**). At the same time, formation of 1,5-dienes is not selective because they are obtained through a radical process.

Treatment of nitrobenzene with a mixture of triallylborane and trimethallylborane (**Scheme 5**) confirmed the contribution of radical processes to the reaction mechanism, since one of the main products was 2-methyl-1,5-hexadiene (52%).



Scheme 5

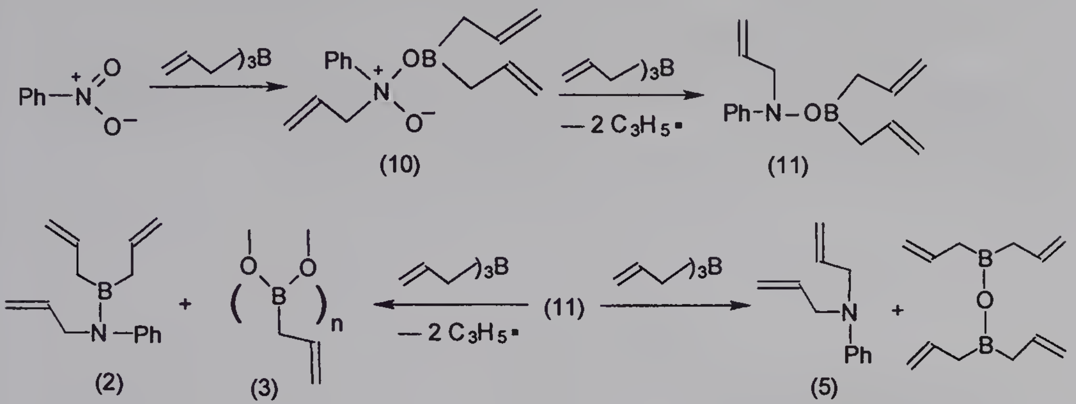
Allylboration of nitrosobenzene affords an aminoborane (2) (δ ^{11}B 44 ppm) and a diallylborinic ester (9) (δ ^{11}B 51 ppm). Deboronation of these products gave *N*-allylaniline (4) (87%) and allyl alcohol (96%) (**Scheme 6**).



Scheme 6

Allyl alcohol is here obtained in nearly quantitative yield, whereas its yield in the reaction of $ArNO_2$ with All_3B does not exceed 5%. Consequently nitrosoarenes are not intermediates in the reductive allylboration of nitroarenes.

A plausible mechanism of the reaction of nitroarenes with allylboranes is shown in **Scheme 7**. We believe that in the first stage of the reaction, "normal" addition of a B-allyl moiety to the N=O bond occurs which is accompanied by the allylic rearrangement via a six-membered transition state. The allyl group adds to the nitrogen atom whereas boron is bonded to the oxygen atom since the energy of the B-O bond (120 - 130 kcal/mol) is significantly greater than that of the B-N bond (105 kcal/mol). Intermediate (10) is further reduced to hydroxylamine derivative (11) by the excess of All_3B. The latter may be transformed in two different ways. The major reaction is a further redox process, accompanied by the formation of allyl radicals, leading to diallyl (as a result of recombination) and aminoborane (2). The cleavage of the N-O bond in (11), followed by a shift of the allylic group from boron to nitrogen and formation of *N,N*-diallylaniline (5), is a minor process.



Scheme 7

CONCLUSIONS

A series of reactions of nitroarenes with triallyl-, trimethallyl- and tricrotylborane have been studied. It has been established that the major process is reductive allylboration of nitro-groups accompanied by an allylic rearrangement. As a result, a new convenient method of the synthesis of *N*-allylanilines has been elaborated.

References

1. B. M. Mikhailov and Yu. N. Bubnov. "Organoboron Compounds in Organic Synthesis", Harwood Acad. Sci. Publishers, London, N-Y, 1984, 781 pp.
2. H. Hepworth. *J. Chem. Soc.*, 1920, **117**, 1004.
3. D. N. Kursanov and P. A. Solodkov. *Zh. Obshch. Khim.*, 1935, **5**, 1487 [Russ. *J. Gen. Chem.*, 1935, **5** (Engl. Transl.)].
4. Y. Yost, H. R. Gutmann and C. C. Muscoplat. *J. Chem. Soc. (C),* 1971, 2119.
5. G. Bartoli, E. Marcantoni, M. Bosco and R. Dalpozzo. *Tet. Lett.*, 1988, **29**, 2251.
6. G. Bartoli, G. Palmieri, M. Petrini, M. Bosco and R. Dalpozo. *Gazz. Chim. Ital.*, 1990, **120**, 247.
7. G. Bartoli, *Acc. Chem. Res.*, 1984, **5**, 109.
8. G. Bartoli, M. Bosco, R. Dalpozzo and P. E. Todesco. *J. Org. Chem*, 1986, **51**, 3694.
9. P. Buck and G. Köbrich. *Tet. Lett.*, **1967**, 1563.
10. R. A. Sadykov. *Izv. RAN. Ser. Khim.* **1998**, 1979 [*Russ. Chem. Bull.*, **1998**, (Engl. Trans.)].
11. V. I. Savin. *Zh. Îrg. Khim.* 1978, **14**, 2090 [*Russ. J. Org. Chem.*, 1978, **14** (Engl. Transl.)].
12. Y. Takahashi, M. Tokuda, M. Itoh and A. Suzuki, *Synthesis,* 1976, 616.

The Reaction of β-Ketoacids with Allylboronates

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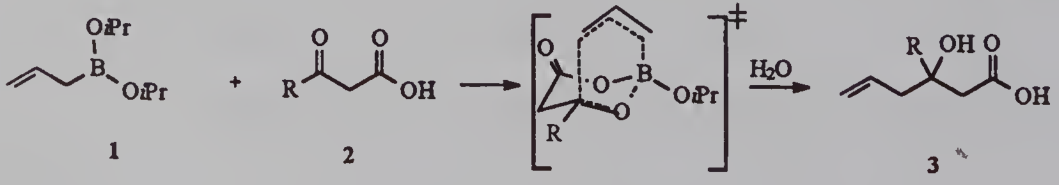
1 INTRODUCTION

Allylmetal reagents have been of synthetic, mechanistic, and biochemical importance for more than seventy years because of their well defined stereo- and regiochemistry.[1] Aldol condensations[2] and mechanistically related carbon-carbon coupling reactions[3] play fundamental roles in the synthesis of natural products of propiogenic/acetogenic biosynthetic origins.[4] Over the past decade, the reaction of allyl- and crotylmetal reagents with carbonyl compounds have proven to be important in acylic diastereoselective syntheses.[5]

2 RESULTS AND DISCUSSION

In earlier studies, we reported remarkable rate and diastereoselectivity enhancements in allyl- and crotylborations involving α-hydroxyketones,[6] α-oxocarboxylic acids[7] and β-hydroxyaldehydes and ketones.[8] We now wish to report that *B*-allyldiisopropoxyborane reacts with ß-ketoacids to produce tertiary homoallylic ß-hydroxycarboxylic acids. The reaction presumably proceeds through a bicyclic transition state (Scheme 1) to yield the desired product in good yield (Table 1).

Unlike other neighboring group assisted allylborations which require a base such as Et_3N,[6,7] the allylboration of β-ketoacids can be carried out in the absence of added base. In fact, when the reaction is run in the presence of one equivalent of Et_3N, decarboxylation occurs. A solvent study revealed that decarboxylation is also minimized when the reactions are carried out in ethereal solvents as opposed to less polar solvents such as dichloromethane.

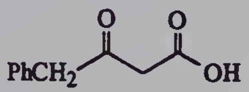
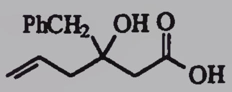
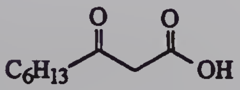
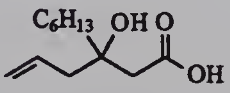
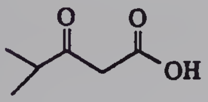
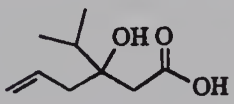


Scheme 1 *Proposed mechanism*

3 EXPERIMENTAL

The ß-ketoacids and *B*-allyldiisopropoxyborane were prepared according to published procedures.[9,10] In a typical experiment, the allylboronate (3 mmol in 20 mL of ether) is added dropwise to the ß-ketoacid (3 mmol in 20 mL of ether) at –10 °C. The reaction is warmed to room temperature and allowed to stir overnight. Aqueous $NaHCO_3$ (50 mL of a 5% solution) is then added to the reaction mixture. The aqueous layer is separated, acidified to pH ~1, and the product extracted into ethyl acetate (3 x 15 mL). The combined organic extracts are dried over anhydrous $MgSO_4$, filtered, and the solvent removed under reduced pressure. The product is then purified by column chromatography.

Table 1 *Reaction of β-ketoacids with β-allyldiisopropoxyborane*

β-Ketoacids	Products	Yield[a,b]
		65.0%
		79.8%
		80.8%

[a] Isolated yields. [b] Products characterized by elemental analysis, mass spectrometry, and appropriate NMR spectral data

4 ACKNOWLEDGEMENTS

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5 REFERENCES

1. Reviews of allylic chemistry: (a). Magid, R. M. *Tetrahedron*, **1980**, *36*, 1901; (b) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841.
2. (a) Evans , D. A. in *Asymmetric Synthesis*, Morrison, J. D. Ed. Academic Press, NY, **1984**, *3*, 1; (b) C. H. Heathcock, *Ibid.* **1984**, *3*, 11.
3. (a) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243; (b) Mukaiyama, T. *Challenges in Synthetic Organic Chemistry*, Clarendon Press, Oxford, **1990**.
4. Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489.
5. Hoffmann, R. W. *Chem. Rev.* **1989**, *86*, 1841.
6. Wang, Z; Meng, X.–J; Kabalka, G.W. *Tetrahedron Lett.* **1991**, *32*, 1945.
7. (a) Wang, Z; Meng, X.–J; Kabalka, G. W. *Tetrahedron Lett.* **1991**, *32*, 4619; (b) Wang, Z; Meng, X.–J; Kabalka, G. W. *Tetrahedron Lett.* **1991**, *32*, 5677.
8. Kabalka, G. W.; Narayana, C; Reddy, N. K. *Tetrahedron Lett.* **1996**, *37*, 2181.
9. Barnick, K.; Bann J. L.; Bickelhaupt, F. *Synthesis* **1979**, 787.
10. Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868.

Resolution of Racemic Diols and Amino Alcohols via Diastereomeric Borate Complexes

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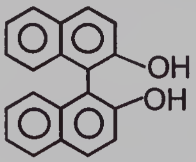
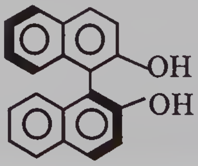
1. INTRODUCTION

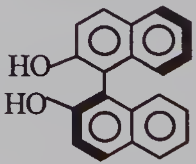
The chiral 1,1'-bi-2-naphthol **1**, has become one of the most widely used chiral compounds in chemistry.[1] The C_2 symmetry, rigid structure and highly stable chiral configuration of **1** play an important role in the use of chiral derivatives containing this moiety in stoichiometric and catalytic asymmetric organic reactions. Moreover, the 3,3'-, 4,4'- and 6,6'- positions can be selectively functionalised which further expands the scope of fine tuning the chiral discriminating ability of this moiety.



1-S and 1-R

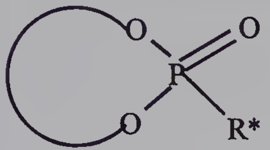


1-S



1-R

The racemic bi-2-naphthol can be readily produced on a large scale through oxidative coupling of 2-naphthol by air in the presence of a copper (II) catalyst.[2] Although asymmetric synthesis has been reported,[3] the preparation of enantiomerically pure bi-2-naphthol in large scale is generally carried out through resolution.[1] One of the versatile resolution methods involves the preparation and crystallisation of the phosphate complexes of the type **2**.[4] However, such phosphate complexes require $LiAlH_4$ for cleavage to obtain the bi-2-naphthol.[4] We have envisaged the preparation of the corresponding diastereomeric borate complexes **3-6** for use in resolution. Such borate complexes are expected to be solid derivatives and could be cleaved by hydrolysis to obtain bi-2-naphthol. Also, they can be readily prepared using inexpensive boric acid, diols, amines, amino acids and amino alcohols. Hence, in principle, it should be possible to devise resolution procedures for not only bi-2-naphthol but also a variety of other important chiral compounds based on such borate complexes. We have undertaken efforts to examine these possibilities. The results are described here.



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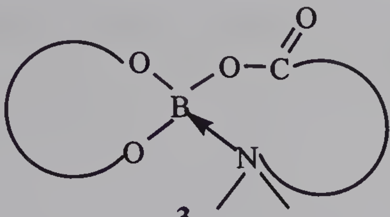

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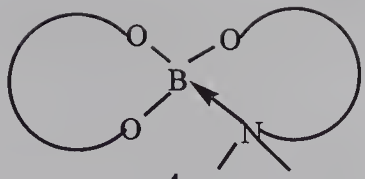

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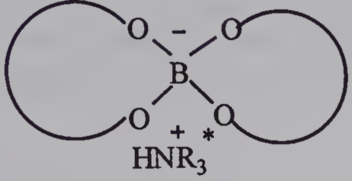

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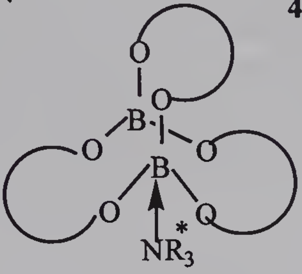
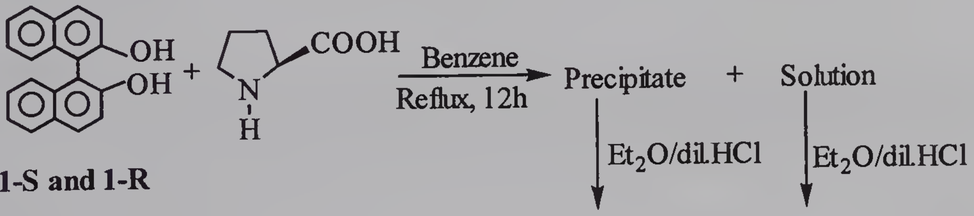


6

2. RESOLUTION OF RACEMIC 1,1'-BI-2-NAPHTHOL AND OTHER DIOLS USING S-PROLINE

Initially, studies on the preparation of the borate complexes of the type **3** using bi-2-naphthol, S-proline and $B(OH)_3$ were carried out. These experiments revealed that the bi-2-naphthol and S-proline form a 2:1 diastereomeric inclusion complex in the absence of boric acid (Scheme 1).[5] Unfortunately, efforts to improve the optical purity through crystallisation did not yield fruitful results. However, both the enantiomers can be obtained in pure forms by carrying out the experiments again using the partially resolved samples.[5]

Scheme 1



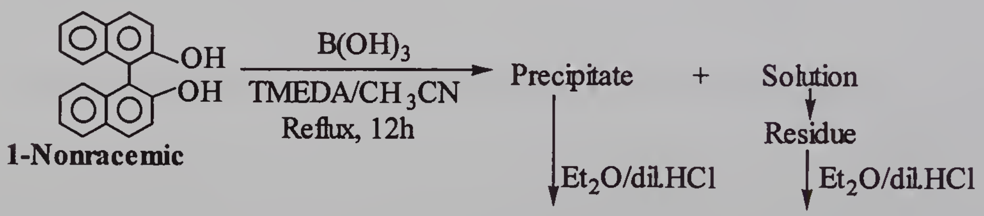
1-S and 1-R

1-S and 1-R, 0% ee	1-S, 65% ee (43%)	1-R, 44% ee (51%)
1-S, 10% ee	1-S, 64% ee (65%)	1-R, 70% ee (25%)
1-S, 65% ee	1-S, 87% ee (66%)	1-S, 06% ee (22%)
1-R, 44% ee	1-R, 90% ee (45%)	1-R, 06% ee (41%)
1-S, 87% ee	1-S, >99% ee (77%)	1-S, 35% ee (11%)
1-R, 90% ee	1-R, 98% ee (70%)	1-R, 28% ee (18%)

Later, it was observed that such partial resolutions can be also carried out in other solvents such as methanol, CH_2Cl_2 and CH_3CN to obtain enriched samples of 40% to 60% ee.[6] Also, some other racemic compounds (eg. 1,1,2-triphenylethane-1,2-diol and 2,3-diphenylsuccinic acid) were resolved via preparation of diastereomeric complexes using S-proline under similar conditions.[7]

It has been reported that the racemic bi-2-naphthol reacts with $BrBH_2.SMe_2$ complex to give a C_3 symmetric borate propeller of the type **6**.[8] The X-ray crystal structure analysis revealed that only the RRR and SSS isomers are formed and the RRS or SSR isomers are not formed in this reaction.[8] We have observed that this C_3 symmetric propeller can be readily prepared by heating bi-2-naphthol with $B(OH)_3$ in benzene.[6] Based on these observations, we have envisaged the enhancement of the enanantiomeric excess of partially resolved samples of bi-2-naphthol using calculated amounts of $B(OH)_3$. Indeed, this has been realised using $B(OH)_3$ and TMEDA in CH_3CN (Scheme 2).[6,9]

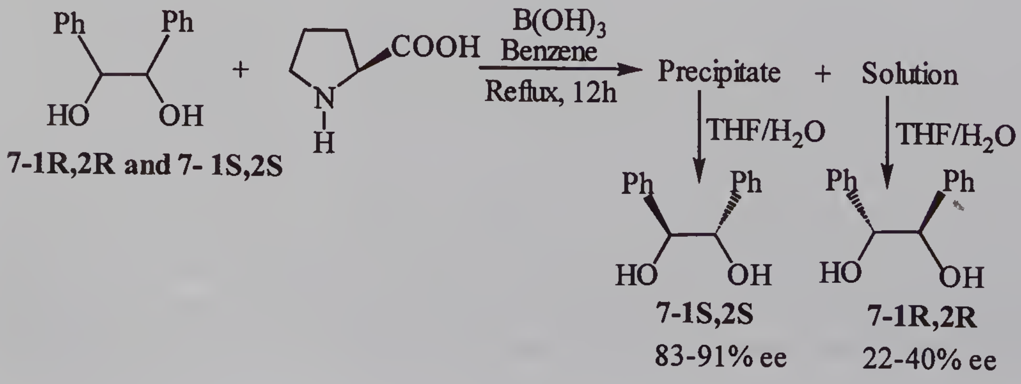
Scheme 2



1-R, 17% ee →	1-R, 89% ee (11%)	1-R, 03% ee (76%)
1-R, 34% ee →	1-R, 93% ee (31%)	1-R, 05% ee (55%)
1-R, 80% ee →	1-R, 94% ee (77%)	1-S, 06% ee (10%)
1-S, 18% ee →	1-S, 90% ee (13%)	1-S, 05% ee (75%)
1-S, 34% ee →	1-S, 96% ee (28%)	1-S, 01% ee (54%)
1-S, 76% ee →	1-S, 96% ee (77%)	00% ee (10%)

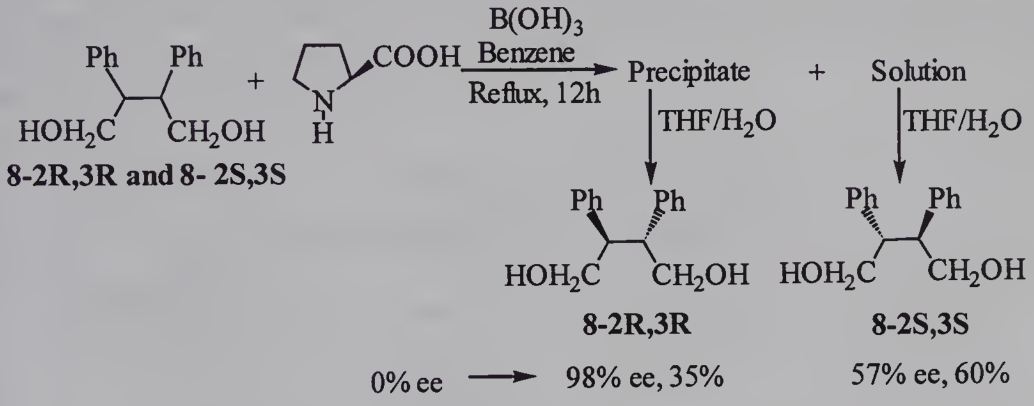
We have also examined the use of $B(OH)_3$ and S-proline for the resolution of several other diols. It was observed that 1,2-diphenylethane-1,2-diol 7, can be resolved through formation of borate complexes of the type **3** (Scheme 3).[7]

Scheme 3



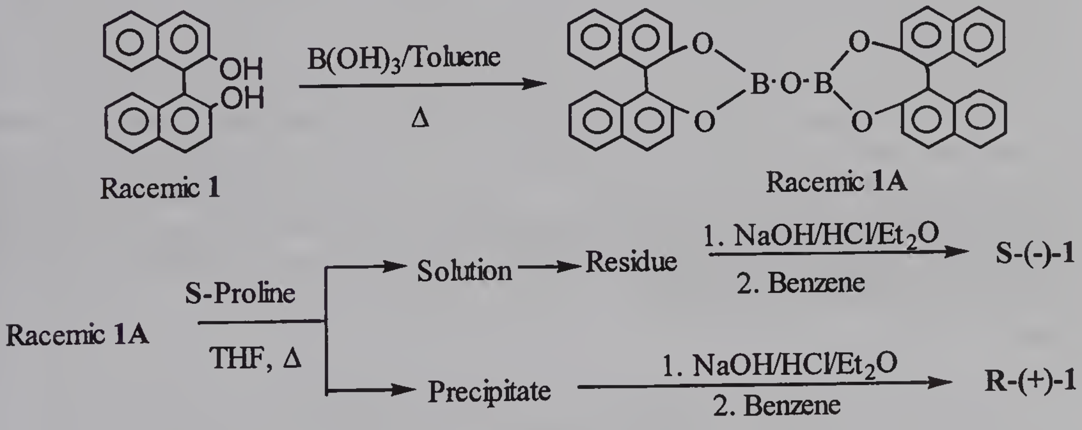
The racemic 2,3-diphenylbutane-1,4-diol **8**, can be prepared via oxidative coupling of phenylacetic acid esters using $TiCl_4/Et_3N$[10] followed by $NaBH_4/I_2$ reduction.[11] We have examined the resolution of this valuable racemic diol using $B(OH)_3$ and S-proline. The results are outlined in Scheme 4.[11b]

Scheme 4



Recently, Zhao *et al* reported that the bi-2-naphthol can be also resolved using S-proline through prior preparation of borates using $B(OH)_3$ followed by reaction with the amino acid (Scheme 5).[12]

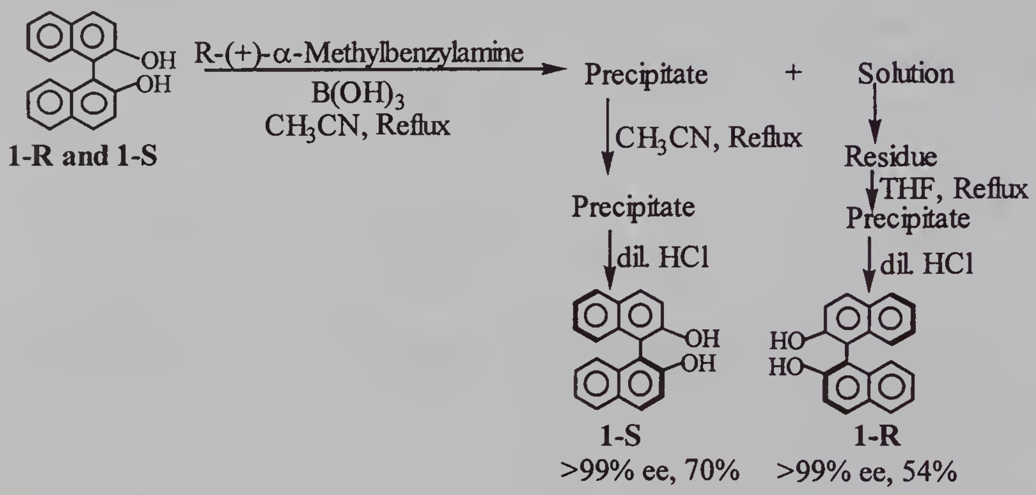
Scheme 5



3. RESOLUTION OF RACEMIC1,1'-BI-2-NAPHTHOL USING α-METHYLBENZYLAMINE AND $B(OH)_3$

Although the racemic bi-2-naphthol can be resolved using S-proline via diastereomeric inclusion complexes followed by enhancement of ee using $B(OH)_3$ and TMEDA[5,6,9] or preparation of a borate complex followed by reaction with S-proline,[12] it is somewhat difficult to recover the water soluble S-proline after work up. Hence, we have decided to investigate the use of readily available, inexpensive chiral amines such as α-methylbenzylamine for this purpose. After extensive investigations, it was observed that the chiral α-methylbenzylamine forms a Bronsted acid ammonium salt of the type **5** upon heating a mixture of the bi-2-naphthol, $B(OH)_3$ and the chiral amine in CH_3CN. The structure of the complex was further confirmed by X-ray crystal structure analysis.[13] We have also observed an interesting solvent effect on this reaction. Whereas the borate complex prepared from R-α-methylbenzylamine and S-bi-2-naphthol is insoluble in CH_3CN, the complex obtained using the same amine and R-bi-2-naphthol is insoluble in THF. This interesting solubility difference has been exploited in resolving (±)-bi-2-naphthol to obtain the enantiomers in >99% ee as shown in Scheme 6.[13] The chiral amine can be recovered in 90% yield after the resolution.

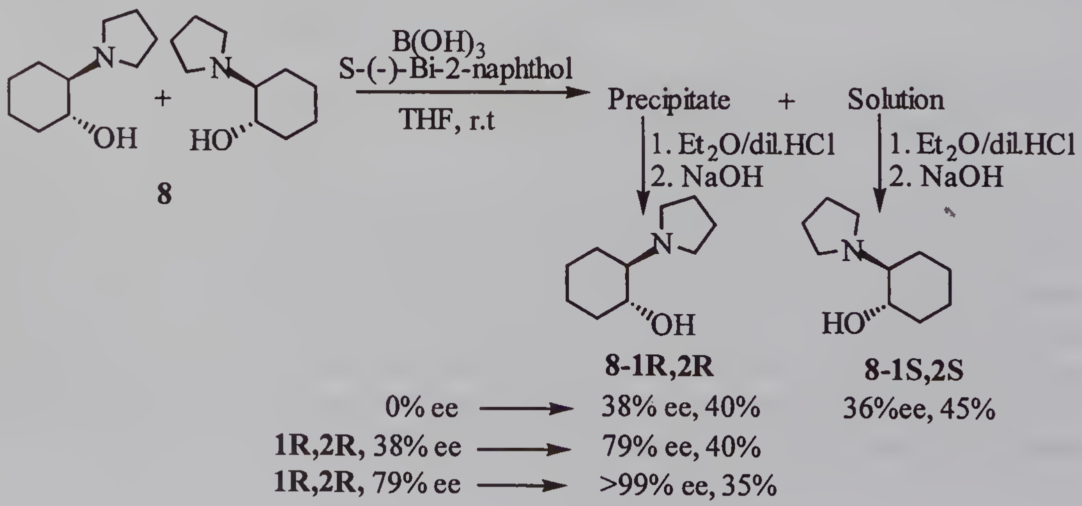
Scheme 6



4. RESOLUTION OF RACEMIC AMINO ALCOHOLS AND PUIFICATION OF DIASTEREOMERIC AMINO ALCOHOL USING CHIRAL BI-2-NAPHTHOL AND B(OH)$_3$

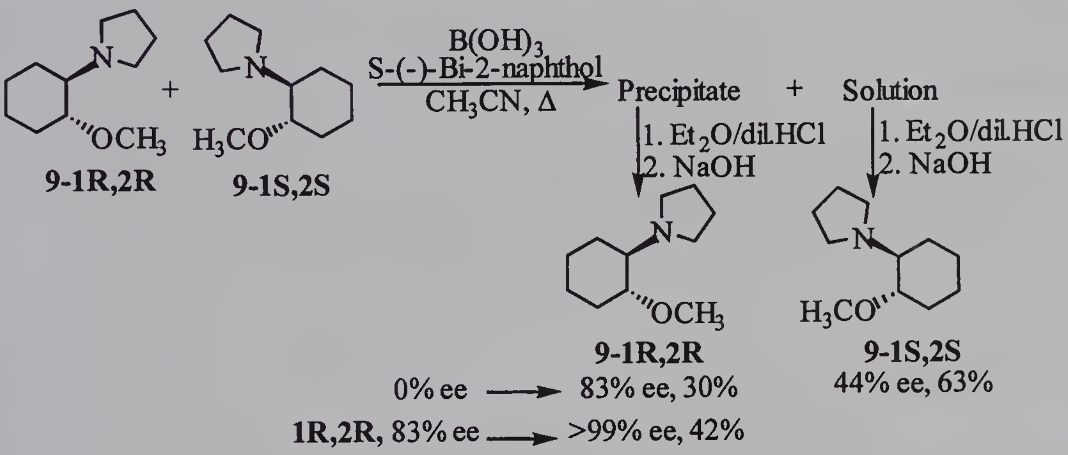
The chiral amino alcohols are important organic compounds, useful as chiral auxiliaries and starting materials for the synthesis of biologically active products. Some of them are also useful as therapeutic agents. A very simple way to access racemic amino alcohols is through opening of epoxides using amines.[14] We have examined the resolution of the racemic amino alcohols obtained in this way via preparation of diastereomeric borate complexes using chiral bi-2-naphthol.

Scheme 7



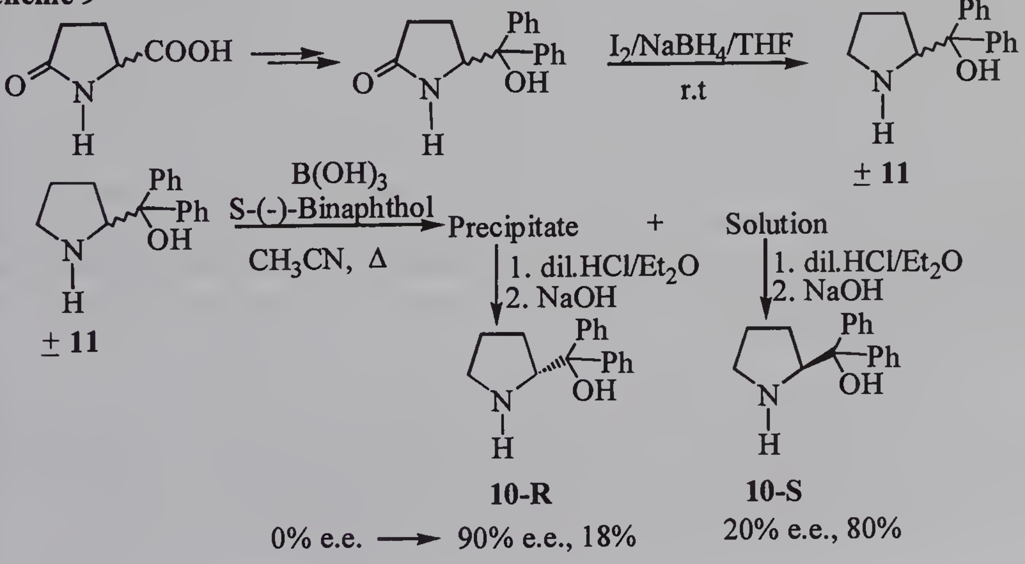
It was anticipated that the amino alcohol would form one of the borate complexes of the type **3-6** with bi-2-naphthol in the presence of boric acid. Indeed, this has been observed. The racemic amino alcohol **8** was resolved to obtain **8-1R,2R** in >99% ee in 3 repetitive operation shown in Scheme 7.[15] The IR spectrum indicated the presence of hydroxy group in the borate complex involved in this reaction (Scheme 7). However, the solid was not suitable for X-ray crystal structure analysis. Fortunately, however, the corresponding racemic methyl ether **9** gave better results in this resolution method (Scheme 8).[15] Also, X-ray crystal structure analysis indicated that the borate complex formed in this reaction is the Bronsted acid salt of the type **5**.[15]

Scheme 8



We have also examined the use of chiral bi-2-naphthol to resolve some other racemic amino alcohols. The S-diphenylpyrrolidinemethanol **S-10**, synthesised from S-proline is useful in the preparation of the CBS oxazaborolidine catalyst,[16] widely used in catalytic asymmetric reductions. Accordingly, the corresponding **R-10** enantiomer is also a valuable chiral compound.

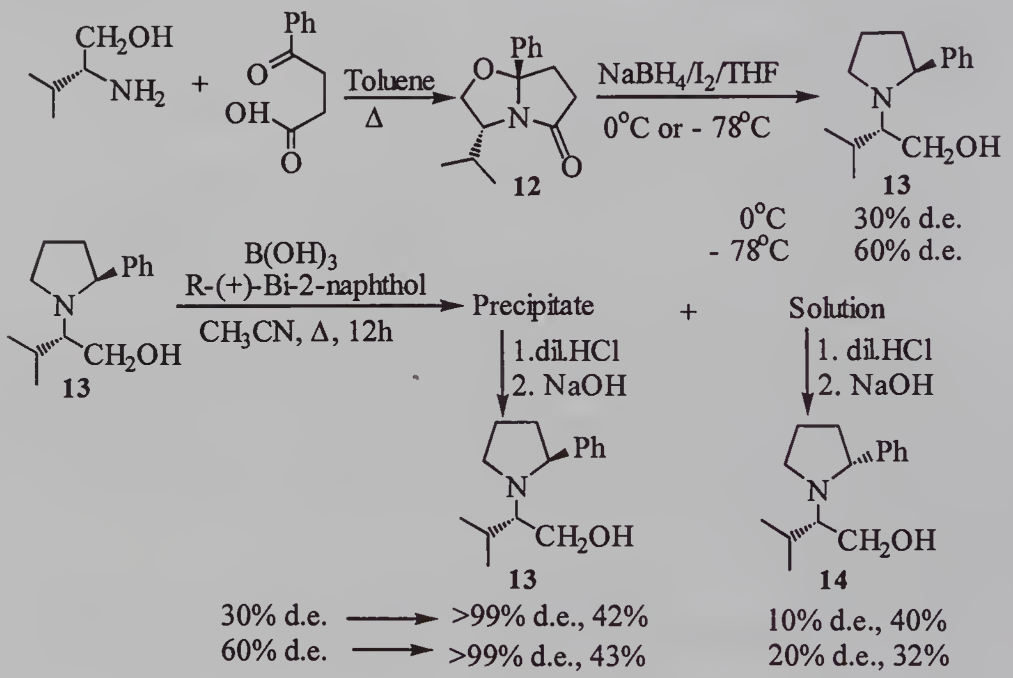
Scheme 9



It was of interest to examine the use of chiral bi-2-naphthol to resolve the racemic amino alcohol **11** that can be prepared starting from pyroglutamic acid (Scheme 9). Preliminary studies revealed that the resolution can be readily carried out using $B(OH)_3$ and chiral bi-2-naphthol (Scheme 9).[17] Further optimisation of the results and structural analysis of the borate complex involved in this reaction are under way.

The Meyers lactam **12**,[18] prepared starting from S-valinol, on reductive cleavage using the $NaBH_4/I_2$ reagent gives the amino alcohol **13**. Unfortunately, the product was not obtained in diastereomerically pure form (Scheme10). Fortunately, the mixture can be readily purified to obtain the amino alcohol in >99% d.e using chiral bi-2-naphthol and $B(OH)_3$.[19]

Scheme 10



In conclusion, simple, convenient methods have been developed for the resolution of racemic bi-2-naphthol **1**, the diols **7**, **8**, the amino alcohol derivatives **9**, **10** and **11** and purification of the diastereomeric amino alcohol **13**. Since some of these chiral diols and amino alcohols are widely used in large scale in asymmetric syntheses, it is anticipated that the new resolution procedures involving diastereomeric borate complexes described here will also find wide applicability.

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References

1. For an excellent recent review on the 1,1'-bi-2-naphthyl system see: L. Pu, *Chem. Rev.,* **1998**, 98, 2405.
2. (a) M. Noji, M. Nakajima and K. Koga, *Tetrahedron Lett.*, **1994**, 35, 7983. (b) Q. -S. Hu, D. Vitharana and L. Pu, *Tetrahedron: Asymmetry*, **1995**, 6, 2123. (c) M. Nakajima, *Chem. Pharm. Bull.*, **1998**, 46, 1814
3. (a) J. Brussee, A. C. A. Jansen, *Tetrahedron Lett.*, **1983**, 24, 3261. (b) M. Smrcina, M. Lorenc, V. Hanus, P. Sedmera and P. Kocovsky, *J. Org. Chem.*, **1992**, 57, 1917
4. (a) J. Jacques, F. Fouguey and R. Viterbo, *Tetrahedron Lett.,* **1971**, *4617.* (b) E. P. Kyba, G. W. Gokel, F. D. Jong, K. Koga, L. R. Sonsa, M. G. Siegel, L. Kaplan, G. D. Y. Sogah and D. J. Gram *J. Org. Chem.* **1977**, 42, 4173. (c) B. Gong, W. Chen and B. Hu, *J. Org. Chem.*, **1991**, 56, 423. (d) J. M. Brunel and G. Buono. *J. Org. Chem.*, **1993**, 58, 7313.
5. (a) M. Periasamy, *Pure & Appl. Chem.*, **1996**, 68, 663 (Presented at the IUPAC international conference in organic synthesis (ICOS 10), December 11-16, 1994, Bangalore, India, Abstract No. SL 36) (b) M. Periasamy, A. S. B. Prasad, J. V. B. Kanth and Ch. K. Reddy. *Tetrahedron: Asymmetry* **1995**, 6, 341.
6. M. Periasamy, L. Venkatraman and K. R. J. Thomas, *J. Org. Chem.*, **1997**, 62, 4302.
7. M. Periasamy, C. R. Ramanathan, A. S .B. Prasad and J. V. B. Kanth, *Enantiomer*, **1998**, 3, 3.
8. D. Kaufmann and R. Boese, *Angew. Chem. Int. Ed.*, **1990**, 29, 545.
9. L. Venkatraman and M. Periasamy, *Tetrahedron: Asymmetry*, **1996**, 7, 2471.
10. Y. Matsumura, M. Nishimura, H. Hiu, M. Watanabe and N. Kise, *J. Org. Chem.* **1996**, 61, *2809.*
11. (a) A. S. B. Prasad, J. V. B. Kanth and M. Periasamy, *Tetrahedron*, **1992**, 48, 4623 (b) V. Dharma Rao and M. Periasamy, *Unpublished results.*
12. Z. Shan, Y. Xiong, W. Li and D. Zhao. *Tetrahedron: Asymmetry*, **1998**, 9, 3985.
13. M. Periasamy, L. Venkatraman, S. Sivakumar, N. Sampathkumar and C. R. Ramanathan, *J. Org. Chem.* in press.
14. (a) L. Radesa, W. D. Bowen, L. D. Paolo and B. R. Decosta, J. Med. Chem., **1991**, 34, 3058. (b) G. Sekar and V. K. Singh, *J. Org. Chem.*, **1999**, 64, 287.
15. M. Periasamy, C. R. Ramanathan and N. Sampathkumar, *Tetrahedron: Asymmetry* in press.
16. E. J. Corey, R. K. Bakshi and S. Shibata, *J. Am. Chem. Soc.*, **1987**, 109, 5551. (b) E. J. Corey and C. J. Helal, *Angew. Chem. Int. Ed.*, **1998**, 37, 1986.(c) J. V. B. Kanth and M. Periasamy, *Tetrahedron*, **1993**, 49, 5127. (d) E. J. Corey, A. Guzman-perez and S. E. Lazerwith, *J. Am. Chem. Soc.*, **1997**, 119, 11769.
17. S. Sivakumar and M. Periasamy, *Unpublished results.*
18. A. I. Meyers and L. E. Burgess, *J. Org. Chem.* **1992**, 57, 1656.
19. V. Dharma Rao and M. Periasamy, *Unpublished results.*

Recent Developments in the Use of α,β-Unsaturated Boronates as Partners in Diels–Alder Cycloadditions

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1 INTRODUCTION

The Diels-Alder reaction of dibutyl vinylboronate with cyclopentadiene was first reported by Matteson and co-workers in 1963 [1]. A mixture of dibutyl endo-norboneneboronate (1) and its exo-isomer (2) in roughly equal amounts was obtained.

(1) (2)

C-substituted vinylboronic esters were investigated by Evans and co-workers [2]. These early reports have shown that vinylboronic esters are sluggish dienophiles. This may be due to the back bonding from the ligands to the vacant p-orbital of boron. This is corroborated by the fact that vinyldiaminoboronic derivatives are completely unreactive towards cyclopentadiene even at 170°C [3]. Singleton and Martinez have shown that 9-vinyl-9 BBN is a much more reactive dienophile than vinylboronic esters and reacts 200 times faster than methylacrylate with butadiene at 25°C [4]. It is also considered as an omniphilic dienophile in that it is relatively insensitive to the structure of the diene [5]. Quantum mechanical calculations indicate that the boron atom bonds significantly to the terminal carbon atom of the diene in the endo transition state, and that the B-C distances in the exo transition state are longer. The relative transition state energies fits the experimental results well [6]. 9-(trimethylsilylethynyl)-9-BBN was also found to be a useful dienophile [7,8]. Nevertheless, one drawback of these dienophiles is their sensitivity to oxidation and moisture. This report focuses on synthesis of vinylboronates bearing an electronwithdrawing group on the double bond β to the boryl group and their reactivity towards dienes. These compounds appeared to be air stable and reactive dienophiles. The second topic presented in this report deals with the synthesis of 1-dialkoxyboryl-1,3 dienes, their use as partners in the Diels-Alder cycloaddition-homoaldolisation tandem reaction and the corresponding 1,3-dienylborates as well.

2 RESULTS AND DISCUSSION

2.1 Synthesis of vinylboronates β–substituted by an electron withdrawing group [9]

Since boronates derived from pinacol are air stable, we decided to prepare olefins of type (4) according to the following sequence :

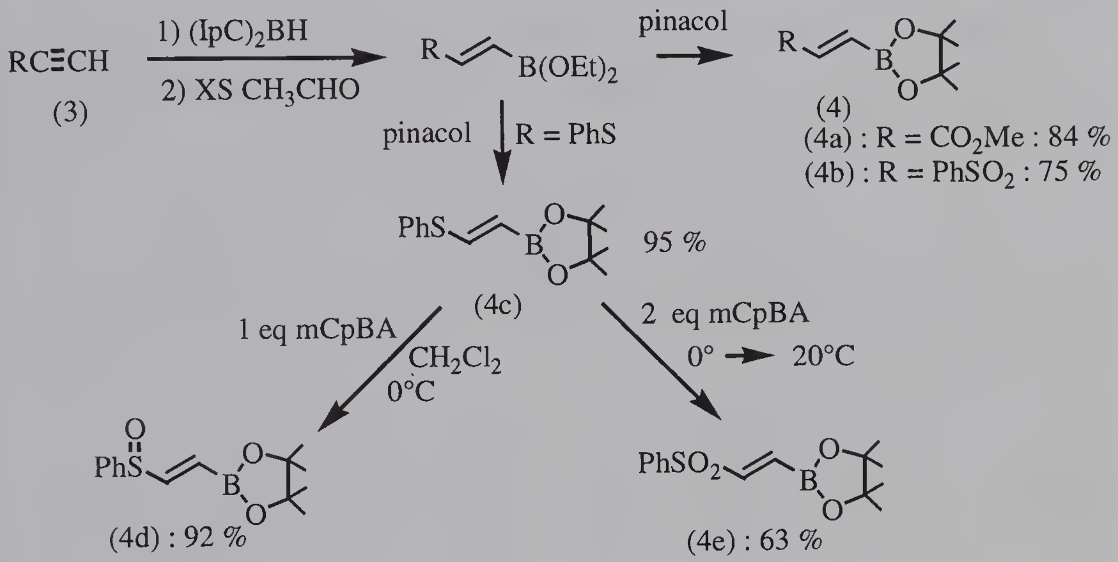


Figure 1 *Synthesis of vinylboronates (4a-e)*

The hydroboration of acetylenes (3) with diisopinocampheylborane $(IpC)_2BH$ in THF led after refunctionalisation and transesterification to the olefins (4a, b, c) isolated in good yields. Monooxidation with mCpBA led to the sulfoxide (4d) whereas the sulfone (4e) was obtained with two equivalents of mCpBA. The same sulfone (4e) could also be obtained in an excellent overall yield by radical addition of phenylsulfonyl iodide to the pinacol ester of vinylboronic acid followed by a dehydroiodination in the presence of Et_3N (87 % overall yield). The carboxylic ester (4a) could be transformed into the corresponding carboxylic acid (4f) (79 % yield) [11] which led to the acid chloride (4g) by treatment with freshly distilled thionyl chloride at 0°C (91 % yield). β–keto vinylboronates are easily accessible by oxidation of the corresponding protected allylic alcohol according to the following scheme :

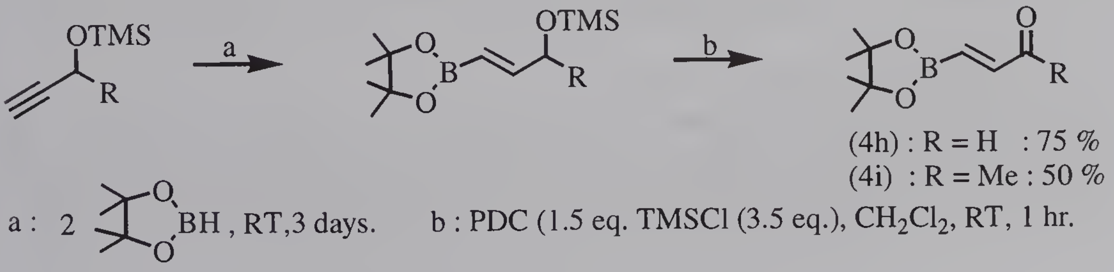
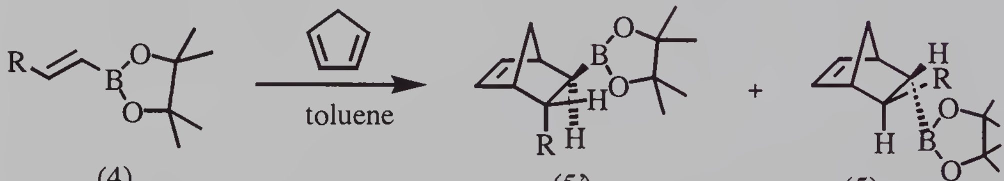


Figure 2 *Synthesis of vinylborates (4h) and (4i).*

Hydroboration of (5) with an excess of pinacolborane at room temperature for 3 days in the absence of solvent followed by oxidation with PDC in the presence of an excess of TMSCl led to the aldehyde (4h) and the ketone (4i) (75 % and 50 % from (5h) and (5i) respectively after bulb to bulb purification) [12,13]. Several other β-keto vinylboronates were obtained in good yields via the addition of organozinc or organocuprates to the aldehyde (4h) followed by a PCC oxidation of the corresponding allylic alcohols [14].

2.2 Diels-Alder cycloaddition of boronic esters 4

Boronic esters (4a-4i) are good dienophiles [9,10,13,15] and can react with cyclopentadiene even at -10°C as shown below.



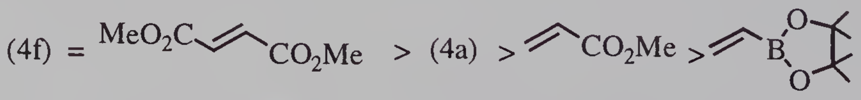
(4) (5') (5)

R	50°C(1)		20°C(1)		-10°C(1)	
	Time(1)	5/5'(2)	time(1)	5/5'(2)	time(1)	5/5'(2)
COOMe	14 hrs	81/19	3 days	88/12	7 days	89/11
COOH	2 hrs	88/12	6 hrs	89/11	2 days	91/09
COCl	45 min	91/09	1.5 hrs	93/07	5 hrs	95/05
p-$MeC_6H_5SO_2$	4 hrs	84/16	12 hrs	86/14	7 days	93/07
CH_3CO	8 hrs	75/25	-		-	
HCO	-		2 hrs	86/14	30 hrs	90/10

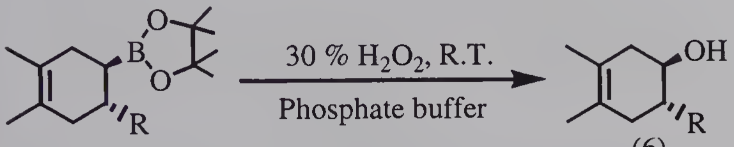
(1) time and temperature for the reaction to go to completion. (2) endo/exo ratio

Figure 3 *[4+2] cycloaddition of boronic esters (4) with cyclopentadiene.*

It is worth mentioning that the endo selectivity is quite good at room temperature or below and that the endo directing groups are the R groups. The reactions with other 1,3-dienes also proceed in good yields at higher temperatures, typically 80 to 110°C, as expected, leading to a wide variety of cyclohexenylboronates. A comparative study establishes the following order of reactivity [15].



The Lewis acid catalysed Diels-Alder cycloaddition of the ketone (4i) with cyclopentadiene allows a complete endo selectivity to be reached. Accordingly, the reaction of (4i) with 1.5 equivalents of cyclopentadiene in the presence of one equivalent of $Cl_2Ti(OiPr)_2$ in toluene at 0°C for12 hrs led exclusively to (5i) which has been isolated in 70 % yield. In the presence of 1.5 equivalents of the oxazaborolidine derived from L-Nmesitylsulfonylvaline and borane dimethylsulfide, an 66 % yield of the endo adduct (5i) was obtained in an 49 % ee [13]. Further transformations of the cyclohexenylboronates obtained from these cycloadditions can be performed. Two examples follow. First, the oxidation by H_2O_2 in the presence of phosphate buffer at room temperature in THF of 2,3-dimethylbutadiene adducts led to the corresponding trans cyclohexenols (6) in good yields (figure 4).

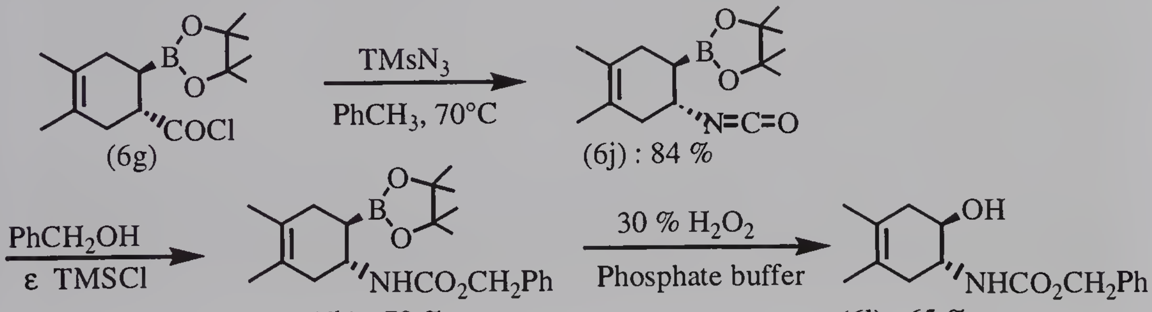


(6)

R	% yield
$ArSO_2$	57
CO_2CH_3	68
CO_2H	68

Figure 4 *oxidation of the C-B bond of some D.A. adducts.*

The two functional groups of (6g) could also be transformed i,e the acid chloride into the isocyanate (6j) (84 %) via a Curtius rearrangement and then into the carbamate (6k) (78%) which oxidation led to the amino alcohol (6l) (65 %). All these transformations are stereoselective (Figure 5).



(6g)

(6j) : 84 %

(6k) : 78 %

(6l) : 65 %

Figure 5 *Functional group transformations in (6g)*

The intramolecular Diels-Alder reactions involving boryl-3-propenoic acid derivatives has been addressed to. So, heating the trienylamide (7) at 80°C in toluene for 15 hours led to a 1/3 mixture of the cycloadducts (8) and (8') isolated in 72 % yield (figure 6) [17]. The trienylamide (9) could not be isolated since the IMDA occured at the temperature of the coupling step, i,e below 0°C in ether for 30 minutes. This very fast cyclisation led to a 85/15 mixture of cycloadducts (10) and (10') having respectively a cis and trans junction in the bicyclic structure. The cis bicyclic structure (10) results from an endo approach of the diene and the dienophile. This is in agreement with literature data [18].

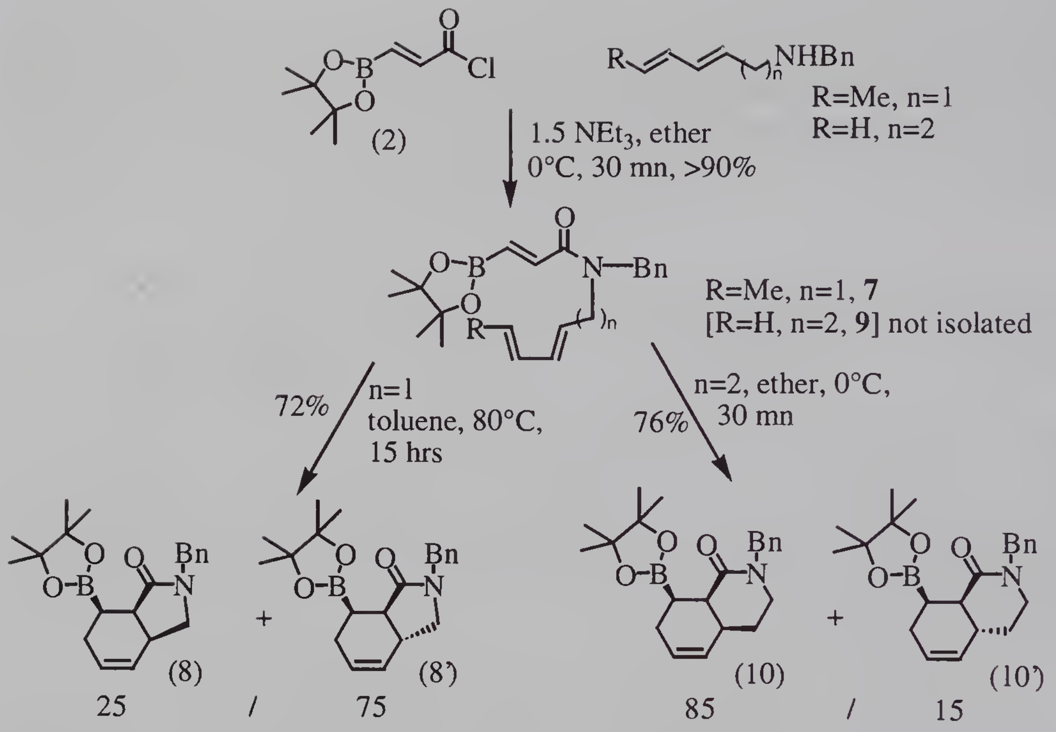
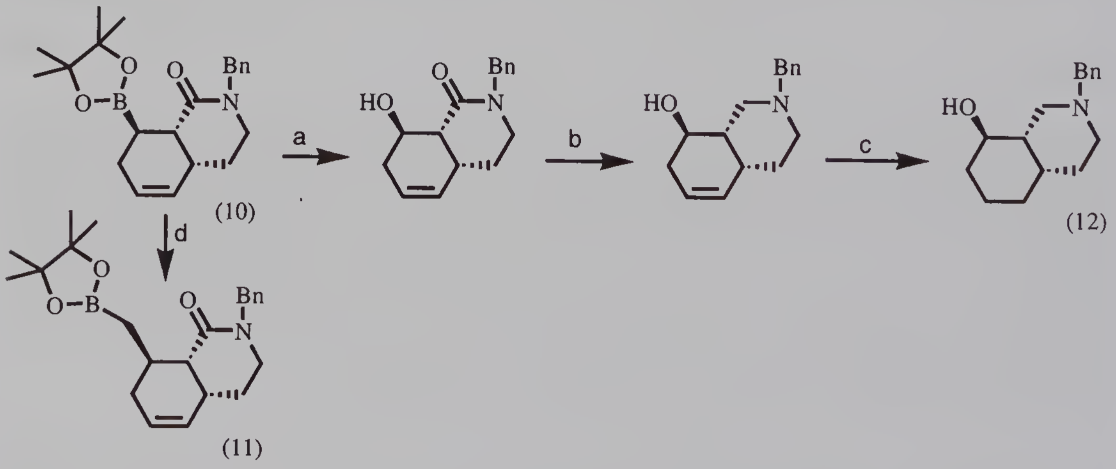


Figure 6 *IMDA of trienamides (7) and (9)*

Further transformations of the easily purified lactam (10) could be achieved. For example, homologation led to the new boronate (11) in 70 % yield whereas an oxidation followed by reductions led to the decahydroisoquinolin-8-ol (12) according to the following sequence (figure 7).

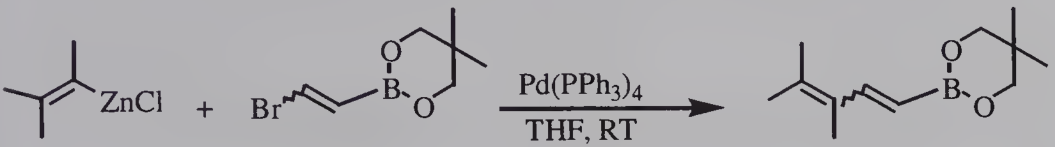


(a) H_2O_2, THF-phosphate buffor, 71%; (b) $LiAlH_4$, ether, 71%; (c) H_2, Pd/C.AcOEt, 63%; (d) $LiCH_2Br$, THF. -95°C, 70%.

Figure 7 *Some further transformations of the IMDA adduct (10)*

2.3 Synthesis and reactivity of 1-(dialkoxyboryl)-1,3-dienes

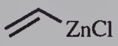
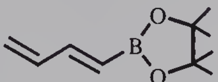
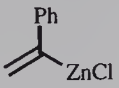
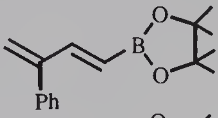
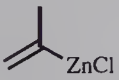
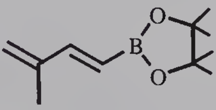
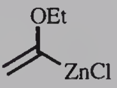
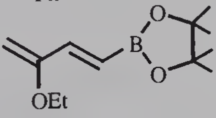
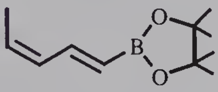
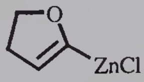
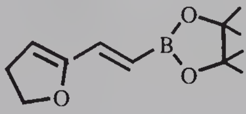
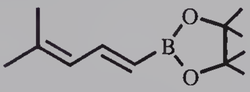
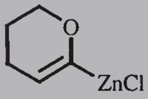
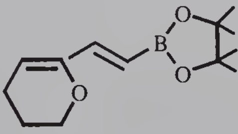
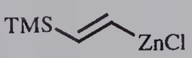
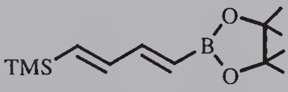
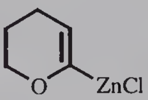
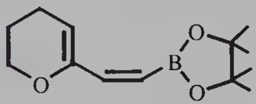
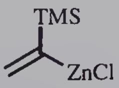
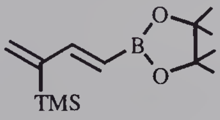
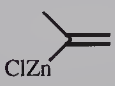
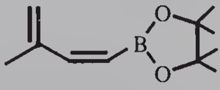
These 1,3-budienyl-1-boronic esters are of particular interest since their Diels-Alder cycloaddition leads to allylboronates with a fixed Z configuration, their double bond which is part of the cyclohexenyl moiety. One possible preparation of these compounds is the hydroboration of enynes with disubstituted boranes such as diisopinocampheylborane, dicyclohexylborane or catecholborane [18,19]. A much more general and stereoselective sequence involves a palladium (O) catalyzed cross-coupling reaction of the boronic esters (13) and (14) with various alkenyl zinc according to figure 8 [21].



(13) : E
(14) : Z
(15)

Figure 8 *Synthesis of dienylboronates by coupling*

E and Z boronic esters (13) and (14) were made easily accessible by bromoboration of acetylene followed by esterification of the resulting dibromoboranes [21,22]. The Pd(O) cross-coupling reaction occurs under mild conditions at room temperature leading to a wide variety of the butadienylboronic esters (15) with all possible combination of configurations of the conjugated double bonds as related in table 1.

Organozinc	Diene (15)	Yields%[(a)]	Organozinc	Diene (15)	Yields%[(a)]
		51			67
		79			62
		72			63
		65			66
		82			50
		79			65

[(a)] Yields refer to isolated pure (15).

Table 1 *Synthesis of 1,3-butadienyl-1-boronic esters (15)*

These dienes (15) can be engaged in a tandem sequence [4 + 2] cycloaddition followed by the allylboration of an aldehyde which leads to cyclohexenyl alcohols after hydrolysis. This is illustrated below by a sequence involving a D.A cyloaddition with maleic anhydride (figure 9) [19,22]. The excellent diastereoselectivity of this multistep sequence and the very good isolated yields of the bicyclic lactones (16) must be pointed out. Another interesting feature is that an allylsilane (16) is obtained when R = Me_3Si which opens the way for further functionalisation.

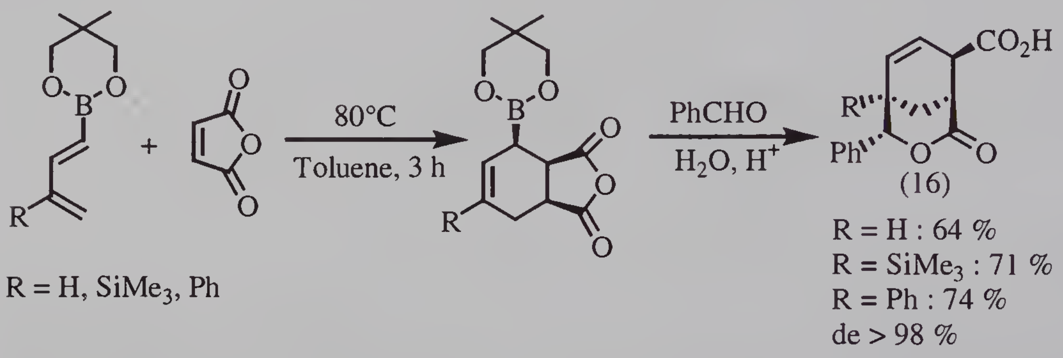


Figure 9 *Tandem D.A-homaldolisation*

This sequence has been used by the group of Lallemand in an approach to the total synthesis of clerodine including the use of chiral 1,3-dienylboronates [23]. Extension of this work to the IMDA is illustrated in figure 10 [24]. The bicyclic lactone (18) has been obtained stereoselectively in an 47 % isolated yield from the yne diene (17) in a one pot sequence with control of the relative stereochemistry of five asymmetric centers including a quaternary one.

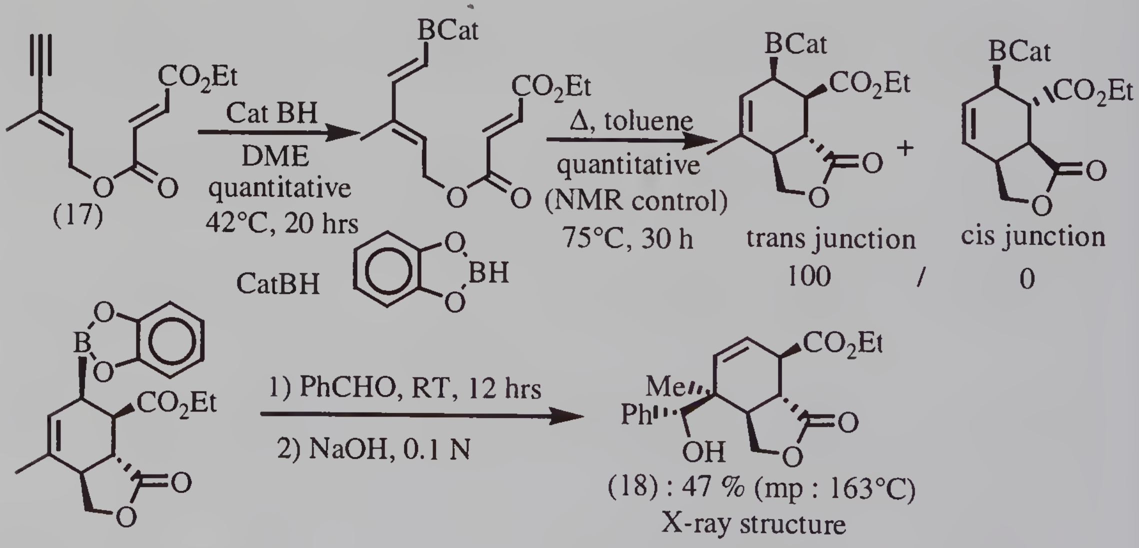
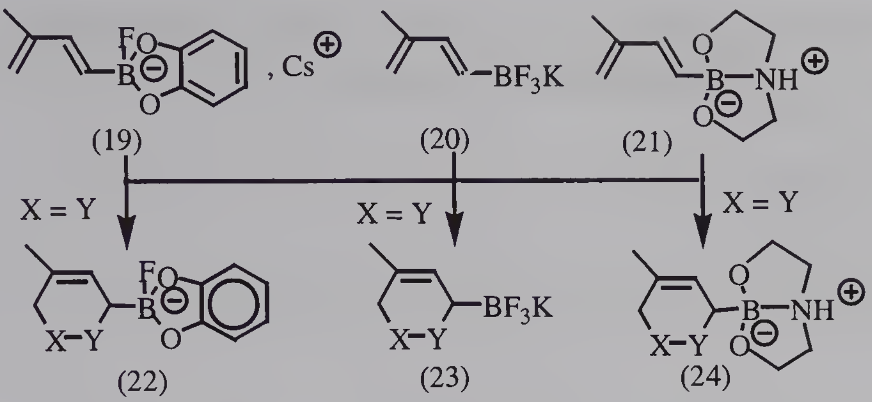


Figure 10 *IMDA-homoaldolisation-hydrolysis sequence involving 1,3-butadienyl-1-boronic esters*

In an extension of this work, we have shown that 1,3-dienylborates including compounds (19), (20), (21) are exceptionally reactive and stereoselective dienes, far more reactive than dienylboronates (15) in Diels-Alder reactions [25]. Interestingly, the reaction could be carried out in aqueous medium in some cases and led to the adducts (22), (23), (24) (figure 11).



(19) (20) (21)

(22) (23) (24)

Figure 11 *[4 + 2] cycloaddition of 1,3-dienylborates*

References

1. D.S. Matteson and J.O. Waldbilig, *J. Org. Chem.*, 1963, **28**, 366.
2. D.A. Evans, A.M. Golob, N.S. Mandel and G.S. Mandel, *J. Am. Chem. Soc.*, 1978, **100**, 8170.
3. G. Goindard and J. Braun, *Bull. Soc. Chim. Fr.*, 1972, 817.
4. D.A. Singleton and J.P. Martinez, *J. Am. Chem. Soc.*, 1990, **112**, 7423.
5. D.A. Singleton, J.P. Martinez and J.V. Watson, *Tetrahedron Letters,* 1992, **33**, 1017.
6. D.A. Singleton, *J. Am. Chem. Soc.*, 1992, **114**, 6563.
7. D.A. Singleton and J.P. Martinez, *Tetrahedron Letters,* 1991, **32**, 7365.
8. D.A. Singleton and A.M. Redman, *Tetrahedron Letters,* 1994, **35**, 509.
9. C. Rasset-Deloge, P. Martinez-Fresneda and M. Vaultier, *Bull. Soc. Chim. Fr.*, 1992, **129**, 285.
10. P. Martinez-Fresneda and M. Vaultier, *Tetrahedron Letters*, 1989, **30**, 2929.
11. E.D. Laganis and B.L. Chenard, *Tetrahedron Letters,* 1984, **25**, 5831.
12. C. Rasset-Deloge and M. Vaultier, *Bull. Soc. Chim. Fr.*, 1994, **131**, 919.
13. C. Rasset-Deloge and M. Vaultier, *Tetrahedron*, 1994, **50**, 3397.
14. G. Lorvelec, Ph.D. Thesis, University of Rennes, 1998.
15. E. Jehanno and M. Vaultier, *Tetrahedron Letters*, 1995, **36**, 4439.
16. C. Rasset-Deloge, Ph.D. Thesis, University of Rennes, 1992.
17. B. Lorvelec and M. Vaultier, *Tetrahedron Letters,* 1998, **39**, 5185.
18. J.L. Gras and M. Bertrand, *Tetrahedron Letters,* 1979, **20**, 4549.
19. M. Vaultier, F. Truchet, B. Carboni, R.W. Hoffmann and I. Denne, *Tetrahedron Letters*, 1987, **28**, 4169.
20. F. Truchet, Ph.D. Thesis, University of Rennes, 1987.
21. C. Mazal and M. Vaultier, *Tetrahedron Letters*, 1994, **35**, 3089.
22. C. Mazal and M. Vaultier, unpublished results.
23. P.Y. Renard and J.Y. Lallemand, *Bull. Soc. Chim. Fr.*, 1996, **133**, 143. G. Ohanessian, Y. Six and J.Y. Lallemand, *Bull. Soc. Chim. Fr.*, 1966, **133**, 1143. P.Y. Renard and J.Y. Lallemand, *Tetrahedron Asymmetry,* 1996, **7**, 2523. P.Y. Renard, Y. Six and J.Y. Lallemand, *Tetrahedron Letters*, 1997, **38**, 6589. Y. Six and J.Y. Lallemand, *Tetrahedron Letters*, 1999, **40**, 1295.
24. P. Bouju and M. Vaultier, to be published.
25. L. Garnier, B. Plunian, J. Mortier and M. Vaultier, *Tetrahedron Letters*, 1996, **37**, 6699. J. Mortier, M. Vaultier, B. Plunian and L. Toupet, *Heterocycles*, 1999, **50**, 703.

Novel Silyl-mediated 10-TMS-9-BBD Organoborane Reagents for Asymmetric Synthesis

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INTRODUCTION

Organoboranes have evolved over the past three decades to play a central role in the hierarchy of reagents for asymmetric synthesis.[1] Applications of these versatile intermediates to asymmetric processes include, among others, reduction,[1f,g] hydroboration,[1a,f,g] allylboration,[1e-g,2] homologation,[1b,f] enolboration (crossed aldol condensation)[1c,d,h] and allenylboration.[1i,j] Chirality transfer normally results through reagent/substrate stereoelectronic interactions which lead to energetically different transition states for each of the possible diastereomeric boron products with one being produced preferentially. Through an oxidative or hydrolytic work-up, the boron-containing moiety is removed, resulting in an optically active product. In the present study, three (3) of these asymmetric processes, namely asymmetric hydroboration, allylboration and allenylboration will be examined employing the new chiral stationary boron ligation, the 10-trimethylsilyl-9-borabicyclo[3.3.2]decane (10-TMS-9-BBD] ring system.

The most commonly employed asymmetric stationary chiral ligation is derived from optically active terpenes, amino alcohols and acids, tartrates, diols, diamines or sugars.[1] The ability of these ligands to provide an asymmetric environment for reactions which occur at the boron center determines their effectiveness for the specific application under consideration. Many chiral ligands have proven useful in this regard, a fact due in no small part to the fact that boron forms strong bonds to carbon, nitrogen and oxygen providing chiral organoboranes which retain their integrity once they are assembled as an asymmetric intermediate. Representative examples[1b,e-j,2] of these chiral auxiliaries which have found useful applications in asymmetric synthesis are shown in Figure 1.[3]

For the asymmetric hydroboration of prochiral alkenes, three reagents: diisopinocampheylborane (Ipc_2BH, *cf* **h**),[4] monoisopinocampheylborane ($IpcBH_2$, *cf* **o**),[5] and Masamune's borolane (2,5-DMB, *cf* **f**)[6] have been proven to be highly useful. Each has unique properties which add to their value for specific applications and also limit their value for others. The first is effective for unhindered *cis*-alkenes (*cis*-2-butene (98.4% ee)), the second for *trans* and tri-substituted alkenes (~70% ee) and the third for all three (~99% ee). To gain a broader perspective on the scope and limitations of these reagents, it is important to examine these asymmetric hydroborating agents in more detail. The Ipc_2BH reagent is effective only for *cis*-alkenes and related cyclo- and heterocyclic alkenes because more hindered alkenes react sufficiently slowly so that the reagent undergoes dehydroboration producing α-pinene and $IpcBH_2$. Since $IpcBH_2$ hydroborates alkenes faster than does Ipc_2BH

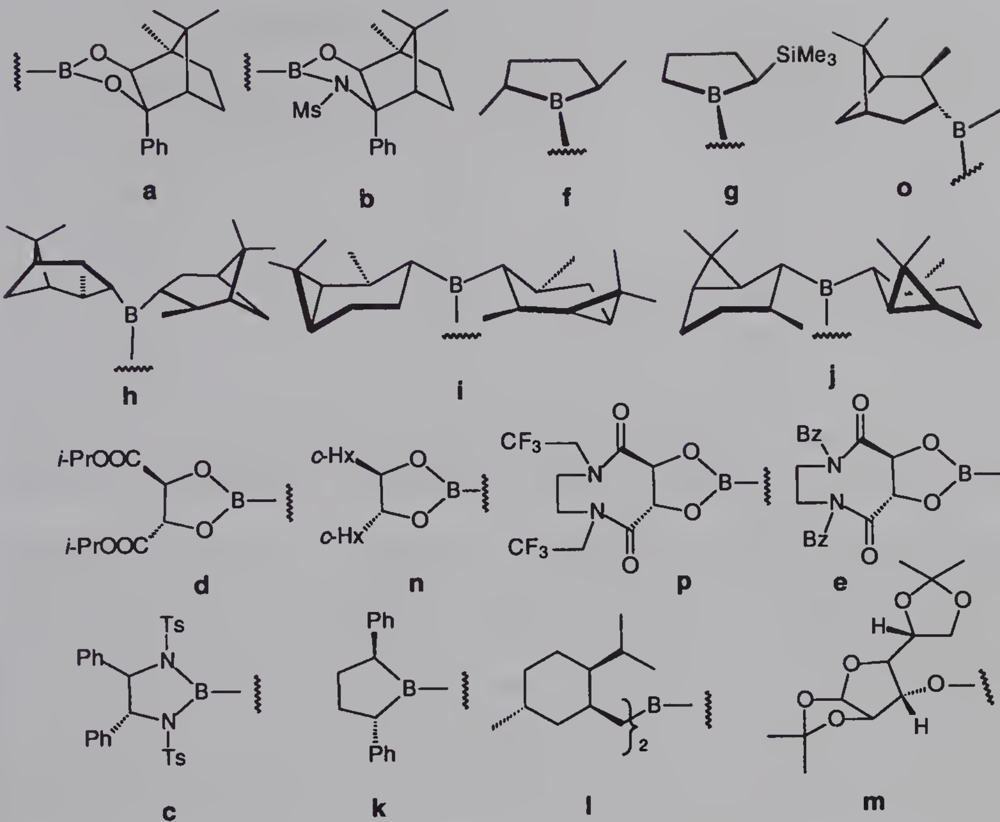


Figure 1 *Common chiral ligation for asymmetric organoborane conversions*

exhibiting the opposite enantiofacial selectivity, low ee's are obtained from more hindered alkenes. Thus, for the asymmetric hydroboration of these more hindered systems (*trans* and tri-substituted alkenes), IpcBH$_2$ is synthetically useful giving ~70% ee. For selected substrates, the selectivity is higher and in some cases, the enantiomerically pure dimeric adducts crystallize from solution giving optically pure organoboranes which are highly useful for many organoborane processes. However, this is not a general phenomenon. The 2,5-DMB reagent is highly selective for *cis*- and *trans*-as well as for tri-substituted alkenes (>97% ee). The problem with this reagent is its lack of accessibility being prepared through a multi-step process which requires two separate resolutions. None of the reagents are effective for 1,1-disubstituted alkenes. Many of the systems shown in Figure 1 are highly effective for the asymmetric allylboration process and the tartrate (**d**) and 1,3,2-diazaborolane (**c**) have been also successfully applied to the analogous allenylboration process.[1i,j]

RESULTS AND DISCUSSION

Preparation of the 10-TMS-9-BBD ring system

As a dialkylborane, 9-borabicyclo[3.3.1]nonane (9-BBN-H) is unrivaled in both stability and selectivity, making it one of the most useful hydroborating agents known.[7] The trialkylborane adducts derived from this reagent are also generally thermally stable and isolable in pure form. For many conversions, the 9-BBN moiety functions effectively as spectator ligation (*e. g.* Suzuki-Miyaura coupling).[8] However, for other processes, the 9-BBN ring can participate or even dominate the observed chemistry. This phenomenon

Table 1 *TMSCHN$_2$ insertion into **2** to provide 10-TMS-9-BBDs (**1**)*

Series	*R*	*Yield of **1** (%)*[a]	*^{11}B NMR (δ)*[b]
a	Me	82	80.5
b	Bu	100	80.9
c	*c*-Hx	100	81.0
d	*t*-Bu	NR	(84.3)[c]
e	*trans*-(*t*-Bu)CH=CH	100	74.3
f	OMe	76	55.0
g	*s*-Bu	96	85.4

[a] Yields are reported for spectroscopically pure material with the exception of **1a** and **1f** which are yields of distilled products. [b] 96 MHZ, C_6D_6 solution. [c] Prepared by an alternative route (*vide infra*).

commonly occurs for processes involving 1,2-migrations (*c.f.* Figure 2), for which the trimethylamine *N*-oxide oxidation of *B*-R-9-BBNs serves as representative.[9] The resulting borinate esters (OBBDs) are remarkably resistant to further oxidation even being stable in the open atmosphere. Moreover, in contrast to **2**, the BBD ring systems are very stable toward further insertion processes providing the desired BBD derivatives in high yield. This suggested that mechanistically related processes could be used to produce the 9-borabicyclo[3.3.2]decanes (*e.g.* **1**) through the insertion of TMSCHN$_2$. Precedence for this reactivity was available from the early studies of Hooz, *et al.* from the reaction of ethyl diazoacetate with **2** which give oxidation products that indicate ring B-C rather than B-R bond insertion occurs with 9-BBN derivatives.[10]

The reaction of TMSCHN$_2$ was carried out with representative examples of **2** which, with the exception of R = *t*-Bu, undergo clean insertion in 1-2 h at reflux temperature in hexane solution providing **1** efficiently (Table 1). These intermediates which contain the boron atom in a rigid bicyclic system represent a new generation of asymmetric boron ligation, one which not only can provide a well-defined chiral environment, but also, a stable bicyclic ring system which neither participates in the organoborane conversion nor undergoes isomerization nor decomposition under a wide variety of reaction conditions.

Consistent with the resistance of a *t*-Bu group to occupy an axial position in a cyclohexyl ring system (*cf* TS model, Figure 2), **2d** failed to react with TMSCHN$_2$ even with prolonged heating. This derivative **1d** was prepared by the reaction of **1f** with LiBu-*t* in pentane which requires 20 h at 25 °C to reach completion (*cf* **1b** (<1 h) from **1f** and LiBu).

As can be inferred from the data presented in Table 1, the TMSCHN$_2$ ring insertion process appeared to be a very general route to 10-TMS-9-BBD systems, the reactivity of 9-BBN-H dimer was examined as a potential

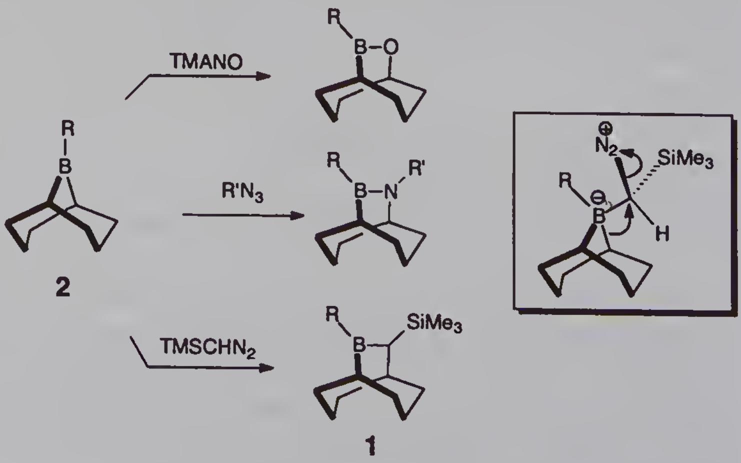
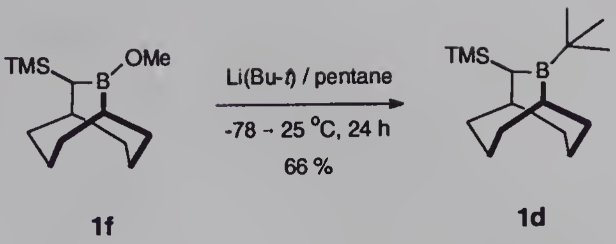
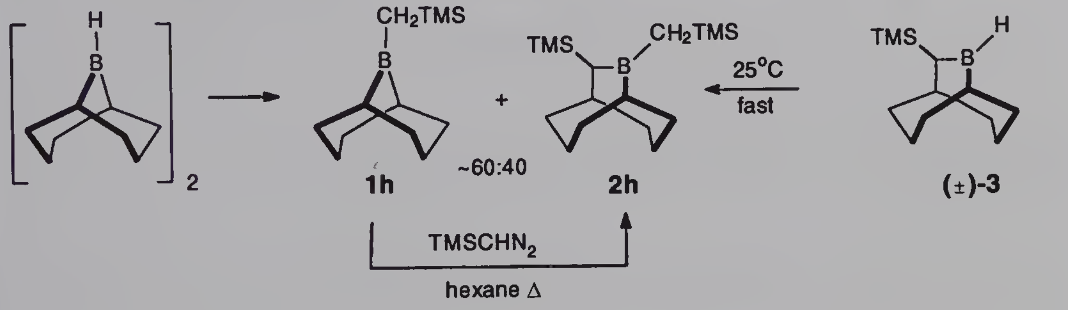


Figure 2 *Selected insertion processes for **2***



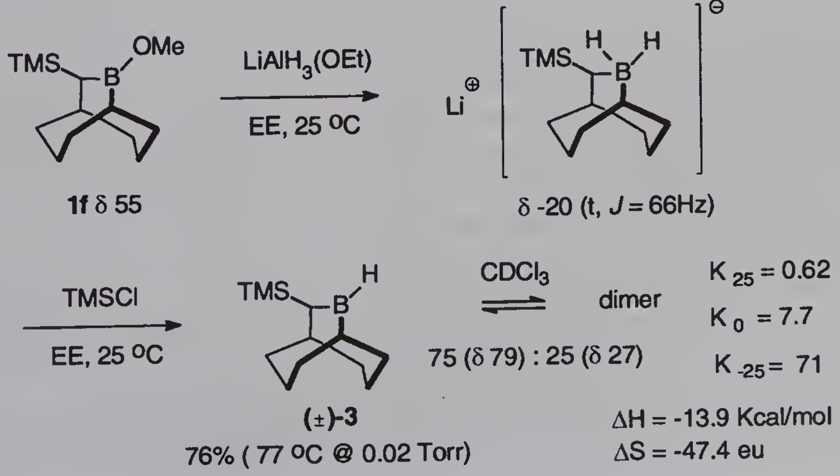
route to the B-H derivative **(±)-3**. However, it proved to exhibit exceptional reactivity producing a 60:40 product mixture of *B*-TMSCH$_2$-9-BBN (**1h**) and **2h** (R = CH$_2$TMS), but none of the desired **(±)-3**.

Fortunately, **(±)-3** was readily in 76% yield from **1f** following the Singaram, Cole, Brown method[11] which takes full advantage of the insolubility of dialkoxyalanes in ether. The addition of TMSCl (1.0 equiv) to the borohydride (^{11}B NMR δ -20 (t, *J* = 66 Hz)) releases the free borane which distills as a monomer, but exists in solution as a 3:1 monomer/dimer mixture at 25 °C in CDCl$_3$ (Scheme 1). In separate experiments, it was confirmed that the reaction of TMSCHN$_2$ was

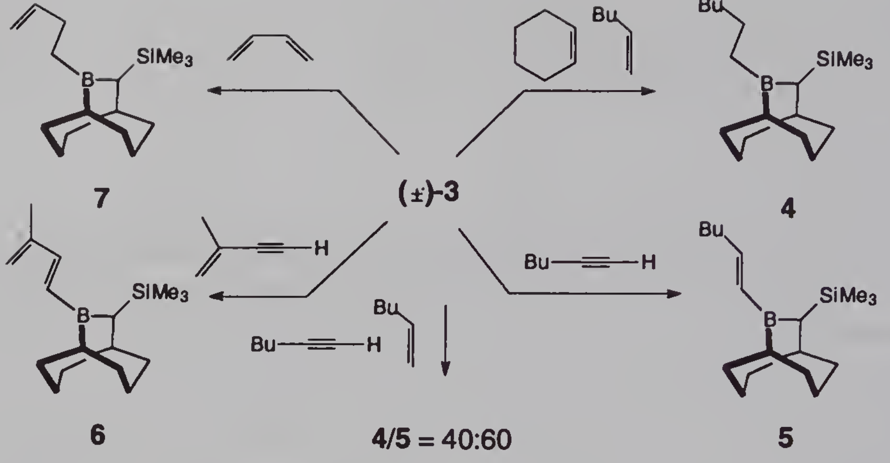


very rapid with **(±)-3**, but slow for **1h**, indicating that the lack of selectivity for (9-BBN-H)$_2$ in the insertion process is due to the fact that H-migration is competitive with ring migration and any **(±)-3** produced reacts faster than it is formed. This suggests that H migration is inherently favored over C migration despite the more favorable conformational bias favoring the ring B-C migration. It is also important to note that **(±)-3** exists largely at or above ambient temperature as the reactive monomeric form of the reagent in marked contrast to the dimeric 9-BBN-H.[13] This would also favor its more rapid reaction with TMSCHN$_2$ than with 9-BBN-H which is present only in minute concentration under the reaction conditions (*i.e.* hexane solution). Moreover, employing variable temperature ^{11}B NMR, the monomer-dimer equilibrium constants were measured and the thermodynamic parameters were determined from a plot of ΔG/T *vs* 1/T. This revealed a large entropy factor in the dimerization of **(±)-3** (-47.4 eu (-198 J/mol K)).

Scheme 1



Scheme 2



Hydroborations and resolution of the 10-TMS-9-BBD system

With **(±)-3** in hand, its reactivity and selectivity in the hydroboration of representative alkenes and alkynes was briefly examined for comparison to the related behavior of 9-BBN-H (**3**) (Scheme 2). While these results are only preliminary, they clearly suggest that, like 9-BBN-H, **(±)-3** is a very selective hydroborating agent, but differing from 9-BBN-H in that whereas it hydroborates alkynes and alkenes with nearly the same rates in competitive experiments (*cf* **4/5**), it exhibits the clean monohydroboration of 1-alkynes. Initially, the exclusive monohydroboration of 2-methylbut-1-en-3-yne was puzzling. However, the steric inhibition to the hydroboration of 1,1-disubstituted alkenes is considerable as will be discussed below, a fact that contributes to the selectivity observed in this process. The monohydroboration of 1,3-butadiene (*cf* **7**) is also noteworthy as is the exclusive hydroboration of 1-alkenes (*cf.* **4**) in the presence of 1,2-disubstituted alkenes (*e.g.* cyclohexene). However, by far the most intriguing feature of the new reagent was revealed in the hydroboration of the 2-butenes. *The cis and trans olefins give different diastereomers!* To the author's knowledge, this is an un-precedented result for any known chiral hydroborating agent. This result was reconfirmed and cross-checked by an INADEQUATE-based rigorous ^{13}C NMR analysis of each of the diastereomers comparing each to the mixture obtained from the TMSCHN$_2$ insertion into **(±)-2g**. These data are illustrated in Figure 3.

The significance of this finding lies in the greater sensitivity to differences in the substitution pattern at the *beta* rather than *alpha* carbon of the double bond undergoing hydroboration. Thus, the orientation of the α-CHMe (*i. e.* C-2') is reversed in *cis vs. trans* alkenes and the opposite relative configuration is obtained for these isomers after the boron adds to this center. Consistent with this hypothesis, the hydroboration of α-methylstyrene is slow (*ca* 96 h, 25 °C), but produces the β-boryl adduct in 61% de, a remarkable result! The reaction intermediates were characterized by ^{13}C NMR a

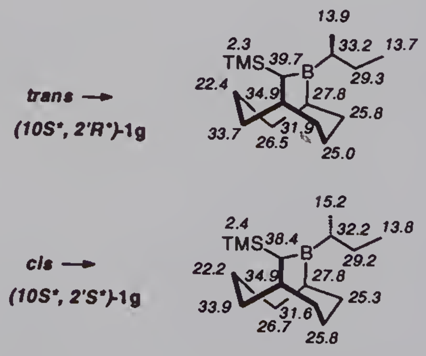
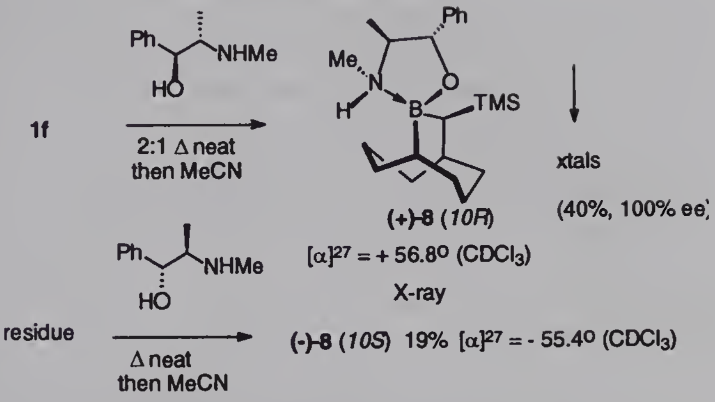


Figure 3 *^{13}C NMR assignments for the* ***1g*** *diastereomers*

technique which provides a direct analysis of the boranes.[12] together with the racemic reagent **1g**. However, quite clearly the resolution of **3** was required to ultimately provide enantiomerically enriched products in asymmetric organoborane conversions.

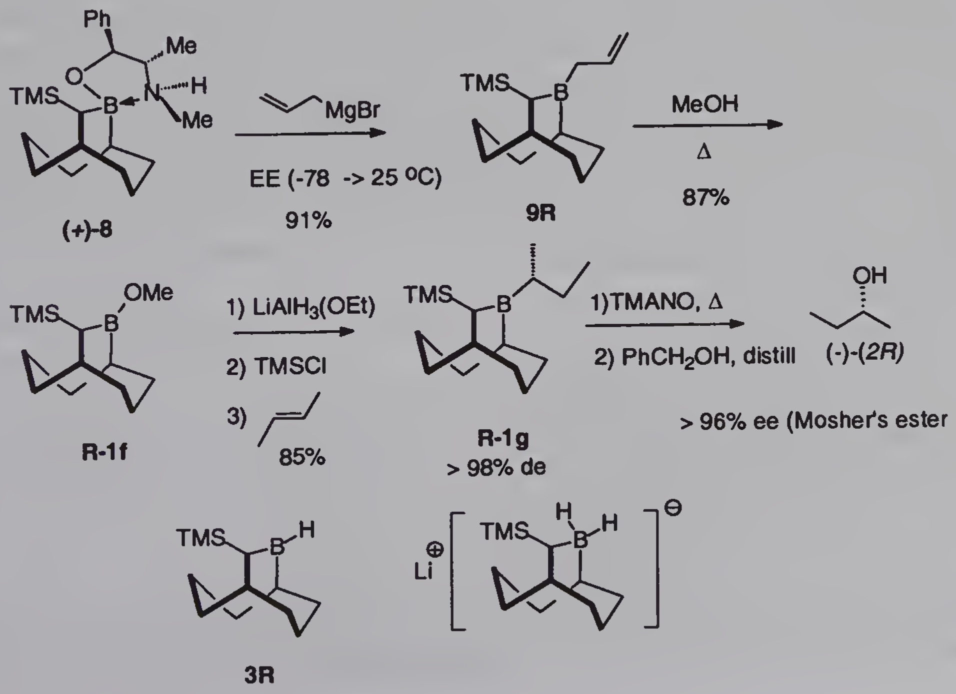
Scheme 3



Toward this end, a modified Masamune procedure[1h,6] was examined using readily available optically active amino alcohols for the resolution of **3**. A systematic computational study (MMX level) of the energetics of intramolecular *N*-complexation in the borinate derivatives of the BBD system revealed large differences for the *10R vs. 10S* form of the reagent for (*1S, 2S*)-(+)-pseudoephedrine (Scheme 3). Heating (±)-**1f** with this alcohol (0.5 equiv) effects the transesterification and the enantiomerically pure air-stable crystalline complex (+)-**8** is obtained in 40% (80% of 50%) yield from acetonitrile. In solution both the open and closed form of (+)-**8** are present (^{11}B-NMR δ 56.3 and 23.7). However, in the solid state, the closed structure and absolute stereochemistry were *confirmed by single crystal X-ray analysis* (see representation in Scheme 3).[13] A sample of (-)-**8** was obtained from the addition of (-)-pseudoephedrine to the concentrated residue, heating and added acetonitrile.

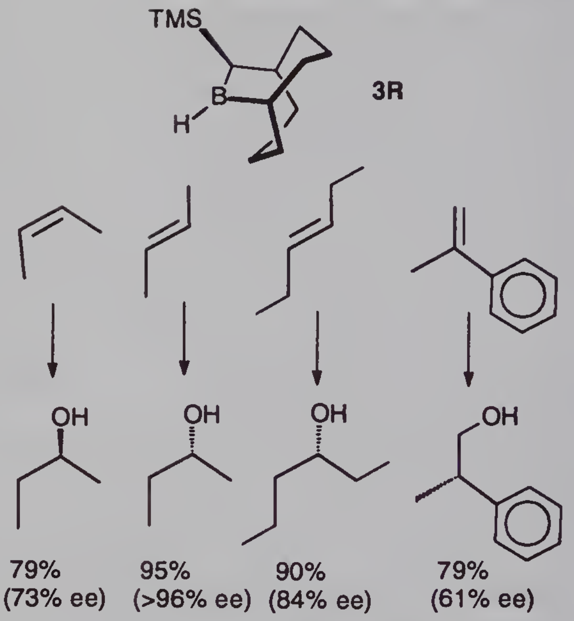
The conversion of (+)-**8** to **R-1f** was accomplished through the intermediate *B*-allyl species **9R** (Scheme 4).[1h] The **1f**→**3** conversion was carried out as is outlined in Scheme 1 to give **3R** which produces the (*10R, 2'S*) isomer ***R*-1g** in >98% de and (-)-(2*R*)-butanol in >96% ee after trimethylamine *N*-oxide (TMANO) oxidation. Preliminary results have also been obtained for 2,3-dihydrofuran (84% de), *cis*-2-butene (>85% de from 95:5 *c/t* mixture),

Scheme 4



t-3-hexene (>90% de) and α-methylstyrene (61% de). The last three adducts were oxidized (H_2O_2, NaOH) to the alcohols Scheme 5). Most notable among these is the last which produces (2*S*)-phenyl-1-propanol in 61% ee, an unprecedented level of enantiofacial selectivity for the asymmetric hydroboration of 1,1-disubstituted alkenes.[14]

Scheme 5



Asymmetric allylboration with the 10-TMS-9-BBD system

Allylboranes are extremely valuable intermediates for carbon-carbon bond formation.[1e] For two decades it has been known that with chiral boron ligation, these reagents can be used for the asymmetric synthesis of homoallylic alcohols (**10**), a feature of the process which markedly enhances the value of the process.[2] The reaction can be viewed as the addition of an allyl group to aldehydes via a chair-like transition state, with the hydrolysis of the intermediate borane ultimately giving **10**.[1e] Exhibiting high diastereoselectivities in their subsequent conversions (*e.g.* epoxidation, iodocyclizaton),[15] these alcohols are extremely useful intermediate in organic synthesis have proven value in the asymmetric synthesis.[3] As noted above, the new chiral organoborane reagent, *B*-allyl-10-(trimethysilyl)-9-borabicyclo[3.3.2]decane (**9**) is readily prepared in either enaniomeric form through the reaction of allylmagnesium bromide with either (+) or (-)-**8**. converted , its conversion to optically pure allylboranes, (+)- and (-)-**9**). Their remarkable selectivities with representative aldehydes is the subject of this Section (Scheme 6).

The asymmetric allylboration of representative aldehydes with either **9R** or **9S** was examined in EE (3h, -78 °C). In all cases, the homoallylic alcohols **10** were obtained in ≥96% ee. These results are summarized in Table 2. The intermediates **11** were isolated in excellent yields in essentially pure form after solvent removal. For the reactions of **9R**, solutions (~0.5 M) of **5*R*** and (*1S*, *2S*)- (+)- pseudoephedrine (1.0 equiv) in MeCN were heated at reflux temperature to effect the transesterification with crystalline (+)-**8** being isolable by simple filtration. An analogous procedure was used for the **9*S*** reactions employing (-)-pseudoephedrine to provide (-)-**8**. The homoallylic alcohols **10** were isolated in good to excellent yields by simple distillation.

The best known chiral boron ligation for asymmetric allylborations for which comparative data is available are included in Figure 1.[2] Comparing the product ee's achieved by these systems with those from **9** reveals that this new asymmetric reagent equals or exceeds the selectivity observed for any of these reagents at -78 °C (*cf* Table 3).

Scheme 6

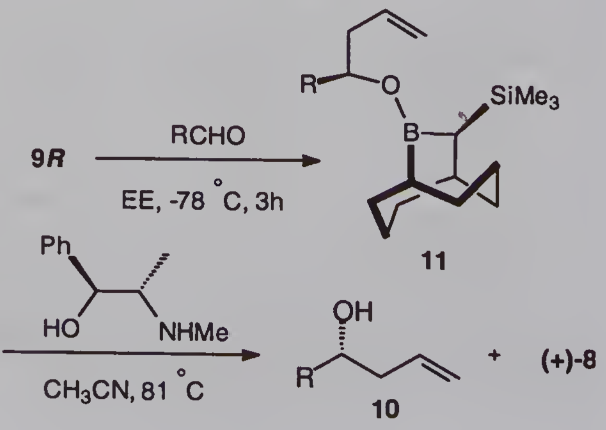


Table 2 *Allylboration with B-allyl-10-TMS-9-BBD (9).*

entry	*R in RCHO*	*9*	*Series*	*Yield (%)*			*%ee*
				11	***8***	***10***	
1	Ph	*S*	**a**	92	84	80	≥98 (*S*)[a, c]
2	Vi	*S*	**b**	87	77	71	≥98 (*S*)[a, c]
3	*i*-Pr	*S*	**c**	91	67	62	≥99 (*S*)[b]
4	*t*-Bu	*R*	**d**	94	71	77	≥98 (*R*)[a]
5	*n*-Pr	*R*	**e**	100	79	79	≥98 (*S*)[b]
6	Me	*R*	**f**	99	73	71	96 (*S*)[a]

[a] Product ee determined by conversion to the Mosher ester and analysis by ^{13}C NMR. [b] Determined by conversion to the Mosher ester and analysis by ^{1}H NMR and ^{13}C NMR. [c] Determined by conversion to the Mosher ester and analysis GC chromatography.

Table 3 *Comparative data for asymmetric allylboration*[a]

RCHO								*%ee*			
R	*a*[b]	*b*[c]	*c*[d]	*d*[e]	*e*[f]	*f*[g]	*g*[h]	*h*[i]	*i*[i]	*j*[i]	*9*[j]
Me	86	96						92(≥99)	94(≥99)	98(≥99)	96
n-Pr	72	96	95	79	94	93	96	86(96)	88(98)	94(≥99)	≥98
i-Bu	70	94				85	96	88(96)	95(98)	94(≥99)	≥99
t-Bu	45	88		82	96	86	97	83(≥99)	88(≥99)	99(≥99)	≥98
C_2H_3			98				97[k]	92(96)	93(98)	98(≥99)	≥98
Ph		88	95	71	85			94(96)	87(98)	95(≥99)	≥98

[a] Excepting those for **9**, data was taken from ref. 1g. [b] -78 °C → 25 °C, overnight. [c] -78 °C, 2 h, -78 °C → 25 °C. [d] -78 °C, 2 h. [e] -78 °C, 1 h. [f] -78 °C, 2-3 d. [g] -78 °C, 1 h, -78 °C → 25 °C. [h] -100 °C, 3 h. [i] Under Mg salt-free conditions at -78 °C (-100 °C). [j] -78 °C. Product % ee determined by conversion to the Mosher ester and analysis by ^{1}H NMR and/or ^{13}C NMR. [k] For crotonaldehyde.

The new reagent **9** is efficiently prepared in three (3) steps from **1** in either enantiomeric form. Moreover use of the reagent does not necessitate temperatures lower than −78 °C, and, in fact, studies indicate that the reactions may be conducted at considerably higher temperatures (*i.e.* 25 and 0 °C) without significant loss of selectivity. This is in contrast to the behavior of the diisopinocampheylborane reagent (*c.f.* Table 4.)[16]

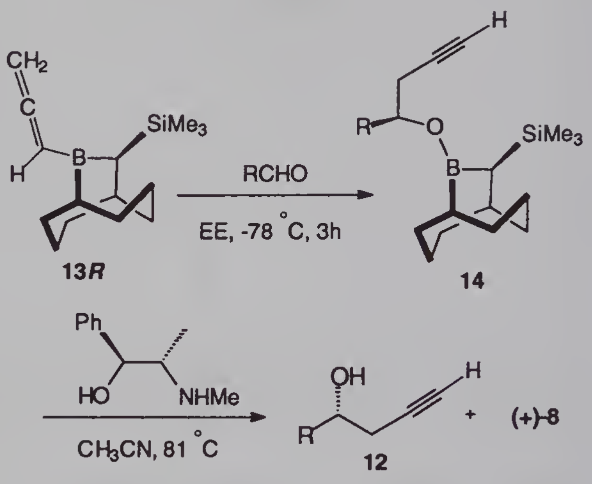
Table 4 *Temperature effects in the allylboration reaction with* ***9***

	% ee with 9 (Ipc_2BAll)[a]	
temp, °C	*PhCHO*	*MeCHO*
25	90.0	93.8
0	93.0[b]	93.0 (79.4)
-25	94.0	98.0 (85.4)
-78	≥98.0	96.0 (93.0)

[a] From ref. 14. [b] For **9*S***. ^{13}C NMR analysis of the Mosher esters.

Asymmetric allenylboration with the 10-TMS-9-BBD system

Scheme 7



Closely related to the above asymmetric allylboration process, allenylboration has been demonstrated to provide an effective entry to optically active homopropargylic alcohols (**12**). Initial studies by H. Yamamoto, *et al.*[1i] effectively employed tartrate esters (*cf* Fig. 1, **d**) to prepare allenylboronic esters which produce **12** in high ee (73-99%) for various aldehydes with aromatic derivatives (*e.g.* PhCHO) being less effective substrates than their aliphatic counterparts. The relative complexity and low yields (40-60%) of the starting allenylboronic acid coupled with the requirement that the chiral boronic esters have to be freshly prepared immediately before their use in the allenylboration detract somewhat from the overall value of the process as do the long reaction times (20 h, -78 °C), the hydrolysis of the chiral boron ligation upon work-up and the relative inefficiency of chirality transfer for aromatic substrates.

Improvements in this process were reported by Corey, *et al.*[1j] with his demonstration that chiral *B*-allenyl-1,3,2-diazaborolanes (*cf* Fig. 1, **c**) are effective asymmetric allenylborating agents providing **12** in high yield (74-82%) and ee (91-98%). Generated *in situ* from the corresponding *B*-Br boracycle and propargyltriphenyltin, the chiral *bis*-p-sulfonamide of the 1,2-diphenyl-1,2-diaminoethane was also recoverable (90%). The versatility of this process is further enhanced by the fact that allenyltins can also be used to prepare allenyl carbinols by an analogous process.[17]

***Table 5** Allenylboration with B-allenyl-10-TMS-9-BBD (13)*

entry	*R in RCHO*	*13*	*Series*	*Yield (%)*		*$[\alpha]_D^{28}$, deg*	*%ee(config)*[a]
				8	*12*	*(c in MeOH)*	
1	Ph	*R*	**a**	84	92	-29.2 (2.2)	93 (*R*)
2	Vi	*R*	**b**	85	74	-36.79 (2.1)	94 (*R*)
3	*i*-Pr	*R*	**c**	80	81	-3.45 (1.2)	93 (*R*)
4	*t*-Bu	*R*	**d**	81	75	+45.37 (1.1)	94 (*R*)
5	*n*-Pr	*R*	**e**	84	82	-28.18 (2.2)	93 (*S*)
6	Furaldehyde	*R*	**f**	80	80	-6.61 (2.4)	95 (*R*)

[a] Product ee determined by conversion to the Mosher ester and analysis by ^{1}H NMR and ^{13}C NMR.

We felt that an improvement in the overall process would be made through the direct preparation of a stable *B*-allenyl chiral boron reagent from allenylmagnesium bromide thereby circumventing the need to both prepare an additional intermediate precursor to the reagent and generate the reagent each time prior to use. Toward this end, we found as for the above allyl system (*i.e.* **9*R***) the pseudoephedrine complex (+)-**8** provided the ideal substrate for the preparation of the allenylborane **13*R*** (93%) from a Grignard procedure. The stable new reagent undergoes clean reaction with representative aldehydes producing, after a pseudoephedrine work-up, the homopropargylic alcohols **12** in 74-92% yields and 93-95% ee (Scheme 7, Table 5). In addition, the chiral organoborane complex **(+)-8** is recovered in 80-86% yield by its crystallization from acetonitrile in all cases through this simple procedure.

CONCLUSIONS

The 10-TMS-9-BBD system is readily prepared from many 9-BBN derivatives through the clean insertion of the stable, commercially available reagent, trimethylsilyldiazomethane. Resolution of the chiral bicyclic system is efficiently accomplished (40%) through its pseudoephedrine complex which is readily converted to the *B*-H (**3**), *B*-allyl (**9**) or *B*-allenyl-10-TMS-9-BBD derivatives. These new reagents have been demonstrated to function as highly useful asymmetric hydroborating, allylborating and allenylborating agents, respectively. Studies are currently underway to further develop related reagents in other asymmetric organoborane conversions.

ACKNOWLEDGMENT

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REFERENCES

1. a) A. Pelter, K. Smith, and H. C. Brown, 'Borane Reagents', Academic Press, London, UK, 1988; b) D. S. Matteson, *Chem. Rev.* 1989, **89**, 1535. c) L. Deloux and M. Srebnik, *Chem. Rev.* 1993, **93**, 763. d) K. Maruoka and H. Yamamoto in 'Catalytic Asymmetric Synthesis', I. Ojima, Ed., VCH Publishers, Inc., NY, 1993. e) Y. Yamamoto and N. Asoa, *Chem. Rev.* 1993, **93**, 2207. (f) J. A. Soderquist in 'Encyclopedia of Inorganic Chemistry, R. B. King, Ed., J. Wiley & Sons, Ltd., London, UK ,1994, Vol. 1, pp 401-433. g) H. C. Brown and P. V. Ramachandran in 'Advances in Asymmetric Synthesis', A. Hassner, Ed., JAI Press: Greenwich, CT, 1995, Vol. 1, pp 147-210. h) C. J. Cowden and I. Paterson, *Org. React.* 1997, **51**, 1. i) N. Ikeda, I. Arai and H. Yamamoto, *J. Am. Chem. Soc.* 1986, **108**, 483. j) E. J. Corey, C-M. Yu and D-H. Lee, *J. Am. Chem. Soc.* 1990, **112**, 878.
2. a) T. Herold and R. W. Hoffmann, *Angew. Chem. Int. Ed. Engl.* 1978, **17**, 768. b) R. W. Hoffmann and T. Herold, *Chem. Ber.* 1981, **114**, 375. c) M. T. Reetz and T. Zierke, *Chem. Ind.* 1988, 663. d) E. J. Corey,C. Yu and S.S. Kim *J. Am. Chem. Soc.* 1989, **111**, 5495.e) W. R. Roush, A. E. Walts and L. K. Hoong, *J. Am. Chem. Soc.* 1985, **107**, 8786. f) W. R. Roush and L. Banfi, *J. Am. Chem. Soc.* 1988, **110**, 3979. g) J. Garcia, B. Kim, B. and S. Masamune, *J. Org. Chem.* 1987, **52**, 4831. h) R. P. Short and S. Masamune, *J. Am. Chem. Soc.* 1989, **111**, 1892.i) H. C. Brown and P. K. Jadhav, *J. Am. Chem. Soc.* 1983, **105**, 2092. (j) H. C. Brown and P. K. Jadhav *J. Org. Chem.* 1984, **49**, 4089. k) H. C. Brown, R. S. Randad, K. S. Bhat, M. Zaidlewicz and U. S. Racherla, *J. Am. Chem. Soc.* 1990, **112**, 2389.l) W. R. Roush and P. T. Grover, *J. Org. Chem.* 1995, **60**, 3806.
3. See, for example: a) K. C. Nicolau, R. D. Gronberg, N. A. Stylianides and T. Miyazaki, *J. Chem. Soc., Chem. Commun.* 1990, 1275. b) G. Khandekar, G. C. Robinson, N. A. Stacey, P. G. Steel, E. J. Thomas, E. J. and S. Vather, *ibid.* 1987, 877. c) E. Merifield, P. G. Steel, and

E. J. Thomas, *ibid.* 1987, 1826. d) S. L. Schreiber and M. Goulet, *J. Am. Chem. Soc.* 1987, **109**, 8120. e) D. D. Martin, N. R. Kotecha, S. V. Ley, S. Mantegani, J. C. Menedez, H. M. Organ and A. D. White, *Tetrahedron* 1992, **48**, 7899. f) A. L. Smith, C. K. Hwang, E. Pitsinos, G. R. Scarlato and K. C. Nicolau, *J. Am. Chem. Soc.* 1992, **114**, 3134. g) A. G. M. Barrett, J. J. Edmunds, J. A. Hendrix, J. Malech and C. J. Parkinson, *J. Chem. Soc., Chem. Commun.* 1992, 1240. h) Y. M. Bubnov, L. L. Lavinovich, A. Y. Zykov and A. V. Ignatenko, *Mendeleev Commun.* 1992, 86. i) Z. Wang and D. Deschenes, *J. Am. Chem. Soc.* 1992, **114**, 1090. j) R. B. Bates, *Tetrahedron Asym.* 1993, **4**, 69. k) W. R. Roush and J. A. Hunt, *J. Org. Chem.* 1995, **60**, 798. l) J. Kriiger and R. W. Hoffmann, *J. Am. Chem. Soc.* 1997, **119**, 7499.

4. H. C. Brown, M. C. Desai and P. K. Jadhav, *J. Org. Chem.* 1982, **47**, 5065.
5. a) H. C. Brown, J. R. Schwier and B. Singaram, *J. Org. Chem.* 1978, **43**, 4395. b) H. C. Brown, P. K. Jadhav and A. K. Mandal, *J. Org. Chem.* 1982, **47**, 5065.
6. S. Masamune, B. M. Kim, J. S. Petersen, T. Sato, S. J. Veenstra and T. Imai,. *J. Am. Chem. Soc.* 1985, **107**, 4549.
7. a) J. A. Soderquist and H. C. Brown, *J. Org. Chem.* 1981, **46**, 4559. b)J. A. Soderquist and A. Negron, *Org. Synth.*, 1991, **70**, 169. c) J. A. Soderquist in *Encyclopedia of Reagents for Organic Synthesis, Vol. 1*, L. A. Paquette, Ed., J. Wiley & Sons, Ltd., London, UK, 1995, pp 622-630.
8. a) N. Miyaura and A. Suzuki, *Chem. Rev.* 1995, **95**, 2457. b) K. Matos and J. A. Soderquist, *J. Org. Chem.*, 1998, **63**, 461.
9. a) J. A. Soderquist and M. R. Najafi, *J. Org. Chem.* 1986, **51**, 1330. b) J. A. Soderquist and C. L. Anderson, *Tetrahedron Lett.* 1986, **27**, 3961.
10. J. Hooz and D. M. Gunn, *Tetrahedron Lett.* 1969, 3455.
11. B. Singaram, T. E. Cole and H. C. Brown, *Organometallics* 1984, **3**, 1520.
12. For early related examples of this technique, see: a) H. C. Brown and J. A. Soderquist, *J. Org. Chem.* 1980, **45**, 846. b) J. A. Soderquist and H. C. Brown, *J. Org. Chem.* 1980, **45**, 3571. c), J. A. Soderquist and A. Hassner, *J. Org. Chem.* 1983, **48**, 1801.
13. The X-ray structure of (+)-**3** will be reported elsewhere(unpublished studies with S. D. Huang).
14. M. Srebnik and P. V. Ramachandran, *Aldrichimica Acta*, 1987, **20**, 9.
15. a) P. A. Bartlett and K. K. Jernstedt, *J. Am. Chem. Soc.* 1977, **99**, 4829. b)P. A. Bartlett and K. K. Jernstedt, *Tetrahedron Lett.* 1980, **21**, 1607. c) G. Cardillo, M. Orena, G. Porzi and S. Sandri, *J. Chem. Soc., Chem. Commun.* 1981, 465. d) M. F. Haslanger and S. Ahmed, *J. Org. Chem.* 1981, **46**, 4808. e) E. D. Mihelich, K. Daniels and D. Eickhoff, *J. Am. Chem. Soc.* 1981, **103**, 7690.
16. P. K. Jadhav, K.S. Bhat, P. T. Perumal and H. C. Brown, *J. Org. Chem.* 1986, **51**, 432.
17. See also: H. C. Brown, U. R. Khire and G. Narla, *J. Org. Chem.* 1995, **60**, 8130.

Theoretical and Computational Studies

Distortion by Hyperconjugation and by Formation of a Three-center-two-electron Bond Between Three Boron Atoms

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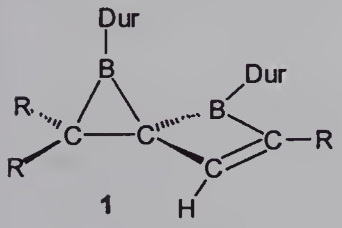
1 INTRODUCTION

Molecules containing borirane rings connected at carbon to *one* additional boron atom can be undistorted like **1**[1], slightly distorted like **2a**,[2] strongly distorted like **3**[1] and extremely distorted, i. e. rearranged into nonclassical structures like **4u**[2] and **4a**.[3] The latter have two three-center-two-electron (3c,2e) bonds between *two* boron atoms and a carbon or a hydrogen.



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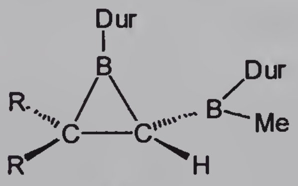
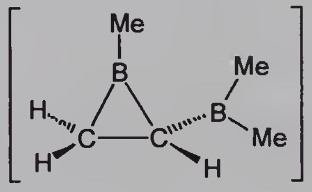
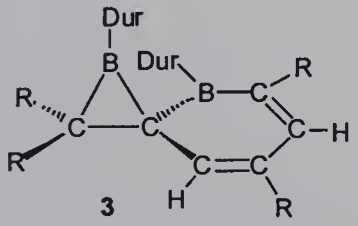


2a



2u

Dur = 2,3,5,6-tetramethylphenyl R = $SiMe_3$



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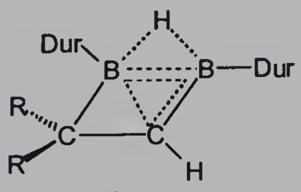
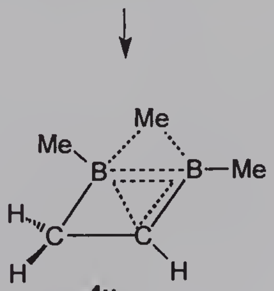


4a



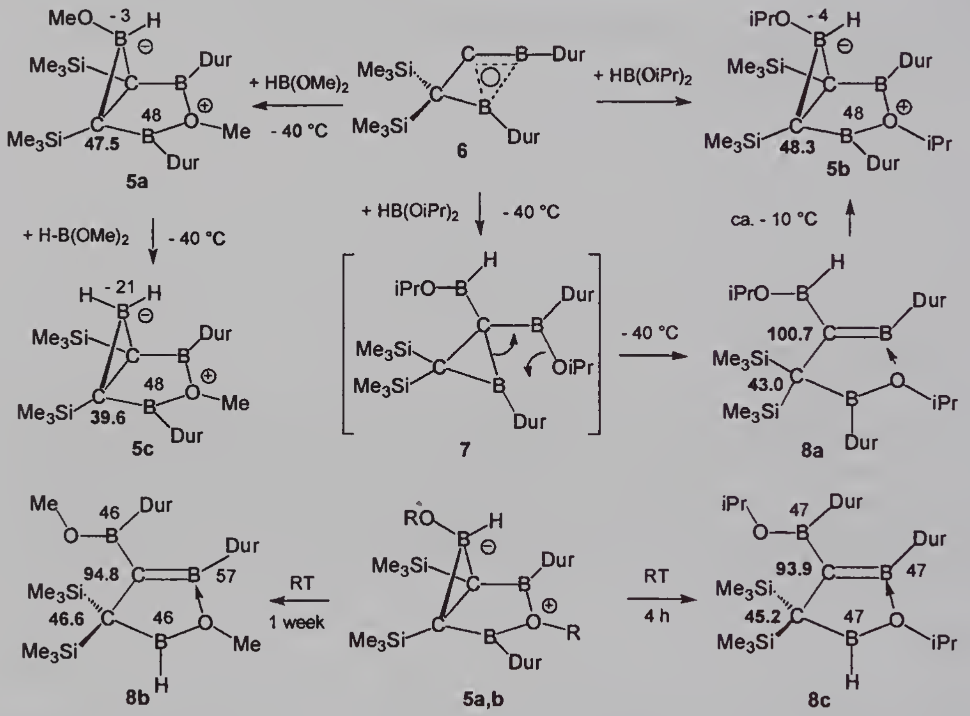
4u

We describe here molecules containing boriranes and boratiranes connected to *two* additional boron atoms - one at each carbon atom - as well as their distortions even into nonclassical polyhedra. The presence of three boron atoms in a bicyclic molecule also can result in extreme distortion by formation of a 3c,2e bond between *three* boron atoms: two electron reduction leads to a polyhedral dianion.

2 DISTORTION BY HYPERCONJUGATION

2.1 Synthesis of Bicycles Containing Boratirane Anions or Boriranes

Zwitterionic bicyclic compounds **5a-c** are obtained when **6**[4] is allowed to react with dimethoxyborane or di(isopropoxy)borane at temperatures below -10°C. The constitution of **5c** is established by the crystal structure shown in Figure 1 (left side). The similarity of the NMR data of **5a** and **5b** to those of **5c** (relevant chemical shifts are included in the formulas through-out this report; $\delta^{13}C$ in bold and $\delta^{11}B$ in plain text) proves the constitutions of **5a** and **5b**.



Compounds **5a-c** contain a hitherto unknown diboryloxonium cation as well as a boratirane anion, derivatives of which have been described by Schuster.[5] Some insight into the mechanism of the formation of compounds **5a,b** is obtained, when **6** is reacted with di(isopropoxy)borane at -40°C. Intermediate **8a** which forms can be explained by addition of the borane to the formal C-B double bond[6] of **6** leading to 1,1-diborylborirane **7** which then rearranges to **8a**. The constitution of **8a** is deduced by comparison of its ^{13}C NMR chemical shifts to those of the related **8c** and **8b**. The crystal structure of **8b** is shown in Figure 1 (right side).

Compounds **8b** and **8c** are formed by spontaneous rearrangement of **5a** and **5b**, respectively, in $CDCl_3$ solution. Note that **8c** cannot be obtained from **7** by intramolecular attack of the second boryl substituent which carries a hydrogen atom.

If **6** is reacted with chlorodimethoxyborane instead of dimethoxyborane, the primary product is **8d** (established by comparison of its ^{13}C chemical shifts to those of **8a-c**). In $CHCl_3$, **8d** transforms spontaneously to **9a**, probably via **5d** as intermediate (compare **8a** → **5b**). The boron chemical shifts of **9a** are close to those calculated for **9au** at GIAO- SCF/6-31G*//MP2/6-31G*.[7]

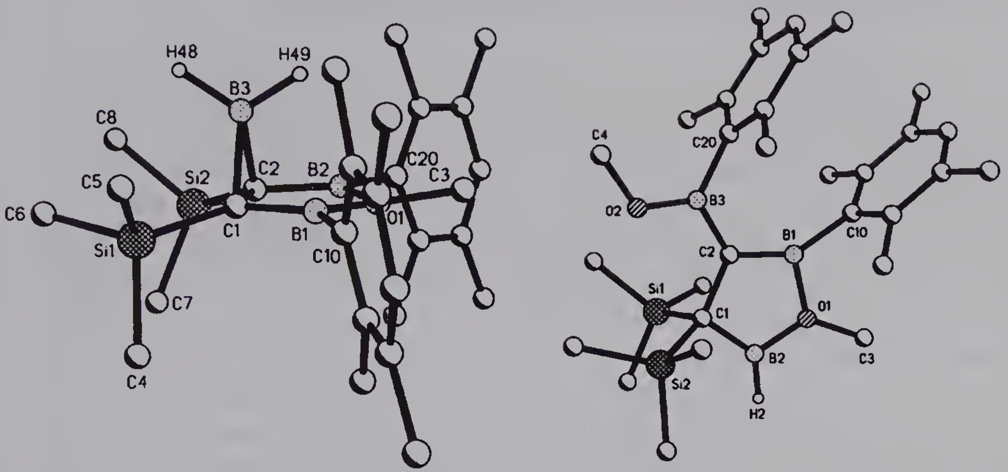
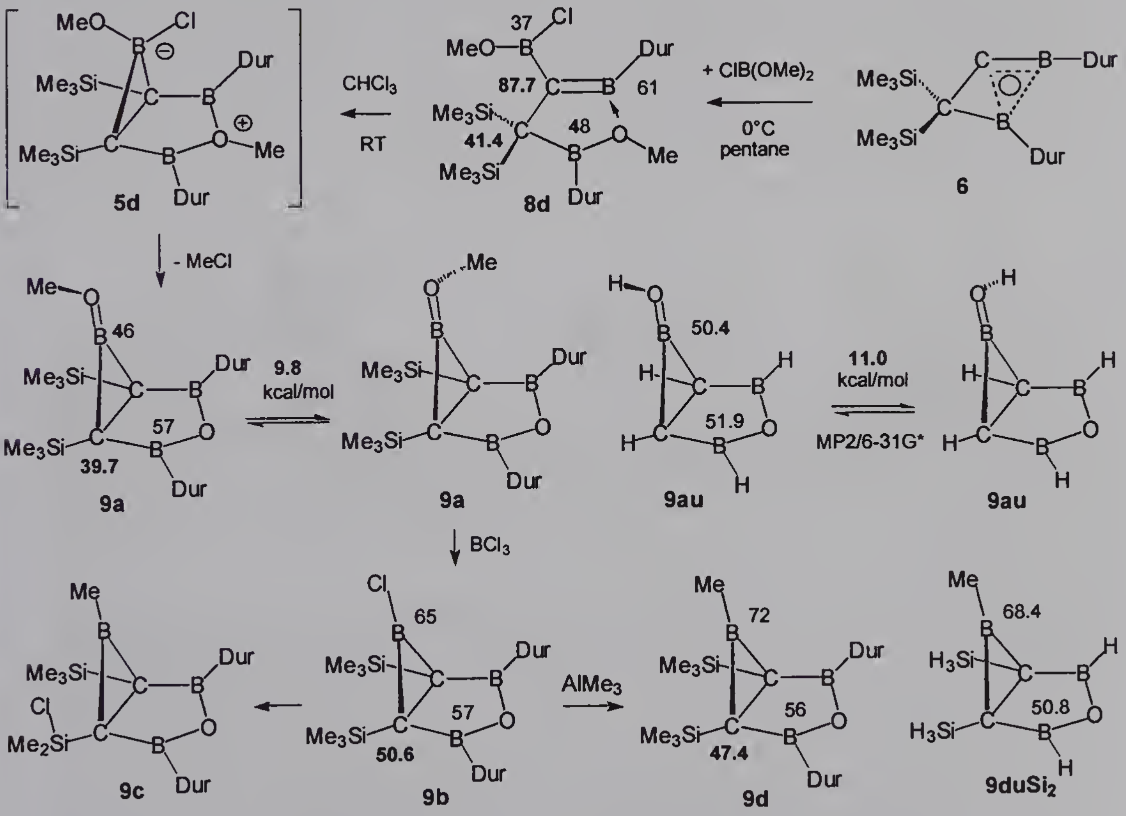


Figure 1: X-ray molecular structures of **5c** (left) and **8b** (right)

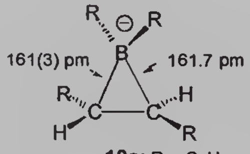
The 9.8 kcal/mol barrier of rotation of the methoxy group of **9b**, determined by analysis of its temperature dependent NMR spectra, is in reasonable agreement with the value (11.0 kcal/mol) calculated for **9au** at MP2/6-31G*.



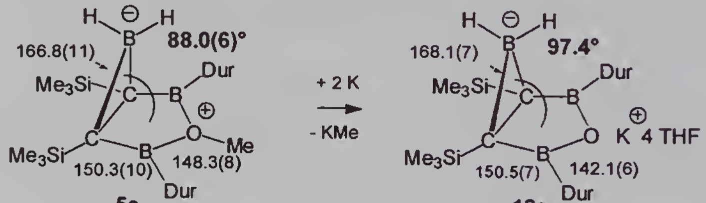
Reaction of **9a** with BCl_3 gives **9b**, the first derivative of chloroborirane. The crystal structure of **9b** is shown in Figure 2 (left side). The high reactivity of **9b** is evident from its spontaneous rearrangement into **9c** in $CHCl_3$ solution. The chlorine of **9b** can be exchanged by a methyl group with $AlMe_3$ below 0°C to yield **9d**. Its boron chemical shifts agree reasonably with those calculated for the model, **9duSi₂**.

2.2 Hyperconjugation in Bicycles Containing Boratirane Anions

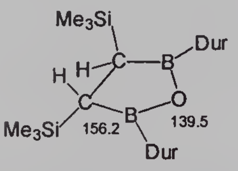
The small 88.0° angle between the three- and five-membered rings of **5c** is remarkable. In addition, the C-B bonds of its three-membered ring (166.8(11) pm) are longer than in Schuster's[5] boratirane **10a** (161(3) pm) and calculated for **10u** (161.7 pm). The C-B bonds of the five-membered ring, however, are relatively short as compared to those in the 1-oxa-2,5-diboracyclopentane **11** (150.3(10) versus 156.2(4) pm). The B-O bonds of **5c** (148.3(8) pm) are considerably longer than those in **11** (139.5(3) pm). Short B-O bonds in **11** indicate double bond character due to delocalization of an oxygen lone pair. σ(C-B) → p(B) hyperconjugation is the origin for the geometric deformations in **5c**: Two factors make the C-B bonds of the three-membered ring excellent σ-donors: a) ring strain and b) the additional, negatively charged substituent at B (H^- in **5c**). In addition, the electron deficiency of the boron atoms is not reduced much by the presence of the neighboring O. The additional (positively charged) ligand at oxygen in **5c** minimizes the potential de-localization of the remaining nonbonding electron pair at oxygen into the formally empty boron p-orbitals. Instead, the boron atoms hyperconjugate strongly with the C-B bonds of the three-membered ring. This interaction causes the described geometric deformations.



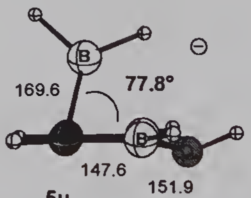
10a: R = C_6H_5
10u: R = H



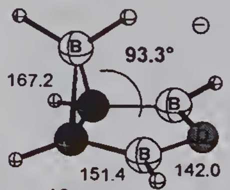
5c **12a**



11



5u



12u

This interpretation is supported by NBO analyses[8] on the unsubstituted prototypes **5u** and **12u**. The MP2/6-31+G* optimized geometry **5u** shows an even smaller angle (77.8°) between the three- and five-membered rings, even longer C-B bonds of the three-membered ring (169.6 pm), and shorter (147.6 pm) C-B and longer (151.9 pm) B-O bonds in the five-membered ring.

In compounds of type **12** (lacking the methyl group at the oxygen atom), the electron deficiency of the boron atoms of the five-membered ring is reduced considerably due to conjugation with an oxygen lone pair. This is evident from an NBO analysis and is also shown by the shorter B-O distance of **12u** as compared to **5u** (142.0 and 151.9 pm, respectively). As a consequence, hyperconjugation with the C-B bonds of the boratirane ring is weaker in **12u** according to an NBO analysis and as seen from the larger inter-planar angle of 93.3°, longer C-B bonds (151.4 pm) in the five-membered ring and shorter C-B bonds (167.2 pm) in the three-membered ring. Experimentally, shorter B-O bonds and an increased interplanar angle of 97.4° clearly confirm the decreased hyperconjugative interaction in **12a** (see the crystal structure shown in Figure 2, right side). This compound is obtained by reductive cleavage of the O-Me bond of **5c** by potassium.

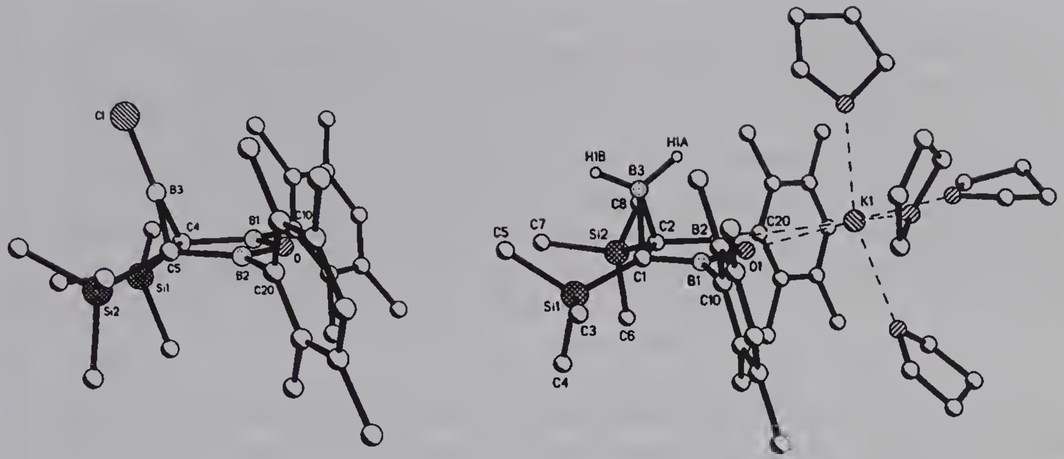
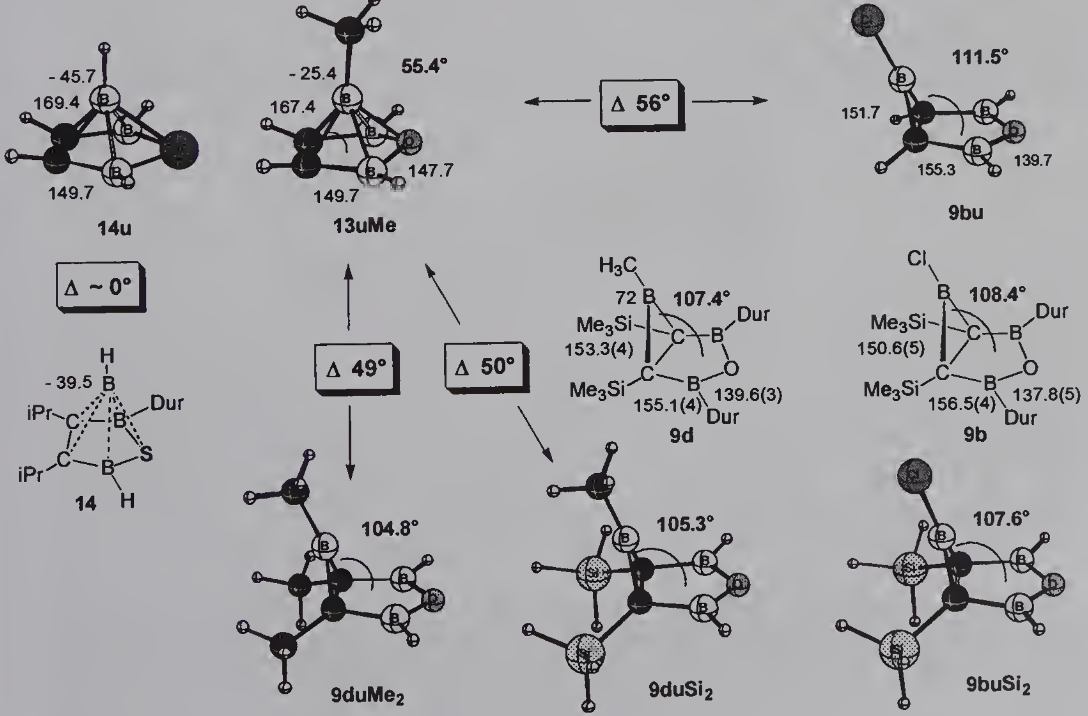


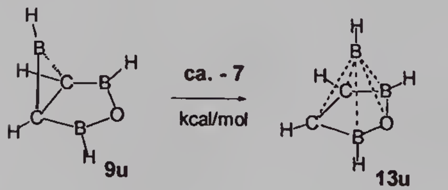
Figure 2: Molecular structures of **9b** (left) and **12a·K·4 THF** (right) in the crystal.

2.3 Remarkable Effects of Substituents on Interplanar Angles

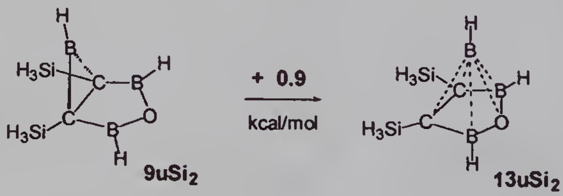
The interplanar angle between the three- and five-membered rings is increased to 111.5° in **9bu** (//MP2/6-31+G*) and 108.4° in **9b**, where the boratirane anion moieties of **12u** and **12a**, respectively, are replaced by a neutral borirane ring carrying an electronegative chlorine substituent. The C-B bonds of **9b** and **9bu** are neither shortened in the five- nor lengthened in the three-membered rings. Hence, hyperconjugation involving the boron atoms of the five-membered ring with the C-B bonds of the three-membered ring is further reduced as compared to **12u** and **12a**.



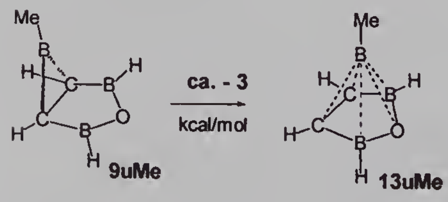
This can be explained by a reduced σ-donor ability due to the increased s-contribution in the B-hybrids of the three membered ring B-C bonds when the negatively charged BH_2^- is replaced by the neutral BCl. This exchange opens up the possibility for additional hyperconjugation between the C-B bonds of the five-membered ring and the B atom of the three-membered ring. This interaction is less important than that involving the strained three-membered ring C-B bonds, but nevertheless may be strong enough to have large geometric consequences. In **9bu**, however, it is even further reduced in significance by the π-donating Cl substituent at B. The bicyclic **9bu** is more stable than the isomeric cluster **13uCl**, but only by 4.1 kcal/mol (//MP2/6-31+G*). H and CH_3 substituents do not donate electron density to the boron p-orbital as effectively as Cl. Hence, the hyperconjugation with the five-membered ring C-B bonds is more important and leads to a strong decrease in the interplanar angle (55.4° for **13uMe**) and the collapse of the structure to a nido-polyhedral cluster. A change in interplanar angles of 56° is, to the best of our knowledge, the biggest effect on geometry ever found upon replacement of a chlorine by a methyl substituent. There is a drastic opposite change when the hydrogen atoms at the carbon skeleton atoms of **13uMe** are replaced by silyl substituents: the interplanar angle is widened from 55.4° to 105.3° in **9duSi₂**, a 50° change! Experimentally, we observe 107.4° for **9d** in nice agreement with 105.3° calculated for **9duSi₂**. Introduction of methyl substituents at the skeleton carbon atoms of the oxapolyhedral **13uMe** has a comparable strong effect as shown by the bicyclic structure **9duMe₂**. Silyl substituents have small effects on the interplanar angles of the bicyclic structures **5u, 12u** (see above) and **9bu** (111.5° to 107.5° in **9buSi₂**). In contrast to **13uMe**, the corresponding thiapolyhedral **14u**, is insensitive to alkyl substituents: derivative **14** with isopropyl groups has a polyhedral structure.[9]



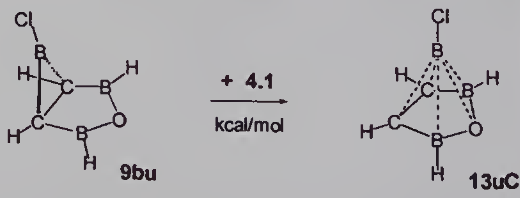
9u **13u**



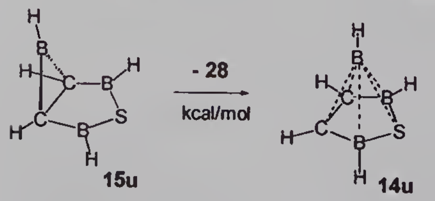
9uSi₂ **13uSi₂**



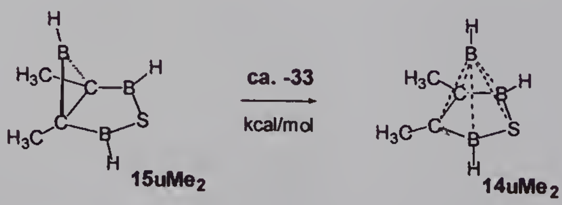
9uMe **13uMe**



9bu **13uCl**



15u **14u**



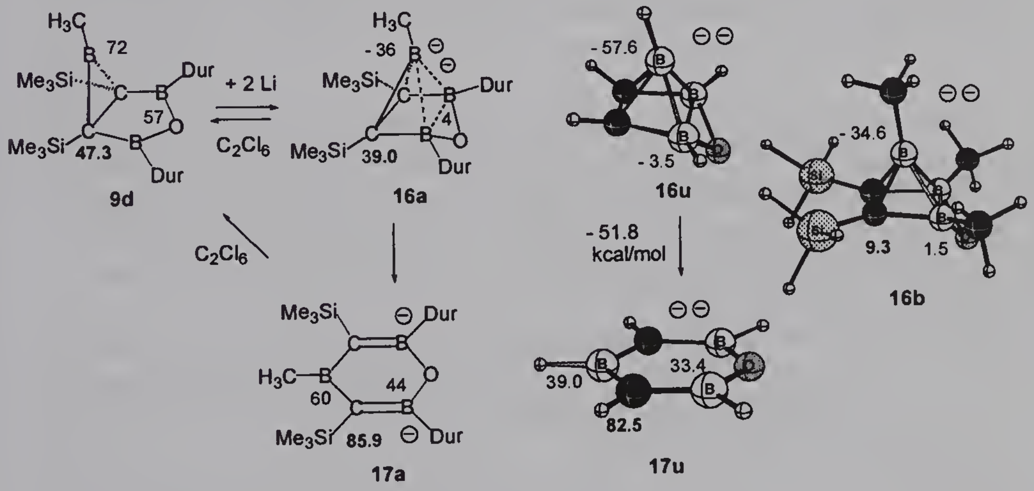
15uMe₂ **14uMe₂**

The energetic differences between bicyclic structures of type **9** and the oxapolyhedra of type **13** are small: about 7 kcal/mol between **9u** and **13u**, and only about 3 kcal/mol between **9uMe** and **13uMe**. (This estimation is based on classical structures with interplanar angles fixed to 105.3°; other parameters were optimized.) Substituent effects like those of chlorine at the three membered ring boron atom or of trimethylsilyl at the carbon atoms of this ring can compete in strength with the small energetic preference of the oxapolyhedron: bicyclic **9bu** is preferred over polyhedral **13uCl** by 4.1 kcal/mol and bicyclic **9uSi$_2$** by 0.9 kcal/mol over polyhedral **13uSi$_2$**. This explains why substituents can have such drastic geometric effects.

When oxygen is replaced by sulfur, however, the energy difference between bicyclic **15u** and the thiapolyhedral **14u** is large (28 kcal/mol). Interestingly, in this case methyl substituents favor the cluster **14uMe$_2$** more than the bicyclic **15uMe$_2$**. Obviously, the more electronegative oxygen is more reluctant to contribute two electrons for three-dimensional six electron aromaticity[10] than sulfur.

3 DISTORTION BY 3c,2e BOND FORMATION BETWEEN THREE BORONS

The interplanar angle between the three- and five-membered ring of **9d** is decreased strongly by introduction of two additional electrons forming a 3c,2e bond between the three boron atoms. This is evident from the strong shielding of the boron atoms after reduction with lithium in diethyl ether. The broad ^{11}B NMR signals of **9d** at 72 (1B) and 57 ppm (2B) are replaced by new sharp signals at 4 (2B) and -36 ppm (1B) of **16a**. During attempts to crystallize **16a**, it transformed spontaneously in three days to **17a**. Computations show that **17u** is much lower in energy than **16u** (by 51.8 kcal/mol at MP2/6-311+G** + 0.93 ZPE(MP2/6-31G*)).



Since all attempts to obtain single crystals of **16a** were unsuccessful we performed GIAO-SCF/6-31G*//BLYP/6-31G* calculations for the model **16b** with methyl substituents at all boron atoms and SiH$_3$-substituents at the two skeleton carbon atoms. The calculated ^{11}B chemical shifts of -34.6 (1B) and 1.5 ppm (2B) are in convincing agreement with those obtained experimentally for **16a**. An NBO analysis for **16u** reveals the presence of a 3c,2e bond between three boron atoms which is responsible for the large change upon reduction of **9d**. The interplanar angles, as defined above, are 58.0° in **16u** and 61.3° in **16b**.

Experimental evidence for the dianionic nature of **16a** is obtained by its spontaneous iso-merisation to **17a** and by the finding that **16a** and **17a** can be reoxidized to **9d** by C_2Cl_6.

4 SUMMARY

We described boratiranes and boriranes with one boron substituent at each ring carbon atom. The geometrical distortions found experimentally in the X-ray structures as well as by model computations can be understood in terms of variably strong hyperconjugation between σ(C-B) bonds and the formally empty p-orbitals of more or less electron deficient boron atoms. Two electron reduction of an oxatriborabicyclohexane leads to ex-treme distortion of the bicyclic to a cluster structure by formation of a 3c,2e-BBB-bond.

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5 REFERENCES

1. C. Balzereit, C. Kybart, H.-J. Winkler, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 1487 (1668).
2. P. Willershausen, G. Schmidt-Lukasch, C. Kybart, J. Allwohn, W. Massa, M. L. McKee, P. von R. Schleyer, A. Berndt, *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 1384.
3. D. Steiner, C. Balzereit, H.-J. Winkler, N. Stamatis, M. Hofmann, P. von R. Schleyer, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 2303.
4. M. Unverzagt, G. Subramanian, M. Hofmann, P. von R. Schleyer, S. Berger, K. Harms, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 1469.
5. M. A. Kropp, M. Baillargeon, K. M. Park, K. Bhamidapaty, G. B. Schuster, *J. Am. Chem. Soc.* 1991, **113**, 2155.
6. A. Berndt, D. Steiner, D. Schweikart, C. Balzereit, M. Menzel, H.-J. Winkler, S. Mehle, M. Unverzagt, T. Happel, P. von R. Schleyer, G. Subramanian, M. Hofmann in *Advances in Boron Chemistry* (Ed.: W. Siebert), The Royal Society of Chemistry, Cambridge, 1997, p.61.
7. Gaussian 94, Revision D.3 was used for all computations reported in this work: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
8. A. E. Reed, F. Weinhold, Chem. Rev. 1988, 88, 899.
9. V. Beez, P. Greiwe, H. Pritzkow, M. Hofmann, P. v. R. Schleyer, W. Siebert, *Eur. J. Inorg. Chem..* 1996, 1775.
10. E. D. Jemmis, P. von R. Schleyer, *J. Am. Chem. Soc.* 1982, **104**, 4781.

Ab Initio Study of Boron–Hydrogen Spheres

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Abstract

Applying *ab initio* quantum-chemical methods and density functional theory in the local density approximation, different $(BH)_n$ spherical clusters for $n = 12, 20, 32, 42$ and 92 have been investigated. Most of the clusters show nearly icosahedral symmetry. The hydrogen atoms are bonded to the spherical surface as prickles. The relative stability of the spheres measured as the binding energy per molecule has been analyzed. All the clusters studied are very stable, and the spherical $(BH)_{32}$ cluster seems to be the most stable structure. The effect of the hydrogen atoms is to increase the stability of the bare boron clusters.

1. Introduction

Owing to its rich structural chemistry and crystallography, boron is one of the most fascinating elements. Boron is a trivalent atom characterized by a short covalent radius and a tendency for sp^2 hybridization. It forms strong directional chemical bonds that produce semiconducting solids. As an impurity, or when bonded to other elements, boron is known by its electron deficiency. Boron has relevant thermal and mechanical properties due to its high melting point of 2300°C, about one thousand degrees higher than silicon, and a hardness similar to that of diamond.

Previous theoretical investigations of pure boron clusters, based on *ab initio* quantum chemical and density functional theoretical methods, have shown that pure boron has stable structures forming a new class of boron materials. These structures can be classified into four topological groups: convex, spherical, quasiplanar and tubular clusters. The new forms contain basically two units: a pentagonal and an hexagonal pyramid. All these clusters can easily be generated by both units with the help of an "Aufbau Principle" proposed for boron[1].

In the meantime the quasiplanarity, predicted in Ref. [2], has theoretically been confirmed by several authors[3,4,5]. On the other hand, Perkins *el al.*[6] experimentally confirmed that, by breaking intra-icosahedral bonds on the (100) surface of icosahedral solid YB_{66} crystals, hexagonal and pentagonal pyramidal forms are observed as open "umbrellas". Due to the fact that pure boron spheres like B_{32} are less stable in comparison to boron sheets or tubes[7], in the present work we look for the stabilizing effect of the hydrogen atoms by eliminating the dangling bonds in the boron spheres.

2. Theoretical Details

Ab initio restricted Hartree-Fock (HF) self-consistent field (SCF) and density functional theoretical (DFT) methods were applied to calculate structures and total energies of the $(BH)_n$ clusters for $n = 12, 20, 32, 42$ and 92. At the HF-SCF level we used the standard STO-3G minimal basis set and the larger 6-31G basis set. A linear search of minima on the potential energy surface was carried out by applying the method of analytical gradients. First we used the STO-3G basis set to generate initial geometries that provide the starting geometries and symmetries for a subsequent optimization with the 6-31G basis set.

For large systems $(BH)_{32}$, $(BH)_{42}$ and $(BH)_{92}$ we have applied the DFT-LCAO method in the local density approximation (LDA) using an atomic basis set. The structural relaxation was performed without symmetry restrictions within the pseudopotential total-energy scheme, so that the final geometry loses its initial symmetry. The pseudopotentials were generated following the prescription of Troullier-Martins. For the valence electrons we used a basis set of double-ζ quality. The exchange-correlation functional is given by Perdew and Zunger. A conjugate gradient approach is used to perform the geometrical minimization[8].

3. Results and Discussion

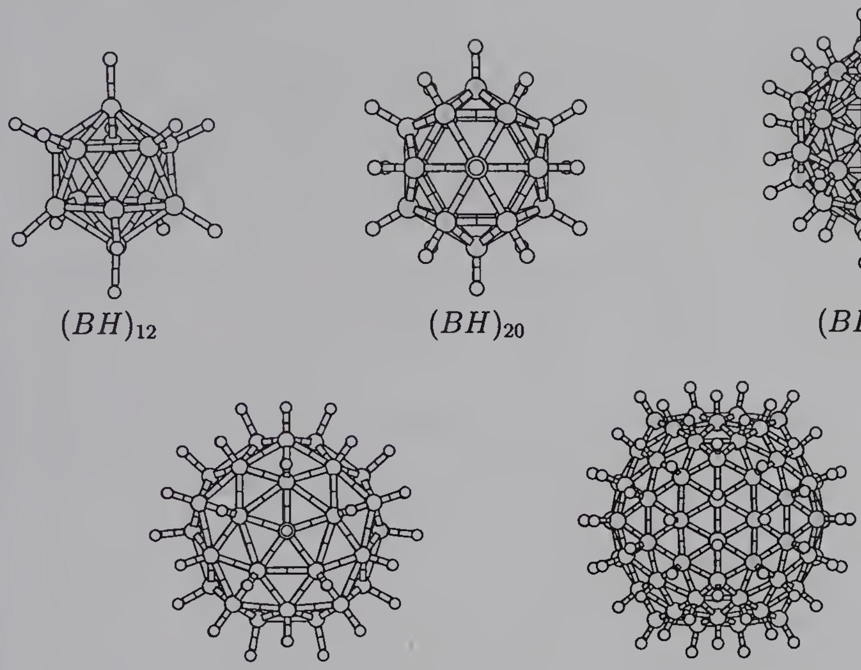
Small systems like $(BH)_{12}$, $(BH)_{20}$ were investigated at the HF-SCF/6-31G level by performing all-electron calculations. Pure boron spheres, B_{32}, B_{42} and B_{92}, were generated at the HF-SCF/STO-3G level, and then investigated at the LDA level including the hydrogen atoms as prickles. In order to compare the cluster stability, determined by the same method, we consequently recalculated the $(BH)_{12}$ and $(BH)_{20}$ clusters at the LDA level of theory. The optimized geometries are given in (Figure 1) and the corresponding energies are listed in (Table 1). The stability of the clusters E_b, also given in (Table 1), is defined as the binding energy per BH unit,

$$E_b = E(BH) - E(BH)_n/n \tag{1}$$

where $E(BH)$ is the energy of the BH unit, and $E(BH)_n$ is the energy of the cluster with the size n. The common structure between boron hydrides is the $(BH)_{12}$ cluster, has nearly an icosahedral structure and is a highly stable configuration. Nevertheless, the corresponding E_b value of 6.189 eV/BH places this cluster only in fourth place within the five clusters of the (Table 1). The structure of the next sphere $(BH)_{20}$, which is an alternative geometry to the dodecahedron, is composed of three hexagonal rings capped on the upper and lower sides, and has initial D_{6h} symmetry. Its E_b value of 6.269 eV/BH places it as the second most stable sphere. $(BH)_{32}$ was first suggested by Lipscomp and Massa[9] as an analogous to fullerenes. Their mapping is geometric only and based on the Euler formula:

$$N + F = e + 2 \tag{2}$$

where N is the number of vertices, F is the number of faces and e is the number of edges. The 32 vertices of this sphere correspond to the 32 faces of C_{60}. With an E_b of 6.274 eV/BH, $(BH)_{32}$ is the most stable structure between all spheres studied here. The initial I_h symmetry transforms to a prolate form during the optimization process due to a Jahn-Teller distortion . The following configuration is the $(BH)_{42}$ sphere.



$(BH)_{12}$ $(BH)_{20}$ $(BH)_{32}$

$(BH)_{42}$ $(BH)_{92}$

Figure 1. *Spherical boron hydrides $(BH)_n$. The scaffold denotes the boron atoms and the prickles the hydrogen atoms.*

The 42 boron vertices correspond to the 42 faces of C_{80}. Slight distortion of its initial I_h symmetry occurs during the optimization process. The E_b of $(BH)_{42}$ is 6.224 eV$/BH$ that places it as the third most stable sphere. The final cluster is the $(BH)_{92}$ sphere and has a nearly icosahedral symmetry. Its vertices correspond to the 60 vertices and the 32 faces of C_{60}. These 32 faces, 12 pentagons and 20 hexagons, are replaced by boron atoms at their centers. This sphere contains dove-tailed pentagonal and hexagonal pyramids, which are the basic units of the most stable boron clusters. The corresponding E_b is 5.994 eV$/BH$. This value degrades it to the less stable sphere. The average bond length of all $(BH)_n$ spheres is given in (Table 1). It varies between 1.78 and 1.85 Å for B-B bonds and between 1.18 and 1.23 Å for B-H bonds.

Recently, Quong *et al.*[10] studied $(BH)_{12}$ and $(BH)_{32}$ besides small boron hydrides as the dual of fullerenes using LDA methods. They found that $(BH)_{12}$ is more stable than the $(BH)_{32}$ cluster by 0.08 eV$/BH$. In our calculations the relative stability is the opposite. The $(BH)_{32}$ sphere is more stable than the $(BH)_{12}$ sphere by 0.08 eV$/BH$ and more stable than the $(BH)_{20}$ sphere only by 0.005 eV$/BH$. However, the discrepancy between our results and those of Quong *et al.* needs further investigation.

The high stability of all the $(BH)_n$ spheres can be related to the saturation effect of hydrogen atoms, that is the elimination of dangling bonds, perpendicular to the spherical surfaces. In contrast to pure boron spheres, boron sheets[2] and nanotubes[8] are highly stable. Other reasons for the high stability of the $(BH)_n$ may be related to the high coordination of boron and to less tension at the surface. The possible gas-phase synthesis of these clusters could open a route for the design of new class of cluster-based materials. New structures arising by substitution of H by molecules, e.g. $B_{32}H_{31} - CH_3$, could have applications in boron chemistry.

Table 1 *LDA-LCAO Energies of the* $(BH)_n$ *Spheres*

Cluster	$(R_{B-B})^a$	$(R_{B-H})^a$	$E(LDA)^b$	$(E_b)^c$
$(BH)_{12}$	1.78	1.23	−1112.1456	6.189
$(BH)_{20}$	1.75	1.21	−1855.1755	6.269
$(BH)_{32}$	1.82	1.22	−2968.4275	6.274
$(BH)_{42}$	1.85	1.21	−3893.9605	6.224
$(BH)_{92}$	1.86	1.21	−8508.4522	5.994
$(BH)_1$	--	1.23	−86.4896	--

[a] *Average bond length of B-B and B-H (Å).*
[d] *LDA-LCAO energies (eV).*
[c] *Binding energy per BH unit (eV/BH), see Eq. 1.*

Starting with the basic units, the pentagonal and hexagonal pyramids, and with help of the "Aufbau principle", proposed in Ref. [1], one can generate highly stable pure boron or boron hydride clusters in form of convex, quasiplanar, tubular and spherical structures. The idea of Lipscomp and Massa for a geometrical mapping between fullerenes and boron is consistent with our *ab initio* proved proposals. Besides their equality in the number of carbon faces and boron vertices and vice versa we may add another equality to generate new spheres: that is, the number of vertices and faces of carbon fullerenes are equal to the number of boron vertices. This is demonstrated by the $(BH)_{92}$ sphere shown in (Figure 1).

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References

1. I. Boustani, *Phys. Rev.*, 1997, **B 55**, 16426.
2. I. Boustani, *Surf. Sci.*, 1997, **370**, 355.
3. A. Ricca and C. W. Bauschlicher Jr., *Chem. Phys.*, 1996, **208**, 233.
4. F. L. Gu, X. Yang, A. C. Tang, H. Jiao and P. v. R. Schleyer, *J. Comput. Chem.*, 1998, **19**, 203.
5. J. E. Fowler and J. M. Ugalde, *J. Amer. Chem. Soc.*, to be published.
6. C. L. Perkins, M. Trenary and T. Tanaka, *Phys. Rev.*, 1998, **B 58**, 9980.
7. I. Boustani, A. Rubio and A. J. Alonso, *Chem. Phys. Lett.*, 1999, submitted
8. I. Boustani, A. Quandt, E. Hernandez and A. Rubio, *J. Chem. Phys.*, 1999, **110**, 3176.
9. W. N. Lipscomp and L. Massa, *Inorg. Chem.*, 1992, **31**, 2297.
10. A. Quong, M. R. Pederson and J. Q. Broughton, *Phys. Rev.*, 1994, **B 50**, 4787.

nido-6<V> Versus *nido*-6<IV> Configurations for the Known Species, $C_2B_4H_6^{2-}$ and $N_2B_4H_6$, and some Calculated Analogs, $B_6H_6^{4-}$, $CB_5H_6^{3-}$, $NB_5H_6^{2-}$, $SB_5H_5^{2-}$, $OB_5H_5^{2-}$, $NCB_4H_6^{1-}$, $SCB_4H_5^{1-}$, $OCB_4H_5^{1-}$, SNB_4H_5, ONB_4H_5, $S_2B_4H_4$, OSB_4H_4 and $O_2B_4H_4$

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1 INTRODUCTION

In 1987 Wade [1] and Williams [2] reported [3] two independent procedures to estimate the charges assigned to the variously coordinated boron-vertices on the surfaces of the many diverse *closo*-$B_nH_n^{2-}$, *nido*-$B_nH_n^{4-}$ and *arachno*-$B_nH_n^{6-}$, clusters. These two disparate procedures gave identical charge distributions and thus were mutually reinforcing.

1.1 Configurational Alternatives

The differing charge distributions about the open faces of the nido-6<V> configuration, $\mathbf{1}_V$, for *nido*-$B_6H_6^{4-}$ and the (at that time undiscovered) nido-6<IV> structure ,$\mathbf{1}_{IV}$, (Figure 1) caused us to question why the former structure is so prevalent. It is known that carbon atoms in carborane analogs of the polyboranes seek out lowest coordinated sites when substituting for boron atoms and that they "prefer" nonadjacent locations when possible. [4] It was also noted that while the ni-6<IV> configuration would have two ideal 3kp sites for carbon atoms that there would be no edge locations available for bridge hydrogens between boron atoms. Suspecting that the presence of bridge hydrogens sometimes "forced" the selection of the ni-6<V> configuration over the ni-6<IV> configuration we suggested to Professor Paul Schleyer that the nido-dianion, $C_2B_4H_6^{2-}$, devoid of bridge hydrogens, would possibly favor the ni-6<IV> structure, $\mathbf{2}_{IV}$. Schleyer subsequently reported [5] [3] that his ab initio calculations supported the ni-6<V> configuration for *nido*-$C_2B_4H_6^{2-}$, $\mathbf{2}_V$, see Figure 1. At the same conference [3] Professor Peter Paetzold reported the discovery of a peralkyl derivative of the parent *nido*-$N_2B_4H_6$, and that it had the ni-6<IV> structure, $\mathbf{3}_{IV}$, see Figure 1.

In 1987 we were not yet persuaded of the accuracy of ab initio calculations and since *nido*-$C_2B_4H_6^{2-}$, $\mathbf{2}_V$, and *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$, were isoelectronic, but apparently not isostructural, it was decided to add (experimentally) two electrons to derivatives of both *closo*-1,2-$C_2B_4H_6$ [6] and *closo*-1,6-$C_2B_4H_6$, [7] to see if *nido*-$C_2B_4H_6^{2-}$ actually had the ni-6<V> structure, $\mathbf{2}_V$ (see Figure 2). Our experimental results, as illustrated in Figure 2, fully vindicated Schleyer's calculations [5]

Years later we repeated the calculations on the ni-6<IV> and ni-6<V> isomers of Paetzold's compound, *nido*-$N_2B_4H_6$, and found the ni-6<IV> configuration was only 0.9 kcal mol-1 more stable than the ni-6<V> structure. The two structures, $\mathbf{3}_{IV}$,and $\mathbf{3}_V$, were energetically almost equivalent.

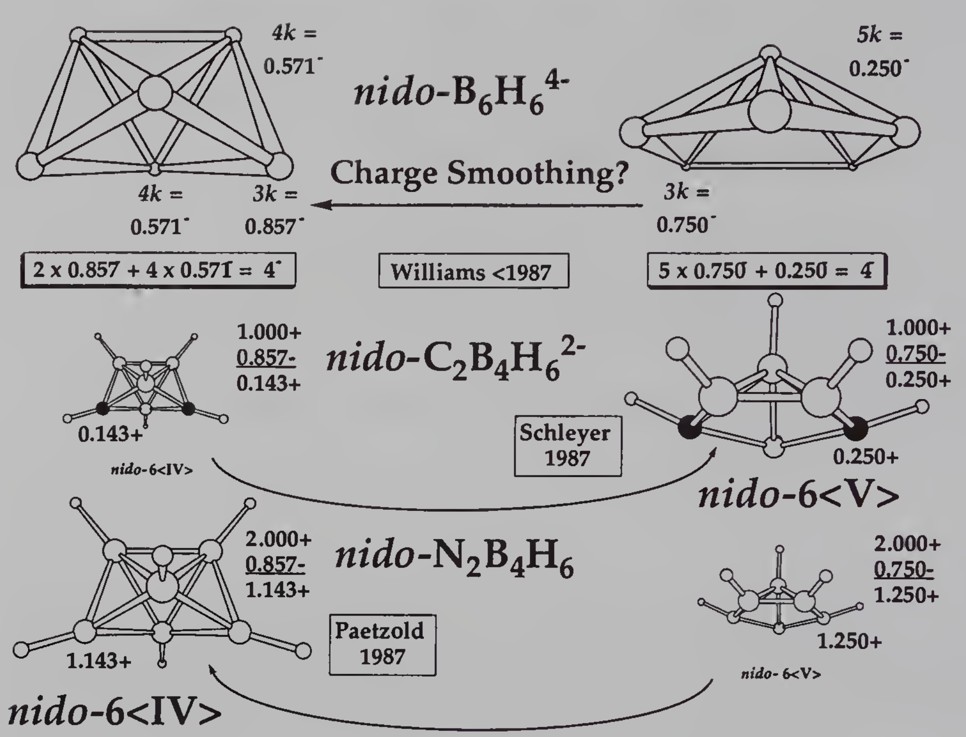


Figure 1 *nido-2,4-*$C_2B_4H_6^{2-}$*, 2V, and nido-*$N_2B_4H_6$*, 3IV, Structures*

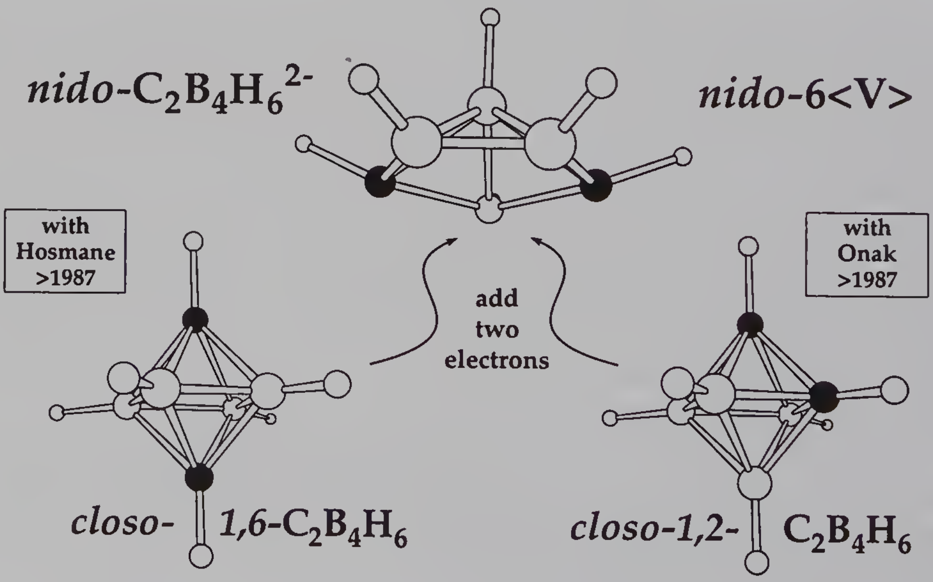
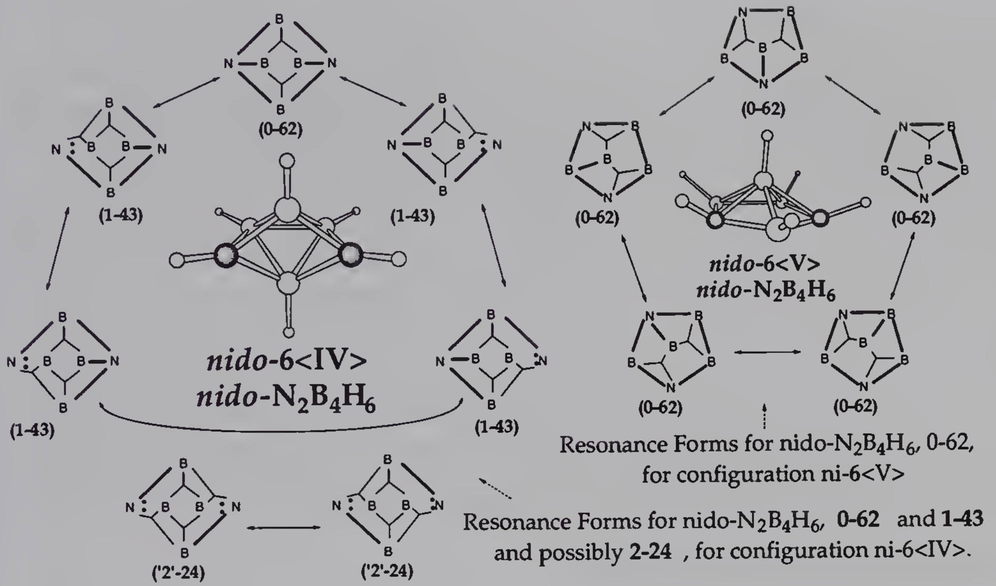


Figure 2 *closo-1,2-*$C_2B_4H_6$ *and closo-1,6-*$C_2B_4H_6$ *+ 2e yield nido-2,4-*$C_2B_4H_6^{2-}$, 2_V

1.2 Electron Distribution Alternatives; No Decision

In Paetzold's view [8] the "electronic structure" for *nido*-$N_2B_4H_6$, 3_{IV}, Figure 1, in terms of three-center two electron (3c2e) bonds and 2c2e bonds, places the two 3c2e bonds in locales involving boron atoms only while the nitrogen atoms interact with 2c2e bonds only, see Figure 3. The two nitrogen atoms are in essence in electron precise environments, as in an ammonium cation.



Resonance Forms for nido-$N_2B_4H_6$, 0-62, for configuration ni-6<V>

Resonance Forms for nido-$N_2B_4H_6$, **0-62** and **1-43** and possibly **2-24**, for configuration ni-6<IV>.

Figure 3 *nido-$N_2B_4H_6$, 3IV, , 3V, Structures: Alternative Perspectives*

Alternatively, Williams views the "electronic structure(s)" of *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$ and $\mathbf{3}_V$, in Figure 3, to be represented by resonance structures wherein the boron and nitrogen atoms are both involved with 3c2e bonds and 2c2e bonds. Incorporation of lone pairs of electrons on nitrogen ("1c2e bonds"), in the $\mathbf{3}_{IV}$ structure, are considered as contributors (see Figure 3). [9] We are not in a position, at this time, to endorse either viewpoint with regards to the "electronic structure" of *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$. Perhaps many resonance forms contribute to the structure with the most influential form being the one preferred by Paetzold. On the other hand the resonance structure(s) of *nido*-$N_2B_4H_6$, $\mathbf{3}_V$, in Figures 3, (only 0.9 kcal mol^{-1} less stable than the $\mathbf{3}_{IV}$ isomer) must incorporate nitrogen atoms that are involved with 3c2e bonds. There is no reason to invoke lone pairs on nitrogen in the $\mathbf{3}_V$ isomer.

Our view is based upon our attitude that the nido-6-atom structure (with a pentagonal open face) has access to 8 skeletal electron pairs while the closo-6-atom structure (with trigonal faces) has access to 7 skeletal electron pairs. Might not something in between like a nido-6-atom structure (with a tetragonal open face) be favored if one of the 8 skeletal electron pairs was unavailable for connecting the skeletal electrons? It is also recognized that less electrons lead to more connections via 3c2e bonds. In the $\mathbf{3}_V$ structures in Figure 3 there are, in all cases, "zero 1c2e", six 2c2e and two 3c2e bonds. This situation is identified as the 0-62 electron pair distribution. Only ***two*** of the eight skeletal electron pairs are 3c2e bonds and a rather open ni-6<V> structure is produced. In contrast, if one endo lone pair is present then a 1-43 electron pair distribution results (seen only in selected *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$, structures illustrated in Figure 3). In this case only seven electron pairs are available for connecting the skeletal atoms to each other as the lone electron pair (the 1 in 1-43 label) is not accessible for intra-skeletal bonding. There are ***three*** 3c2e bonds in this case and a more closed ni-6<IV> structure is produced. Such a "seven electron pair situation", for connecting the skeletal atoms to each other is normal in the closo-6-atom cluster that has a 0-34 electron pair distribution, see Figure 2. There are ***four*** 3c2e bonds, out of seven, and the totally closed clo-6<III> structure is produced. We theorized that the production of endo-lone pairs may be what drives the choice of the ni-6<IV> structure (1-43) over the ni-6<V> structure (0-62) and that the substitution of even more electronegative heteroatoms might more strongly favor the ni-6<IV> structures.

2 RESULTS AND DISCUSSION

Ab initio calculations were carried out on both the ni-6<IV> and ni-6<V> configurations of *nido*-$B_6H_6^{4-}$ and fourteen other mono- and di-heteroatom substituted analogs (see Figure 4). The heteroatoms (followed by Pauling's electronegativity values in brackets, {}) included C{2.5}, N{3.1 }, S{2.4}, and O{3.5}, to be compared with B{2.0}.

In the case, *nido*-$B_6H_6^{4-}$, the "input" ni-6<IV> geometry spontaneously "optimized" to the ni-6<V> geometry as noted by the [XX→] sign in Figure 4. In two cases the reverse was true. Thus in *nido*-$O_2B_4H_4$ and *nido*-OSB_4H_4, the "input" ni-6<V> geometries spontaneously "optimized" to the ni-6<IV> geometries as noted by the sign [←XX]. In these cases we could not obtain indications of the differences in energy of the two isomers. These examples were frustrating as we wished to know, not only which isomers were most stable, but in each case, by what amount, i. e. "the difference value" in kcal mol^{-1}, was one of the isomers more stable than the other isomer. Additionally, in two cases, *nido*-$CB_5H_6^{3-}$and *nido*-$SB_5H_5^{2-}$, the "input" ni-6<IV> geometries "optimized" to a distorted ni-6<?IV?> geometries as noted by the [X→] sign. [10] The desired difference values were considered questionable in these examples.

2.1 Unmixed Heteroatom Compounds

Even with half of the numbers missing or suspect, it appeared that perhaps some "trial and error" attempts to ferret out patterns might be worthwhile. In Figure 5 we compare four series involving nine structures. Only two species are known (boxed). Note that the numbers below each formula are measures of how much more stable that structure is, compared to its less stable isomer. As an example the most stable isomer, *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$ (E_{rel} = 0.0), may be compared with the slightly less stable isomer, *nido*-$N_2B_4H_6$, $\mathbf{3}_{V}$ (E_{rel} = 0.9). For our purposes in Figure 5 we note that the most stable isomer, *nido*-$N_2B_4H_6$, $\mathbf{3}_{IV}$, is more stable than *nido*-$N_2B_4H_6$, $\mathbf{3}_{V}$, by 0.9 kcal mol^{-1}.

In the series *nido*-$B_6H_6^{4-}$ to *nido*-$NB_5H_6^{2-}$ to *nido*-$N_2B_4H_6$ we had at least some confidence in the "difference value" of 27.7 kcal mol^{-1} (solid arrow) between *nido*-$NB_5H_6^{2-}$ (0.9) and *nido*-$N_2B_4H_6$ (26.8); both values were calculated. Absent intuition or guidance we also assigned the difference between *nido*-$B_6H_6^{4-}$ and *nido*-$NB_5H_6^{2-}$ a value of 27.7 kcal mol^{-1} (dotted arrow). This dubious procedure led to an *extrapolated value* of (54.5) for *nido*-$B_6H_6^{4-}$. This assumed that the ni-6<V> configuration (E_{rel} = 0.0) was 54.5 kcal mol^{-1} more stable than the ni-6<IV> structure (E_{rel} = 54.5) of *nido*-$B_6H_6^{4-}$ for which no minimum could be found.

A crime, once committed and unpunished, becomes successively easier to repeat. In the top series, *nido*-$B_6H_6^{4-}$ (54.5), *nido*-$CB_5H_6^{3-}$ (?42.3?) and *nido*-$C_2B_4H_6^{2-}$ (35.3), the middle value of 42.3 was not trusted. However, if we accept the extrapolated 54.5 and calculated 35.3 values as correct and "split the difference" then an extrapolated value of 44.9 for *nido*-$CB_5H_6^{3-}$ emerges which is not that much different from the calculated ?42.3?. In the third series, *nido*-$B_6H_6^{4-}$ (54.5), *nido*-$SB_5H_5^{1-}$ (?19?) and *nido*-$S_2B_4H_4$ (17.5), the middle value of 19 was again not trusted, but if we accept the 54.5 and 17.5 values and "split the difference" a value of 18.5 emerges which is very close to ?19?.

In the fourth series, *nido*-$B_6H_6^{4-}$ (54.5), *nido*-$OB_5H_5^{1-}$ (10.7) and *nido*-$O_2B_4H_4$, the latter value was not known, but if we accept the extrapolated 54.5 and calculated 10.7 values, the difference is 43.8. Using this same difference value of 43.8 we can extrapolate that the ni-6<IV> structure for *nido*-$O_2B_4H_4$ is ?33.1? kcal mol^{-1} more stable than its ni-6<V> analog for which we could find no minimum. These suspect patterns look interesting but can any of these numbers be tested? Calculations on more analogs were needed.

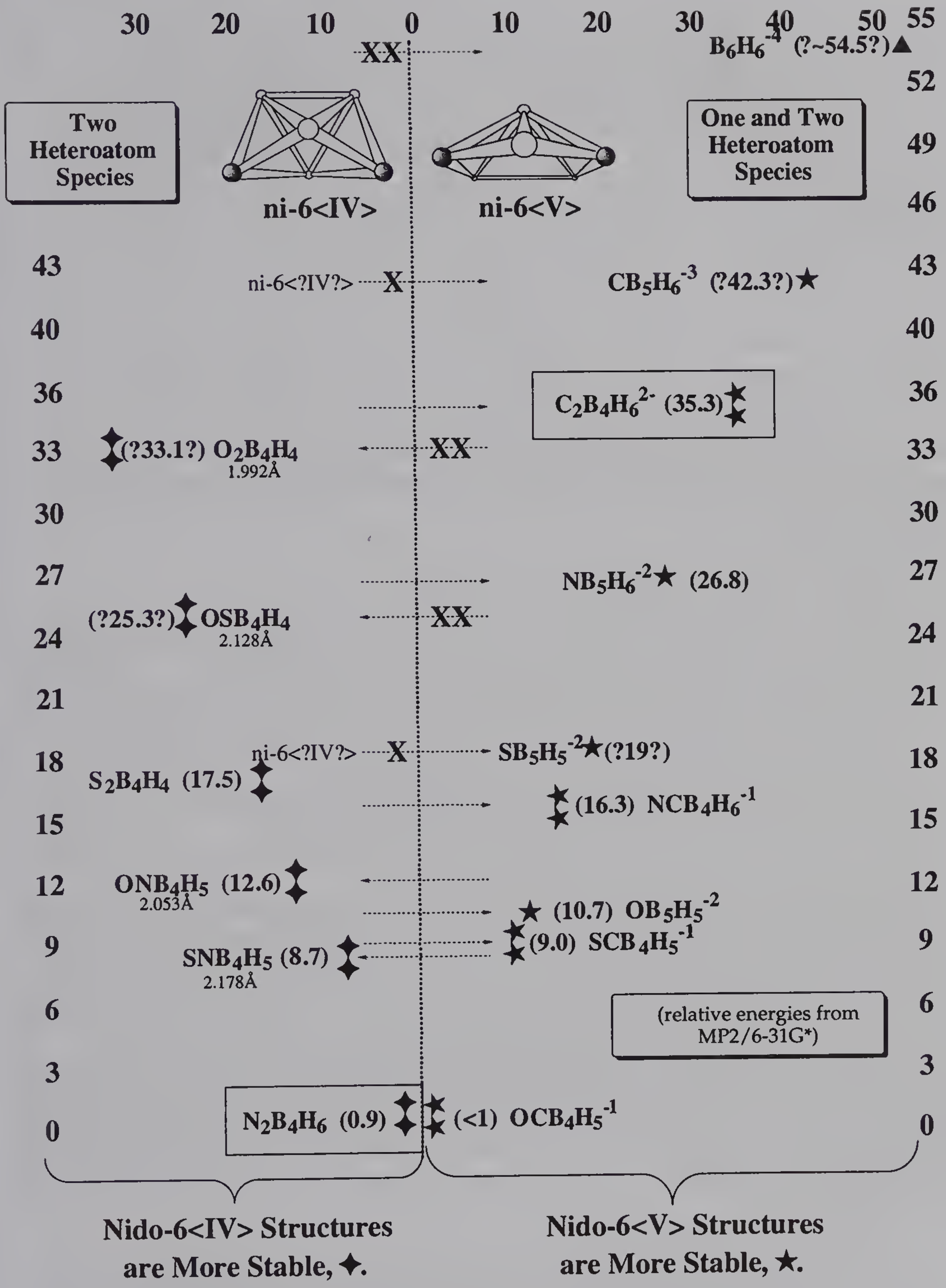


Figure 4 *"Zero-",mono- and di-heteroatom substituted analogs (C, N, S and O)*

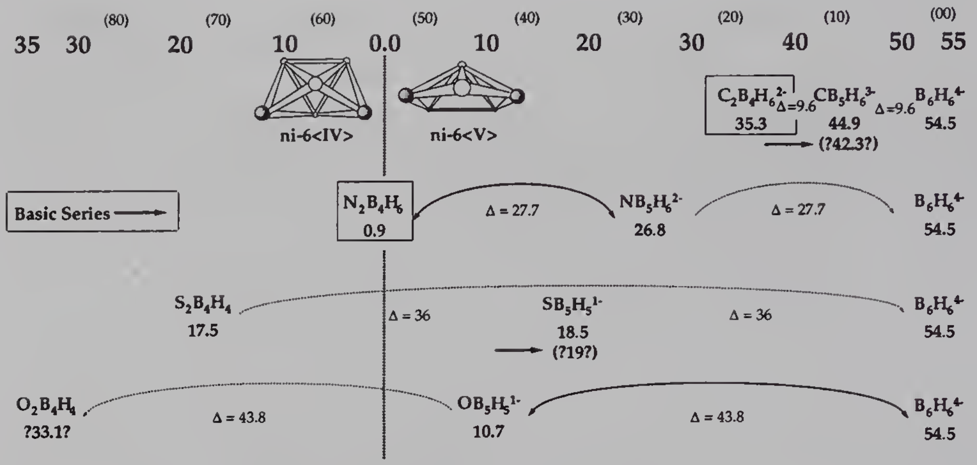


Figure 5 *nido-*$B_6H_6^{4-}$ *in series with the four pairs: nido-*$CB_5H_6^{3-}$ *plus nido-*$C_2B_4H_6^{2-}$*; nido-*$NB_5H_6^{2-}$ *plus nido-*$N_2B_4H_6$*; nido-*$SB_5H_5^{1-}$ *plus nido-*$S_2B_4H_4$ *and nido-*$OB_5H_5^{1-}$ *plus nido-*$O_2B_4H_4$

2.2 Carbon and Other Heteroatom Compounds

There are a number of questions that should test the highly suspect conclusions drawn from Figure 5. These conclusions are:

(a) that the ni-6<V> configuration of *nido*-$B_6H_6^{4-}$, is 54.5 kcal mol^{-1} more stable than the ni-6<IV> alternative for which no minimum could be found and,
(b) that substitutions of carbons for borons results in a "movement" of 9.6 kcal mol^{-1} in the direction of favoring a ni-6<IV> structure and,
(c) that substitutions of nitrogens for borons results in a "movement" of 27.7 kcal mol^{-1} in the direction of favoring a ni-6<IV> structure and,
(d) that substitutions of sulfurs for borons results in a "movement" of 36 kcal mol^{-1} in the direction of favoring a ni-6<IV> structure and,
(e) that substitutions of oxygens for borons results in a "movement" of 43.8 kcal mol^{-1} in the direction of favoring a ni-6<IV> structure.

If these conclusions are correct then the mixed species, $NCB_4H_6^{1-}$, $SCB_4H_5^{1-}$, $OCB_4H_5^{1-}$, should have ni-6<V> structures, that are more stable than their ni-6<IV> analogs by 17.2, 8.9 and 1.1 kcal mol^{-1} respectively. The 1.1 estimated value is probably too close to call as calculations may vary by a kcal or so.

As illustrated in Figure 6 these projections are far "better" than we had any right to expect. The calculated value for $NCB_4H_6^{1-}$ is 16.3 to be compared to the 17.2 projected from Figure 5. The calculated value for $SCB_4H_5^{1-}$ is 9.0 to be compared to the 8.9 projected from Figure 5 and the calculated value for $OCB_4H_5^{1-}$ is <1 to be compared to the 1.1 projected from Figure 5.

2.3 Mixed Heteroatom Compounds

There are a number of questions that should further test the conclusions drawn from Figure 5. If these conclusions are correct then the mixed species, SNB_4H_5, ONB_4H_5, OSB_4H_4, should have ni-6<IV> structures that are more stable than their ni6<IV> analogs by ?9.2?, ?17? and 25.3 kcal mol^{-1}. In Figure 7 it is seen that the calculated value of 8.7 for SNB_4H_5 is very close to the extrapolated value of ?9.2?. On the other hand the calculated value of 12.6 for ONB_4H_5 differs by 4.3 kcal mol^{-1} from the extrapolated value of ?17?; this is the worst mismatch encountered! The extrapolated value of ?25.3? for OSB_4H_4, ni-6<IV> isomer, is not in contention as the OSB_4H_4, ni-6<V>, analog does not optimize to a minimum and thus no comparison can be made.

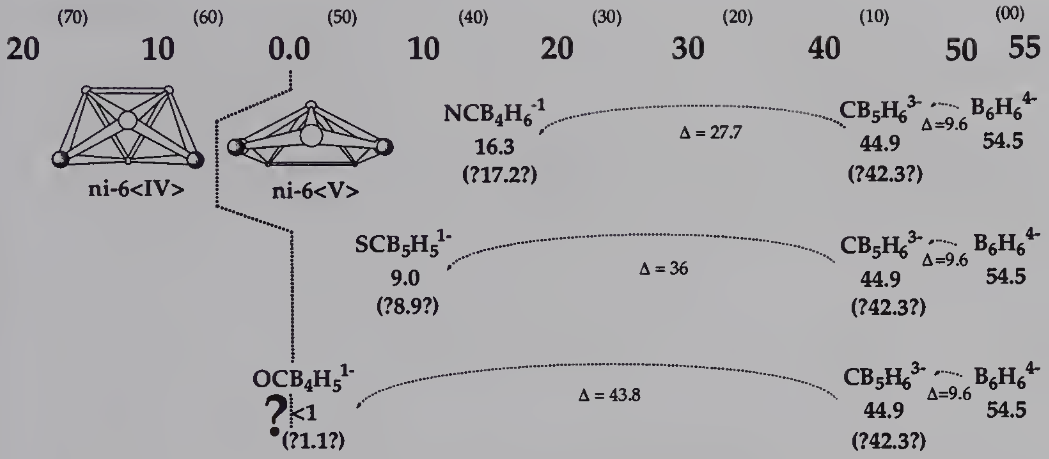


Figure 6 *Extrapolated Versus Calculated Stability Advantages for the mixed species,* $NCB_4H_6^{1-}$, $SCB_4H_5^{1-}$ *and* $OCB_4H_5^{1-}$

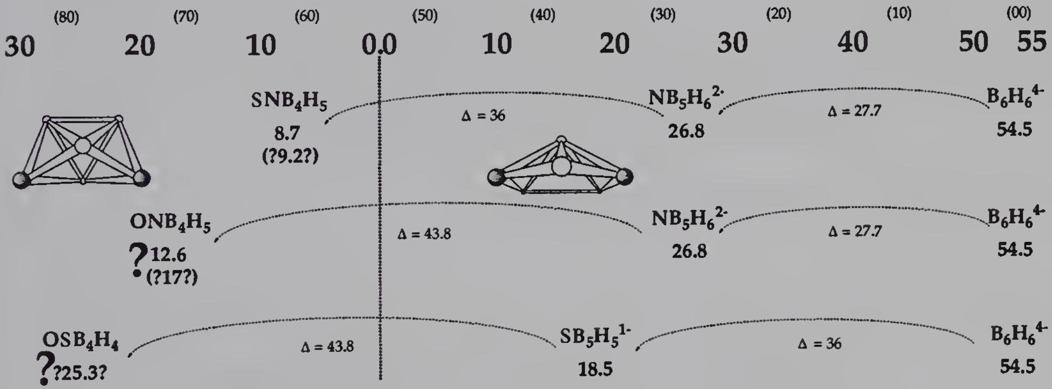


Figure 7 *Extrapolated Versus Calculated Stability Advantages for the mixed species,* SNB_4H_5, ONB_4H_5 *and* OSB_4H_4

2.4 Comparison of "Difference Values" and Electronegativities

The idea that first-row heteroatoms, in the order C{2.5}, N{3.1} and O{3.5}, when substituted for B{2.0} might tend increasingly to favor the ni-6<IV> structure seems to be valid, see Figure 8. There also seems to be an even stronger second-row "inflation effect" in that sulfur, S{2.4}, with an electronegativity less than carbon, C{2.5}, has an "influence" half way between N{3.1} and O{3.5}. We would suspect that phosphorous and silicon substitution for boron would have similar second-row "inflation effects".

2.5 Protonation of *nido*-$N_2B_4H_6$ to Produce *nido*-$N_2B_4H_7^{1+}$

As illustrated in Figure 1, *nido*-$N_2B_4H_6$ favors the ni-6<IV> structure over the ni-6<V> structure by 0.9 kcal mol^{-1}. As the driving force was considered to be associated with the absence of bridge hydrogens we felt that the ni-6<V> configuration would be favored if a proton was added to produce *nido*-$N_2B_4H_7^{1+}$. In Figure 9 the nido-6<V> structure for *nido*-$N_2B_4H_7^{1+}$ is illustrated. Attempts to find a nido-6<IV> based structure with endo-hydrogens on either boron or nitrogen failed.

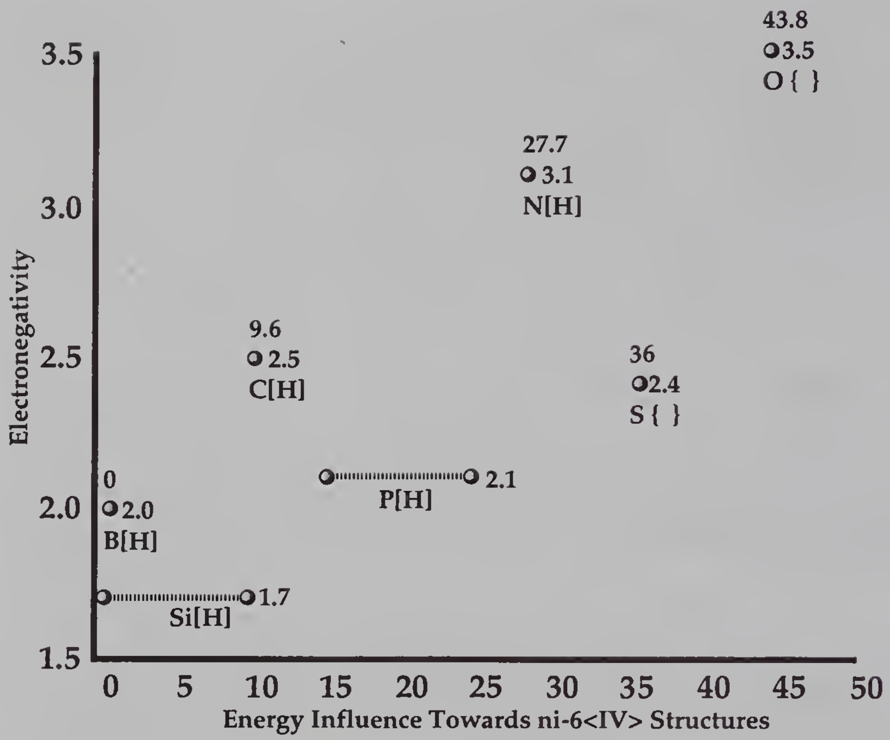


Figure 8 *"Difference Values" amd Electronegativities*

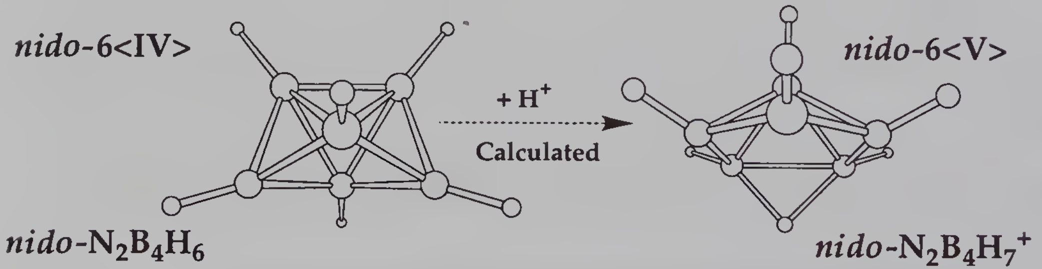


Figure 9 *Protonation of nido-$N_2B_4H_6$ to Form nido-$N_2B_4H_7{}^{1+}$*

3 CONCLUSIONS

The ni-6<V> structure is favored by all nido-6-atom boron hydrides and carboranes. When one heteroatom substitutes for Boron, B{2.0}, including C{2.5}, N{3.1 }, S{2.4}, and O{3.5}, the ni-6<V> structure is still favored. When two heteroatoms substitute for boron, B{2.0}, including N{3.1 }, S{2.4}, and O{3.5}, the ni-6<IV> structure is favored. The trend seems to follow the relative electronegativities with respect to the atoms, B{2.0}, C{2.5}, N{3.1 } and O{3.5}. Sulfur, S{2.4}, (the only second row heteroelement tested) is out of line as it has an "inflated influence" in between N{3.1 } and O{3.5}. [11]

The influence in kcal mol^{1} (in the direction of favoring the ni-6<IV> configuration) following the substitution for boron, B{2.0}, by the various heteroelements seems to be surprisingly constant. The influence for carbon, C{2.5}, is 9.6; the influence for nitrogen, N{3.1 }, is 27.7; the influence for sulfur, S{2.4 }, is 36; and the influence for oxygen, O{3.5 }, is 43.8.

Calculations suggest that protonation of *nido*-$N_2B_4H_6$, would favor *nido*-$N_2B_4H_7{}^{1+}$ with a ni-6<V> structure in order to accommodate one bridge hydrogen, BHB.

REFERENCES

[1] Wade, K., Chapter 1, pp. 3-25 in *"Boron Chemistry"*, Ed. S. Hermanek, World Scientific, Singapore, 1987.

[2] Williams, R. E., Chapter 2 in *"Electron Deficient Boron and Carbon Clusters"*, G. A. Olah, K. Wade and R. E. Williams Eds., Wiley-Interscience, New York, 1991.

[3] IMEBORON-VI Conference, June 22-26, 1987 in Bechyne, Czech Republic.

[4] Williams, R. E. and Gerhart, F. J., *J. Am. Chem. Soc.*, 1965, ***87***, 3513.

[5] P. v. R. Schleyer, personal communication to R. E. Williams in 1987. [3]

[6] *closo*-1,2-Me_2-1,2-$C_2B_4H_6$ furnished by T. P. Onak

[7] Hosmane, N. S.; Lei, J.; Zhang, H.; Bausch, J. W.; Prakash, G. K. S.; Onak T. P. and Williams R. E. *Inorg. Chem.*, 1991, ***30***, 3793.

[8] Paetzold, Chapter 20, pp 446-475 in *"Boron Chemistry"*, Ed. S. Hermanek, World Scientific, Singapore, 1987.

[9] Williams, R. E., Chapter 1 in *"The Borane, Carborane, Carbocation Continuum"*, Ed. J. Casanova, Wiley-Interscience, New York, 1998.

[10] It was as if the lone carbon and sulfur atoms were "being extruded" as electron precise groups.

[11] Sulfur seemingly has greater influence in promoting smaller open faces in the nido-8-atom [12] and nido-9-atom clusters as well.

[12] Tebbin, A. J.; Ji, G.; Bausch J. W. and Williams, R. E., *Inorg. Chem.*, 1998, *37*, 2189-2197.

Defective Vertices and Unsaturation in Borane Deltahedra

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The most stable molecular boron cages such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ are based on icosahedral structures.[1,2] In addition, icosahedral cages are found in the stable allotropes of boron and many of the most stable metal borides.[3,4] This paper presents a new approach to the description of non-icosahedral boron deltahedra in terms of their deviation of their local vertex surroundings from those found in ideal icosahedra, where a deltahedron is considered to be a polyhedron in which all faces are triangles. This method complements other methods for the study of borane deltahedra including the topological methods of Lipscomb[5] leading to localized bonding models as well as methods based on graph theory[6] or tensor surface harmonics[7] for study of three-dimensional aromaticity.

The characteristic feature of the geometry of the regular icosahedron is the presence of twelve equivalent vertices of degree 5 where the degree of a vertex is the number of edges meeting at that vertex. If the unusual stability of borane icosahedra can be attributed to the special stability of degree 5 boron vertices, then vertices of degrees other than 5 can be considered to be defects in the deltahedral structure. The most favorable borane deltahedra will be those with a minimum number of such defective vertices and with the defective vertices as widely spaced as possible. Conversely, the defective vertices are potential sites of chemical reactivity in borane deltahedra.

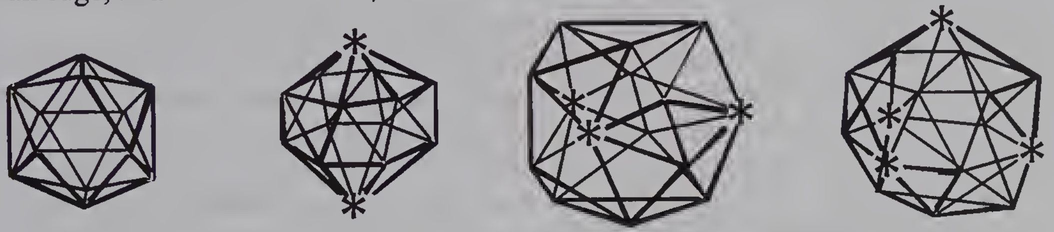
This idea of defective vertices is not original but was used by Frank and Kasper more than 40 years ago to study polyhedra found in metal alloy structures.[8] In such polyhedra the defective vertices are vertices of degree 6. Frank and Kasper showed that there are only four polyhedra (Figure 1) with only degree 5 and 6 vertices and with "isolated" degree 6 vertices, i.e., no pair of degree 6 vertices is connected by an edge. The four Frank-Kasper polyhedra are significant not only in metal alloy structures but also in metal carbonyl cluster chemistry in describing the polyhedra formed by the carbonyl ligands in polynuclear metal carbonyls.[9]

The deltahedra for the stable cage boranes (Figure 2) are characterized by having no degree 3 vertices and only degree 4 and 5 vertices except for the $B_{11}H_{11}^{2-}$ polyhedron which is topologically required to have at least one degree 6 vertex.[10] In such borane deltahedra, the defective vertices can be considered to be the vertices of degree 4. Among borane deltahedra other than the icosahedron only the bicapped square antiprism of $B_{10}H_{10}^{2-}$ and the tricapped trigonal prism of $B_9H_9^{2-}$ are seen to meet a Frank-Kasper-like criterion of non-adjacent degree 4 vertices.

These topological observations relate to the experimentally observed chemistry of the deltahedral borane anions $B_nH_n^{2-}$. For example the hydrolytic stability of the deltahedral boranes[11] decreases in the approximate sequence:

$$B_{12}H_{12}^{2-} > B_{10}H_{10}^{2-} > B_{11}H_{11}^{2-} > B_9H_9^{2-} \sim B_8H_8^{2-} \sim B_6H_6^{2-} > B_7H_7^{2-}$$

The most hydrolytically stable borane anions are thus those in which there are no adjacent degree 4 vertices, notably $B_{10}H_{10}^{2-}$ and $B_9H_9^{2-}$ as well as $B_{11}H_{11}^{2-}$. In addition the generation of $B_nH_n^{2-}$ by the pyrolysis of CsB_3H_8 is known to lead only to $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_9H_9^{2-}$, i.e. deltahedral boranes with no pair of degree 4 vertices connected by an edge, in addition to $CsBH_4$.[12]



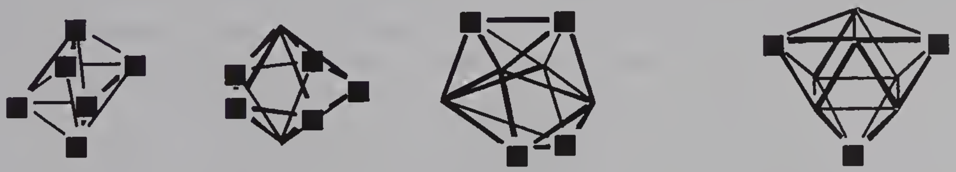
12 vertices:
Icosahedron
I_h

14 vertices:
Bicapped Hexagonal Antiprism
D_{6d}

15 vertices:
Staggered 3^5 Stack
Föppl $3:[(3):3]_2$
D_{3h}

16 vertices:
Tetracapped Truncated Tetrahedron
T_d

Figure 1 *The four Frank-Kasper polyhedra. In the figures degree 4 vertices are indicated by ■ and degree 6 vertices by* ✻.

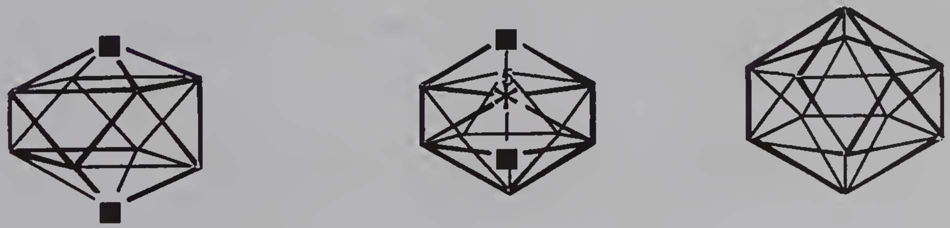


6 vertices:
Octahedron

7 vertices:
Pentagonal Bipyramid

8 vertices:
Bisdisphenoid
("D_{2d} Dodecahedron")

9 vertices:
3,3,3-Tricapped Trigonal Prism



10 vertices:
4,4-Bicapped Square Antiprism

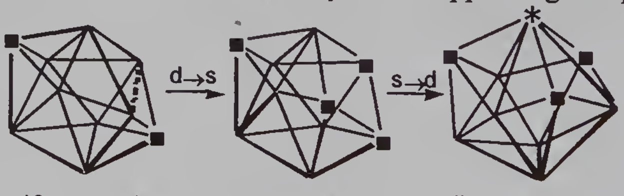
11 vertices:
Edge-coalesced Icosahedron

12 vertices:
Icosahedron

Figure 2 *The polyhedra for the deltahedral borane anions* $B_nH_n^{2-}$.

The special reactivity associated with BH groups at degree 4 rather than degree 5 vertices is also related to some aspects of the chemical reactivity of the octahedral $B_6H_6^{2-}$ which has only degree 4 vertices and thus should be reactive. In this connection $B_6H_6^{2-}$, although highly symmetrical, is only obtainable in low yield in cage borane syntheses.[13,14] Furthermore, $B_6H_6^{2-}$ may be regarded as an "unsaturated" deltahedral borane, since it is unusually reactive towards addition reactions in which its degree 4 vertices effectively become degree 5 vertices through bonding to external groups. For example, protonation of $B_6H_6^{2-}$ to give $B_6H_7^-$ occurs much more readily ($pK_a = 7.00$)[15] than the protonations of other $B_nH_n^{2-}$ ions to give the corresponding $B_nH_{n+1}^-$ ions so that aqueous solutions of alkali metal salts of $B_6H_6^{2-}$ are significantly basic owing to the equilibrium $B_6H_6^{2-} + H_2O = B_6H_7^- + OH^-$. In $B_6H_7^-$ the "extra" hydrogen atom caps one of the triangular faces of the $B_6H_6^{2-}$ octahedron so that 3 of the degree 4 vertices become degree 5 vertices through multicenter bonding with this "extra" hydrogen atom. Similarly $B_6H_6^{2-}$ acts as a tridentate ligand in metal complexes such as $[nBu_4N][(\eta^3\text{-}B_6H_6)_2Cd]$,[16] $[Ph_4P][PhHg(\eta^3\text{-}B_6H_6)]$,[17] $(Ph_3P)_2M(\eta^3\text{-}B_6H_6)$ (M = Cu and Au),[18] and $[nBu_4N][Ni(\eta^5\text{-}C_5H_5)(\eta^3\text{-}B_6H_6)]$.[14]

The development of metallaborane chemistry in recent years has led to the discovery of some metallaborane structures containing the so-called *isocloso* deltahedra, which have a transition metal atom (e.g., Ru, Rh, Ir) located at a degree 6 vertex.[19,20] Such *isocloso* metalla-borane deltahedra, except for the 11-vertex structures, are topologically different from the *closo* borane deltahedra found in the simple boranes $B_nH_n^{2-}$ and the corresponding carboranes $C_2B_{n-2}H_n$ but may be derived from the *closo* deltahedra by one or more diamond-square-diamond processes (Figure 3). The *isocloso* deltahedra with v vertices have $2v$ skeletal electrons rather than the $2v+2$ skeletal electrons for *closo* deltahedra implying a different bonding topology, possibly 2-electron 3-center B–B–B bonds in v of the $2v-4$ faces of the *isocloso* deltahedron rather than the single v-center core bond and v 2-electron 2-center bonds in the surface of the *closo* deltahedron.[6,7] The most prevalent *isocloso* metallaborane deltahedra are those with 10 and 11 vertices in which the degree 4 boron vertices are isolated from each other but connected to the degree 6 metal vertex (Figure 3). The equilateral triangle pattern of the three degree 4 vertices in the 10-vertex *isocloso* metallaborane deltahedron (Figure 3) is similar to that in the 9-vertex *closo* borane deltahedron, namely the tricapped trigonal prism (Figure 2).



10-vertex *closo* polyhedron (D_{4d} bicapped square antiprism)

The 10-vertex *isonido* polyhedron

The (C_{3v}) 10-vertex *isocloso* polyhedron

11-vertex *closo* polyhedron (C_{2v} "edge-coalesced icosahedron")

The 11-vertex *isonido* polyhedron

The 11-vertex *isocloso* polyhedron (Also a C_{2v} edge-coalesced icosahedron)

Figure 3 *The 10- and 11-vertex isocloso deltahedra found in metalloboranes and their formation by diamond-square-diamond (d→s→d) processes.*

A question of interest in deltahedral borane chemistry is whether supraicosahedral boranes $B_nH_n^{2-}$ ($n \geq 13$) can be prepared and whether the Frank-Kasper polyhedra (Figure 1) are suitable models for their structures. The supraicosahedral metallacarborane $(C_5H_5)_2Co_2B_{10}C_2H_{12}$ is known[21] and has a structure based on the Frank-Kasper bicapped hexagonal antiprism with the cobalt atoms at the degree 6 vertices. Recent computations[22] suggest that the still unknown metal-free supraicosahedral boranes $B_nH_n^{2-}$ (n = 13 to 17) should be stable although the design of suitable synthetic methods might be rather challenging in order to avoid getting trapped in the icosahedral $B_{12}H_{12}^{2-}$ energy sink. The geometry optimization in these computations led to the Frank-Kasper polyhedra for $B_{14}H_{14}^{2-}$ and $B_{15}H_{15}^{2-}$ but not for $B_{16}H_{16}^{2-}$, which had an optimized structure with two square faces.

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REFERENCES

1. E. L. Muetterties, ed., Boron Hydride Chemistry, Academic Press, New York, 1975.
2. R. N. Grimes, Carboranes, Academic Press, New York, 1970.
3. J. L. Hoard and R. E. Hughes, in E. L. Muetterties, ed., The Chemistry of Boron and its Compounds, Wiley, New York, 1967, pp. 25–154.
4. D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Woods, eds., Boron-Rich Solids, American Institute of Physics Conference Proceedings 140, American Institute of Physics, New York, 1986.
5. W. N. Lipscomb, Boron Hydrides, Benjamin, New York, 1963, Chapter 2.
6. R. B. King and D. H. Rouvray, J. Am. Chem. Soc., 1977, **99**, 7834.
7. A. J. Stone and M. J. Alderton, Inorg. Chem., 1982, **21**, 2297.
8. F. C. Frank and J. S. Kasper, Acta Crystallogr., 1958, **11**, 184.
9. R. B. King, Inorg. Chim. Acta, 1995, **235**, 111.
10. R. B. King and A. J. W. Duivestijn, 1990, **178**, 55.
11. R. L. Middaugh, in E. L. Muetterties, ed., Boron Hydride Chemistry, Academic Press, New York, 1975, p. 283.
12. F. Klanberg and E. L. Muetterties, in W. L. Jolly, ed., Inorganic Syntheses, McGraw-Hill, New York, 1968, vol. 11, p. 27.
13. J. L. Boone, *J. Am. Chem. Soc.*, 1964, **86**, 5036.
14. R. M. Kabbani, *Polyhedron*, 1996, **15**, 1951.
15. W. Preetz, A. Heinrich, and J. Thesing, *Z. Naturforsch.*, 1988, **43b**, 1319.
16. T. Schaper and W. Preetz, *Inorg. Chem.*, 1998, **37**, 363.
17. T. Schaper and W. Preetz, *Z. Naturforsch.*, 1997, **52b**, 57.
18. T. Schaper and W. Preetz, *Chem. Ber. Rec.*, 1997, **130**, 405.
19. J. D. Kennedy and B. Štibr, in *Current Topics in the Chemistry of Boron*, ed., G. W. Kabalka, Royal Society of Chemistry, Cambridge, 1994, pp. 285-292.
20. J. D. Kennedy, in *The Borane-Carborane-Carbocation Continuum*, ed., J. Casanova, Wiley, New York, 1998, ch. 3, pp. 85–116.
21. W. J. Evans and M. F. Hawthorne, *J. Chem. Soc. Chem. Comm.*, 1974, **38**.
22. P. v. R. Schleyer, K. Najafian, and A. M. Mebel, *Inorg. Chem.*, 1998, **37**, 6765.

The Dianions of *o*-, *m*-, *p*-Carboranes from *Ab Initio* Calculations

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1. INTRODUCTION

Although the existence of $C_2B_{10}H_{12}^{2-}$ ions derived from the *o*-, *m*- and *p*-carboranes were reported already during the 1960'ies[1-6], their number and their structures have remained largely unknown. The chemistry of the dianions has been extensively explored, but they have not yet been isolated as salts. In the present study we discuss the uptake of one and two electrons by each of the three carboranes, based on *ab initio* calculations, and present the resulting optimized structures and relative stabilities of the neutral carboranes and their anions.

2. RESULTS AND DISCUSSION

2.1 The neutral $C_2B_{10}H_{12}$ carboranes

2.1.1 Relative stabilities of the o-, m-, and p-compounds. Geometry optimisations at the Hartree-Fock 3-21G*, 6-31G* and 6-31G** levels were carried out using the program Spartan 4.1 [7] and the Gaussian 94/DFT program [8]. The optimized geometries of the neutral $C_2B_{10}H_{12}$ carboranes are found in the left column of **Fig. 1**, together with their relative energies. The relative energy values change very little between the three basis sets. It is well known (Grafstein[2]) that, on heating, *o*-carborane is converted to *p*-carborane via the *m*-compound. The experimental heats of formation for the three carboranes in the solid state confirm this stability trend: -176 kJ/mol, -246 kJ/mol and -315 kJ/mol for *o*-, *m*-, and *p*-carborane, respectively (average values from Gmelin[9]). Our calculated total energies at the 6-31G* and 6-31G** levels give that the *m*-carborane is ~75 kJ/mol more stable than the *o*-carborane, in reasonable agreement with experiment. However, the calculations show *p*-carborane to be only ~10 kJ/mol more stable than the *m*-carborane, *i.e.* we get a much smaller stability difference than given by the experimental heats of formation. Moreover, the experimental molar sublimation enthalpies are 70.3, 65.3 and 66.3 kJ/mol for the *o*-, *m*- and *p*-carboranes[9], respectively, which suggests that the crystal packing enthalpies do not vary greatly for the carborane crystals, and we are therefore inclined to conclude that there exists a real discrepancy between the experimental and computed stabilization energies for the *m*- and *p*-molecules. Our total energies and our stabilization energies are (of course) in total agreement with the earlier calculations on the neutral, unsubstituted carboranes[10-12]. It

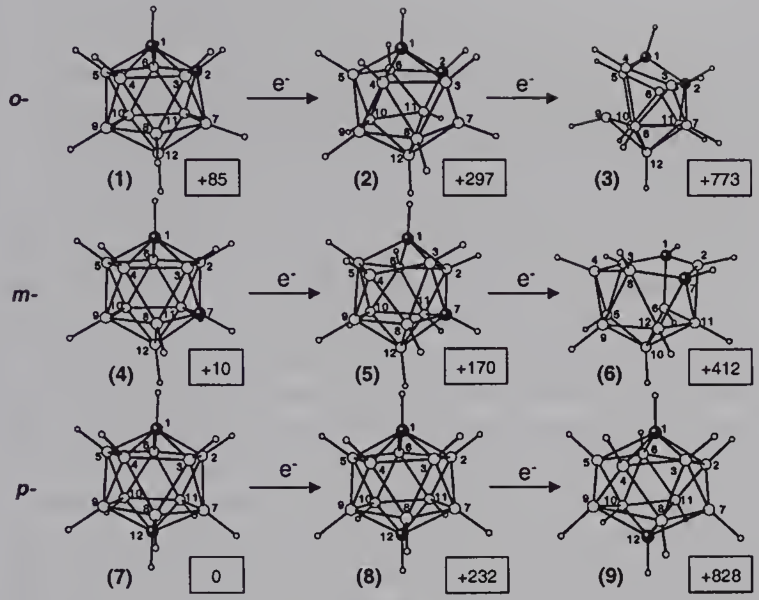

Fig.1 The optimized HF/6-31G* structures of the *o*-, *m*-, and *p*-carboranes and their mono-anions and di-anions. The framed numbers are the realtive energies in kJ/mol of each structure with respect to the neutral *p*-carborane. Note that in structure (3) the B9-B10 bond is hidden exactly behind the B8-B9 bond. The distance limit for drawing a bond was set to 1.95 Å.

should be mentioned, that another series of experiments do support our calculated stability results: Zakharkin *et al.*[13-15] established that the rearrangement of *m*- to *p*-carborane at 925-975K in the gaseous phase is a reversible process with an equilibrium mixture containing 53% of *m*-carborane and 47% of *p*-carborane. Zakharkin's numbers indicate a $\Delta G(p\text{-}m)$ difference of +1.0 kJ/mol, *i.e.* a close similarity in thermodynamic stability between these two species, contrary to the conclusions from the heats of formation[9]. We have made a normal-mode and thermochemical analysis using the Gaussian program, for the meta and para compounds at 975 K, and find that the meta compound has a slightly higher entropy than the para compound, giving rise to a $T\Delta S$ term of 6.5 kJ/mol at 975K with the 6-31G* basis set. Our computed approximation to $\Delta G(p\text{-}m) = \Delta E(p\text{-}m) - T\Delta S(p\text{-}m)$ is thus equal to $(-9.9 + 6.5) = -3.4$ kJ/mol, *i.e.* very small, in agreement with Zakharkin's experiments[13-15].

2.1.2 Atomic charges. The carbon atoms (electronegativity=2.6) carry negative charge relative to their nearest boron neighbours (electronegativity=2.0), and the C atoms in the *m*- and *p*-carboranes, having only B atoms as neighbours, are more negative than those in the *o*-compound. In all three isomers, boron atoms with no C neighbours have Mulliken charges in a narrow range around -0.10 (with the 6-31G* basis), those with one C neighbour lie around -0.02, and those with two C around 0.06. The H atoms bound to C are 0.20 *e* more positive that those bound to B atoms. In conclusion, for all the atoms here, the Mulliken charge trends reflect well their immediate environment.

2.2 The dianions

2.2.1 Previous ab initio results. McKee[16] and McKee *et al.*[17] have studied the $C_2B_{10}H_{12}^{2-}$ dianion using *ab initio* calculations, starting their optimizations from a few plausible model nido-structures. They thus considered three nido-isomers, each with an open six-membered face with two carbons either in the 2,4 or in the 2,5 positions. Two different symmetries were used in the case of the 2,4 isomer: C_s and C_1. Geometry optimizations at the HF/3-21G level followed by single-point energy calculations at the MP2/6-31G* level and ZPE corrections gave that the unsymmetrical (C_1) 2,4-isomer was about 10 kcal/mol more stable than the symmetrical (C_s) 2,4-isomer, which was 3 kcal/mol more stable than the 2,5-molecule (C_s) cage. These large energy differences (10 and 13 kcal/mol) suggest that the unsymmetrical 2,4-isomer would be the only species present in solution at room temperature, unless kinetic aspects play a significant role.

2.2.2 Our ab initio results. Starting from the geometries of the neutral carborane cages, we have optimized the structures of the monovalent and divalent *o*-, *m*- and *p*-carborane anions with the three basis sets discussed in this paper. **Fig. 1** shows the resulting optimised geometries at the 6-31G* level. The addition of the electrons has a striking effect on the molecular geometries. Already the singly charged molecules show large distortions. In $[o\text{-carborane}]^-$ the spherical cage has started to open up: the B4-B5 and B7-B11 distances are 0.16 Å longer than in the neutral cage. The $[o\text{-carborane}]^{2-}$ dianion (**3**) is heavily distorted and the B4-B5 distance, for example, is now 0.87 Å longer than in the neutral cage.

It is the *m*-compound which becomes the most distorted on electron-capture; the singly charged structure still looks like a cage (**5**), although distorted, with a quadilateral face formed by C1-B3-B4-B5 and then the cage opens up to a *nido* structure (**6**) for the dianion. The cage thus becomes a basket with the opening formed by a "rather planar" six-ring consisting of the C1-B2-C7-B8-B4-B3 atoms. One face is quadrilateral, consisting of the C1-B2-B11-C6 atoms. McKee *et al.*[17] also found a 4-ring in their optimized unsymmetrical (C_1) 2,4-isomer. Some structural features (like the quadrilateral face) seem to be common to both our structure and that of McKee *et al.*[17], and it is not unlikely that their unsymmetrical (C_1) 2,4-isomer is equivalent to (**6**). We base this conclusion on the fact that we performed a new optimization, at the 3-21G level like McKee[16], but starting from our 6-31G*-optimized structure (**6**). Our 3-21G-optimized structure is the same as (**6**) within 0.04 Å for all nearest-neighbour distances, and the HF/3-21G energy of this dianion is close to the energy to the unsymmetrical 2,4-isomer of McKee *et al.*[17].

For *p*-carborane, the cage shape is not quite as drastically affected by the electron uptake, but the interatomic distances still do change drastically. Many of the B-B distances lie around 2.10 Å in this dianion, and here the distance limit in **Fig. 1** has been set to 2.10 Å, since it gives a more representative impression of the new shape of the molecule.

For all three compounds, the captured electron(s) become distributed over all the H atoms, which each takes up about 0.10 electrons in the singly charged molecules and 0.2 electrons in the doubly charged molecules (Mulliken values). This systematic uptake of electrons occurs for all H atoms in all the isomers and is little dependent on the local environment around the H atom. It is interesting to note that the B-H and C-H distances are not drastically affected by the electron uptake; they increase by between 0.01 and 0.03 Å.

3. CONCLUDING REMARKS

Previous experiments on the *protonated* $C_2B_{10}H_{12}^{2-}$ suggest that there are (at least) two different such ions of importance[20], and accompanying calculations suggest that both are nido-cages, one with a B-C-B-B-B five-ring on top, the other with a C-B-C-B-B-B six-ring. The many transition metal-$C_2B_{10}H_{12}^{2-}$ compounds studied crystallographically all contain a nido-cage with a six-ring. No experimental structural information exists for the pure $C_2B_{10}H_{12}^{2-}$ ions. Previous *ab initio* calculations by McKee *et al.*[17] on isolated dianions found one isomer which lies substantially below other minima; this isomer is a nido structure with a six-ring on top and the C atoms in *meta* position. Our own Hartree-Fock calculations give three local minima for the $C_2B_{10}H_{12}^{2-}$ ion, namely structures **(3)**, **(6)** and **(9)** in **Fig. 1**. None of these has a five-ring. Our most stable structure, akin to that of Ref. 17, has a six-ring with the C atoms in *meta* position. The relative energies of the three isomers are vastly different, and based solely on energetic arguments, only the nido-cage would be found in solution.

Existing experimental data that could help sheding light on this unclear situation is scarce. Dunks *et al.*[18] and Stanko *et al.*[19] have performed ^{11}B NMR measurements for the dianions derived from *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$, and the existence of two different dianions was suggested, but unfortunately, no definite structural conclusions can be drawn, because of the broad NMR spectral lines. Whether or not the two dianions have the same structure thus needs to be more closely examined experimentally. We find such a possibility quite likely, and suggest that the dianion structure observed should be close to the nido-structure **(6)**.

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REFERENCES

1. Fein, M.; Bobinski, J.; Mayes, N.; Schwartz, N.; Cohen, M.S. *Inorg. Chem.* **1963**, *2*, 1111-1115.
2. Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128-1135.
3. Zakharkin, L.; Kalinin, V.; Podvisotskaya, L. *Izv. Akad. Naukuk SSSR, Ser. Khim.* **1967**, 2310.
4. Zakharkin, L.; Kalinin,V., *Izv. Akad. Naukuk SSSR, Ser. Khim.* **1969**, 194.
5. Stanko, V.; Gol`tyapin, Yu. V.; Brattsev, V. *Zh. Obsch. Khim.* **1969**, *39*, 1175.
6. Stanko, V.; Brattsev, V.; Gol`tyapin, Yu. V. *Zh. Obsch. Khim.* **1969**, *39*, 2686.
7. *SPARTAN 4.0*, Wavefunction, Inc., 18401 Von Karman, Suite 370, Irvine, California 92715.
8. *Gaussian 92/DFT, Revision G.4.* Frisch, M. J.; Trucks, G.W.; Schlegel, H. B.; Gill, P.M.W.; Johnson, B.G.; Wong, M.W.; Foresman, J.B.; Robb, M.A.; Head-Gordon, M.; Replogle, E.S.; Gomperts,; R.; Andres, J.L.; Raghavachari, K.; Binkley, J.S.; Gonzalez, C.; Martin, R.L.; Fox, D.J.; Defrees, D.J.; Baker, J.; Stewart, J.J.P. ; Pople, J.A. Gaussian, Inc., Pittsburgh PA, 1993.
9. Average values from Table 2/4 page15 in Gmelin Handbuch der Anorganische Chemie Borverbindungen 11.
10. Diaz, M.; Jaballas, J.; Arias, J.; Lee, H.; Onak, T. *J. Amer. Chem. Soc.* **1996**, *118*, 4405-4410.
11. Ott, J.J.; Gimarc, B.M. *J. Comput. Chem.* **1986**, *7*, 673-692.
12. Wales, D.J. *J. Am. Chem. Soc.* **1993**, *115*, 1557-1567.
13. Zakharkin, L.I.; Kalinin, V.N.; Podvisotskaya, L.S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 1197.
14. Zakharkin, L.I.; Kalinin, V.N.; Podvisotskaya, L.S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1297.
15. Zakharkin, L.I. *Pure. Appl. Chem.* **1972**, *29*, 513-526.
16. McKee, M. L. *J. Am. Chem. Soc.* **1992**, *114*, 5856-5858.
17. McKee, M.L.; Bühl, M.; Schleyer, P.v.R. *Inorg. Chem.* **1993**, *32*, 1712-1715.
18. Dunks, G.B.; Wiersma, R.J.; Hawthorne, M.F. *J. Am. Chem. Soc.* **1973**, *95*, 3174.
19. Stanko, V.I.; Babushkina, T.A.; Brattsev, V.A.,; Klimova, T.P.; Alymov, A.M.; Vassilyev, A.M.; Knyazev, S.P. *J. Organometal. Chem.* **1974**, *78*, 313-322.
20. See discussion and references in: Hermansson, K.; Wójcik, M.; Sjöberg, S *Inorg.Chem.* In press.

Boron Carbon 'Ligands' Stabilized in Rare Earth Metal Solid State Compounds: A Theoretical Approach

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1 INTRODUCTION

The combination of boron and carbon with rare earth metals leads to the formation of ternary rare earth metal borocarbide solid-state compounds which receive increasing attention because of their mechanical, magnetic and electrical properties.[1] In these materials of general formula $M_xB_yC_z$ (M = Sc, Y, Ln, An), boron and carbon atoms form two-dimensional (2-D) networks which alternate with 2-D sheets of metal atoms, one-dimensional (1-D) carbon-branched zig-zag boron chains running into channels built by the metal atoms, or finite pseudo-molecules of various sizes trapped into holes made by the metallic matrix. Such a broad diversity of original topologies, especially with respect to the bonding within the nonmetal frameworks, renders these compounds of interest for the theoretical chemists.[2]

According to electronegativities of the elements into play, charge transfer must proceed from the rare earth metals to boron and carbon. Using the Zintl-Klemm concept,[3] i.e. assuming an ionic bonding mode between fully oxidized metal atoms (usually M^{3+}) and the anionic B/C system, an averaged valence electron count (VEC) per nonmetal atom can be defined. For an $M_xB_yC_z$ compound, VEC = $(3x + 3y + 4z)/(y + z)$ if a number of three valence electrons is assumed for M. These VEC values calculated for all the characterized $M_xB_yC_z$ compounds allow a crude rationalization of the dimensionality of the nonmetal network present in these compounds as function of the number of electrons. Compounds containing 2-D boron-carbon networks are associated with the lowest VECs, ca. 4.[4-5] This is the case for instance of $Gd_2B_3C_2$ (VEC = 4.6), which adopts a layered structure made alternatively of metal sheets and boron-carbon layers resulting from the assemblage of linear B-C-B-C-B units (see Figure 1).[5] Compounds with 1-D nonmetal zigzag chains are characterized by VEC values of ca. 5,[6] as exemplified by YBC (VEC = 5).[7] Larger VECs are found for the phases encapsulating finite boron-carbon chains such as Sc_2BC_2 (VEC = 5.67) which contains BC_2 "molecules".[8] Indeed augmentation of VEC corresponds to formal addition of supplementary electrons in antibonding orbitals of the boron-carbon network. Consequently, bond breaking is expected, inducing a decreasing of the connectivity between the atoms and thus of the dimensionality of the nonmetal network.

Although it provides a rough rationalization of the dimensionality of the B/C sublattice in the $M_xB_yC_z$ phases, the calculation of VEC is not sufficient to fully understand the local environment of the boron and carbon atoms. Various theoretical analyses using quantum-mechanics calculations have been carried out, especially in my laboratory,[2] in order to obtain a deeper insight into the bonding encountered in these compounds. Results were interpreted in a somewhat personal way from a molecular viewpoint, regarding these solid state compounds as giant "metal complexes". More precisely, one can think of these materials as solid state coordination compounds containing boron carbon "ligands" in which the classical bonding scheme of σ-donation, sometimes supplemented by some π-back-donation, is present. Interestingly, the boron carbon "ligands" can often be seen as inorganic analogs of organic compounds. I would like to illustrate this point by discussing briefly the following specific examples.

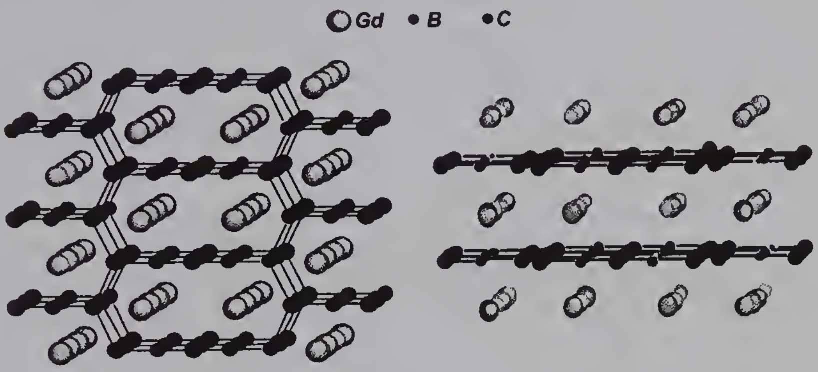


Figure 1 *Top view (left) and side view (right) of the structural arrangement of* $Gd_2B_3C_2$

2 Sc_2BC_2: A SOLID STATE COORDINATION COMPOUND CONTAINING BC_2 "MOLECULES"

The crystal structure of Sc_2BC_2 depicted in Figure 2 is related to that of CaC_2.[9] The metal atoms form regular 2-D square nets which stack in such a way to form bi-capped cubic holes in which symmetrical and linear C-B-C units are embedded.[8] The B-C distance (1.48 Å) suggests double bonds. Unprecedented for a while, such BC_2 units are now commonly observed in different solid-state compounds.[10-12]

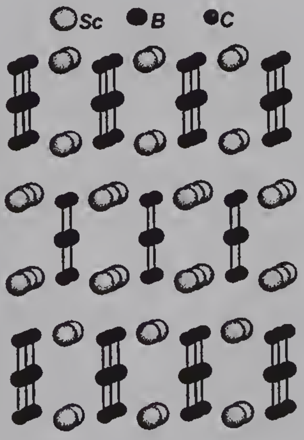


Figure 2 *Structural arrangement of* Sc_2BC_2

In order to tackle the bonding in this compound, the recipe generally used for molecular coordination compounds can be employed. Sc_2BC_2 can formally be fragmented in the metallic sublattice on one hand and the set of the boron carbon chains on the other hand. To reconstruct Sc_2BC_2, we need to know the electronic structure of the fragments. Being isolated from each other, we start by looking at the bonding properties of one BC_2 unit. Its EHMO diagram is shown in Figure 3. Its level ordering is qualitatively similar to that of CO_2, with a favored valence electron count of 16 leading to a formal charge of 5-.[8] For such an electron count, all the bonding and non-bonding levels are occupied and separated from the empty antibonding orbitals by a large HOMO/LUMO gap. Ab initio calculations at the MP2 level on the 16-eletron $(BC_2)^{5-}$ anion located in a modelized cationic environment lead to an optimized distance of 1.49 Å, a value in good agreement with that measured in Sc_2BC_2 (1.48 Å).[11]

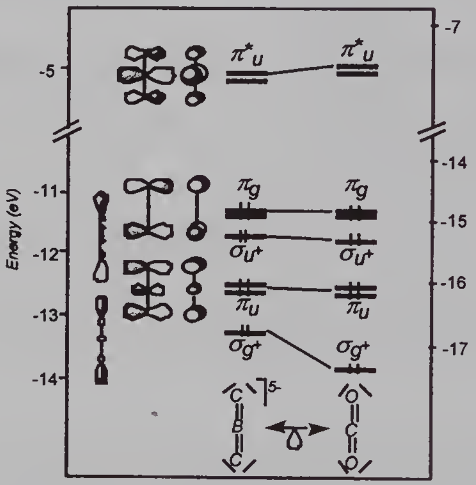


Figure 3 *Highest occupied and lowest unoccupied molecular orbitals of the linear $(BC_2)^{5-}$ and CO_2 entities*

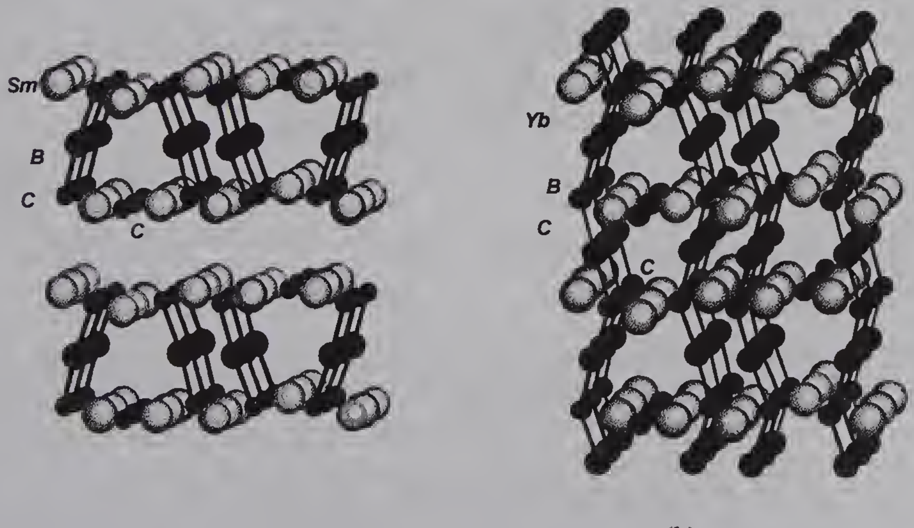
Occupied MOs (σ_{g+}, π_u, σ_{u+} and π_g) at relatively high energy and vacant MOs (π_u*) at relatively low energy provide the ingredients for the $(BC_2)^{5-}$ ligands being good σ-donor, and forming, as in a classical molecular coordination compound, metal-ligand covalent bonding. This was confirmed by extended Hückel tight-binding (EHTB) and density-functional theory (DFT) calculations on the 3-D Sc_2BC_2 compound.[8,13] The major bonding interaction occurs via an electron donation from the occupied bonding and non-bonding orbitals of the $(BC_2)^{5-}$ units into empty states of the metallic d-band, supplemented by fairly weak π-back-donation from occupied metallic states into acceptor orbitals of the $(BC_2)^{5-}$ chains. The electron occupation of the BC_2 frontier orbitals in the 3-D solid after interaction with the metallic host are consistent with the $(BC_2)^{5-}$ charge assignation, leading to an averaged formal oxidation state of 2.5+ for the metal atoms. With half an electron per metal atom occupying the very bottom of the conduction band, Sc_2BC_2 is expected to be an electrical conducting material.

3 TOWARD THE SYNTHESIS OF AN INORGANIC ANALOG OF CARBYNE?

Longer "molecular" B_mC_n chains up to 13 atoms can be observed in other ternary and quaternary compounds.[11-12] The chains are not rigourously linear. It is known that a small bending of organic cumulene and cumulenone molecules is not costly in energy and is facilitated as they become longer.[14] Extended Hückel and ab initio calculations on different B_mC_n units indicate the same phenomenon, i.e. the energy of the real geometries do not differ much from those obtained for idealized linear structures.[11] A cumulene-like character (formal double bonds along the chains) is computed for particular negative charges. This renders these B_mC_n anionic entities isoelectronic to hypothetical $(C_n)^{4-}$ cumulenic oligomers.

One of the great challenges in carbon chemistry is the preparation of infinite linear 1-D rods made of sp-type carbon atoms, called "carbyne".[15] Theoretical studies predict that carbyne will adopt the acetylenic form -(C≡C)- rather than the cumulenic form =(C=C)=.[16] Indeed, the finite B_mC_n anionic entities can be considered as pieces of carbyne with the cumulenic-like form which follows the octet rule. From this viewpoint, it appears that the synthesis of a rare earth metal borocarbide compound containing infinite $(B{=}C)^-$ rods would constitute a good inorganic analog of the hypothetical metastable linear (C=C) modification of carbon (see Scheme 1). Having in mind the different structural arrangements which were characterized for ternary rare earth metal borocarbides and knowing their electronic structure, the hypothetical "$Yb_5B_4C_5$" compound with a formal charge partitioning $(Yb^{2+})_5[(BC)^-]_4(C^{4-})$ is quite appealing for this purpose. Its structural arrangement can conceptually be derived from that encountered for $Sm_5B_2C_5$ which contains BC_2 units and isolated carbon atoms (see Figure 4a).[17] Linking the BC_2 units by additional boron atoms leads to the formation of infinite $(BC)^-$ chains (see Figure 4b). Note that infinite $-[(B^-){\equiv}(B^-)]-$ boryne chains isolelectronic to carbyne under its acetylenic form were very recently found embedded in a lithium matrix.[18]

Scheme 1



(a) (b)

Figure 4 *Structural arrangement of (a) $Sm_5B_2C_5$ and (b) "$Yb_5B_4C_5$"*

Carbon rods of different length can easily be stabilized when spanned by organometallic caps.[19] Close ties between these molecular organometallic species and the solid state rare earth metal borocarbides containing finite boron-carbon chains are evident. For instance, a $(C_3)^{4-}$ group, isolectronic to $(BC_2\ )^{5-}$ contained in Sc_2BC_2, is present in the molecular complex $[\{Re(C_5Me_5)(NO)(PPh_3)Mn(C_5H_5)(CO)_2\}(\mu\text{-}C_3)]^{+}$.[20] The study of the bonding in such species indicates that, as observed in our finite-chains-containing borocarbides, ligand-to-metal electron transfer is rather strong whereas metal-to-ligand back-donation is fairly weak.[21]

4 ZIGZAG BORON CARBON CHAINS IN YBC: INORGANIC ANALOGS OF POLYKETONE

A large interest is currently devoted to conjugated organic polymers because of their potentially interesting physical and structural properties. Interestingly enough, polymeric analogs can be encountered in rare earth metal borocarbides as illustrated in YBC (see Figure 5).[7] In this compound the metal atoms depict trigonal prisms which condense along one direction through square faces and along another direction through the triangular faces, forming infinite 2-D slabs. Boron atoms are located at the center of the metal trigonal prisms forming infinite zigzag chains which are branched by terminal carbon atoms. The YBC slabs which are formed stack in such a way that they face to each other, leading to long $C\cdots C$ interslab separations. Boron chains are regular with $d_{B\text{-}B} = 2.00$ Å and $d_{B\text{-}C} = 1.64$ Å.[7]

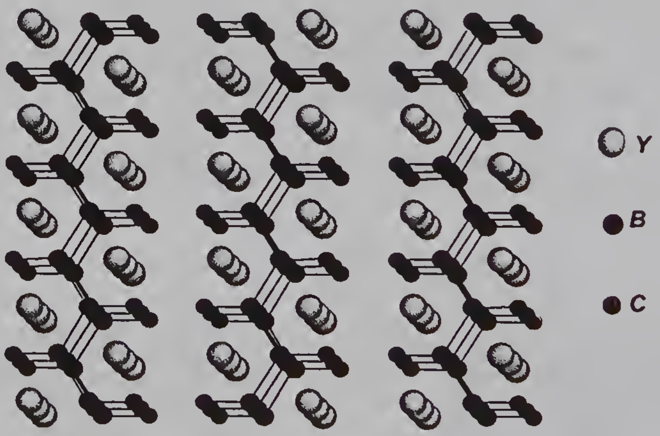


Figure 5 *Structural arrangement of YBC*

The bonding within a regular infinite zigzag (BC) chain can be nicely understood from the analysis of its band structure recalled in Figure 6.[22] The π MO diagram of the (B_2C_2) unit cell which can be compared to butadiene orbitals is shown on the left side of the figure. In the extended chain, each of these π levels generates a band (set of wave functions associated with energies depending on translational symmetry). Because of the presence of a screw axis along the regular chain, these π bands are degenerate at the edge of the Brillouin zone (X point). Assuming the charge partitioning $(Y^{3+})(BC)^{3-}$, the Fermi level (i.e. the HOMO for a solid) lies very close to the bottom of the π_3 band. With (slightly more than) two occupied π bands per B_2C_2 repeat motif (π_1 and π_2), the bonding in the infinite $(BC)^{3-}$ chain can be described by a Lewis formula which presents two π-electron pairs per B_2C_2 unit. With such a formal electron distribution the $(BC)^{3-}$ chain is isoelectronic to the yet unsynthesized polymer of CO named polyketone (see Scheme 2), which in fact, exhibits a very similar band structure.[23] Indeed, a recent ab initio study on polyketone suggests that this kind of chain is thermodynamically stable.[24] The potential energy surface associated to the rotation around the C-C single bonds is particularly flat, despite the expectation of some second-order Peierls (i.e. second order Jahn-Teller) instability arising from the σ/π band crossing near the Fermi level (see Figure 6). Therefore, the observed planarity of the 1-D chains in YBC may be imposed by the interaction with the metal atoms.[22] As noted previously for Sc_2BC_2, calculations on the 3-D YBC compound indicate a strong covalent character between the metal atoms and the boron carbon chains with the Fermi level crossing the bottom of the metallic d band and the top of the B-B bonding band.[22]

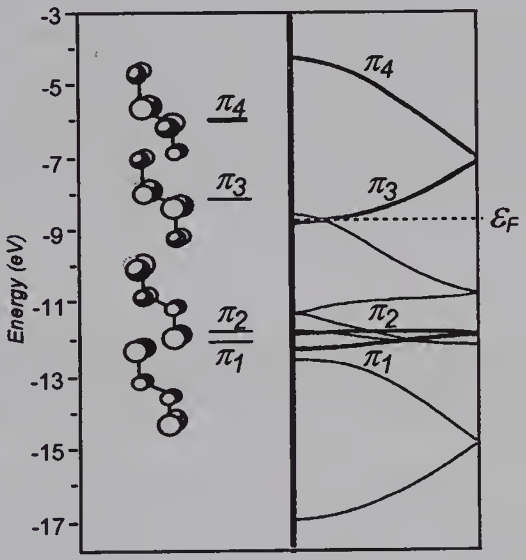
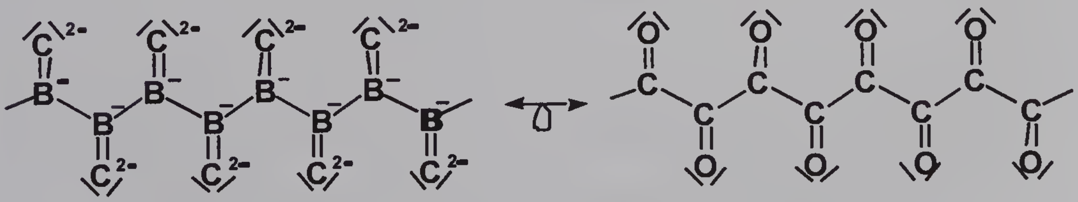


Figure 6 *π MO diagram for the B_2C_2 unit cell (left) and band structure (right) for a regular zigzag $(BC)_\infty$ chain*



Scheme 2

5 CONCLUSION

Although the solid-state language of Zintl-Klemm concept, band structures, and density of states is necessary to rationalize these fascinating solid state compounds, they are governed by the same laws that guide molecular structural chemistry: the relationship between the electron count and the geometrical structure. More precisely, one could think of these compounds as solid state coordination compounds resulting from the complexation of metal cations in a high oxidation state by infinite or finite anionic ligands in which the octet rule is generally satisfied. Interestingly enough, these infinite or finite anionic ligands can often been considered as solid state analogs of organic molecules or polymers. A classical bonding mode, i.e. ligand-to-metal σ-donation, sometimes supplemented by some metal-to-ligand π-back-donation, can be used to describe these materials.

Examples briefly discussed here in which the coordination aspect is important have been chosen in order to emphasize the close ties between this kind of solid state compound, molecular coordination compounds and organic chemistry. Bonding in these materials was described purposely from a molecular viewpoint, regarding them as giant "metal complexes" in order to facilitate excursion of the molecular chemist in the realms of solid-state chemistry.

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References

1. See for instance: (a) G.-Y. Adachi, N. Imakana, Z. Fuzhong, in K.A. Gschneidner, Jr. and L. Eyring (ed.), 'Handbook on the Physics and Chemistry of Rare Earths', Elsevier, Amsterdam, 1991, vol. 15, p. 62. (b) A. I. Gusev, *Russ. Chem. Rev.*, 1996, **65**, 379.
2. Bauer, J.; Halet, J.-F.; Saillard, J.-Y. *Coord. Chem. Rev.*, 1998, **178-180**, 723 and references therein.
3. (a) E. Zintl, *Angew. Chem.*, 1939, **1**, 52. (b) W. Klemm, *Proc. Chem. Soc. London*, 1958, 329.
4. F. Wiitkar, S. Kahlal, J.-F. Halet, J.-Y. Saillard, J. Bauer, P. Rogl, *J. Am. Chem. Soc.*, 1994, **116**, 251.
5. F. Wiitkar, J.-F. Halet, J.-Y. Saillard, P. Rogl, J. Bauer, *Inorg. Chem.*, 1994, **33**, 1297.
6. F. Wiitkar, S. Kahlal, J.-F. Halet, J.-Y. Saillard, J. Bauer, P. Rogl, *Inorg. Chem.*, 1995, **34**, 1248.
7. (a) J. Bauer, H. Nowotny, *Monatsh. Chemie*, 1971, **102**, 1129. (b) J. Bauer, *J. Less-Common Met.*, 1982, **87**, 45.
8. J.-F. Halet, J.-Y. Saillard, J. Bauer, *J. Less-Common Met.*, 1990, **158**, 239.
9. M. Atoji, *Chem. Phys.*, 1961, **35**, 1950. For a theoretical analysis see J. R. Long, H.-J. Meyer, R. Hoffmann, *Inorg. Chem.*, 1992, **31**, 1734.
10. (a) J. Bauer, O. Bars, *J. Less-Common Met.*, 1983, **83**, 17. (b) H. Hillebrecht, F.D. Meyer, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2499.
11. Hj. Mattausch, O. Oeckler, A. Simon, *Inorg. Chim. Acta*, 1999, **289**, 174 and references therein.

12. (a) D. Ansel, J. Bauer, F. Bonhomme, G. Boucekkine, G. Frapper, P. Gougeon, J.-F. Halet, J.-Y. Saillard, B. Zouchoune, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 2098. (b) J. Bauer, G. Boucekkine, G. Frapper, J.-F. Halet, J.-Y. Saillard, B. Zouchoune, *J. Solid State Chem.*, 1997, **133**, 190.
13. R. Gautier, J.-F. Halet, J.-Y. Saillard, unpublished results (1998).
14. C. Liang, L. C. Allen, *J. Am. Chem. Soc.*, 1991, **113**, 1873 and references therein.
15. (a) F. Diederich, Y. Rubin, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1101. (b) F. Diederich, *Nature*, 1994, **369**, 199 and references therein.
16. (a) M.J. Rice, A.R. Bishop, D.K. Campbell, *Phys. Rev. Lett.*, 1983, **51**, 2136. (b) R. Hoffmann, C. Janiak, C. Kollmar, *Macomolecules*, 1991, **24**, 3725.
17. J. Bauer, E. Bidaut, P. Gougeon, J.-F. Halet, R. Pöttgen, unpublished results (1998).
18. M. Wörle, R. Nesper, *Angew. Chem. Int. Ed.*, in press.
19. See for instance: (a) U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 969. (b) M.I. Bruce, *Coord. Chem. Rev.*, 1997, **166**, 91. (c) C. Lapinte, F. Paul, *Coord. Chem. Rev.*, 1998, **178-180**, 431. (d) T. B. Peters, J. C. Bohling, A. M. Arif, J. A. Gladysz, *Organometallics*, 1999, **18**, 3261 and references therein.
20. W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 3824.
21. See for instance: (a) D.L. Lichtenberger, S.K. Renshaw, *Organometallics*, 1993, **12**, 3522. (b) F. Frapper, M. Kertesz, *Inorg. Chem.*, 1993, **32**, 732. (c) Belanzoni, P.; Nazzareno, R.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton Trans.*, 1998, 1825. (d) M.I. Bruce, P. Low, K. Costuas, J.-F. Halet, *J. Am. Chem. Soc.*, in press.
22. F. Wiitkar, S. Kahlal, J.-F. Halet, J.-Y. Saillard, J. Bauer, P. Rogl, *Inorg. Chem.*, 1995, **34**, 1248.
23. (a) C.-X. Cui, M. Kertesz, *Chem. Phys. Lett.*, 1990, **169**, 445. (b) H. Genin, R. Hoffmann, *J. Am. Chem. Soc.*, 1995, **117**, 12328.
24. G. Frapper, C.-X. Cui, J.-F. Halet, J.-Y. Saillard, M. Kertesz, *J. Chem. Soc. Chem. Commun.*, 1997, 2011.

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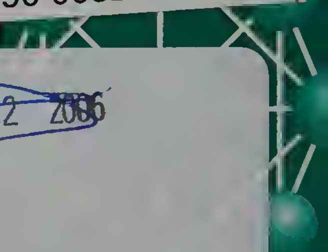

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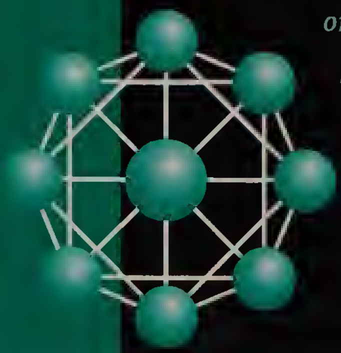

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