

4 Boron

A. S. Weller

Department of Chemistry, University of Bath, Bath, UK BA2 7AY

Molecular wheels of eight- and nine-atom boron clusters have been observed by photoelectron spectroscopy and their structures confirmed by DFT calculations.¹ The first cationic terminal borylene, containing a Fe=B double bond, [Cp*Fe(CO)₂-(Bmesityl)][BAr_{f4}] has been synthesised. DFT calculations support a bonding model in which boron engages in π -bonding to both [Cp*Fe(CO)₂]⁺ and mesityl moieties.² The first thirteen vertex carborane has been prepared by successive reduction of 1,2- μ -{C₆H₄(CH₂)₂}-1,2-*closo*-C₂B₁₀H₁₀ with Na to afford the [7,8- μ -{C₆H₄(CH₂)₂}-7,8-*nido*-C₂B₁₀H₁₀]²⁻ ion followed by addition of PhBCl₂ to give the unprecedented 13-vertex carborane 1,2- μ -{C₆H₄(CH₂)₂}-3-Ph-1,2-C₂B₁₁H₁₀ which has a heneicosahedral structure.³

1 Introduction

This review covers the literature published in 2003. Due to space limitations it is not exhaustive, focusing on what the author considers to be significant contributions to the field in 2003. Descriptions of specific results are often kept to a minimum, with the reader directed to the original paper for more information. The overall approach of this section is similar to that used in previous years, with the inorganic and organometallic aspects of boron reviewed. *Exo* metalla-substituted heteroboranes are included under a separate section, while complexes bearing tris-pyrazolyl type borate ligands, borate complexes acting simply as innocent counter-ions and organoboron compounds, in general, have not been included.

2 Reviews

A review analysing the variety of different structures that small molecular compounds of the subvalent Group 13 elements can adopt has been presented.⁴ The structural connections between the compounds of boron and carbon have been reviewed and extended.⁵ The relationships between five vertex *nido* main group clusters (including boron) have been discussed.⁶ A new class of organic-inorganic hybrid compounds bearing a cyclic η -ligand, an icosahedral carborane moiety, and a bridging group have been reviewed. These versatile ligands can be readily converted into mono-, di-,

tri- and pentaanionic species, leading to the generation of a new class of organometallic compounds in which the carboranyl unit can be cast in the role of a bulky substituent, a η^5 , η^6 , or η^7 -ligand.⁷ Recent advances in metallaborane chemistry have been reviewed.⁸ The trends in cyclopentadienyl-main-group-metal bonding have been reviewed.⁹ A “feature article” reviews the use of $B(C_6F_5)_3$ substituted butadiene metallocenes in olefin polymerisation.¹⁰ The synthesis and chemistry of polydentate Lewis acids based round organoboranes has been reviewed.¹¹ The chemistry of borylene transition metal complexes has been reviewed.¹²

3 Boranes

The dianions of tetraboranes(4) are found to be puckered aromatic four-membered rings that react with electrophiles to afford products that have conserved their aromaticity.¹³ The crystal structure for trimethylboron BMe_3 has been determined and compared with those of the heavier Group 13 trimethyl compounds and represents a new structural type for the Group 13 trimethyl derivatives in the solid state. In contrast to its heavier analogues, which form pseudo tetramers, it consists of layers containing only very weakly interacting BMe_3 molecules.¹⁴ Dimesitylborane dimer exists in equilibrium with dimesitylborane monomer in solution. The solid-state structure of the dimer has been investigated by single crystal X-ray diffraction at 100 K and the position of the bridging hydrogen atoms has been determined accurately, for the first time, by single crystal neutron diffraction at low temperature.¹⁵ A series of stable donor- π -acceptor compounds with a $B(Mes)_2$ acceptor group have been synthesized, along with analogues of these compounds for comparative studies. Comprehensive spectral data demonstrate that the $B(Mes)_2$ acceptor group is not only an excellent single-photon excited fluorescence activator, but also an effective two-photon excited fluorescence fluorophore in the blue-to-green optical region.¹⁶ [1.1]Diborataferrocenophane $[(\eta^5-C_5H_4)_2BMe_2Fe]_2^-$ is a highly efficient Li^+ scavenger, the lithium ion being trapped inside the cavity formed between two ferrocene units and two formally anionic bridging BMe_2 groups.¹⁷

Molecular wheels of eight- and nine-atom boron clusters, $[B_8]^-$ and $[B_9]^-$, have been observed by photoelectron spectroscopy and their structures confirmed by DFT calculations.¹ The structures and energies of $[X_3H_3]^{2-}$, $[X_3H_4]^-$, X_3H_5 and $[X_3H_6]^+$ ($X = B, Al$ and Ga) have been investigated theoretically at the DFT level.¹⁸ The analogy between hypothetical polyhedral boranes with exo multiple bonds being three-dimensional inorganic analogues of quinones has been discussed.¹⁹ *Ab initio* and density functional studies have shown that silylenes can form complexes with BH_3 and the resultant R_2Si-BH_3 complexes possess 3c-2e bridges.²⁰ Structures of the complexes of the guanidinium ion $(H_2N)_3C^+$ with super Lewis acidic BH_4^+ and AlH_4^+ have been calculated using the DFT method. These dicationic complexes contain a hypercoordinate boron or aluminium atom with a two-electron 2e-3c bond.²¹ *Arachno* boranes of the type B_nH_{n+6} and $[B_nH_{n+5}]^-$ ($4 \leq n \leq 10$) have been studied using the “defective vertex” principle and the stabilities of certain compounds have been rationalised in terms of the low number (or absence) of defective vertices.²² The existence of a new class of planar aromatic boranes has been theoretically

predicted. *Ab initio* calculations show that the reduction of a three-dimensional $[\text{B}_6\text{H}_6]^{2-}$ octahedron (for example) leads to the formation of a perfectly stable, planar structure: hexagonal $[\text{B}_6\text{H}_6]^{6-}$. This species is also aromatic. Smaller (B_5) and larger (B_7 and B_{10}) planar structures are also predicted to be stable.²³ Hypothetical tubular boranes of the general formula $[\text{B}_n\text{H}_n]^{2-}$, such as $[\text{B}_{17}\text{H}_{17}]^{2-}$ and $[\text{B}_{27}\text{H}_{27}]^{2-}$, have been investigated by theoretical methods. These *closo*-borane nanotubes obey Wade's $n + 1$ rule, but the traditional explanation based on a partitioning into radial/tangential molecular orbitals is found wanting.²⁴

The topomerization of a distorted diamond-shaped tetraborane(4) and its hydroboration to a *closo*-pentaborane(7) with a *nido* structure has been reported.²⁵ The electrochemical oxidation of the boron subhalide cluster dianions $[\text{B}_6\text{X}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) has been found to occur by a two step process.²⁶ The structure of $[\text{PPh}_3(\text{benzyl})][\text{B}_{10}\text{H}_{11}]$ has been determined. The B_{10} core of $[\text{B}_{10}\text{H}_{11}]^-$ is similar in shape to that of $[\text{B}_{10}\text{H}_{10}]^{2-}$, while the 11th H atom asymmetrically caps a polar face of the cluster. Variable temperature multinuclear NMR studies show that, in addition to the fluxionality of the cluster H atoms, the boron cage is fluxional at moderate temperatures, in contrast to $[\text{B}_{10}\text{H}_{10}]^{2-}$.²⁷ The synthesis of mono- and di-halogenated derivatives of $(\text{Me}_2\text{S})_2\text{B}_{12}\text{H}_{10}$ and subsequent palladium-catalyzed boron-carbon cross-coupling reactions to give *B*-alkyl and *B*-aryl substituted products in good yield has been reported.²⁸ The ammonioborane monoanion $[\text{H}_3\text{NB}_{12}\text{H}_{11}]^-$ can be per-*B*-fluorinated with elemental fluorine in liquid hydrogen fluoride to yield the first member of a new class of weakly coordinating anions: $[\text{H}_3\text{NB}_{12}\text{F}_{11}]^-$. The crystal structure of the trityl salt has been reported, and shows long and weak $\text{BF} \cdots \text{CPh}_3$ interactions in the solid-state.²⁹ The high yield synthesis of $[\text{B}_{12}\text{F}_{12}]^{2-}$ by sequential fluorination with LAHF then 20% F_2/N_2 has been reported. This anion is stable in 98% sulfuric acid and is unchanged after treatment with aqueous 3 M KOH for 10 days. This is in contrast to parent $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{CB}_{11}\text{F}_{12}]^-$ anions which decompose under acidic and basic conditions respectively.³⁰ The double-cage molecules [*o*-, *m*-, and *p*- $\text{CB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_4\text{OB}_{12}\text{H}_{11}]^{2-}$ have been prepared. The high boron content of these molecules makes them potential candidates for the synthesis of agents for boron neutron capture therapy (BNCT).³¹ OH and OEt derivatives of the macropolyhedral borate anion cluster $[\text{B}_{22}\text{H}_{22}]^{2-}$ have been prepared.³²

4 Metallaboranes including borohydride and related complexes

Cp_2ZrCl_2 reacts with varying stoichiometries of LiBH_3CH_3 to give the methyltrihydroborate complexes $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHCH}_3\}$ and $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$. The paramagnetic Ti(III) complex, $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BHCH}_3\}$ is also reported.³³ The reaction of $\text{K}[\text{H}_2\text{BC}_8\text{H}_{14}]$ with Cp_2ZrCl_2 affords $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$ which when reacted with KH yields $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$. The exchange processes of the bridging hydrides has been studied by NMR and deuterium labelling studies.³⁴ The scandium borohydride complex $(\text{Nacnac})\text{Sc}(\text{NHAr})(\text{HBEt}_3)$ ($\text{Nacnac} = \text{ArNC}(\text{CH}_3)\text{CHC}(\text{CH}_3)\text{NAr}$) cleaves the carbon-oxygen bonds in OEt_2 and THF to afford ethoxide $(\text{Nacnac})\text{Sc}(\text{NHAr})(\text{OEt})$ and enolate complex $(\text{Nacnac})\text{Sc}(\text{NHAr})(\text{OCH}=\text{CH}_2)$ respectively.³⁵ The bidentate borohydride complex

$[\text{Ru}(\eta^2\text{-BH}_4)(\text{CO})\text{H}(\text{PMe}_2\text{Ph})_2]$ reacts at low-temperature with 2-electron donors to form $[\text{Ru}(\eta^1\text{-BH}_4)(\text{CO})\text{H}(\text{L})(\text{PMe}_2\text{Ph})_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$, CO , 4-methylpyridine, respectively). On warming with excess L these give $\text{H}_3\text{B}\cdot\text{L}$ and $[\text{Ru}(\text{CO})(\text{H})_2\text{L}(\text{PMe}_2\text{Ph})_2]$.³⁶

Reactions of the hexaborane(10) analogue *nido*-(PPh_3)₂(CO)OsB₅H₉ with bidentate phosphines containing a rigid backbone form linked cluster systems with a phosphine spacer.³⁷ The reactions of $[\text{Cp}^*\text{MH}_2]_2$ ($\text{M} = \text{Fe}$, Ru) with $\text{BH}_3\cdot\text{THF}$ have been explored: $[\text{Cp}^*\text{RuH}_2]_2$ readily reacts with borane to generate *nido*-1,2-(Cp^*RuH)₂B₃H₇ whereas $[\text{Cp}^*\text{FeH}_2]_2$ gives metastable *arachno*-1- $\text{Cp}^*\text{FeB}_4\text{H}_{11}$, which reacts further with $\text{Co}_2(\text{CO})_8$ to give *nido*-1-(Cp^*Fe)₂{ $\text{Co}(\text{CO})_3$ }B₄H₈.³⁸ The complex reactivity of *nido*-1,2-(Cp^*RuH)₂B₃H₇ with alkynes to give metallacarboranes has been presented.³⁹ Eight- and ten-vertex open ruthenaboranes, $[(\text{Cp}^*\text{RuH}_2)_2\text{B}_6\text{H}_8]$ and the “hypo-electronic” $[(\text{Cp}^*\text{Ru})_2\text{B}_8\text{H}_{12}]$, have been synthesized by vigorous heating of $[(\text{Cp}^*\text{Ru})_2\text{B}_4\text{H}_8]$ with $\text{BH}_3\cdot\text{thf}$.⁴⁰ The *isonido* cluster $[\text{1-PPh}_3\text{-}\{\text{1,3-(}\mu\text{-dppm)}\}\text{-isonido-1,2-RhSB}_9\text{H}_8]$ reacts with $[\text{RhCl}(\text{PPh}_3)_3]$ to afford the icosahedral cluster $[\text{2-PPh}_3\text{-2,3-Cl}_2\text{-2,3-(}\mu\text{-Cl)}\text{-3,7-(}\mu\text{-dppm)}\text{-closo-2,3,1-Rh}_2\text{SB}_9\text{H}_8]$ in a reaction wherein the metal reagent inserts into the quadrilateral face of the *isonido* 11-vertex cluster.⁴¹ *nido*-1,2-(Cp^*RuH)₂B₃H₇ reacts with $\text{RC}\equiv\text{CR}'$ (R , $\text{R}' = \text{H}$, Ph ; Me , Me) to yield novel metallacarborane species derived from insertion of the acetylene into the metal–boron framework.⁴²

5 Carboranes and heteroboranes

Theoretical studies have shown that planar (BCO)₆ and other monocyclic boron carbonyl compounds with $4n + 2$ delocalized electrons are aromatic and should be viable synthetic targets. The isolobal equivalence of a BCO with a CH group appears to be capable of considerable extension and predicts a new family of molecules, akin to the metal carbonyls.⁴³ The computational prediction of a new family of related boranes and carboranes which follow the electron counting rule, $6m + 2n$, has been published. These large clusters have been calculated up to C₈B₈₄H₉₂ and are dubbed “sea-urchins” due to their globular shapes and protruding hydrogens.⁴⁴ A quantitative study on cationic *closo*-tricarboranes of formula $[\text{closo-C}_3\text{B}_n\text{H}_{n+3}]^+$ has proved their stability and suggests some possible synthetic strategies to accessing these cluster compounds.⁴⁵ The electronic and molecular structure has been investigated in the diethylaluminium cation-like system $\text{Et}_2\text{Al}(\text{CB}_{11}\text{H}_6\text{X}_6)$ ($\text{X} = \text{Cl}$, Br) and neutral compounds AlX_3 ($\text{X} = \text{Cl}$, Br , Me , C_6H_5) with DFT methods. These find significant ionic character in both Al–Br and Al–Cl bonds and give legitimacy to the designation of these types of compounds as “ion-like”.⁴⁶

The first triboracyclobutane, a two electron homoaromatic having a nonclassical σ skeleton, has been synthesised at low temperature. The crystal structure of the dianion (as the dilithium salt) has also been reported which possesses a classical σ skeleton.⁴⁷ The synthesis of a diboracyclopropane has been described, the structure of which has a planar-tetracoordinate carbon atom and a triborabicyclobutane fragment.⁴⁸ The structure of a triboracyclobutanide has been reported, and shows it to be a four-membered two-electron aromatic compound. Line shape analyses of its temperature-dependent solution NMR spectra show that its skeletal bonds fluctuate

via a distorted triboratetrahedrane anion.⁴⁹ The electronic structures of the 1,3-diboracyclobutane-1,3-diyls has been discussed.⁵⁰

The first 10-vertex *arachno*- and *nido*-phosphamonocarbaboranes, *exo*-6-R-*arachno*-6,7-PCB₈H₁₂ and [6-R-*nido*-6,9-PCB₈H₉][−] (R = C₆H₅, CH₃), have been synthesised by initial reaction of a substituted phosphorus dihalide (RPCl₂) with the [arachno-CB₈H₁₃][−] monoanion followed by an *in situ* dehydrohalogenation. Reaction of the *arachno* cluster with O₂, S₈, BH₃, or Br₂ affords new *arachno*-substituted compounds in which the O, S, BH₃, and Br substituents are bound to the phosphorus at the *endo* position.⁵¹ 10-Vertex phosphadiborabboranes 6-R-*arachno*-6,8,9-PC₂B₇H₁₁ and 6-R-*arachno*-6,5,7-PC₂B₇H₁₁ can be synthesized by *in situ* dehydrohalogenation reactions of RPCl₂ (R = Ph or Me) with the *arachno*-4,5-C₂B₇H₁₃ and *arachno*-4,6-C₂B₇H₁₃ carboranes, respectively. The coordination chemistry of these new cluster compounds with Pt(II) fragments has also been reported.⁵²

Carboranyl C-glycosides have been prepared. These clusters are highly water-soluble and display only a very low cytotoxicity which makes them promising candidates for use in boron neutron capture therapy for the treatment of cancer.⁵³ A combined nucleophilic (deboronation of C₂B₁₀H₁₀ followed by reaction with BI₃) and electrophilic (halogenation) sequential process has allowed for the first time the introduction of nine equal halogen substituents onto C₂B₁₀H₁₂.⁵⁴ C-substituted derivatives of *ortho*-carborane, 1-R-1,2-C₂B₁₀H₁₁ (R = 2-pyridyl, 2-picoyl, 5-bromo-2-pyridyl and 3-pyridyl) have been prepared and the hydrogen bonding between C_{cage}-H...N studied. Calculations at the MP2/6-31G* level of theory have also been used to assess the strength of the hydrogen bonding detected.⁵⁵ The synthesis of the neutral arsa-carborane complexes, 7,8,9,11-, 7,9,8,10- and 7,8,9,10-isomers of *nido*-As₂C₂B₇H₉, by reaction of *arachno*-4,6-C₂B₇H₁₃ with AsCl₃ or AsI₃ in the presence of base, has been reported. Halogenated derivatives are also described.⁵⁶ Deprotonation of the eleven-vertex tricarbaborane zwitterions 7-L-*nido*-7,8,9-C₃B₈H₁₀ [L = H₃N, ^tBuH₂N, Me₂HN], followed by reactions with metal reagents [FeI₂, NiCl₂, and Ni(C₅H₅)₂] leads to the 7 → 8 rearrangement of the *N*-substituted cage carbon atom to yield a series of 8-aminosubstituted derivatives of *nido*-7,8,9-C₃B₈H₁₂.⁵⁷ The synthesis of the first 11-vertex *arachno*-dicarbathiaborane anion [1,6,7-C₂SB₈H₁₁][−] and the elucidation of its structure by the DFT/GIAO NMR method has been reported.⁵⁸

The synthesis and structures of new carborane-substituted cyclotriphosphazenes, exemplified by *gem*-[N₃P₃{(OCH₂)₂C₂B₁₀H₁₀}₃] has been reported.⁵⁹ 1,2- and 1,7- isomers of *para*-phenyl-substituted icosahedral B₁₀-diaryl *closo*-carboranes have been synthesised. These have been used in the formation of carborane macrocycles with an organic linker. The size and geometry of the cycles, the nature of the functional groups in the *para*-position of the phenyl substituents, as well as the nature of the linking moiety can be tuned in a controlled fashion to give a variety of novel structures.⁶⁰ Rigid neutral and anionic carborane rods [1-(4-MeC₆H₄-4-C₆H₄)-*closo*-CB₁₁H₁₀-12-(C₆H₄-4-Me)][−] and [1-Ph-*closo*-1-CB₉H₈-6-(NC₅H₄-4-CH₂Ph)] have been prepared which have van der Waals lengths of 23 and 30 Å respectively.⁶¹ Superacid protonated arenes [H(arene)][carborane] are readily isolated as crystalline salts, thermally stable to >150 °C by protonating benzene, toluene, *m*-xylene, mesitylene, and hexamethylbenzene with the carborane superacid H(CB₁₁HR₅X₆) (R = H, Me; X = Cl, Br).⁶² These anions have also been used to stabilise the [C₅₉N]⁺

carbocation, prepared by oxidation of $(C_{59}N)_2$ with [hexabromo(phenyl)carbazole]-[$CB_{11}H_6Cl_6$]. The counterion to the cationic species is $[Ag(CB_{11}H_6Cl_6)_2]^-$.⁶³

Computations on the stability and three-dimensional aromaticity of all the possible positional isomers of the *closo*-azaboranes $NB_{n-1}H_n$ ($n = 5-12$) reveal substantial differences in the relative energies.⁶⁴ The synthesis of the eight-, nine- and ten-vertex azacarbaboranes: *exo*- and *endo*-7- CH_3 -*hypho*-7,8- NCB_6H_{11} , *nido*-6,8,9- $NC_2B_7H_{10}$, *arachno*-6,5,9- $NC_2B_7H_{12}$ and *arachno*-6,5,10- $C_2NB_7H_{12}$ has been accomplished by reaction between excess *n*- C_4H_9ONO and *arachno*-4,5- $C_2B_7H_{13}$.⁶⁵ The microwave spectrum of 1-thia-*closo*-dodecaborane(11), 1- $SB_{11}H_{11}$, has been investigated and the molecule is found to have C_{5v} symmetry. The structure is in reasonable agreement with the one determined previously by electron diffraction.⁶⁶ The synthesis, by either acid-catalysed electrophilic substitution or recapitation, of four new *B*-labelled diphenyl carboranes based on $C_2B_{10}H_{10}$ has been described.⁶⁷ The first thirteen vertex carborane has been prepared by successive reduction of 1,2- μ - $\{C_6H_4(CH_2)_2\}$ -1,2-*closo*- $C_2B_{10}H_{10}$ with Na to afford $[7,8-\mu\{-C_6H_4(CH_2)_2\}-7,8-nido-C_2B_{10}H_{10}]^{2-}$ ion followed by addition of $PhBCl_2$ to give the unprecedented 13-vertex carborane 1,2- μ - $\{C_6H_4(CH_2)_2\}$ -3- Ph -1,2- $C_2B_{11}H_{10}$ which has a hencicosahedral structure.³

6 Metallacaboranes

Synthetic and structural studies on lanthanacarboranes with two and three “carbons apart” carborane cages, based upon the dianion $[2,4-(SiMe_3)_2-2,4-C_2B_4H_4]^{2-}$, bonding to a Ln(III) metal (Ln(III) = Nd, Gd, Dy, Ho, Er, Tb, Lu) have been reported.⁶⁸ The introduction of organic and inorganic substituents onto η^5 - C_5H_5 ligands in the small cobaltacarboranes such as $CpCo(Et_2C_2B_4H_4)$ and $CpCo(Et_2C_2B_3H_5)$ has been explored, together with metal-promoted C–C coupling to generate polycluster species featuring Cp–Cp and Cp–benzene linkages. Using this methodology triple-sandwich trinuclear and hexanuclear benzene-centered complexes in which three cobaltacarborane units are anchored to a central 1,3,5-(η^5 - C_5H_4) $_3C_6H_3$ hydrocarbon scaffold have been prepared.⁶⁹ A series of *B*-alkynyl-substituted derivatives of CoC_2B_3 , CoC_2B_4 , and $Co_2C_2B_3$ cobaltacarboranes has been prepared and linked together *via* metal-promoted cross-coupling reactions to generate several types of polynuclear molecular complexes. Electrochemical data on the alkynyl-linked compounds indicate that metal–metal communication in oxidized and reduced species occurs to a limited extent in most cases and to a considerable degree (Robin–Day class III) in systems with a C_2B_3 -bridged triple-decker motif.⁷⁰ Stepwise assembly of a tetranuclear species that contains four identical seven-vertex MC_2B_4 cobaltacarborane clusters and features a planar octagonal (tetratruncated square) $\{C_{16}B_8\}$ macrocycle has been described. Electrochemical analysis by cyclic voltammetry revealed two separate one-electron reductions followed by a single two-electron reduction which indicates significant intramolecular electronic communication between the four cobalt centers.⁷¹ The first dendrimers containing metallacarborane modules have been prepared and characterized, *viz*: the 16- and 32-cobalt metalloidendrimers $DAB-dend-[NHC(O)-C_5H_4Co(2,3-Et_2C_2B_3H_5)]_{16}$ and $DAB-dend-[NHC(O)-C_5H_4Co(2,3-Et_2C_2B_3H_5)]_{32}$ (DAB = diaminobutane-dend- $(NH_2)_{16}$).⁷²

Rearrangement processes in the platinum carboranes based upon [3-X-7,8-Ph₂-7,8-*nido*-C₂B₉H₈]²⁻ (X = Et, F) have been discussed.⁷³ The formally seventeen- and eighteen-electron metallacarboranes [1,1,1-(CO)₃-2-Ph-*closo*-1,2-MnCB₉H₉]ⁿ⁻ (n = 1, 2) are a structurally characterized, redox-related pair. The seventeen electron species is a stable radical monoanion and DFT and EPR studies show that the unpaired electron is delocalized over the cluster.⁷⁴ The synthesis and structure of the 11-vertex rhenacarborane dianion [1,1,1-(CO)₃-2-Ph-*closo*-1,2-ReCB₉H₉]²⁻ has been reported. The reactivity toward cationic transition metal fragments to afford products in which the electrophilic metal groups are attached *exo*-polyhedrally to the cage by rhenium-metal bonds supported by three-centre two-electron B-HFM linkages is also reported.⁷⁵ A novel class of hybrid “multiplecluster” in which an {ReIrAu₂} butterfly is constructed on a rhenacarborane {ReC₂B₉} substrate has been described.⁷⁶ The anion [2,3-μ-{N(CH₂)₅}-2,2,2-(CO)₃-*closo*-2,1-MoCB₁₀H₁₀]⁻ has been synthesised by reaction of Li₂[7-NMe₃-*nido*-7-CB₁₀H₁₀] with [Mo(CO)₄-{NH(CH₂)₅}]₂ in THF followed by oxidation. Reaction with coinage metal fragments {M(PPh₃)₃}⁺ (M = Ag, Cu) affords complexes with Mo-M bonds and agostic M-H-B linkages.⁷⁷

The charge compensated ruthenacarboranes [3-*H*-3,3-(PPh₃)₂-8-SR¹R²-1-R-3,1,2-RuC₂B₉H₉] have been prepared and are excellent catalysts for the Kharasch addition of CCl₄ to methyl methacrylate and styrene.⁷⁸ The superior efficiency of these catalyst compared to Cp-containing systems is ascribed to the fine-tuning of the oxidation potential of the Ru catalyst by the ability of the *exo* sulfonium to both donate and to accept electron density from the metal.⁷⁹ The neutral, arene-like, charge compensated carborane [(SMe₂)₂C₂B₉H₉] has been synthesized, and its complex with a metal fragment, viz. [Rh(cod){(SMe₂)₂C₂B₉H₉}] [BF₄]⁻ prepared.⁸⁰

Reaction of SnCl₂ with [{μ-1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀}]₂Na₄(THF)₆]_n gives the Lewis base free stannacarborane {μ-1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀}Sn. The corresponding Lewis base coordinated stannacarboranes {μ-1,2-[*o*-C₆H₄(CH₂)₂]-1,2-C₂B₁₀H₁₀}Sn(L), L = MeCN, THF and DME have been prepared.⁸¹ The compounds [η⁵-σ-Me₂A(C₉H₆)(C₂B₁₀H₁₀)]Zr(NMe₂)₂ (A = C, Si) react with CS₂, PhCN, CH₂=CHCN, ⁿBuNCS, and PhNCO to give the mono-, di-, and tri-insertion products, depending upon the substrates. These unsaturated substances insert exclusively into the Zr-N bonds, and the Zr-C(cage) bond remains intact in all reactions.⁸² 1-SH-2-[HCpCH(Ph)]-*closo*-1,2-C₂B₁₀H₁₀ reacts with Ti(NMe₂)₄ to form the corresponding titanium “constrained geometry” complex [1-(σ-S)-2-(η⁵-C₅H₄CH(Ph))-1,2-C₂B₁₀H₁₀][Ti(NMe₂)₂].⁸³ The multidentate dicarbollide ligand *nido*-7,8-(NMe₂CH₂)₂-7,8-C₂B₉H₁₁ has been prepared and employed in the preparation of the novel mono- and tri-metallic titanium complexes {η⁵:η¹-(NMe₂CH₂)C₂B₉H₉CH₂-NMe₂}Ti(NMe₂)₂ and [η⁵:η¹-(NMe₂CH₂)C₂B₉H₉CH₂NMe₂}Ti(NMe₂)₂]-μ³-OTi(NMe₂)₂.⁸⁴ Three new isomers of [*closo*-(η⁵-C₅H₅)FePC₂B₈H₁₀] have been reported.⁸⁵ Paramagnetic 13-vertex diferratricarboranes of the “*subcloso*”-[(η⁵-C₅H₅)₂Fe₂C₃B₈H₁₁] type have been isolated in low yield from *nido*-[ⁿBuNH-CpFeC₃B₈H₁₀]⁻ and sources of {CpFe}.⁸⁶ New 13-vertex *closo*-metallacarboranes of rare earth metals incorporating *nido*- and *arachno*-carborane ligands have been prepared and structurally characterized.⁸⁷

The cobaltdicarbollide anion containing a bridge between the two cages, [μ-8,8'-C₂H₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻, is formed by a sequential palladium cross coupling

between a starting mono iodo complex followed by an intramolecular hydroboration.⁸⁸ The thioether substituted cobaltdicarbollide anion $[1,1-\mu\text{-}\{\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{-CH}_2\text{CH}_2\text{S}\}\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$, has been isolated in *meso* and *rac*-forms. Both forms coordinate sodium ions but in slightly different ways.⁸⁹ Methyl disubstituted derivatives of $[3,3'\text{-Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ have been synthesised by application of a modified Kumada reaction, *viz.* $\text{Cs}[8,8'\text{-(CH}_3)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$. Molecules containing B–C and B–O are also generated, such as $\text{Cs}[8\text{-CH}_3\text{-}8'\text{-OH-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]$. This compound undergoes a oxodemethylation to afford $[8,8'\text{-}\mu\text{-O-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$.⁹⁰ The synthesis of monosubstituted derivatives $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ that incorporate synthons for conducting organic polymers, such as pyrrolyl, indolyl and carbazolyl, has been reported.⁹¹ Regioselective monoalkylation and monoarylation of the parent $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ has also been reported.⁹²

7 *exo*-Metallacarboranes

The first zirconocene-1,2-dehydro-*o*-carborane complex $[\{\eta^5\text{-}\sigma\text{-Me}_2\text{C}(\text{C}_6\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{-ZrCl}(\eta^3\text{-C}_2\text{B}_{10}\text{H}_{10})][\text{Li}(\text{thf})_4]$, an analogue of a transition metal complex of benzyne, has been reported.⁹³ The new complexes $\{[\eta^5\text{-}\sigma\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2\}_2[\eta^2\text{-}(\text{PhC}\equiv\text{C}\equiv\text{CPh})]$ and $[\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_6\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2(\text{NMe}_2)$ have been reported.⁹⁴ Thermally stable complexes $(\eta^5\text{-Cp}^*)[\eta^5\text{-(C}_5\text{H}_4)\text{CMe}_2\text{CB}_{10}\text{-H}_{10}\text{CR}]\text{MCl}_2$ ($\text{R} = \text{H, Me}$) and $(\eta^5\text{-Cp}^*)[\eta^5\text{-}\eta^1\text{-(C}_5\text{H}_4)\text{CMe}_2(\text{CB}_{10}\text{H}_{10}\text{C})]\text{MCl}$ have been prepared ($\text{M} = \text{Ti, Zr and Hf}$). The titanium and zirconium complexes produce high-density polyethylenes in the presence of modified methylaluminoxane cocatalyst.⁹⁵ Group 4 metallacarboranes of constrained geometries derived from B(cage)- and C(cage)-silylamido-substituted carborane ligands have been prepared.⁹⁶

Gold and silver derivatives with the carborane-selenolate ligand $[\text{closo-B}_{10}\text{H}_{11}\text{C}_2\text{Se}]^-$ have been prepared.⁹⁷ The neutral digold, rigid rod, complexes $[(\text{AuL})_2(1,12\text{-}(\text{C}\equiv\text{C})_2\text{-}1,12\text{-C}_2\text{B}_{10}\text{H}_{10})]$ have been synthesised ($\text{L} = \text{aryl phosphine, CNtBu}$).⁹⁸ The synthesis and characterisation of *exo-closo*-rhodacarboranes $\{[\text{exo}(\text{R}_3\text{P})_2\text{Rh}]\{\text{closo-CB}_{11}\text{H}_{12}\}[\text{R}_3\text{P}=\text{P}(\text{OMe})_3, \text{PCy}_3, \frac{1}{2}\text{dppf}]\}$ has been reported.⁹⁹ The synthesis of $\{\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}^+$ fragments partnered with the monoanionic carboranes $[\text{closo-CB}_{11}\text{H}_{11}\text{Br}]^-$, $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$ and $[\text{closo-HCB}_{11}\text{Me}_{11}]^-$ by silver salt metathesis and hydride abstraction has been reported.¹⁰⁰ The synthesis and characterisation of $[9\text{-}\{\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}\text{-nido-}7,8\text{-C}_2\text{B}_9\text{H}_{12}]$, $[7\text{-}\{\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}\text{-nido-}7,8\text{-As}_2\text{B}_9\text{H}_{10}]$ and $[7\text{-}\{\text{M}(\text{CO})_2(\eta^7\text{C}_7\text{H}_7)\}\text{-nido-}7,8\text{-As}_2\text{B}_9\text{H}_{10}]$ ($\text{M} = \text{Mo or W}$), where the metal fragments are bound *exo* to the cage by B–H–M or As–M interactions have been described.¹⁰¹ Reaction of *nido*- $[7,8,9\text{-PC}_2\text{B}_8\text{H}_{11}]$ with $[\{\text{CpFe}(\text{CO})_2\}_2]$ affords the η^1 -bonded complex $[7\text{-Fp-(}\eta^1\text{-nido-}7,8,9\text{-PC}_2\text{B}_8\text{H}_{10})]$ ($\text{Fp} = \text{CpFe}(\text{CO})_2$). The isomeric complex $[7\text{-Fp-(}\eta^1\text{-nido-}7,9,10\text{-PC}_2\text{B}_8\text{H}_{10})]$ together with the fully sandwiched complexes $[1\text{-Cp-closo-}1,2,4,5\text{-FePC}_2\text{B}_8\text{H}_{10}]$ and $[1\text{-Cp-closo-}1,2,4,8\text{-FePC}_2\text{B}_8\text{H}_{10}]$ can also be accessed.¹⁰² The tetrasubstituted, square planar, polyanions of platinum, palladium and gold, $[\text{M}(\text{SnB}_{11}\text{H}_{11})_4]^{x-}$ ($x = 6, \text{M} = \text{Pd, Pt}; x = 5, \text{M} = \text{Au}$), have been prepared and characterized by single-crystal X-ray crystallography.¹⁰³ Reaction of PPh_3AuCl with $[\text{SnB}_{11}\text{H}_{11}]^{2-}$ results in two different gold–tin clusters: $[(\text{Ph}_3\text{P})\text{Au}(\text{SnB}_{11}\text{H}_{11})_2]^{2-}$ and $[(\text{Ph}_3\text{P})_2\text{Au}_2(\text{SnB}_{11}\text{H}_{11})_3]^{4-}$

both of which have formally Au(0) centres and show significant Au–Au interactions in the solid-state.¹⁰⁴

[Cp₂ZrMe(12-μ-Me-1-*closo*-CB₁₁HMe₁₀)] is isolated by methide abstraction from Cp₂ZrMe₂ using [CPh₃][*closo*-HCB₁₁Me₁₁] and displays an intermolecular Zr···H₃CB interaction in both the solid state and solution.¹⁰⁵ Using an ionic liquid formed from a weakly coordinating carborane anion and *N*-ⁿbutylpyridinium (BP) ions, [BP][*closo*-CB₁₁H₁₂], the compound [*closo*-1,3-{μ-(η²-3-CH₂=CHCH₂CH₂)}-3-H-3-PPh₃-3,1,2-RhC₂B₉H₁₀] is an excellent asymmetric hydrogenation of unsymmetrical aryl ketones in the presence of binap. Intermediates in which the Rh centre is σ bound to the [*closo*-CB₁₁H₁₂] cage have been postulated.¹⁰⁶ Oxidation of the carboranyliridium fullerene complex [(η²-C₆₀)Ir(*o*-HCB₁₀H₉CCH₂PPh₂-B,P)(^tBuNC)₂] by O₂ occurs by a selective insertion of the dioxygen molecule into the longest Ir–C bond to [σ-C₆₀OO-Ir(*o*-HCB₁₀H₉CCH₂PPh₂-B,P)(^tBuNC)₂].¹⁰⁷

8 Boryl complexes and hydroborations

The reactivity of the bridged chloroborylene complex [μ-BCl{(η⁵-C₅H₄Me)-Mn(CO)₂}]₂ toward pyridine was investigated under various conditions. In the presence of protic reagents the formation of the aminoborylene complex [1-(μ-B)-4-H-(NC₅H₅){(C₅H₄Me)Mn(CO)₂}]₂ results, which represents the product of an unprecedented formal 1,4-hydroboration of pyridine.¹⁰⁸ Photolysis of [MnMe(CO)₄(PR₃)] with BH₃·PMe₃ results in the formation of the boryl complexes [Mn(CO)₄(PR₃)(BH₂·PMe₃)] (PR₃ = PMe₂Ph, PET₃) which, on protonation, form the borane σ complexes [Mn(CO)₄(PR₃)(η¹-BH₃·PMe₃)]⁺.¹⁰⁹

The differing steric requirements of phenyl and mesityl substituents have been shown to influence reactivity in asymmetric transition metal haloboryl complexes. Hence, substitution of both halides in PhBCl₂ can be achieved by reaction with an excess of the bulky organometallic nucleophile Na[(η⁵-C₅Me₅)Fe(CO)₂] to afford [(η⁵-C₅Me₅)Fe(CO)₂](μ-CO)(μ-BPh), whereas the mesityl species (η⁵-C₅Me₅)Fe(CO)₂B(X)Mes (X = Cl, Br) are seemingly inert to further Fe–B bond formation.¹¹⁰ The cationic terminal borylene, containing a Fe=B double bond, [Cp*Fe(CO)₂-(Bmesityl)][BAR_{f4}], has been synthesised by halide abstraction from Cp*Fe(CO)₂B-(mesityl)Br using Na[BAR_{f4}] [Ar_f = C₆H₃(CF₃)₂-3,5]. DFT calculations support a bonding model in which boron engages in π-bonding to both [Cp*Fe(CO)₂]⁺ and mesityl moieties.² Irradiation of [(OC)₅Cr=B=N(SiMe₃)₂] in the presence of [(η⁵-C₅H₅)V(CO)₄] affords [(η⁵-C₅H₅)(OC)₃V=B=N(SiMe₃)₂] a half-sandwich complex with a terminal borylene ligand.¹¹¹ The single-crystal X-ray (at 120 K) and neutron (at 20 K) diffraction studies on two Rh-boryl complexes [(PⁱPr₃)₂RhHCl(Bpin)] and [(PⁱPr₃)₂RhHCl(Bcat)] (pin = OCMe₂CMe₂O; cat = 1,2-O₂C₆H₄), provide the first accurate location of the hydride ligands in a hydrido boryl complex. They are best described as Rh(III) hydrido boryl rather than Rh(I) σ-borane (σ-HB(OR)₂) complexes, although there is a modest residual BH interaction in both compounds. DFT calculations show that this latter interaction can occur through both the “empty” BO₂ p(π*) and BO₂ σ* orbitals, which are mutually perpendicular.

The complex *trans*-[Rh(Cl)(CO)(PPh₃)₂] has been found to be an efficient catalyst precursor for the dehydrogenative borylation of alkenes without consumption of half

the alkene substrate by hydrogenation, giving useful vinylboronate esters including 1,1-disubstituted derivatives that cannot be made by alkyne hydroboration.¹¹² High yields and regioselectivity in the aromatic C–H borylation of arenes and heteroarenes has been reported using stoichiometric amounts of pinacolborane and catalyzed by an iridium complex generated from $[\text{Ir}(\text{OMe})(\text{COD})]_2$ and 4,4'-di-*tert*-butyl-2,2'-bipyridine at room temperature in hexane.¹¹³ The direct borylation of five-membered heteroarenes using the same catalyst has also been reported.

Experimental and computational evidence for a boron-assisted, σ -bond metathesis pathway for alkane borylation using the transition metal boryl complex $\text{CpM}(\text{CO})_n\text{BR}_2$ ($\text{M} = \text{Fe}, \text{Ru}, n = 2$; $\text{M} = \text{Mo}, \text{W}, n = 3$) has been presented.¹¹⁴ The iridium-catalyzed borylation of benzene with diboron has been theoretically investigated with the DFT method, focusing on an iridium(I) mono boryl complex and an iridium(III) tris(boryl) complex. It is concluded that it is a iridium(III) tris(boryl) complex that is the active species and an unusual seven coordinate iridium(V) species is involved as a key intermediate in the reaction.¹¹⁵ Reaction mechanisms of the methane and benzene functionalizations by $\text{CpFe}(\text{CO})(\text{BO}_2\text{C}_2\text{H}_2)$ and $\text{CpW}(\text{CO})_2(\text{BO}_2\text{C}_2\text{H}_2)$ have been investigated with the aid of DFT calculations. The results show that functionalizations by the Fe boryl complex favor a one-step mechanism with an oxidatively added transition state, while the functionalizations by the tungsten boryl complex only proceed by a two-step mechanism. The distinct barriers between the functionalizations of methane and benzene by the Fe complex can be explained by the significant stabilization interaction between the “empty” boron p orbital of the boryl group and the π orbitals of the benzene ring.¹¹⁶ DFT calculations have been performed to study the structures and stability of titanocene borane σ -complexes $\text{Cp}_2\text{Ti}(\eta^2\text{-HBcat})\text{L}$ ($\text{L} = \text{HC}\equiv\text{CH}, \text{H}_2\text{C}=\text{CH}_2, \text{SiH}_4, \text{CH}_4, \text{and H}_2$).¹¹⁷ The boron-diylide phenyl{bis(triphenylphosphanemethylenido)}borane has been prepared and forms allyl-type complexes with Zr and Pd fragments.¹¹⁸ DFT calculations have been performed on the structural isomers of borane adducts of $\text{Cp}_2\text{M}(\text{H})$ ($\text{M}/\text{Nb}, \text{Ta}$). These show that O- and N-substituted borane adducts can have various structural isomers including boryl, hydridoborate and s-complex structures.¹¹⁹

9 Perfluorinated boranes

Tris(pentafluorophenyl)borane has been used as catalyst in the formation of P–B bonds by mediating the dehydrocoupling of phosphine–boranes $\text{PhPH}_2\text{-BH}_3$ and $\text{PH}_3\text{-BH}_3$.¹²⁰ The tellurium diimide dimer $[\text{tBuNTe}(\mu\text{-NtBu})_2\text{TeN}^t\text{Bu}]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ form a 1:1 adduct which instigates THF ring opening to give $[\text{tBuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu}](\text{CH}_2)_4\text{OB}(\text{C}_6\text{F}_5)_3$ quantitatively.¹²¹ Propylene polymerization using unsymmetrical *ansa*-metallocene complexes $\text{Me}_2\text{Y}(\text{Ind})\text{CpMMe}_2$ ($\text{Y} = \text{Si}, \text{C}, \text{M} = \text{Zr}, \text{Y} = \text{C}, \text{M} = \text{Hf}$) and the co-initiators methyl aluminoxane (PMAO), $\text{B}(\text{C}_6\text{F}_5)_3$, and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ have been studied at a variety of propylene concentrations. Modelling of the polymer microstructure reveals that the catalysts derived from $\text{Me}_2\text{Si}(\text{Ind})\text{CpZrMe}_2$ and each of these co-initiators function under conditions where chain inversion is much faster than propagation (Curtin–Hammett conditions).¹²² Metallocene polymerization catalyst ion-pair aggregation [with $\text{MeB}(\text{C}_6\text{F}_5)_3$ anions]

has been investigated by cryoscopy and pulsed field gradient spin-echo NMR diffusion measurements. These provide no evidence of significant aggregation at concentrations in the 1–18 millimolar regime. This demonstrates that ion-pair aggregation into ion-quadruples have little relevance to actual olefin enchainment and propagation processes in olefin polymerisation.¹²³ The substituted cyclopentadienyl zirconium complex $[\text{Cp}'''\text{ZrMe}_2]$ ($\text{Cp}''' = \eta^5\text{-C}_5\text{H}_2\text{-1,2,4-(SiMe}_3)_3$) reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to give the two species $[\text{Cp}'''\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ and $[\text{Cp}'''\eta^5\text{-C}_5\text{H}_2\text{-2,4-(SiMe}_3)_2\text{SiMe}_2\text{CH}_2\text{Zr}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ that shows C–H activation of a SiMe_3 group attached to the cyclopentadienyl ligand.¹²⁴

The tris(3-*tert*-butyl-5-methylpyrazolyl)hydroborato zinc and cobalt hydroxide complexes $[\text{Tp}^{\text{But,Me}}\text{MOH}]$ are protonated by $(\text{C}_6\text{F}_5)_3\text{B}(\text{OH})_2$ to yield the aqua derivative $\{[\text{Tp}^{\text{But,Me}}\text{M}(\text{OH})_2][\text{HOB}(\text{C}_6\text{F}_5)_3]\}$. These complexes exhibit a hydrogen bonding interaction between the metal aqua and boron hydroxide moieties. This hydrogen bonding interaction may be viewed as analogous to that between the aqua ligand and Thr-199 at the active site of carbonic anhydrase.¹²⁵ Treatment of the oxovanadium(v) complex $[\text{VO}(\text{OCH}_2\text{CF}_3)_3]_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ leads to aryl/alkoxy group exchange and formation of the unexpected organometallic oxovanadium(v) $[\text{VO}_2\text{OCH}_2\text{CF}_3](\text{OCH}_2\text{CF}_3)(\text{C}_6\text{F}_5)_2$; while with $[\text{VO}(\text{NET}_2)_3]$ the Lewis acid adduct $[(\text{Et}_2\text{N})_3\text{VO}\cdot\text{B}(\text{C}_6\text{F}_5)_3]$ results.¹²⁶ The reaction of $[\text{Cp}_2\text{Ti}(\text{CO})_2]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ leads to the unexpected titanaacylborane $[\text{Cp}_2\text{Ti}(\text{CO})(\eta^2\text{-OCB}(\text{C}_6\text{F}_5)_3)]$.¹²⁷ The zwitterionic η^3 -benzyl complexes $[\text{RR}'\text{C}=\text{NC}_6\text{H}_4\text{C}\{\text{OB}(\text{C}_6\text{F}_5)_3\}_2\text{O}_2\text{N},\text{O}]\text{Ni}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ ($\text{R}, \text{R}' = (\text{CH}_2)_5$, $\text{R} = \text{Et}$, $\text{R}' = \text{Et}$) are active for the polymerization of ethylene.¹²⁸ $\text{Cp}_2\text{Hf}(\text{SiR}_3)\text{Me}$ ($\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3$, Si^iBuPh_2 , SiPh_3) react with $\text{B}(\text{C}_6\text{F}_5)_3$ to quantitatively produce the cationic hafnium silyl complexes $\text{Cp}_2\text{Hf}(\text{SiR}_3)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$. The σ -bond metathesis reaction with Mes_2SiH_2 yielded $\text{HSi}^i\text{BuPh}_2$ and the reactive species $\text{Cp}_2\text{Hf}(\eta^2\text{-SiHMe}_2)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ which was also generated by reaction of $\text{Cp}_2\text{Hf}(\text{SiMes}_2\text{H})\text{Me}$ with $\text{B}(\text{C}_6\text{F}_5)_3$. Spectroscopic data provide evidence for an unusual agostic Si–H interaction. The reaction with arenes has also been studied.¹²⁹

New types of binuclear constrained geometry Ti olefin polymerisation catalysts with the bifunctional bisborane activator $1,4\text{-(C}_6\text{F}_5)_2\text{BC}_6\text{F}_4\text{B(C}_6\text{F}_5)_2$ have been investigated. They exhibit greatly enhanced polymerization activity, polyolefin molecular weight, and comonomer incorporation efficiency compared with the Zr analogues.¹³⁰ Reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with the silanol groups of MCM-41 results in a heterogeneous tris(pentafluorophenyl) borate anion. This immobilised weakly-coordinating anion retains metallocenes, and yields a heterogeneous propene oligomerisation catalyst which has an activity comparable to the corresponding homogeneous catalyst.¹³¹ Reaction of Cp^*ZrMe_3 with the heterogeneous activator $[\equiv\text{SiO-B}(\text{C}_6\text{F}_5)_3]_2[\text{HNEt}_2\text{Ph}]$, generates the well-defined cationic silica-supported metallocenium species $[\equiv\text{SiO-B}(\text{C}_6\text{F}_5)_3][\text{Cp}^*\text{ZrMe}_2(\text{NEt}_2\text{Ph})]$ which is an active olefin polymerisation catalyst.¹³²

Reactions between the cyclic sec. amines pyrrolidine and piperidine and $\text{B}(\text{C}_6\text{F}_5)_3$ yield Lewis acid–base adducts with both *intra*- and *inter*-molecular hydrogen bonding interactions between C–H and N–H groups and aryl-fluorines in the solid state.¹³³ The reaction of Lewis acidic perfluorinated borafluorenes $\text{C}_{12}\text{F}_8\text{BR}$ ($\text{R} = \text{C}_6\text{F}_5$, CH_3) and 9-phenyl-9-borafluorene toward $[\text{Cp}^*\text{Al}]_4$ has been investigated and leads to the formation of thermally robust η^1 Lewis acid–base adducts as the thermodynamically favored products. η^5 products are not observed.¹³⁴ $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of various

substituted imidazoles have been prepared, and their dynamic behavior studied by NMR.¹³⁵ The crystal and molecular structures of boron fluoromes and fluoroxy compounds: Ar_2BF , $\text{Ar}'_3\text{B}$, $\text{Ar}_2\text{B}(\text{OH})$, $\text{Ar}'\text{B}(\text{OH})_2$ and Mes_2BF ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) have been determined ($\text{Ar} = 2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2$, $\text{Ar}' = 2,6\text{-(CF}_3)_2\text{C}_6\text{H}_3$, $\text{Ar}'' = 2,4\text{-(CF}_3)_2\text{C}_6\text{H}_3$).¹³⁶ New ionic-liquids incorporating fluorinated borates have been described.¹³⁷

Reactions of titanium and zirconium derivatives of bis(trimethylsilyl)acetylene with $\text{B}(\text{C}_6\text{F}_5)_3$ have been reported to afford the Ti(III) complex with pendant $\text{B}(\text{C}_6\text{F}_5)_3$ groups on Cp or the acetylene.¹³⁸ The synthesis of half-sandwich bis(pentafluorophenyl)borylsubstituted cyclopentadienyl zirconium, niobium and tantalum complexes has been reported, exemplified by $\text{MCl}_4\{\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2\}$ ($\text{M} = \text{Nb, Ta}$), and $\text{ZrCl}_2(\text{Cp})\{\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2(\text{SMe}_2)\}$ or $\text{ZrCl}_2(\text{Ind})\{\text{C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2(\text{SMe}_2)\}$ ($\text{Ind} = \eta^5\text{-indenyl}$).¹³⁹ Binuclear compounds containing bridging $(\mu\text{-CN})\text{B}(\text{C}_6\text{F}_5)_3$ and $(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3$ groups, such as $[\text{Ir}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\text{PPh}_3)_2\text{CO}]$ and $[\text{Fe}\{(\mu\text{-NC})\text{B}(\text{C}_6\text{F}_5)_3\}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ have been prepared.¹⁴⁰

10 B-Heterocycles

Unsymmetrical 9-borafluorenes have been accessed *via* low-temperature C–H activation of *m*-terphenylboranes. For example $2,6\text{-(4-}^t\text{BuC}_6\text{H}_4)_2\text{C}_6\text{H}_3\text{Li}$ reacts with $\text{H}_2\text{CIB-SMe}_2$ to afford 9-borafluorene 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene.¹⁴¹ The amino borane 1-(NPh_2)-2- $[\text{B}(\text{C}_6\text{F}_5)_2]\text{C}_6\text{H}_4$ has been prepared. Reaction with water or HCl affords zwitterionic compounds, while LiH in the presence of 12-crown-4 leads to the isolation of the aminoborate $[\text{1-(Ph}_2\text{N)-2-[B(H)(C}_6\text{F}_5)_2]\text{C}_6\text{H}_4][\text{Li(12-crown-4)}]$.¹⁴² 2,2'-diborabiphenyl, a Lewis acid analogue of 2,2'-bipyridine has been synthesized. Some Lewis base adducts that include bifunctional pyridazine donors have also been prepared, which lead to novel heterocyclic analogues of polycyclic aromatic hydrocarbons that contain a $\{\text{C}_2\text{B}_2\text{N}_2\}$ core.¹⁴³ The structures of the alkali metal boratabenzenes: $\text{K}([\text{18-crown-6}](\text{C}_5\text{H}_5\text{BMe})$, $\text{K}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{B}\cdot\text{NMe}_2)(\text{THF})_2$ and $\text{K}[3,5\text{-Me}_2\text{C}_5\text{H}_3\text{B}\cdot\text{N}(\text{SiMe}_3)_2]$ have been reported.¹⁴⁴ An *o*-phenylene-bridged bis(1-boratabenzene)zirconium dichloride and 1,1-isobutenyl-bridged bis(1-boratabenzene)zirconium dichloride have been prepared.¹⁴⁵ Reaction of 1,4-dihydro-4-(diisopropylamino)-2,6-dimethyl-1-phenyl-1,4-phosphaborin with Mn and Ru fragments results in sandwich complexes in which the phosphorus bound phenyl group has been lost.¹⁴⁶

11 Boron–pnictogen complexes

Trivinylphosphineborane adducts $(\text{CH}_2=\text{CH})_3\text{PBX}_3$ ($\text{X} = \text{H, Cl, Br, I}$) have been prepared and are stable compounds, whereas with BF_3 polymerization of the phosphine and its adduct occurs. Some factors accounting for this are discussed.¹⁴⁷ $\text{PH}(\text{Me})(\text{Ph})(\text{BH}_3)$ reacts with $\text{Pd}((S,S)\text{-chiraphos})(o\text{-MeOC}_6\text{H}_4)(\text{I})$ to give a mixture of the diastereomers $\text{Pd}((S,S)\text{-chiraphos})(o\text{-MeOC}_6\text{H}_4)(\text{P}(\text{Me})(\text{Ph})(\text{BH}_3))$ showing that Pd–P bond formation proceeded with retention of configuration at phosphorus in this system.¹⁴⁸ The synthesis and reactivity of Pt(II) complexes with

phosphinoborane ligands, models for intermediates of the dehydropolymerisation of phosphine boranes, have been reported.¹⁴⁹ $\text{P}_4\text{O}_6 \cdot \text{BH}_3$, formed from addition of P_4O_6 to $\text{Me}_2\text{S} \cdot \text{BH}_3$, dimerizes spontaneously at -30°C resulting in $\text{P}_8\text{O}_{12} \cdot 2\text{BH}_3$ the crystal structure of which shows two bicyclic $\text{P}_4\text{O}_5 \cdot \text{BH}_3$ subunits connected *via* O bridges.¹⁵⁰ The structures of unknown phosphanyl- and arsanyl-boranes H_2BPH_2 and H_2BASh_2 have been calculated by DFT. By applying the concept of Lewis acid/base stabilisation, $[(\text{CO})_5\text{W}(\text{H}_2\text{EBH}_2 \cdot \text{NMe}_3)]$ ($\text{E} = \text{P}, \text{As}$) derivatives have been synthesised by the metathesis reactions between $\text{Li}[(\text{CO})_5\text{WEH}_2]$ and $\text{ClH}_2\text{BNMe}_3$. UV radiation of the phosphanylborane leads to the dinuclear phosphanido-bridged complex $[(\text{CO})_8\text{W}_2(\mu\text{-PHBH}_2 \cdot \text{NMe}_3)_2]$ by H_2 and CO elimination.¹⁵¹

Reactions of boron atoms with NO molecules in solid argon have been studied using matrix isolation infrared absorption spectroscopy. In solid argon, boron atoms spontaneously react with NO to form the insertion molecule NBO. BNBO and OBNNO molecules were formed by B and NO addition reactions to NBO. The linear BBNO and BBBNO nitrosyls form spontaneously on annealing.¹⁵² The Group 13–15 inorganic analogues of benzene, $[\text{HMYH}]_3$ ($\text{M} = \text{B}, \text{Al}, \text{Ga}; \text{Y} = \text{N}, \text{P}, \text{As}$) as well as mixed heterocycles of the type $[\text{BAlGaNPAs}]_6$ and their dimers have been theoretically examined at the DFT level of theory. B–N bonding strongly stabilizes the mixed heterocycles. Dimerization reactions of the coordinationally unsaturated $[\text{HMYH}]_3$ heterocycles yielding hexamer clusters $[\text{HMYH}]_6$ are found to be exothermic with the exception of borazine, for which, as for benzene, dimerization is strongly endothermic due to the aromaticity of C_6H_6 and $[\text{HBNH}]_3$.¹⁵³ Macrocyclic imidazolylboranes $[\text{imidazolylB}(\text{R}^1)_2]_n$ ($n = 4$ or 5) are obtained from 1-trimethylsilylimidazoles and haloboranes $\text{XB}(\text{R}^1)_2$ by boron/silicon exchange using 2-bromoimidazole and benzimidazole.¹⁵⁴ A full paper describing the mild, catalytic dehydrocoupling route to aminoboranes and borazine derivatives from either primary or secondary amine–borane adducts using late transition metal complexes as precatalysts has been published.¹⁵⁵ The tris(tricholorsilylvinyl)-substituted borazine $(\text{Cl}_3\text{SiCH}=\text{CH})_3\text{B}_3\text{N}_3\text{H}_3$ has been prepared by hydrosilylation of a precursor trialkynylborazine. This complex is transformed into a highly functionalized silica gel by a sol–gel process.¹⁵⁶ The structure of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene- BH_3 has been determined and this high melting solid exhibits head-to-tail alignment of the molecular dipoles in the solid state, with the closest intermolecular contact being a simple well-defined example of an unconventional $[\text{C}-\text{H}\delta^+ \cdots \text{H}\delta^- - \text{B}]$ dihydrogen bond.¹⁵⁷

The dinuclear boryloxycarbyne complexes $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{M}\equiv\text{CO}]_2\text{B}_2(\text{NMe}_2)_2\}$ have been reported ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). The Mo and W complexes proved to be kinetically favoured products and underwent quantitative rearrangement in solution to afford the boryl complexes $\{[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{M}\equiv\text{CO}] \text{B}(\text{NMe}_2)\text{B}(\text{NMe}_2)\{ \text{M}(\text{CO})_3 - (\eta^5\text{-C}_5\text{H}_5) \} \}$.¹⁵⁸ The coordination chemistry of the bis(*tert*-butylamido)phenylborane ligand, $[\text{tBuN-BPh-N}^t\text{Bu}]^{2-}$, has been developed. The reactions of $\text{PhB}(\text{tBuNLi})_2$, with metal halides of zirconium, hafnium, and vanadium generate complexes of general formulae $(\text{tBuN-BPh-N}^t\text{Bu})_2\text{M}(\text{THF})$ ($\text{M} = \text{Zr}, \text{Hf}$), $\text{Li}_2[\text{M}(\text{tBuN-BPh-N}^t\text{Bu})_3]$ ($\text{M} = \text{Zr}, \text{Hf}$), and $\text{M}(\text{tBuN-BPh-N}^t\text{Bu})_2$ ($\text{M} = \text{V}$).¹⁵⁹ Reaction of bis(amino)phosphane $\text{tBuP}(\text{NH}^t\text{Bu})_2$ with BH_3 results in a simple Lewis acid Lewis base adduct at the phosphane centre and not the nitrogen consistent with BH_3 being a soft Lewis acid.¹⁶⁰ The thermal decomposition of hindered amine–borane adducts

leads to high yields of new monomeric (dialkylamino)boranes $R^1R^2N-BH_2$ ($R^1, R^2 =$ alkyl) that are efficient boron sources in the Pd(0) catalyzed borylation reaction that affords monomeric aryl(dialkylamino)boranes $R^1R^2N-BHR^3$ ($R^3 =$ aryl).¹⁶¹ The syntheses, structure and reactivity of 1-[bis(diisopropylamino)boryl]imidazoles have been reported.¹⁶²

12 Boron–chalcogen complexes

The crystal structure of diboronic acid shows that in the solid-state it consists of molecules of $B_2(OH)_4$ hydrogen-bonded into two-dimensional sheets linked by $B \cdots O$ interactions.¹⁶³ Tetraboronic acids that have four $-B(OH)_2$ groups oriented tetrahedrally from cores derived from tetraphenylmethane and tetraphenylsilane have been described. Crystallization produces isostructural diamondoid networks held together by hydrogen bonding of the $-B(OH)_2$ groups.¹⁶⁴ The synthesis and structural characterization of the ferrocenyl diboronic acid complex $[Fe(\eta^5-C_5H_4-B(OH)_2)_2]$ and the pyridyl boronic acid $[Fe(\eta^5-C_5H_4-4-C_5H_4N)(\eta^5-C_5H_4-B(OH)_2)]$ have been determined. The $B(OH)_2$ group provides two hydrogen bonding donor groups and two acceptors, forming mainly cyclic hydrogen-bonded systems in topological analogy with a primary amido group. For the pyridyl complex the $(B)OH \cdots N$ and the $(B)OH \cdots O(B)$ donor–acceptor systems have comparable strength and do not lead to strong topological preferences.¹⁶⁵ $B(C_6F_5)_2OH$ exists as a cyclic trimer in the solid-state, with $B-O(H)-B$ bridges and a cyclohexane-like structure. In solution it exists as a monomer at low-temperature. ¹⁹F NMR data reveal restricted rotation of the OH substituent around the Ar_2B-OH bond as a result of the partial double-bond character of this interaction.¹⁶⁶ A series of octupolar molecules derived from the boroxine framework $[R-C_6H_4-BO]_3$ ($R =$ Ome, SMe, NMe₂) combine excellent transparency in the near UV-visible region with significant first-order hyperpolarisabilities.¹⁶⁷ A series of complexes of dimethylsulfoxonium methylide and various organoboranes X_3B ($X =$ H, Ph, F, C_6F_5) have been prepared and isolated, which are intermediates in the catalysis of the repetitive insertion of methylene from dimethylsulfoxonium methylide to form polymethylene.¹⁶⁸

The reduction of a phenylene-bridged bis(2,2-difluoro-1,3,2-(2H)-dioxaborine) affords a strongly delocalised organic mixed-valence system, which for the first time, allows details of the vibrations coupled to the electron transfer to be extracted from the intervalence band.¹⁶⁹ Placing a longer conjugated bridge between the two dioxaborines affords compounds that exhibit high two-photon cross sections which can be used as sensitizers for the photodeposition of metallic silver lines.¹⁷⁰

13 Boron–halide complexes

The higher Lewis acid strength of BCl_3 in X_3B-NH_3 adducts compared with BF_3 has been investigated by the DFT method. An energy partitioning analysis shows that the stronger bond in the former complex comes from enhanced covalent interactions between the Lewis acid and the Lewis base which can be explained with the energetically lower lying LUMO of BCl_3 .¹⁷¹ The experimentally determined

structures of B_8F_{12} and of a completely new boron subhalide, $B_{10}F_{12}$, both obtained by means of low temperature X-ray crystallography, have been reported.¹⁷² $Fe(NO)_3(\eta^1-BF_4)$ can be synthesized by treating $Fe(NO)_3Cl$ with an equimolar amount of $[Ag][BF_4]$. The iron centres in the $Fe(NO)_3$ fragment exhibit approximately tetrahedral coordination geometries, but the Fe–N–O linkages are distinctly nonlinear. DFT calculations show that these bent Fe–N–O links have an electronic origin and need not be attributed to other factors such as packing forces in the crystal.¹⁷³ The P–B adducts of 3,4-mimethyl-1-phosphaferrocene with bromoboranes have been reported.¹⁷⁴

14 Trispyrazolyl-borate, -methane and related complexes

The homoleptic Group-12 metal bis(mercaptoimidazolyl)borate $[Bm^R]$ complexes of general formula $M(Bm^R)_2$ ($M = Zn, Cd, Hg$) have been prepared.¹⁷⁵ Related dihydrobis(thioxotriazolyl)borato complexes of zinc(II), bismuth(III), and nickel(II) have also been prepared. These complexes show $M \cdots H-B$ interactions in the solid-state that have been further studied by DFT calculations.¹⁷⁶ $[RuH(CO)(PPh_3)\{3-H,S,S''-HB(mt)_3\}]$ ($mt =$ methimazolyl), which contains an agostic B–H–Ru interaction, hydrogenates ethynylbenzene to styrene with formation of the ruthenaboratrane $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ that contains a direct $Ru \rightarrow B$ bond.¹⁷⁷ The preparation of phenyltris[1-adamantyl(thiomethyl)]borate $[PhTtAd]^-$ as the thallium salt, which incorporates the large 1-thioether substituent, has been described. This monoanionic tripodal ligand has been used to prepare a range of four coordinate Ni(I) complexes: $[PhTtAd]Ni(L)$ ($L = CO, PMe, \eta^2-CH_2SAd$).¹⁷⁸

The sterically encumbered, high field, tris(diisopropylphosphino)borate ligand, $[PhB(CH_2P^iPr)_3]^-$ has been partnered with a variety of metal fragments.¹⁷⁹ The related tripodal ligand $Li[PhB(CH_2PPh_2)_3]$ has been used to synthesise a low-spin d^5 iron(III) imide complex $[PhB(CH_2PPh_2)_3]Fe=N-p\text{-tolyl}$.¹⁸⁰ The structural, electronic and mechanistic comparisons relevant to ligand exchange and benzene C–H activation processes in zwitterionic and cationic bis(phosphine) platinum(II) complexes of a range of neutral and anionic tripodal ligands have been presented.¹⁸¹ The zwitterionic complexes exemplified by $[(Ph_2B(CH_2PPh_2)_2)Rh(nbd)]$ and $[(Ph_2B(CH_2NMe_2)_2)Rh(nbd)]$ show good activities in a range of addition reactions such as hydrogenation, hydroboration and hydroacylation.¹⁸²

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