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Contents

Special Issue: Frontiers in Boron Chemistry Dedicated to Professor M. Frederick Hawthorne on his 75th Birthday

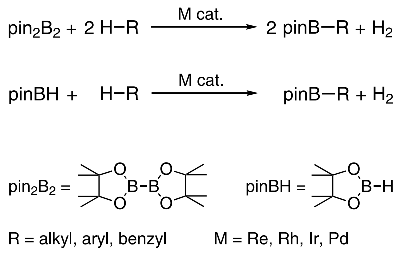
Reviews

Tatsuo Ishiyama, Norio Miyaura

J. Organomet. Chem. 680 (2003) 3

Transition metal-catalyzed borylation of alkanes and arenes via C–H activation

This review describes seminal early works and exciting recent developments of transition metal-catalyzed C–H borylation. Re-, Rh-, Ir- and Pd- catalyzed reactions of alkanes, arenes and benezylic positions of alkylarenes with bis(pinacolato)diboron or pinacolborane provide alkyl-, aryl-, heteroaryl- and benzylboronates, respectively.

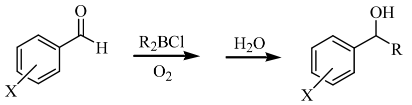


G.W. Kabalka, Zhongzhi Wu, Yuhong Ju

J. Organomet. Chem. 680 (2003) 12

The use of organoboron chlorides and bromides in organic synthesis

Organoboron chlorides and bromides have been found to alkylate aromatic aldehydes in a Grignard-like fashion. Depending on reaction conditions, either arylhalomethane or arylmethanol derivatives are formed. Boron chloride and bromide derivatives can also be used to induce aromatic aldehydes to react with both alkenes and alkynes to generate a wide variety of halogenated products of value to synthetic organic chemists.

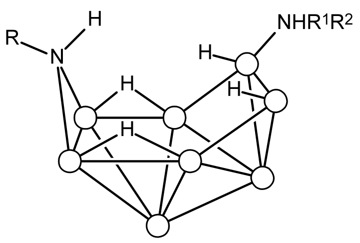


Detlef Gabel, Claudia Bauer,
Mohamed E. El-Zaria, Afaf R. Genady,
Udo Dörfler

J. Organomet. Chem. 680 (2003) 23

The chemistry of the azanonaborane cluster $RNH_2–B_8H_{11}NHR$

The $R^1R^2NH–B_8H_{11}NHR$ cluster is stable to aqueous solutions and can be made water-soluble by the introduction of a few hydrophilic groups. This makes the cluster a good candidate as boron moiety in compounds for boron neutron capture therapy. The introduction of substituents on the nitrogen atoms and the mechanism of its formation are reviewed. Pyridine derivatives of the cluster show electronic interaction between the cluster and the pyridine.



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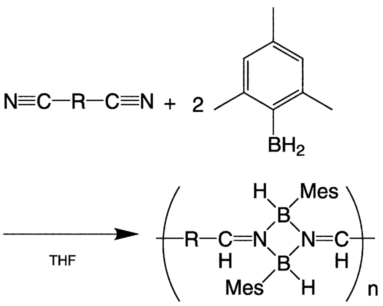
Fukashi Matsumoto, Yoshiki Chujo

J. Organomet. Chem. 680 (2003) 27

Poly(cyclodiborazane)s

Poly(cyclodiborazane)s, which consist of boron–nitrogen four-membered rings, are highly stable against air and moisture. The polymers exhibited interesting properties as a novel type of π-conjugated polymers with intramolecular charge transfer structure. Their stability and potential as functional materials would be important and informative both in industry and boron chemistry.

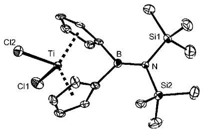


Holger Braunschweig, Frank M. Breitling, Emanuel Gullo, Mario Kraft

J. Organomet. Chem. 680 (2003) 31

The chemistry of [1]borametallocenophanes and related compounds

[1]Borametallocenophanes of early **I** and late transition metals **II** have attracted considerable interest due to their potential use as highly active catalysts for Ziegler–Natta type polymerisation of olefins or as precursors for novel organometallic polymers. The present overview covers corresponding *ansa*-complexes with one three-coordinate boronatom in the bridge and summarizes their structure, synthesis and reactivity.



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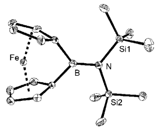


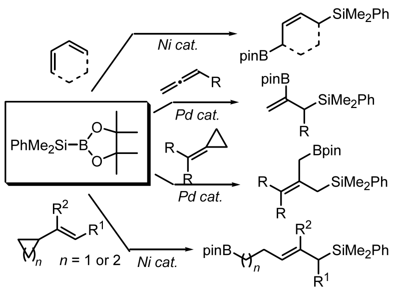
II

Michinori Suginome, Yoshihiko Ito

J. Organomet. Chem. 680 (2003) 43

Regio- and stereoselective synthesis of boryl-substituted allylsilanes via transition metal-catalyzed silaboration

Regio- and stereo-controlled synthesis of boryl-substituted allylsilanes via transition metal-catalyzed additions of silylboranes to unsaturated organic compounds is described.



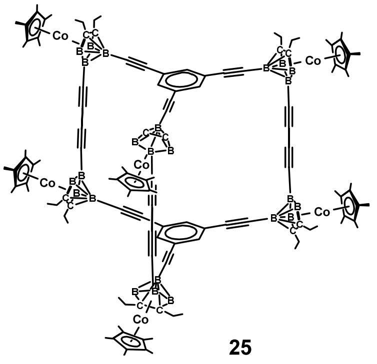
Regular Papers

Haijun Yao, Russell N. Grimes

J. Organomet. Chem. 680 (2003) 51

Small cobaltacarborane clusters in synthesis. Peralkylation, perhalogenation, and macrocycle construction

The molecular engineering of organometallic macromolecules based on small metallacarborane building blocks has been extended in two areas: the synthesis of fully substituted complexes in which all B-H hydrogens are replaced by halogen or alkyl groups, and the construction of new 2- and 3-dimmensioal matallacarborane-based nanoscale macrocycles that are designed with the posibility of the metal-metal electronic communication and other potentially useful properties in mind.



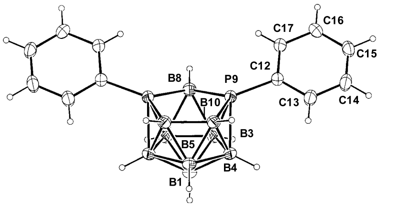
25

Daewon Hong, Patrick J. Carroll,
Larry G. Sneddon

J. Organomet. Chem. 680 (2003) 61

Synthesis and structural characterization of an 11-vertex *nido*-diphosphaborane, 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$

The first neutral 11-vertex *nido*-diphosphaborane 7,9-Ph2-*nido*-7,9-P2B9H9 that is also the first diphosphaborane to thave *exo*-substitutents at the phosphorus cage atom has been synthesized by reaction of Me4N+[*nido*-B9H12-] with PhPCl2 in the presence of NaH. X-ray diffraction and DFT/GIAO/NMR methods have both established that the phosphorus atoms are in non-adjacent positions on the open pentagonal face of the cluster.

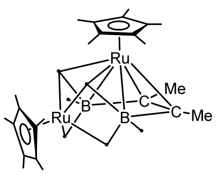


Hong Yan, Alicia M. Beatty,
Thomas P. Fehlner

J. Organomet. Chem. 680 (2003) 66

Reactions of *nido*-1,2-$(Cp^*RuH)_2B_3H_7$ with RC≡CR′ (R, R′ = H, Ph; Me, Me) to yield novel metallacarboranes

Addition of alkyne to *nido*-1,2-$(Cp^*RuH)_2B_3H_7$ leads to novel ruthenacarboranes. For example, good kinetic control leads to the formation of *nido*-1,2-$(Cp^*$-$RuH)_2$-4,5-Me_2-4,5-$C_2B_2H_4$ (**3**) and *nido*-1,6-$(Cp^*Ru)_2$-4,5-Me_2-4,5-$C_2B_2H_6$ (**6**): a pair of unusual framework isomers that do not readily interconvert. Depending on whether internal or terminal alkynes are used, other novel structural types containing an *exo*-polyhedral metal–boron bridging borane fragment on the one hand and an *exo*-polyhedral metal–boron bridging alkylidene fragment on the other are observed. When pushed, more stable *closo*-ruthenacarboranes result including a novel triple-decker complex containing a borole ring.



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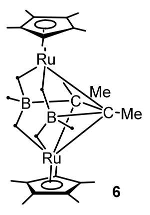

6

George R. Clark, Geoffrey J. Irvine,
Warren R. Roper, L. James Wright

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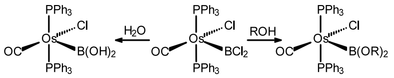
Reactions of the dichloroboryl complex of osmium, $Os(BCl_2)Cl(CO)(PPh_3)_2$, with water, alcohols, and amines
Crystal structures of $Os[B(OH)_2]Cl(CO)$-$(PPh_3)_2$, $Os[B(OEt)_2]Cl(CO)(PPh_3)_2$, and $\mathrm{Os[\overline{BN(CH_3)C_6H_4N}(CH_3)]Cl(CO)(PPh_3)_2}$

The two chloride substituents on boron in the dichloroboryl complex, $Os(BCl_2)Cl(CO)$ $(PPh_3)_2$, are readily replaced through reactions with water, alcohols, and amines giving the corresponding dihydroxy-, dialkoxy- and diamino-boryl complexes. The following compounds, $Os[B(OH)_2]Cl(CO)$-$(PPh_3)_2$, $Os[B(OEt)_2]Cl(CO)(PPh_3)_2$, and $\mathrm{Os[\overline{BN(CH_3)C_6H_4N}(CH_3)]Cl(CO)(PPh_3)_2}$, prepared in this way, have been characterized by X-ray crystallography.

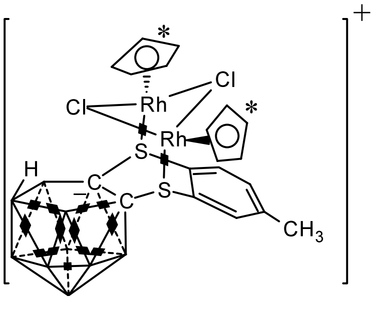


Francesc Teixidor, Mª Rosa Cirera,
Clara Viñas, Raikko Kivekäs,
Reijo Sillanpää, Albert Demonceau

J. Organomet. Chem. 680 (2003) 89

A versatile rigid binucleating ligand for $Rh_2(\mu\text{-}Cl)_2$ moieties: its application as a catalyst in hydrogenation and cyclopropanation
Crystal structure of $[Rh(C_5Me_5)Cl\{7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3(CH_3))S\text{-}C_2B_9H_{10}\}][7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3(CH_3))S\text{-}C_2B_9H_{10}]\cdot THF$

A rigid non-deforming "MCl_2M" binucleating ligand $[7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3(CH_3))S\text{-}C_2B_9H_{10}]^-$ able to held the two rhodium atoms in a cooperative distance has been synthesized. The original two bridging chlorides are retained in $[Rh_2(C_5Me_5)_2$ $Cl_2\{7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3(CH_3))S\text{-}C_2B_9H_{10}\}]^+$. Hydrogenation of 1-hexene is 10 times faster with $[Rh_2(C_5Me_5)_2Cl_2\{7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3$ $(CH_3))S\text{-}C_2B_9H_{10}\}]^+$ than with $[Rh_2(C_5Me_5)_2Cl_4]$. A hydrogenation mechanism has been proposed which assumes that $[Rh_2(C_5Me_5)_2(Cl)(H)\{7,8\text{-}\mu\text{-}S(4'\text{-}C_6H_3$ $(CH_3))S\text{-}C_2B_9H_{10}\}]^+$ is the first generated species in the process.

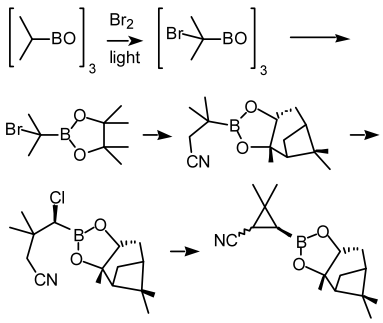


Donald S. Matteson, Dilinie Fernando

J. Organomet. Chem. 680 (2003) 100

Bromination of tri(isopropyl)boroxine and asymmetric synthesis of (2-cyano-3,3-dimethylcyclopropyl)boronic esters

Bromination of triisopropylboroxine to tris(1-bromo-1-methylethyl)boroxine is far more facile than α-bromination of *sec*-alkylboronic esters. Further transformations of the sterically hindered system were carried out, including asymmetric insertion of a chloromethyl group into the C–B bond of a pinanediol ester and cyclization to the corresponding cyclopropylboronic ester.

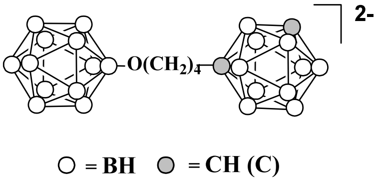


Igor B. Sivaev, Stefan Sjöberg,
Vladimir I. Bregadze

J. Organomet. Chem. 680 (2003) 106

$[C_2B_{10}]$–$[B_{12}]$ double cage boron compounds—a new approach to the synthesis of water-soluble boron-rich compounds for BNCT

A new approach to the synthesis of water-soluble compounds for BNCT was proposed. The *closo*-dodecaborate cage is used as a hydrophilic substituent providing for the water-solubility of the molecule whereas the carborane cage can be used for attachment to biomolecules. The double-cage molecules [*o*-, *m*-, and *p*-$CB_{10}H_{10}C(CH_2)_4OB_{12}H_{12}]^{2-}$ were prepared by the reaction of $[B_{12}H_{11}O(CH_2)_4]^-$ with the corresponding lithiated carboranes.

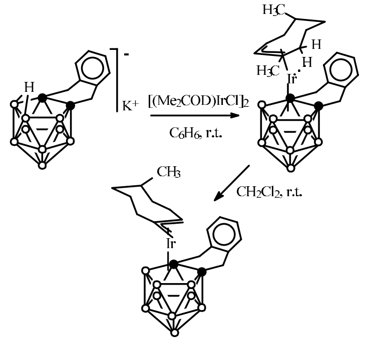


Alexander V. Safronov, Tatiana V. Zinevich,
Fedor M. Dolgushin, Evgenii V. Vorontsov,
Oleg L. Tok, Igor T. Chizhevsky

J. Organomet. Chem. 680 (2003) 111

First agostic *closo*-metallacarboranes with η^3-cyclooctenyl type ligand: synthesis and structural characterization of *closo*-3-[η^3-(*endo*-1,5-dimethylcycloocten-1-yl)]-1,2-μ-(1′,2′-xylylene)-3,1,2-$IrC_2B_9H_9$ and its isomerization to *closo*-3-[η^3-(*exo*-1-methylene-5-methylcyclooctene-1-yl)]-1,2-μ-[η^2-(1′,2′-xylylene)]-3,1,2-$IrC_2B_9H_9$

Novel 12-vertex agostic (C–H···Ir) *closo*-iridacarboranes with η^3-cyclooctenyl type ligands, *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-3,1,2-$IrC_2B_9H_9$ (**3**) and *closo*-3-[η^3-(*endo*-1,5-Me_2COD)]-1,2-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-8-(EtO)-3,1,2-$IrC_2B_9H_8$ (**4**), have been synthesized via the reaction of $[Ir(\eta^4\text{-}1,5\text{-}Me_2COD)Cl]_2$ with [*nido*-7,8-μ-(1′,2′-$CH_2C_6H_4CH_2$–)-7,8-$C_2B_9H_{10}]^-K^+$. Complex **3** in dichloromethane solution is converted to isomeric η^3-exo-allylic complex *closo*-3-[η^3-(1-*exo*-CH_2-5-MeC_8H_{12})]-1,2-μ-[η^2-(1′,2′-$CH_2C_6H_4CH_2$–)]-3,1,2-$IrC_2B_9H_9$ (**5**) in which a weak η^2-coordination of the metal atom with one of the aromatic bonds of *ortho*-xylylene cage substituent has been revealed. The structures of these complexes were elucidated by ^1H- and $^{13}C/^{13}C\{^1H\}$-NMR spectroscopy and crystallography.

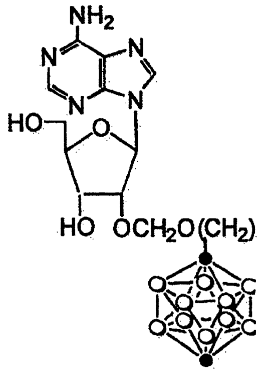


Agnieszka B. Olejniczak, Andrey Semenuk,
Marek Kwiatkowski,
Zbigniew J. Lesnikowski

J. Organomet. Chem. 680 (2003) 124

Synthesis of adenosine containing carborane modification

The carboranyl cage is a new modifying entity for nucleosides and DNA-oligonucleotides. Most of carborane–nucleoside conjugates described so far belong to pyrimidine series. Herein, the first synthesis of adenosine, nucleoside containing purine nucleic base, modified with carborane cluster, is described.

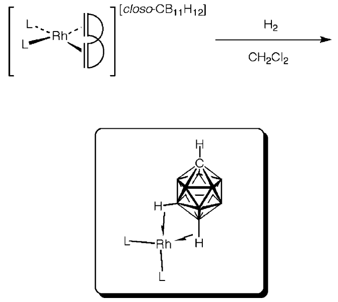


A. Rifat, V.E. Laing, G. Kociok-Köhn, M.F. Mahon, G.D. Ruggiero, A.S. Weller

J. Organomet. Chem. 680 (2003) 127

exo-closo-Rhodacarboranes: synthesis and characterisation of [{*exo*-$(R_3P)_2Rh$}(closo-$CB_{11}H_{12}$)] [$R_3P = P(OMe)_3$, PCy_3, 1/2dppe]

New *exo*-closo-rhodacarboranes have been synthesised by addition of H_2 to precursor diene complexes. The spectroscopic markers that indicate metal-carborane interaction in solution are discussed.



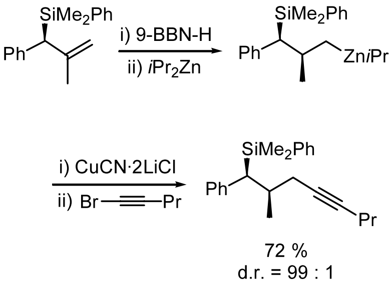
Eike Hupe, M. Isabel Calaza, Paul Knochel

J. Organomet. Chem. 680 (2003) 136

Synthesis and reaction of secondary and primary diorganozinc reagents using a boron–zinc exchange reaction

A useful method for the stereo- and regioselective formation of new carbon–carbon bonds

The boron–zinc exchange reaction allows to considerably enhance the scope of substrate controlled diastereoselective hydroborations. Functionalized chiral secondary alkylzinc reagents can also be prepared by this exchange reaction and used to perform formal enantioselective Michael-additions with umpolung of reactivity. A chemoselective approach to difunctionalized arylsilanes is also described.

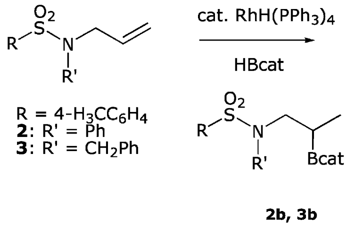


Michael G. Hamilton, Catrin E. Hughes, Alison M. Irving, Christopher M. Vogels, Stephen A. Westcott

J. Organomet. Chem. 680 (2003) 143

Catalyzed hydroboration of allyl sulfonamides

The hydroboration of allyl sulfonamides with catecholborane (HBcat) using different rhodium catalysts has been examined using multinuclear NMR spectroscopy. Reactions give complex product distributions, regardless of the choice of catalyst, arising from a competing isomerization reaction. This isomerization reaction can be used, in conjunction with the hydroboration reaction, to give regioselective formation of one product.

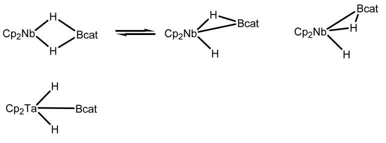


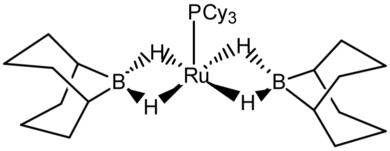
Dan Liu, King-Chung Lam, Zhenyang Lin

J. Organomet. Chem. 680 (2003) 148

Density functional theory studies on structural isomers and bonding of catecholborane adducts of Group 5 metallocene (Nb, Ta) hydride complexes

Complicated structural isomers and bonding of borane adducts of $Cp_2M(H)$ (M = Nb, Ta) as well as substituent effects have been studied using the Becke3LYP density functional theory calculations. The stability of boryl, η^2-HBcat and hydridoborate structures has been discussed.



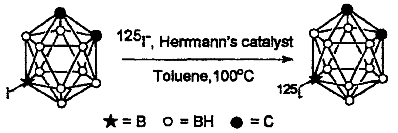

PCy3
H
Ru
H
B
H
H
B

Karl Johan Winberg, Gemma Barberà, Ludvig Eriksson, Francesc Teixidor, Vladimir Tolmachev, Clara Viñas, Stefan Sjöberg

J. Organomet. Chem. 680 (2003) 188

High yield [^{125}I]iodide-labeling of iodinated carboranes by palladium-catalyzed isotopic exchange

A number of iodinated *closo*-carboranes have been radiolabeled with ^{125}iodine in high to excellent yields using the palladacycle Herrmann's catalyst.

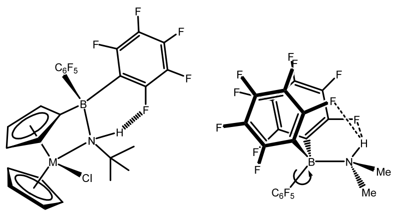


Simon J. Lancaster, Andrew J. Mountford, David L. Hughes, Mark Schormann, Manfred Bochmann

J. Organomet. Chem. 680 (2003) 193

Ansa-metallocenes with B–N and B–P linkages: the importance of N–H···F–C hydrogen bonding in pentafluorophenyl boron compounds

The synthesis of titanium and zirconium complexes with constrained-geometry type Cp–B–E chelate ligands is described (E = N, P). Amido complexes, as well as the adducts of $B(C_6F_5)_3$ with *prim*- and *sec*-amines, are characterised by C–F···H–N hydrogen bonding to one of the *ortho*-F atoms of a C_6F_5 ring, which in some cases is strong enough to persist in solution at room temperature.

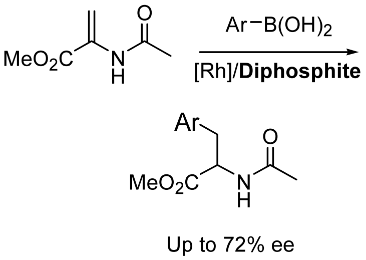


Christopher J. Chapman, Kelly J. Wadsworth, Christopher G. Frost

J. Organomet. Chem. 680 (2003) 206

Enantioselective rhodium-catalysed addition of boronic acids using C_2-symmetric aryl diphosphite ligands

The use of enantiopure C_2-symmetric aryl diphosphite ligands facilitates the efficient preparation of unnatural amino acid esters by a rhodium-catalysed conjugate addition of aryl boronic acids. The products have been obtained in up to 72% ee and with good isolated yield.

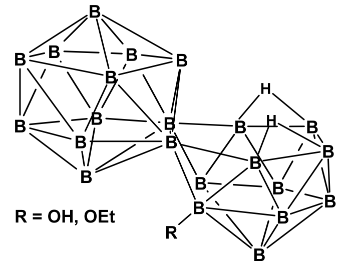


O. Volkov, N.P. Rath, L. Barton

J. Organomet. Chem. 680 (2003) 212

Functionalization of the macropolyhedral borate anion cluster $[B_{22}H_{22}]^{2-}$: isolation and characterization of the OH and OEt derivatives

The first derivatives, $[B_{22}H_{21}OH]^{2-}$ (**1**) and $[B_{22}H_{21}OEt]^{2-}$ (**2**), of the fused macropolyhedral anion $[B_{22}H_{22}]^{2-}$, a cluster involving the conjoining of a *closo*-B_{12} icosahedron with a *nido*-B_{10} cage, are reported. An unusual feature is the lengthening of what was a *nido*-B_{10} gunwale B–B connection adjacent to the junction of the two cages; presumably due to the influence of the substituents.

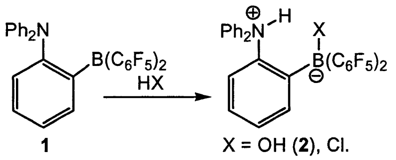


Roland Roesler, Warren E. Piers, Masood Parvez

J. Organomet. Chem. 680 (2003) 218

Synthesis, structural characterization and reactivity of the amino borane 1-(NPh_2)-2-[$B(C_6F_5)_2$]C_6H_4

The bright red, intensely colored aminoborane **1** reacted easily with small acids like H_2O and HCl giving colorless zwitterionic compounds. For **1** and **2** the crystal structures were determined, the latter featuring an ammonium borate structure containing a short intramolecular NH···O hydrogen bond bridge.

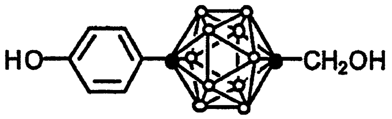


Jayaseharan Johnsamuel, Youngjoo Byun, Thomas P. Jones, Yasuyuki Endo, Werner Tjarks

J. Organomet. Chem. 680 (2003) 223

A new strategy for molecular modeling and receptor-based design of carborane containing compounds

Difficulties associated with computer-aided molecular design (CAMD) of carborane containing molecules have hampered drug development in boron neutron capture therapy (BNCT). A new approach of modeling and docking of carborane containing molecules with the readily available software packages HYPERCHEM, SYBYL and FLEXX is described.

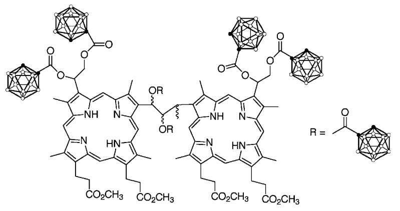


Meden F. Isaac, Stephen B. Kahl

J. Organomet. Chem. 680 (2003) 232

Synthesis of ether- and carbon-linked polycarboranyl porphyrin dimers for cancer therapies

Novel porphyrin dimers bearing up to six *closo* *o*-carborane cages have been prepared. These compounds have potential applications in binary cancer therapies such as boron neutron capture therapy. Porphyrin dimers linked through ether bonds were found to be acid-labile, while those comprised of carbon–carbon links were stable.

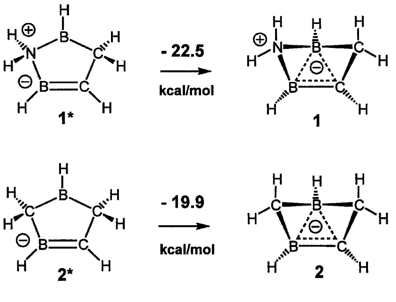


Yüksel Sahin, Andreas Ziegler, Thorsten Happel, Harald Meyer, Michael J. Bayer, Hans Pritzkow, Werner Massa, Matthias Hofmann, Paul von Ragué Schleyer, Walter Siebert, Armin Berndt

J. Organomet. Chem. 680 (2003) 244

Two-electron homoaromatics with heteroatom bridges

The properties of two-electron homoaromatics with heteroatom bridges like **1** are similar to those of the corresponding species with methylene bridges like **2**. A derivative of **1** completes the three-center two-electron boron–carbon series. Computations on prototype models show that the homoaromatic stabilization energies decrease with the number of carbon centers due to the higher electronegativity of carbon than boron.

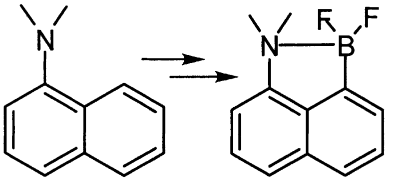


Richard L. Giles, Judith A.K. Howard, Leonard G.F. Patrick, Michael R. Probert, Gillian E. Smith, Andrew Whiting

J. Organomet. Chem. 680 (2003) 257

Synthesis and structure of potential Lewis acid–Lewis base bifunctional catalysts: 1-*N*,*N*-dimethylamino-8-borononaphthalene derivatives

1-*N*,*N*-dimethylaminonaphthalene undergoes directed metallation lithiation in position 8, which after reacting with various borate esters, provided the corresponding boroxine trimer, or boronates esters, with structural support and evidence of B–N chelation from X-ray analysis and ^{11}B-NMR. The boroxine trimer is converted into the difluoroborane with potassium hydrogen fluoride, as evidenced by ^{11}B- and ^{19}F-NMR.

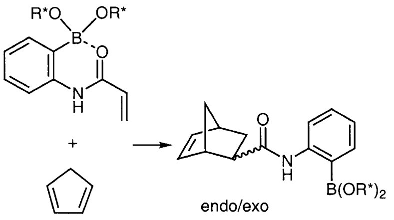


Jason W.J. Kennedy, Dennis G. Hall

J. Organomet. Chem. 680 (2003) 263

Design of chiral boronate-substituted acrylanilides.
Self-activation and boron-transmitted 1,8-stereoinduction in [4+2] cycloaddition

The [4+2] cycloaddition of *ortho*-boronoanilide dienophile **4** with cyclopentadiene was found to proceed faster than both its *para* isomer **8** and the unsubstituted derivative **6**, thereby confirming that self-activation by internal coordination is operative in the case of **4**. Chiral boronic esters derivatives **9**–**13** provided a small level of remote 1,8-stereoinduction transmitted through a putative tetrahedral stereogenic boronate complex. These results show that dialkoxyboronic esters can operate as weak, internal Lewis acids and activate carbonyl-containing functionalities in cycloaddition reactions.

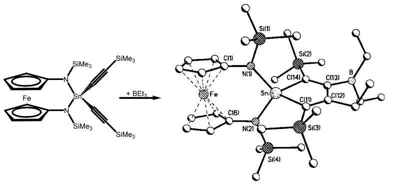


Bernd Wrackmeyer, Heidi E. Maisel, Wolfgang Milius, Max Herberhold

J. Organomet. Chem. 680 (2003) 271

1,3,2-Diazastanna-[3]ferrocenophanes bearing alkyn-1-yl groups at tin and their 1,1-organoboration with triethylborane—molecular structure of a novel spirotin compound

2,2-Di(alkyn-1-yl)-1,3-bis(trimethylsilyl)-1,3,2-diazastanna-[3]ferrocenophanes were prepared, and treatment with triethylborane gave spirotin compounds containing both a 1,3,2-diazastanna-[3]ferrocenophane and a stannacyclopentadiene ring. Extensive multinuclear magnetic resonance studies (in solution and in the solid state) were carried out, and one of the new spirotin compounds was characterised by X-ray structural analysis.

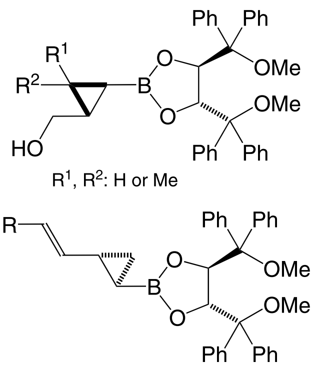


Pilar Garcia Garcia, Erwin Hohn, Jörg Pietruszka

J. Organomet. Chem. 680 (2003) 281

Synthesis of enantiomerically pure vinylcyclopropylboronic esters via cross-metathesis

The potent antibiotic ambruticin caused us to investigate two new aspects of cyclopropylboronic ester chemistry: we established the analytical basics for all 1,2,3-trisubstituted diastereoisomers as well as the cross-metathesis as a tool to synthesise vinylcyclopropylboronic esters.

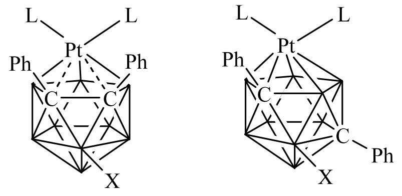


Susan Robertson, David Ellis,
Georgina M. Rosair, Alan J. Welch

J. Organomet. Chem. 680 (2003) 286

Platination of [3-X-7,8-Ph_2-7,8-*nido*-$C_2B_9H_8]^{2-}$ (X = Et, F)
Synthesis and characterisation of slipped and 1,2 → 1,7 isomerised products

Slipped, non-isomerised (X = Et) and 1,7 C atom isomerised (X = Et, F) bis-phosphine platinacarboranes (L = PMe_2Ph) have been prepared and characterised. Their structures are discussed in the context of the mechanism of isomerisation of carboranes.

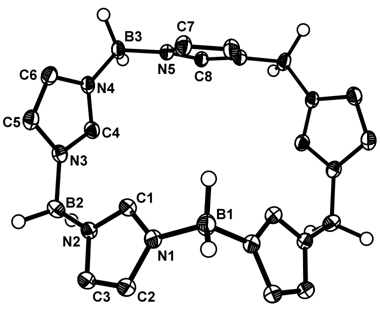


Andre Weiss, Victor Barba, Hans Pritzkow,
Walter Siebert

J. Organomet. Chem. 680 (2003) 294

Synthesis, structures and reactivity of macrocyclic imidazolylboranes

Tetrameric and pentameric imidazolylboranes [imid.$B(R^1)_2]_n$ are obtained from 1-trimethylsilylimidazoles and haloboranes $XB(R^1)_2$, using 2-bromoimidazole and benzimidazole. A new access to oligomeric imidazolylboranes involves the cyclization of bis(imidazolyl)boronium chlorides. The macrocycles are formally zwitterionic and contain imidazolyl rings linked through their nitrogen atoms by BH_2, $B(R^1)_2$, or BR^1X units. X-ray crystal structures of several compounds are reported.

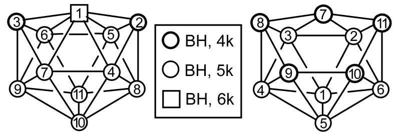


Oleg Volkov, Peter Paetzold

J. Organomet. Chem. 680 (2003) 301

The chemistry of the undecaborates

The octadecahedron of *closo*-$B_{11}H_{11}^{2-}$ represents a unique structure because of its skeletal fluxionality, which includes 11!/2 degenerate tautomers, and because of one vertex with the unusual high skeletal connectivity of 6. The series of *nido*-species $B_{11}H_{15}$, $B_{11}H_{14}^-$, $B_{11}H_{13}^{2-}$, $B_{11}H_{12}^{3-}$, and the hypothetical $B_{11}H_{11}^{4-}$, exhibit a rigid B_{11} skeleton, derived from a B_{12} icosahedron by removing one vertex, thus forming a pentagonal aperture. A survey is given on the formation, structure, and reactivity of the B_{11} clusters.



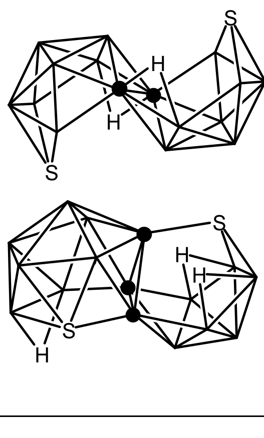
closo-$B_{11}H_{11}{}^{2-}$ *nido*-$B_{11}H_{11}{}^{4-}$

Pervinder K. Dosangh, Jonathan Bould,
Michael G.S. Londesborough,
Tomáš Jelínek, Mark Thornton-Pett,
Bohumil Štíbr, John D. Kennedy

J. Organomet. Chem. 680 (2003) 312

Macropolyhedral boron-containing cluster chemistry. Aspects of the $S_2B_{16}H_{16}$ system. Preparation, structure, NMR spectroscopy and isomerism

Thermolysis of [*arachno*-4-SB_8H_{12}] gives [*n*-$S_2B_{16}H_{16}$] and [*iso*-$S_2B_{16}H_{16}$]. [*n*-$S_2B_{16}H_{16}$] resembles *nido* ten-vertex: *nido* ten-vertex [*anti*-$B_{18}H_{22}$], but with S vertices at the 9 and 9′ positions; [*iso*-$S_2B_{16}H_{16}$] consists of *nido* 11-vertex {SB_{10}} and *nido*-type {B_8} subclusters fused via a common {B_2}edge and a sulphur atom *exo* to the {SB_{10}} unit and *endo* to the {B_8} unit.

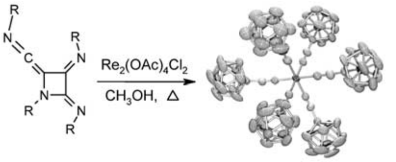


Paul Schaffer, James F. Britten,
Alan Davison, Alun G. Jones,
John F. Valliant

J. Organomet. Chem. 680 (2003) 323

Synthesis of homoleptic Re(I) complexes of isocyano-carboranes and the X-ray structure of hexakis(*p*-carboran-1-yl-isonitrile)Re(I)

Two homoleptic Re(I) complexes of *ortho* and *para*-carborane isocyanide ligands were prepared as a new class of BNCT/BNCS agents. The latter complex was prepared from a carborane-derived azetidine.

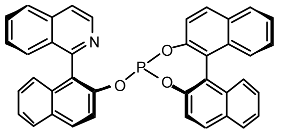


Andrei Korostylev, Ilya Gridnev,
John M. Brown

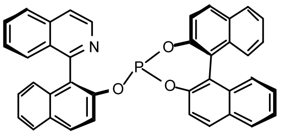
J. Organomet. Chem. 680 (2003) 329

Mechanistic and synthetic aspects of hydroboration with a simple atropisomeric ligand prepared from 1-(1′-(isoquinolyl)-2-naphthol

A novel triarylphosphite ligand has been prepared directly from both enantiomers of BINOL and a single enantiomer of 1′-(isoquinolyl)-2-naphthol. In one of the two cases cationic Rh complex proved to be reasonably effective in the asymmetric hydroboration of electron-poor styrenes.



(*aS*,*R*)-**3**



(*aS*,*S*)-**3**

Application to Rh-catalysed hydroboration

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