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Contents

Special Issue: EUROBORON II: 2nd European Symposium on Boron Chemistry

Reviews

Bohumil Štíbr, Bernd Wrackmeyer

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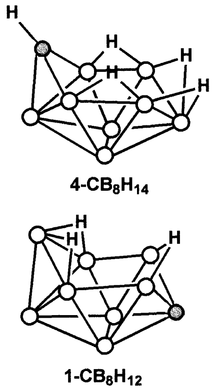
Recent developments in the chemistry of the nine-vertex monocarbaboranes

A short review is presented on the synthesis and reactivity of the nine-vertex monocarbaboranes *arachno*-4-CB_8H_{14} and *nido*-1-CB_8H_{12}. These compounds have become important starting materials for the preparation of a family of 'smaller-cage' seven-, eight-, and nine-vertex *closo* monocarbaborane anions $[2\text{-}CB_6H_7]^-$, $[1\text{-}CB_7H_8]^-$, and $[4\text{-}CB_8H_9]^-$, new candidates for weakly coordinated anion chemistry. Included are also recent syntheses leading to new phosphacarboranes containing one, two, and three phosphorus atoms in the cage.

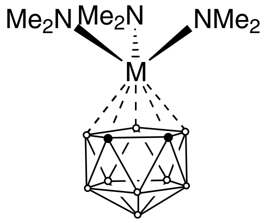


Andrew K. Hughes

J. of Organomet. Chem. 657 (2002) 9

Imide- and amide-supported Group 5 and 6 metallacarboranes

Synthesis, structures and spectroscopy of three isomeric Group 5 metallacarboranes $(C_2B_9H_{11})M(NMe_2)_3$ (M = Nb, Ta) are described, together with the reactions of the 3,1,2 isomer. Base-sensitive *nido*-11-Me-2,7-$C_2B_9H_{12}$ can be metallated by $Ta(NMe_2)_5$ to 4,4,4-$(NMe_2)_3$-3-Me-4,1,2-*closo*-$TaC_2B_9H_{10}$ without rearrangement. Acetonitrile reacts with 3-N^tBu-3,3-$(NH^tBu)_2$-*closo*-3,1,2-$WC_2B_9H_{11}$ to give the *N*,*N*-dimethyl acetamidine adduct of $W(N^tBu)_2(C_2B_9H_{11})$, containing a hydrogen bond to a bent imide.

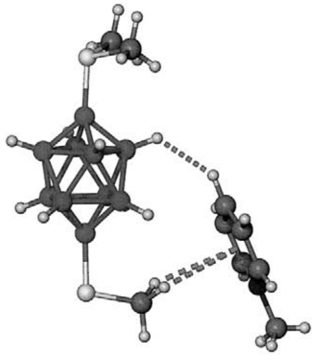


Caroline O'Dowd, John D. Kennedy, Mark Thornton-Pett

J. of Organomet. Chem. 657 (2002) 20

The use of Kitaigorodskii's *Aufbau* principle in the solid-state study of crystalline borane compounds. A preliminary account

Kitaigorodskii's *Aufbau* principle (KAP) is exemplified by consideration of the molecular arrangements in the 'wrap-around' encapsulation of 4,4′-bipyridyl with [6,9-(4,4′-bipyridyl)$_2$-*arachno*-$B_{10}H_{12}$] in their 1:1 co-crystal, the complex three-dimensional dihydrogen-bonding network in the crystal structure of H_3BNH_3, solvent channels in the structure of the co-crystal of *n*-hexane with $[C_5H_5NMe][1\text{-}(SMe)\text{-}10\text{-}(SMe_2)$-*closo*-$B_{10}H_8]$, and systematic variations within the crystal structures of [6,9-$(NC_5H_4\text{-}4\text{-}R)_2$-*arachno*-$B_{10}H_{12}$], where R is Me, Et and *n*-Pr.



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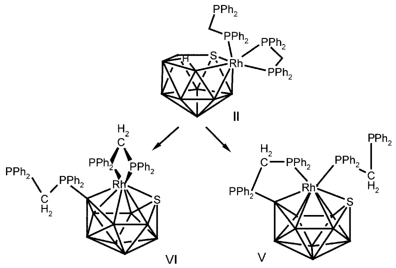
Regular papers

**Oleg Volkov, Ramon Macias,
Nigam P. Rath, Lawrence Barton**

J. of Organomet. Chem. 657 (2002) 40

Chemistry on a metallathiaborane cluster Part 4: reactions of 11-vertex rhodathiaboranes with bidentate phosphines and their subsequent rearrangements

Thermal rearrangement of the species [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**II**) affords a red compound whose identity appears to be a mixture of the two isomers shown herein. The study does not unambiguously identify **V** or **VI** but analogues of **VI** are well known and a species related to **V** in which there is a PPh_3 moiety instead of dppm is structurally identified in the study.



Yasuyuki Endo, Chalermkiat Songkram, Ryu Yamasaki, Aya Tanatani, Hiroyuki Kagechika, Kojiro Takaishi, Kentaro Yamaguchi

J. of Organomet. Chem. 657 (2002) 48

Molecular construction based on icosahedral carboranes and aromatic *N*,*N*′-dimethylurea groups. Aromatic layered molecules and a transition metal complex

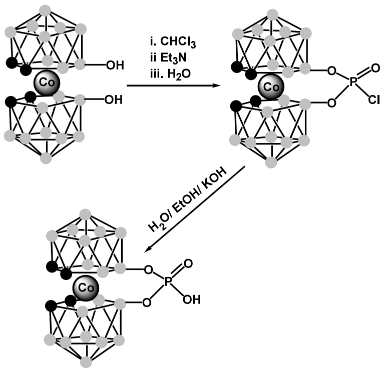
cis-Preference of *N*-methyl aromatic ureas in combination with regulation of the *C*-substituent on an *o*-carborane cage is applicable to construct structurally unique macromolecules. Aromatic ureas with multilayer structure and an aromatic urea containing an intramolecular *nido*-carborane–cobalt complex were synthesized and their structures were determined by X-ray crystallography.

**Jaromír Plešek, Bohumír Grüner,
Ivana Císařová, Jiří Báča, Pavel Selucký,
Jiří Rais**

J. of Organomet. Chem. 657 (2002) 59

Functionalized cobalt bis(dicarbollide) ions as selective extraction reagents for removal of M^{2+} and M^{3+} cations from nuclear waste, crystal and molecular structures of the [8,8′-μ-ClP(O)(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co]HN(C_2H_5)$_3$ and [8,8′-μ-Et_2NP(O)-(O)$_2$<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co](HN(CH_3)$_3$)

New reliable synthetic methods leading to derivatives of the *closo*-[(1,2-$C_2B_9H_{11}$)$_2$-3,3′-Co]$^-$ (**1**) anion **1** with phosphorus containing substituents on the cage boron atoms have been successfully developed, starting from its 8-OH (**2**) and 8,8′-(OH)$_2$ (**3**) hydroxyderivatives. Extraction properties of the anionic ligating species for M^{3+} have been tested, best results being obtained for the bridged series.

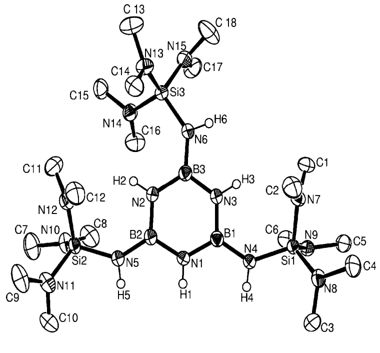


**F. Cheng, B. Toury, S.J. Archibald,
John S. Bradley**

J. of Organomet. Chem. 657 (2002) 71

Synthesis and structure of 2,4,6-tris[tris(dimethylamino)silylamino]borazine: {[(CH_3)$_2$N]$_3$SiNH}$_3B_3N_3H_3$

Lithium tris(dimethylamino)silylamide [(CH_3)$_2$N]$_3$SiNHLi reacts with 2,4,6-trichloroborazine $Cl_3B_3N_3H_3$ leading to the formation of a new compound: 2,4,6-tris[tris(dimethylamino)silylamino]borazine {[(CH_3)$_2$N]$_3$SiNH}$_3B_3N_3H_3$. The molecular structure has been determined on the basis of its FTIR, NMR and X-ray crystallographic analysis.

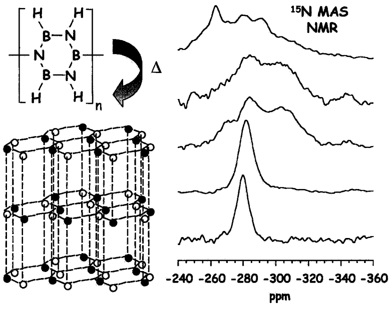


Christel Gervais, Florence Babonneau

J. of Organomet. Chem. 657 (2002) 75

High resolution solid state NMR investigation of various boron nitride preceramic polymers

Hexagonal boron nitride (h-BN) ceramics can be prepared from polymeric precursors by heat treatment under inert atmosphere. The purpose of this paper is to illustrate the strategy that can be followed to characterize by ^{15}N and ^{11}B solid state NMR the polymers as well as their pyrolysis derivatives. A suitable choice of NMR techniques, combined with isotopic enrichment, can lead to a good qualitative as well as quantitative description of the local environment of B and N sites in such complex samples.

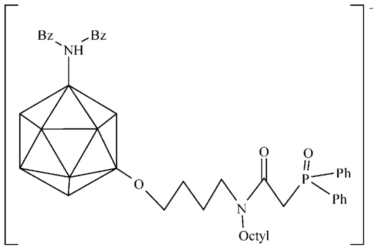


R. Bernard, D. Cornu, B. Grüner, J.-F. Dozol, P. Miele, B. Bonnetot

J. of Organomet. Chem. 657 (2002) 83

Synthesis of $[B_{12}H_{12}]^{2-}$ based extractants and their application for the treatment of nuclear wastes

Several *closo*-hydroborates bearing phosphite oxide, phosphine oxide or CMPO groups were synthesised. The abilities of $Na[Bz_2N(H)B_{12}H_{10}(OCH_2CH_2)_2P(O)(O\text{-}Bu)_2]$ (**5**) and $Na[Bz_2N(H)B_{12}H_{10}O(CH_2)_4\text{-}N(octyl)C(O)CH_2P(O)(Ph)_2]$ (**10**) to extract selectively the radionuclides ^{241}Am and ^{152}Eu from nuclear waste solutions were investigated using a liquid–liquid extraction technique. Promising results were obtained with compound **10**, which exhibits enhanced hydrophobicity and solubility in organic extraction solvent.

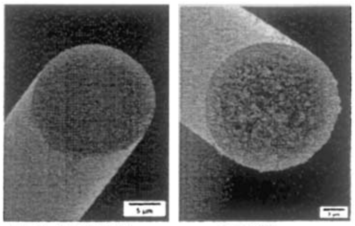


S. Bernard, D. Cornu, P. Miele, H. Vincent, J. Bouix

J. of Organomet. Chem. 657 (2002) 91

Pyrolysis of poly[2,4,6-tri(methylamino)borazine] and its conversion into BN fibers

The pyrolysis process of poly[2,4,6-tri(methylamino)borazine]-based fibers has been studied in detail. The condensation of polymer leads to infusible fibers with a three-dimensional polymeric network from 70 to 400 °C. A polymer–mineral transition occurs since 400 to give amorphous hydrogenated fibers at 1000 °C. The chemical conversion process is complete at 1400 °C and the BN fibers crystallize up to 1800 °C.



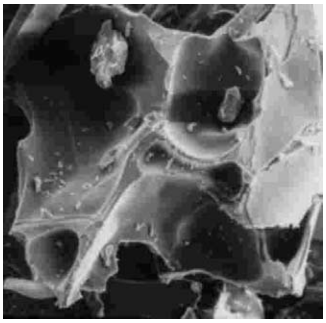
PolyMAB fiber BN fiber

José Antiono Perdigon-Melon, Aline Auroux, David Cornu, Philippe Miele, Bérangère Toury, Bernard Bonnetot

J. of Organomet. Chem. 657 (2002) 98

Porous boron nitride supports obtained from molecular precursors.
Influence of the precursor formulation and of the thermal treatment on the properties of the BN ceramic

Boron nitride (BN) porous samples have been prepared in order to be used as noble metal catalyst support from various molecular precursors. Three types of precursors have been tested: ammonia borane, polyborazylene and several aminoborazines and derived polymers. Specific surfaces of 30 m^2 g^{-1} were currently obtained from aminoborazines. Foams exhibiting a surface of more than 50 m^2 g^{-1} have been obtained when polyborazylene based precursor was pyrolysed.



Christophe Duriez, Eric Framery, Bérangère Toury, Pascaline Toutois, Philippe Miele, Michel Vaultier, Bernard Bonnetot

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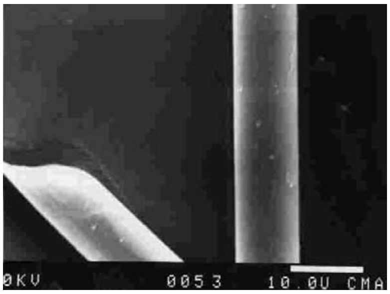
Boron nitride thin fibres obtained from a new copolymer borazine–tri(methylamino)borazine precursor

Boron nitride thin fibres have been obtained using the melt drawn technique from a new molecular precursor prepared by reacting borazine $(HBNH)_3$ with trimethylamino-borazine $(CH_3NHBNH)_3$, (MAB). The best copolymer prepared was with a borazine/MAB molar ratio of 90/10. A mother fibre was extruded at 85° with a diameter of about 200 μm but its stretching was difficult. Samples of BN fibres have been obtained but with a too short length to be tested.

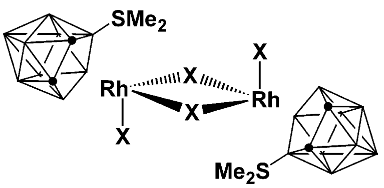


Alexander R. Kudinov, Dmitry S. Perekalin, Pavel V. Petrovskii, Konstantin A. Lyssenko, Gennadii V. Grintselev-Knyazev, Zoya A. Starikova

J. of Organomet. Chem. 657 (2002) 115

Synthesis and structure of rhodium complexes with monoanionic carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$

Rhodacarborane halide complexes **4a**–**c**, which are analogous to $[Cp^*RhX_2]_2$, were synthesized by reaction of $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(cod)$ (cod = 1,5-cyclooctadiene) with HX. 2e-Ligands destroy the dimeric structure of **4** to give the adducts $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhLX_2$. Complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(dppe)Cl]^+$ (**7**), $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}C_5R_5)]^+$ (**11a**: R = H, **11b**: R = Me) and $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}7,8\text{-}C_2B_9H_{10})$ were also prepared. Structures of **7**BF_4 and **11b**PF_6 were confirmed by X-ray diffraction study.



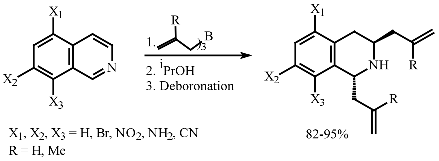
4a: X = Cl; **4b**: X = Br; **4c**: X = I

Fedor V. Pastukhov, Ilia V. Yampolsky, Yuri N. Bubnov

J. of Organomet. Chem. 657 (2002) 123

Allylboration of functionalized isoquinolines

Functionalized isoquinolines react with triallylborane to produce 1,3-diallylated 1,2,3,4-tetrahydroisoquinolines **1**–**8** with excellent chemo- and stereoselectivity.

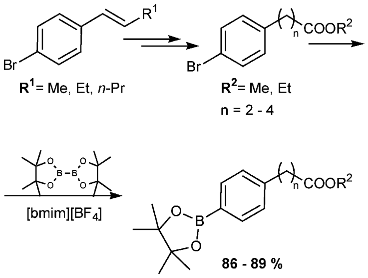


Marek Zaidlewicz, Andrzej Wolan

J. of Organomet. Chem. 657 (2002) 129

Syntheses with organoboranes. XIII. Synthesis of ω-(4-bromophenyl)alkanoic acids and their borylation

ω-(4-Bromophenyl)alkanoic acids were obtained from 1-bromo-4-alkenylbenzenes by hydroboration–thermal isomerization–oxidation. Their esters were transformed in good yields into the corresponding boronates by the cross-coupling reaction with bis(pinacolato)diboron in an ionic liquid, $[bmim][BF_4]$.



Sabine Thormeier, Bertrand Carboni, Dieter E. Kaufmann

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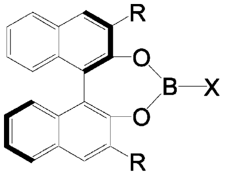
Chiral boronates—versatile reagents in asymmetric synthesis

New, axially chiral borates and boronates are representatives of three different structural types. They have proved to be efficient catalysts or reagents in asymmetric synthesis: Diels–Alder reactions, reductions, allylborations and homologization reactions. Activated vinylboronates can serve as cyclophiles in [3+2] cycloaddition reactions with methylenecyclopropanes giving borylated methylenecyclopentanes.



R = H, Br, $Si(CH_3)_3$
X = H, C_2H_3, C_3H_5, C_6H_5, OC_6H_5

Bernd Wrackmeyer, Moazzam H. Bhatti, Saqib Ali, Oleg L. Tok, Yuri N. Bubnov

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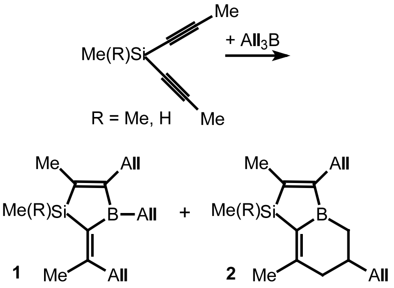
Reactivity of some poly-1-alkynylsilicon and -tin compounds towards triallylborane—routes to novel heterocycles

Triallylborane reacts with many di-1-alkynylsilanes to give the novel 2-alkylidene-1,3-silaborolenes as the result of an intermolecular 1,1-allylboration followed by an intramolecular 1,2-allylboration. Upon heating, a second intramolecular 1,2-allylboration takes place to give 1,7-borasilabicyclo[4.3.0]nona-5,8-diene derivatives. Corresponding tin derivatives are also accessible. All products were characterised by extensive multinuclear magnetic resonance spectra (^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si-, and ^{119}Sn-NMR).



E.S. Shubina, E.V. Bakhmutova, A.M. Filin, I.B. Sivaev, L.N. Teplitskaya, A.L. Chistyakov, I.V. Stankevich, V.I. Bakhmutov, V.I. Bregadze, L.M. Epstein

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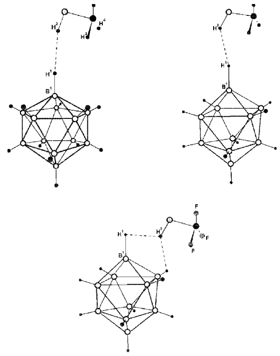
Dihydrogen bonding of decahydro-*closo*-decaborate(2−) and dodecahydro-*closo*-dodecaborate(2−) anions with proton donors: experimental and theoretical investigation

H-bonding in complexes of $[Bu_4N]_2[B_{10}H_{10}]$ and $[Bu_4N]_2[B_{12}H_{12}]$ with various proton donors in low polarity media was investigated. Spectral (IR, NMR) evidence for the BH···HO hydrogen bonding between the boron hydrides and the OH proton donors in solution is presented. Geometry, energy, and electron distribution in the complexes were analyzed using ab initio HF/6-31G approximation. An increase of the proton donor ability of the acids leads to formation of a bifurcate H-bond.

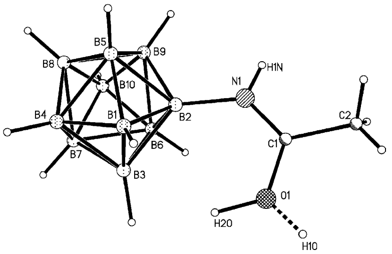


Igor B. Sivaev, Natal'ya A. Votinova, Vikentii I. Bragin, Zoya A. Starikova, Lyudmila V. Goeva, Vladimir I. Bregadze, Stefan Sjöberg

J. Organomet. Chem. 657 (2002) 163

Synthesis and derivatization of the 2-amino-*closo*-decaborate anion $[2\text{-}B_{10}H_9NH_3]^-$

A new method of synthesis of the $[2\text{-}B_{10}H_9NH_3]^-$ anion was elaborated. The method includes reaction of the $[B_{10}H_{10}]^{2-}$ anion with acetonitrile in the presence of acid followed by hydrolysis of the nitrilium derivative $[2\text{-}B_{10}H_9NCMe]^-$ to the acetamide derivative $[2\text{-}B_{10}H_9NH_2COMe]^-$ and then to the amine. The crystal molecular structure of $(Bu_4N)[2\text{-}B_{10}H_9NH{=}C(OH)Me]$ was determined. The reaction of $[2\text{-}B_{10}H_9NH_3]^-$ with aromatic aldehydes gives *N*-protonated Schiff bases $[2\text{-}B_{10}H_9NH{=}CHR]^-$. Reduction of the Schiff bases with $NaBH_4$ gives the monoalkylamino derivatives $[2\text{-}B_{10}H_9NH_2CH_2R]^-$.

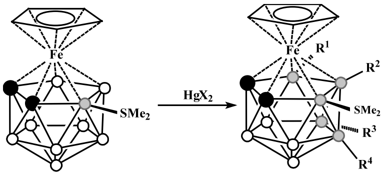


Vladimir I. Bregadze, Irina A. Lobanova, Sergey V. Timofeev, Alexander R. Kudinov, Vladimir I. Meshcheryakov, Oleg L. Tok, Pavel V. Petrovskii, Zoya A. Starikova

J. of Organomet. Chem. 657 (2002) 171

Polysubstituted derivatives of 3-(η^5-Cp)-4-SMe$_2$-3,1,2-FeC$_2$B$_9$H$_{10}$. X-ray structure of 3-(η^5-Cp)-4-SMe$_2$-7,8-(CF$_3$COO)$_2$-12-HgCl-3,1,2-FeC$_2$B$_9$H$_7$

The electrophilic mercuration of 3-(η^5-Cp)-4-SMe$_2$-3,1,2-FeC$_2$B$_9$H$_{10}$ (**1**) was investigated. The reaction of **1** with the excess of mercury trifluoroacetate in dichloromethane at 20 °C gives complexes containing from two to four substituents depending on the ratio of reagents. All new compounds were separated and characterized by elemental analysis and NMR spectra. The positions of substitution were established by ^{11}B-NMR and ^{11}B-^{11}B COSY NMR spectra. X-ray structure of 3-(η^5-Cp)-4-SMe$_2$-7,8-(CF$_3$COO)$_2$-12-HgCl-3,1,2-FeC$_2$B$_9$H$_7$ was determined.



Andreas Franken, Colin A. Kilner, Mark Thornton-Pett, John D. Kennedy

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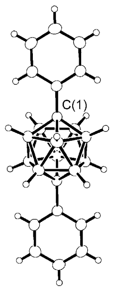
Polyhedral monocarbaborane chemistry
The C,B-*para*-diphenyl monocarbadodecaborane anion [1,12-Ph$_2$-*closo*-1-CB$_{11}$H$_{10}$]$^-$

Iodination of Cs$^+$[1-Ph-*closo*-1-CB$_{11}$H$_{11}$]$^-$ with I$_2$ in CH$_3$COOH solution gives Cs$^+$[1-Ph-*closo*-1-CB$_{11}$H$_{10}$-12-I]$^-$, which with PhMgBr and [PdCl$_2$(PPh$_3$)$_2$] in thf solution gives the [1,12-Ph$_2$-*closo*-1-CB$_{11}$H$_{10}$]$^-$ anion.



Andreas Franken, Colin A. Kilner, Mark Thornton-Pett, John D. Kennedy

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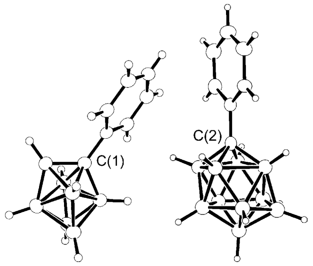
Polyhedral monocarbaborane chemistry
The *closo*-[PhCB$_7$H$_7$]$^-$ and *closo*-[PhCB$_{10}$H$_{10}$]$^-$ anions: the two missing species in the *closo*-[PhCB$_n$H$_n$]$^-$ sequence

In a cluster-dismantling sequence, reaction of the ten-vertex *nido*-[PhCB$_9$H$_{11}$]$^-$ anion with FeCl$_3$ gives the nine-vertex *arachno*-[PhCB$_8$H$_{13}$]$^-$ anion, which on treatment with NEt$_3$ gives the eight-vertex *closo*-[PhCB$_7$H$_7$]$^-$ anion. Conversely, in a cluster-*Aufbau* reaction, the *nido*-[PhCB$_9$H$_{11}$]$^-$ anion with [BH$_3$(THF)] gives the eleven-vertex *nido*-[PhCB$_{10}$H$_{12}$]$^-$ anion which, on treatment with I$_2$ gives the eleven-vertex *closo*-[PhCB$_{10}$H$_{10}$]$^-$ anion.



Sari Paavola, Francesc Teixidor, Clara Viñas, Raikko Kivekäs

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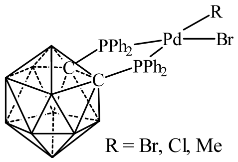
Pd(II) bromide complexes of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane. Crystal structures of [PdBr$_2$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)]·CH$_2$Cl$_2$, [PdBr$_{1.133}$Cl$_{0.867}$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)]·CH$_2$Cl$_2$ and [PdBrCl$_{0.541}$Me$_{0.459}$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)]·CHCl$_3$

The revised synthesis of [PdBr$_2$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)] is described. The pure complex was obtained by several days reaction of [PdCl$_2$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)] with an excess of KBr. Shorter reaction time of 2 h produced partially brominated product [PdBr$_{1.133}$Cl$_{0.867}$(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)]. These three strucutures are isostructural. The reaction of Mg and an excess of MeBr with [PdClMe(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)] yielded a mixture of novel complexes [PdBrCl(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)] and [PdBrMe(1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)].



Hiram I. Beltrán, Luis S. Zamudio-Rivera, Teresa Mancilla, Rosa Santillan, Norberto Farfán

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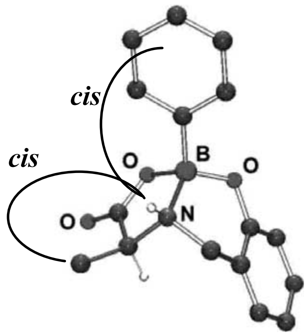
X-ray analysis and structural characterization of 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononenenones

Nine new monomeric boronates of the type 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones were prepared from *N*-(2-hydroxybenzyl)-α-aminoacids **1a**–**1i** and phenylboronic acid **2**. The spectroscopic evidence and the X-ray structures established that the configurations at the nitrogen and boron atoms are '*R*' and '*S*', respectively and the transannular fusion is *cis*. SAM1 calculations supported the experimental results whereby geometrical measurements give useful tendencies to predict the preferred product.

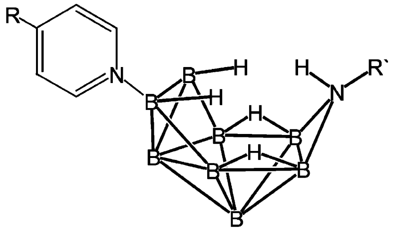


Claudia Bauer, Detlef Gabel, Tobias Borrmann, John D. Kennedy, Colin A. Kilner, Mark Thornton-Pett, Udo Dörfler

J. of Organomet. Chem. 657 (2002) 205

Azanonaborane-pyridine derivatives $[(R'C_5H_4N)B_8H_{11}NHR'']$: synthesis, structure and some molecular-orbital calculations

The azanonaborane-pyridine derivatives $[(R'C_5H_4N)B_8H_{11}NHR'']$ are synthesized by ligand-exchange reactions of azanonaboranes $[(RH_2N)B_8H_{11}NHR'']$ with pyridine and substituted pyridines. The products of these reactions show different colours that depend on the substituent R′ on the pyridine ring.

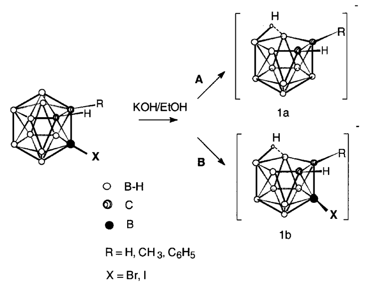


G. Barberà, C. Viñas, F. Teixidor, A.J. Welch, G.M. Rosair

J. of Organomet. Chem. 657 (2002) 217

Retention of the B(3)–X (X = Br, I) bond in *closo*-*o*-carborane derivatives after nucleophilic attack. The first synthesis of $[3\text{-X-7-R-7,8-}nido\text{-}C_2B_9H_{10}]^-$ (X = Br, I). Crystal structure of $[HNMe_3][3\text{-I-7,8-}nido\text{-}C_2B_9H_{11}]$

The synthesis of new 3-halogeno *nido* derivatives of *o*-carborane, $[3\text{-X-7-R-7,8-}C_2B_9H_{10}]^-$ (X = Br, I; R = H, CH_3, C_6H_5) is described. The halogen atom remains attached to the boron atom in the partially degraded products. The influence of the halogen moiety on both the B(3) resonance and that of the bridge proton are discussed.

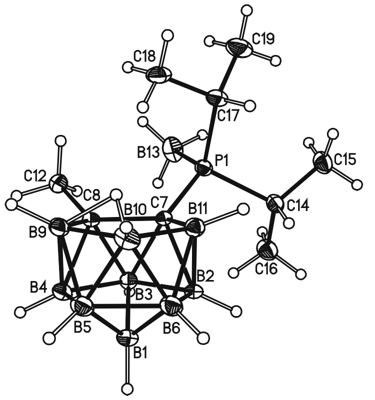


Rosario Núñez, Clara Viñas, Francesc Teixidor, Reijo Sillanpää, Raikko Kivekäs

J. of Organomet. Chem. 657 (2002) 224

Phosphine–boranes incorporating the carborane cluster

Nido-carboranylmonophosphines react with the $BH_3\cdot THF$ Lewis acid leading to the corresponding phosphine–borane adducts, which incorporate a *nido*-cluster. In contrast, practically non-reactivity has been shown by the *closo*-carboranylmonophosphines. This behavior, together with the NMR indicators based on ccs, ^1J(B, H) and ^1J(P, B), indicates that the *nido*-carboranylmonophosphines are much better coordinating ligands than the corresponding *closo*-ones. The X-ray structure of tetrabuthylammonium diisopropyl[7-(8-methyl - 7,8 - dicarba - *nido* - undecaborate)]-phosphine–borane has been determined.

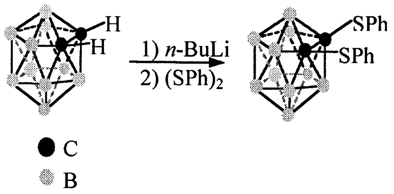


Jordi Llop, Clara Viñas, Josep M. Oliva, Francesc Teixidor, Miquel Angel Flores, Raikko Kivekas, Reijo Sillanpää

J. of Organomet. Chem. 657 (2002) 232

Modulation of the C–C distance in disubstituted 1,2-R_2-*o*-carboranes. Crystal structure of *closo* 1,2-$(SPh)_2$-1,2-$C_2B_{10}H_{10}$

The $C_c\cdots C_c$ distance in 1,2-C_c-substituted *o*-carboranes can be modeled as function of the carbon atom substituents. The more plausible explanation is the transfer of electron density from the available lone pairs on the carbon substituents to the Ψ^* orbitals, producing a decrease in the $C_c\cdots C_c$ bond order and, an increase in the $C_c\cdots C_c$ distance.

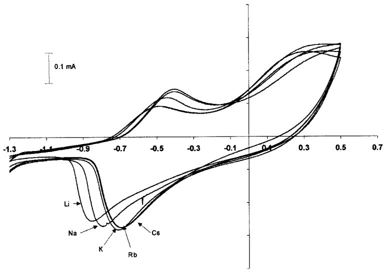


C. Masalles, F. Teixidor, S. Borrós, C. Viñas

J. of Organomet. Chem. 657 (2002) 239

Cobaltabisdicarbollide anion $[Co(C_2B_9H_{11})_2]^-$ as doping agent on intelligent membranes for ion capture

It has been proven that the weakly coordinating anion $[Co(C_2B_9H_{11})_2]^-$ can be highly relevant as doping agent for conducting organic polymers. This anion provides enhanced properties to polypyrrol (PPy). The most striking one is the high over oxidation resistance. The PPy$[Co(C_2B_9H_{11})_2]$ membranes act as cation capture and release devices, the selectivity being controlled by their outer sphere coordination.

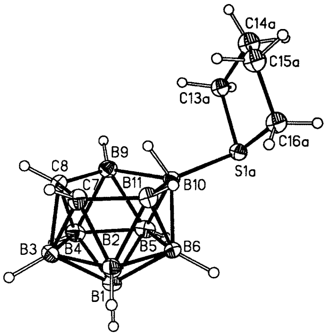


Oscar Tutusaus, Francesc Teixidor, Rosario Núñez, Clara Viñas, Reijo Sillanpää, Raikko Kivekäs

J. of Organomet. Chem. 657 (2002) 247

Recent studies on RR′S·$C_2B_9H_{11}$ charge-compensated ligands
Crystal structures of 10-$(S(CH_3)_2)$-7,8-$C_2B_9H_{11}$ and 10-$(S(CH_2)_4)$-7,8-$C_2B_9H_{11}$

Three new carborane derivatives of the series 10-SRR′-7-R^1-8-R^2-7,8-$C_2B_9H_9$ have been synthesized and the X-ray structures of 10-$(S(CH_3)_2)$-7,8-$C_2B_9H_{11}$ and 10-$(S(CH_2)_4)$-7,8-$C_2B_9H_{11}$ determined. Thermolysis of the 10-SRR′-isomer leads to a mixture of the respective 9-SRR′-isomer and the *closo*-2,3-$C_2B_9H_{11}$. By tuning up the reaction conditions, the 9-SRR′-isomers free of *closo*-2,3-$C_2B_9H_{11}$ can be obtained. These isomers have the same charge as the Cp or Cp* and can find a good application in catalysis.



Jonathan Bould, Michael G.S. Londesborough, Daniel L. Ormsby, J.A. Hugh MacBride, Kenneth Wade, Colin A. Kilner, William Clegg, Simon J. Teat, Mark Thornton-Pett, Robert Greatrex, John D. Kennedy

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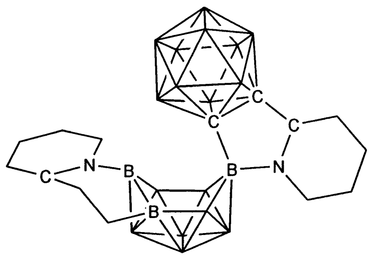
Macropolyhedral boron-containing cluster chemistry
Models for intermediates en route to globular and discoidal megaloborane assemblies. Structures of $[$*nido*-$B_{10}H_{12}($*nido*-$B_5H_8)_2]$ and $[(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}(NC_5H_4$-*closo*-$C_2B_{10}H_{10})]$ as determined by synchrotron X-ray diffraction analysis

$[($*nido*-$B_{10}H_{12})($*nido*-$B_5H_8)_2]$, from the oligomerisation of B_5H_9, and $[\mu$-$(CH_2CH_2C_5H_4N)$-*arachno*-$B_{10}H_{10}$-μ-$(NC_5H_4$-*closo*-$C_2B_{10}H_{10})]$, from the reaction of $[B_{10}H_{12}(NCMe)_2]$ with *ortho*-ethynyl-pyridine, demonstrate possible initial steps for the *Aufbau* construction of globular and discoidal megaloborane assemblies via the accumulation of boron hydride units around a central core.

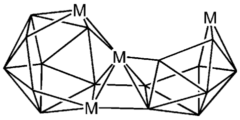


Michael G.S. Londesborough, Colin A. Kilner, Mark Thornton-Pett, John D. Kennedy

J. of Organomet. Chem. 657 (2002) 262

Macropolyhedral boron-containing cluster chemistry
A novel triple-cluster structural motif. Isolation and characterisation of contiguous twenty-vertex $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)_2]$

Twenty-vertex $[(PPh_3)_4ClPd_4B_{16}H_{17}(PPh_3)]$, from the thermolysis of $[(PPh_3)_2PdB_8H_{12}]$ in refluxing toluene solution, has a core *nido* five-vertex $\{Pd_2B_3\}$ unit that has opposing triangular faces in common with an *arachno* ten-vertex $\{Pd_2B_8\}$ unit and a *nido* eleven-vertex $\{Pd_3B_8\}$ unit.

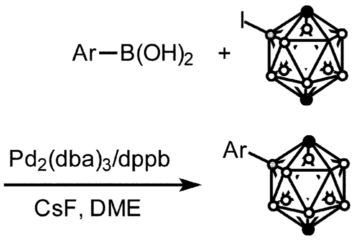


Ludvig Eriksson, Irina P. Beletskaya, Vladimir I. Bregadze, Igor B. Sivaev, Stefan Sjöberg

J. of Organomet. Chem. 657 (2002) 267

Palladium-catalyzed cross-coupling reactions of arylboronic acids and 2-I-*p*-carborane

p-Carborane has been arylated on the 2-*B*-atom in high yields, using the Suzuki–Miyaura reaction. Thus, the reaction between 2-I-*p*-carborane and various arylboronic acids gave the corresponding 2-aryl-*p*-carboranes in DME solution when reacted in the presence of cesium fluoride and the catalytic $Pd_2(dba)_3$–dppb system.



Matthias Hofmann, Sascha Karl Goll

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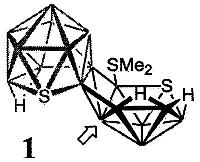
Macropolyhedral thiaboranes with unusual *arachno* subclusters—a computational investigation

Conjuncto boranes may prefer subcluster structures different from those realized for isolated clusters. The unexpected macropolyhedra of experimentally identified $[S_2B_{17}H_{17}\cdot SMe_2]$, **1**, and $[S_2B_{18}H_{19}]^-$, **2**, with unusual six coordinate vertices (marked by arrows) in the arachno subclusters are computed to be more stable than alternatives incorporating the expected arachno subclusters, although the latter are more stable when no nido subcluster is attached.



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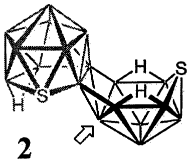

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