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Special Issue: III EUROBORON Conference

Preface 2693

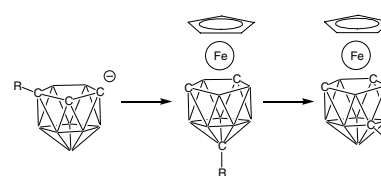
Reviews

Bohumil Štíbr

J. Organomet. Chem. 690 (2005) 2694

Chemistry related to cluster-borane analogues of the cyclopentadienide anion and ferrocene: New developments

A review on cluster-borane analogues of the cyclopentadienide anion (Cp) and ferrocene is presented. Triheteroboranes of general structure [*nido*-E₃B₈H₈][−] (where E = CH or P and their combinations) were used as effective ligands for the preparation of “half- and full-sandwich” complexes [CpFeE₃B₈H₈] and [Fe(E₃B₈H₈)₂], respectively – analogues of ferrocene.

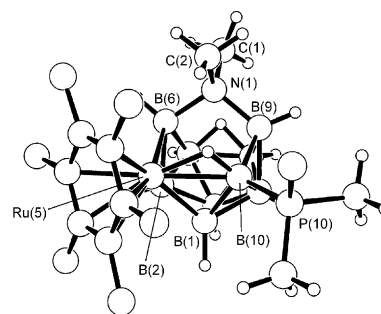


**Jonathan Bould, Mark Bown,
Richard J. Coldicott, Evert J. Ditzel,
Norman N. Greenwood, Ian Macpherson,
Peter MacKinnon, Mark Thornton-Pett,
John D. Kennedy**

J. Organomet. Chem. 690 (2005) 2701

Metallaborane reaction chemistry. Part 12. Some interactions of acetylenes and isocyanides with selected metallaboranes

An overview of reactions of acetylenes and isocyanides with metallaboranes of general type {MB₉H₁₃} and {MB₈H₁₂} is presented. Reductions, oligomerisations, reductive oligomerisations, and complete or partial cluster-incorporation of the unsaturated species have been observed.



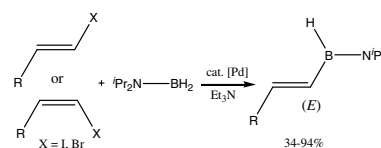
Regular papers

**Lisenn Euzénat, David Horhant,
Cédric Brielles, Gilles Alcaraz,
Michel Vaultier**

J. Organomet. Chem. 690 (2005) 2721

Stereospecific palladium-catalyzed borylation reaction of 1-alkenyl halides with diisopropylaminoborane

B_{sp²}-H containing (*E*)-1-alkenyl boron derivatives as stable and isolable species are accessible stereospecifically in medium to high yields from 1-alkenyl halides via a palladium-catalyzed borylation reaction involving diisopropylaminoborane as an efficient BH transferring agent.

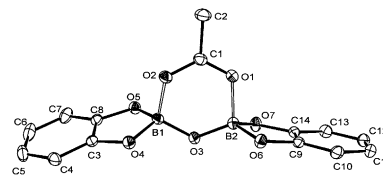


**Natalie D. Coombs, Simon Aldridge,
Gavin Wiltshire,
Deborah L. Kays (née Coombs),
Christopher Bresner, Li-ling Ooi**

J. Organomet. Chem. 690 (2005) 2725

Complementary anion binding by bidentate boron-containing Lewis acids

Anion binding by the pyroborates (catB)₂O (**1**, cat = O₂C₆H₄-1,2) and (*S,S*-Ph₂C₂H₂O₂-B)₂O (**2**) has been investigated by spectroscopic, structural and titration methods; **1** has been shown to act as a bifunctional Lewis acid in the complementary (1:1) binding of acetate both in the solid state and in solution (for which a binding constant of 1500 ± 550 M⁻¹ has been determined).

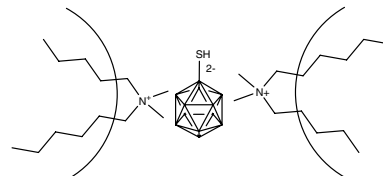


**Doaa Awad, Irene Tabod, Silke Lutz,
Holger Wessolowski, Detlef Gabel**

J. Organomet. Chem. 690 (2005) 2732

Interaction of Na₂B₁₂H₁₁SH with liposomes: Influence on zeta potential and particle size

Positively charged liposomes interact with Na₂B₁₂H₁₁SH, leading to changes in the electrophoretic mobility and the size of the liposomes.

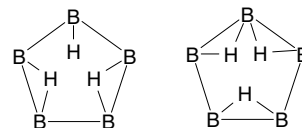


**Oleg Volkov, Krzysztof Radacki,
Rhodri Ll. Thomas, Nigam P. Rath,
Lawrence Barton**

J. Organomet. Chem. 690 (2005) 2736

A new look at the *nido*-undecaborate system

Structural and calculational studies on the *nido*-undecaborate anion, [B₁₁H₁₄]⁻, and some derivatives, suggest that the disposition of bridging- and *endo*-hydrogen atoms in the open face may be represented by the two structures shown herein. They differ by only 0.36 kJ/mol effectively rendering them indistinguishable.

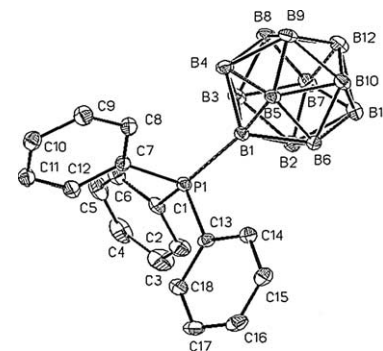


**R. Bernard, D. Cornu, D. Luneau,
D. Naoufal, J.-P. Scharff, P. Miele**

J. Organomet. Chem. 690 (2005) 2745

Synthesis and X-ray structural characterization of the triphenylphosphine derivative of the *closo*-dodecaborate anion, *closo*-[1-B₁₂H₁₁P(C₆H₅)₃][N(*n*-C₄H₉)₄]

Reaction of *closo*-[B₁₂H₁₁I][N(*n*-C₄H₉)₄]₂ with tetrakis(triphenylphosphine)palladium (0) yields *closo*-[1-B₁₂H₁₁P(C₆H₅)₃][N(*n*-C₄H₉)₄]. Its molecular structure was determined by X-ray diffraction analysis. We suggested a two-step mechanism for the formation of the title compound consisting in a oxidative addition of the palladium complex followed by a reductive elimination involving P(C₆H₅)₃ and assisted by Na₂CO₃.

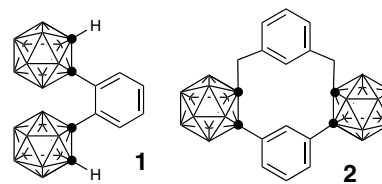


**Yasuyuki Endo, Chalermkiat Songkram,
Kiminori Ohta, Kentaro Yamaguchi**

J. Organomet. Chem. 690 (2005) 2750

Synthesis of distorted molecules based on spatial control with icosahedral carboranes

In the crystal structure of 1,2-bis(*o*-carboranyl)benzene (**1**), the benzene ring is remarkably twisted out of planarity, owing to the steric bulkiness of two adjacent carboranyl groups. In the carboracycle (**2**), the two benzene rings are slantingly stacked owing to spatial control by the carborane cages.

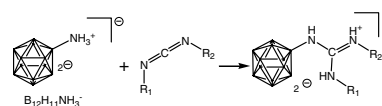


**Sascha Hoffmann, Eugen Justus,
Michal Ratajski, Enno Lork, Detlef Gabel**

J. Organomet. Chem. 690 (2005) 2757

$B_{12}H_{11}$ -containing guanidinium derivatives by reaction of carbodiimides with $H_3N-B_{12}H_{11}(1-)$. A new method for connecting boron clusters to organic compounds

The $B_{12}H_{11}NH_3^-$ boron cluster can be easily connected to organic substituents via the connection to carbodiimides. This easy and convenient synthetic way allows the formation of a wide variety of several new boron cluster containing organic compounds for possible use in BNCT (boron neutron capture therapy).

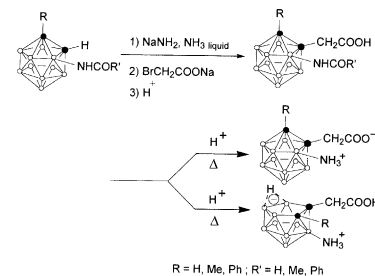


**Valentina A. Ol'shevskaya, Rami Ayuob,
Zhanna G. Brechko, Pavel V. Petrovskii,
Elena G. Kononova, Galina L. Levit,
Victor P. Krasnov, Valery N. Charushin,
Oleg N. Chupakhin, Valery N. Kalinin**

J. Organomet. Chem. 690 (2005) 2761

Synthesis of carborane analogues of γ -aminobutanoic acid

A high yield strategy for obtaining *N*-protected carboranyl amino acids from readily available 3-amino-*o*-carboranes was elaborated. Deprotection of *N*-acylated carborane amino acids is studied in acidic media. Depending on the procedure employed, *closo*- or *nido*-carborane amino acids were obtained.

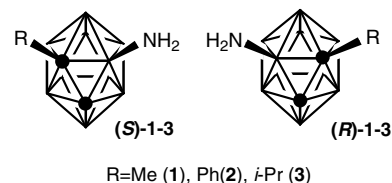


**Mikhail I. Kodess, Marina A. Ezhikova,
Galina L. Levit, Victor P. Krasnov,
Valery N. Charushin**

J. Organomet. Chem. 690 (2005) 2766

NMR determination of enantiomeric composition of 1-substituted 3-amino-1,2-dicarba-*closo*-dodecaboranes using $Eu(hfc)_3$

Experimental conditions for determination of enantiomeric composition of 1-substituted 3-aminocarboranes by 1H and ^{13}C NMR spectroscopy using chiral shift reagent $Eu(hfc)_3$ have been found.

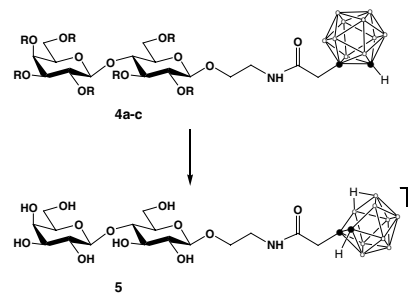


Leonid O. Kononov, Anna V. Orlova,
Alexander I. Zinin, Boris G. Kimel,
Igor B. Sivaev, Vladimir I. Bregadze

J. Organomet. Chem. 690 (2005) 2769

Conjugates of polyhedral boron compounds with carbohydrates. 2. Unexpected easy *closo*- to *nido*-transformation of a carborane-carbohydrate conjugate in neutral aqueous solution

A novel 1,2-dicarba-*closo*-dodecaborane-lactose conjugate, when dissolved in water or methanol, is subject to unexpected deboronation in *neutral* conditions leading to the formation of the corresponding *nido*-counterpart as detected by ^{11}B NMR spectroscopy.

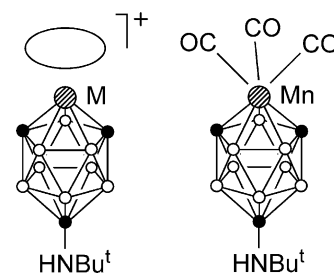


Dmitry S. Perekalin, Konstantin A. Lyssenko,
Pavel V. Petrovskii, Josef Holub,
Bohumil Štíbr, Alexander R. Kudinov

J. Organomet. Chem. 690 (2005) 2775

Metal complexes with an aminosubstituted tricarbollide ligand

Reactions of the aminosubstituted tricarbollide anion $[7\text{-}t\text{BuNH-}7,8,9\text{-C}_3\text{B}_8\text{H}_{10}]^-$ (**1**) with labile solvate complexes, $[(\text{cod})\text{Rh}(\text{THF})_x]^+$, $[\text{Cp}^*\text{Rh}(\text{THF})_3]^{2+}$, and $[(\text{C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{THF})_3]^{2+}$, give the corresponding metalla-tricarbollides in good yields. The tricarbollide analogue of cymantrene, $[1,1,1\text{-}(\text{CO})_3\text{-}12\text{-}t\text{BuNH-}1,2,4,12\text{-MnC}_3\text{B}_8\text{H}_{10}]$, was obtained by refluxing $[\text{Mn}(\text{CO})_3(\text{MeCN})_3]^+$ with **1** in THF and investigated by a single-crystal X-ray diffraction analysis.

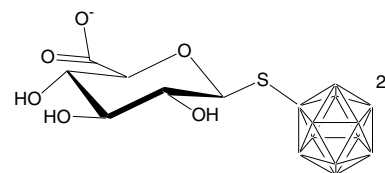


Björn Lechtenberg, Detlef Gabel

J. Organomet. Chem. 690 (2005) 2780

Synthesis of a $(\text{B}_{12}\text{H}_{11}\text{S})^{2-}$ containing glucuronoside as potential prodrug for BNCT

A first boron-containing glycoside of glucuronic acid is described. It may find use as a prodrug for boron neutron capture therapy.

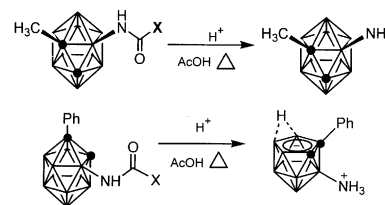


Galina L. Levit, Alexander M. Demin,
Mikhail I. Kodess, Marina A. Ezhikova,
Liliya Sh. Sadretdinova,
Valentina A. Ol'shevskaya, Valery N. Kalinin,
Victor P. Krasnov, Valery N. Charushin

J. Organomet. Chem. 690 (2005) 2783

Acidic hydrolysis of *N*-acyl-1-substituted 3-amino-1,2-dicarba-*closo*-dodecaboranes

Acidic hydrolysis of diastereomeric amides of 1-methyl-3-amino-1,2-dicarba-*closo*-dodecaborane resulted in the partial racemization of the target 3-amino-1-methylcarborane. Under the similar conditions the hydrolysis of *N*-acyl-3-amino-1-phenyl-1, 2-dicarba-*closo*-dodecaboranes resulted in amide bond cleavage accompanied by simultaneous deboronation with the removal of boron atom at position 6 of carborane cage and formation of 7,8-dicarba-*nido*-undecaborane derivative according to ^{11}B and ^1H NMR spectroscopy.

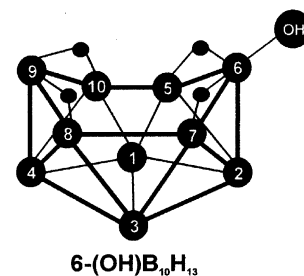


Daoud Naoufal, Maher Kodeih, David Cornu, Philippe Miele

J. Organomet. Chem. 690 (2005) 2787

New method of synthesis of 6-hydroxy-nido-decaborane 6-(OH)B₁₀H₁₃ by cage opening of closo-[B₁₀H₁₀]²⁻

Reaction of closo-[B₁₀H₁₀](NH₄)₂ with concentrated acid in inert solvent yield 6-hydroxy-nido-decaborane 6-(OH)B₁₀H₁₃. We suggested two possible mechanisms for the formation of the title compound based on the opening of the [B₁₀H₁₀]²⁻ cage.



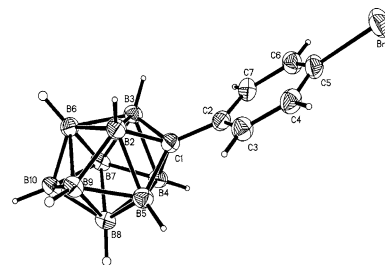
Igor B. Sivaev, Zoya A. Starikova, Pavel V. Petrovskii, Vladimir I. Bregadze, Stefan Sjöberg

J. Organomet. Chem. 690 (2005) 2790

The synthesis of functional derivatives of the [1-CB₉H₁₀]⁻ anion by Brelochs reaction

Reactions of decaborane with various aldehydes in alkaline media were studied. The reactions with HCOH and 2-MeOC₆H₄CHO give the corresponding *arachno*-carboranes

[6-*R*-*arachno*-CB₉H₁₃]⁻, whereas the reactions with C₆H₅CHO, 4-BrC₆H₄CHO, 4-MeCONHC₆H₄CHO, and 2-SC₄H₃CHO result in the *nido*-carboranes [6-*R*-*nido*-CB₉H₁₁]⁻. Both the *arachno*- and the *nido*-carboranes can be easily oxidized with elemental iodine in an alkaline aqueous solution to the *closo*-derivatives [2-*R*-*closo*-2-CB₉H₉]⁻, which under heating in solution, undergo rearrangement to [1-*R*-*closo*-1-CB₉H₉]⁻. The structure of (Bu₄N)[1-(4-BrC₆H₄)-1-CB₉H₉] was determined using single crystal X-ray diffraction.

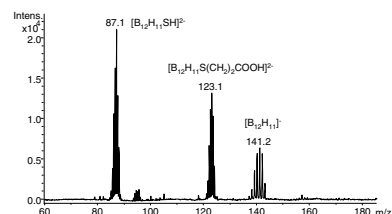


Irina Slepukhina, Thomas Duelleks, Hans-Martin Schiebel, Detlef Gabel

J. Organomet. Chem. 690 (2005) 2796

Fragmentation of B₁₂H₁₁S-R(2-) in electrospray mass spectrometry

The electrospray ionization (ESI) mass spectrometry (MS) of (3-carboxyethyl)-thio-undecahydro-*closo*-dodecaborate(2-) shows the appearance of additional peaks corresponding to B₁₂H₁₁SH(2-) and B₁₂H₁₁(1-).

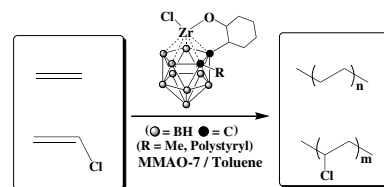


Zhu Yinghuai, Zhong Yulin, Keith Carpenter, John A. Maguire, Narayan S. Hosmane

J. Organomet. Chem. 690 (2005) 2802

Syntheses and catalytic activities of Group 4 metal complexes derived from C_(cage)-appended cyclohexyloxocarborane trianion

Constrained-geometry half-sandwich titana- and zirconacarborane complexes, derived from the trianionic C_(cage)-appended cyclohexyloxocarborane ligand, and the corresponding polymer-supported species were synthesized, spectroscopically characterized, and their catalytic activities in polymerization of ethylene and vinyl chloride have been explored.



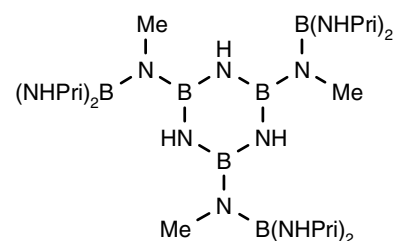
**Philippe Miele, Bérangère Toury,
David Cornu, Samuel Bernard**

J. Organomet. Chem. 690 (2005) 2809

Borylborazines as new precursors for boron nitride fibres

Schematic representation of a borylborazine molecular precursor of high performance BN fibres. A series of borylborazine-based polymers have been prepared

by thermal or chemical route. Function of the polycondensation and of the kind of monomer, the polymers display different structure established from the linkage of borazine units through direct B–N bonds or 3 atoms “–N–B–N–” bridges. This study demonstrated that high melt-spinning ability, which influences in a large extent the mechanical properties of the resulting BN fibres, is directly linked to a good stretching ability of the polymer; the latter being enhanced by the presence of flexible 3 atom bridges within the polymer.

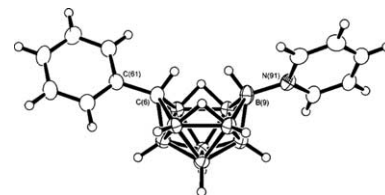


**Neil J. Bullen, Andreas Franken,
Colin A. Kilner, Simon J. Teat,
William Clegg, John D. Kennedy**

J. Organomet. Chem. 690 (2005) 2815

Polyhedral monocarbaborane chemistry. Reactions of the [6-Ph-*nido*-6-CB₉H₁₁][−] anion with two-electron donors to yield a series of neutral *arachno* and *closo* ten-vertex monocarbaborane derivatives

Two-electron donor ligands L with [6-Ph-*nido*-6-CB₉H₁₁][−] in the presence of {FeCl₃(OH₂)₆} give neutral *arachno* ten-vertex monocarbaboranes [6-Ph-9-L-*arachno*-6-CB₉H₁₂]. When L is a pyridine-type ligand neutral *closo* ten-vertex monocarbaboranes [1-Ph-6-L-*closo*-1-CB₉H₈] are formed on prolonged treatment with {FeCl₃(OH₂)₆}.

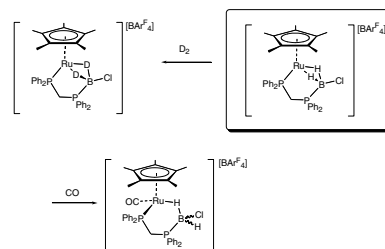


**Nicolas Merle, Christopher G. Frost,
Gabriele Kociok-Köhn, Michael C. Willis,
Andrew S. Weller**

J. Organomet. Chem. 690 (2005) 2829

Ruthenium (II) complexes of the chelating phosphine borane H₂CIB·dppm

[RuCp⁺(η²-H₂CIB·dppm)][BAF₄[−]] has been synthesised, that contains the chelating phosphine borane ligand H₂CIB·dppm. Reactions with CO and D₂ are discussed.

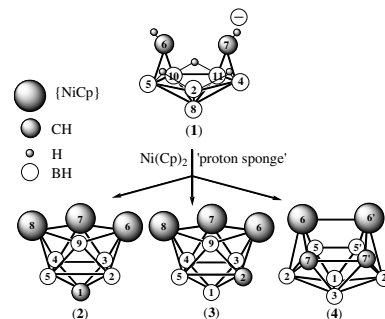


**Michael G.S. Lodesborough, Tomáš Jelínek,
Bohumír Grüner, Bohumil Štíbr,
Ivana Čisářová, Michael J. Carr**

J. Organomet. Chem. 690 (2005) 2835

Metallacarborane chemistry of the *hypho*-[6,7-C₂B₆H₁₃][−] anion: Reaction with nickelocene and the formation of three multimetallic nickel–boron clusters

The reaction of the *hypho*-[6,7-C₂B₆H₁₃][−] anion (1) with nickelocene and an excess of ‘proton sponge’ (1,8-bis-(dimethylamino)naphthalene) in boiling acetonitrile leads to the formation of a pair of isomeric trimetallic nickel–boron clusters, [6,7,8-(CpNi)₃-1-CB₅H₆] (2) and [6,7,8-(CpNi)₃-2-CB₅H₆] (3), in a combined yield of 55%.

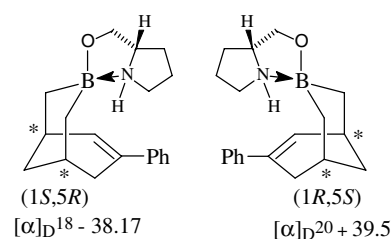


M.E. Gurskii, A.L. Karionova,
A.V. Ignatenko, K.A. Lyssenko,
M.Yu. Antipin, Yu.N. Bubnov

J. Organomet. Chem. 690 (2005) 2840

The first preparation of (1*S*,5*R*)-(-)- and (1*R*,5*S*)-(+)-7-phenyl-3-borabicyclo[3.3.1]non-6-enes and their application for synthesis of chiral cyclohexene derivatives

(1*S*,5*R*)-(-)- and (1*R*,5*S*)-(+)-7-phenyl-3-borabicyclo[3.3.1]non-6-enes that differed only by the location of the double bond were prepared by the resolution of diastereomeric intramolecular chelates with l- and d-prolinol.



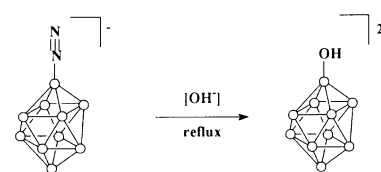
Communications

Vikentii I. Bragin, Igor B. Sivaev,
Vladimir I. Bregadze, Natal'ya A. Votinova

J. Organomet. Chem. 690 (2005) 2847

Synthesis of the 1-hydroxy-*closo*-decaborate anion [1- $B_{10}H_9OH$]²⁻

Reactions of the diazonium derivative of *closo*-decaborate anion with oxygen nucleophiles were studied. The reaction of [1- $B_{10}H_9N_2$]⁻ with hydroxide ion gives the corresponding hydroxy derivative [1- $B_{10}H_9OH$]²⁻ in high yield. The reactions with OR (R = Me, Et, *i*-Pr, Ph) result in mixture of [1- $B_{10}H_9OR$]²⁻ and [*a*²- $B_{20}H_{18}OH$]⁴⁻.

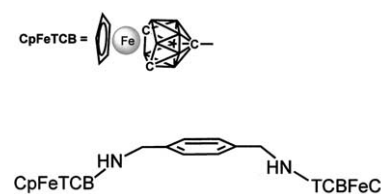


Bohumír Grüner, Jaroslav Bačkovský,
Ivana Čisářová, Bohumil Štíbr

J. Organomet. Chem. 690 (2005) 2850

Towards rod-shaped molecules based on the twelve-vertex ferratricarbollides

Reported is the first example of single- and double-spacer molecular constructions based on extremely stable cyclopentadienyl-ferratricarbollide (CpFeTCB) cages.

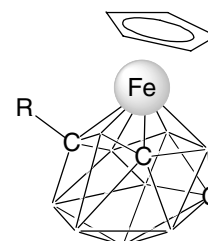


Bohumír Grüner, Libor Mikulášek,
Ivana Čisářová, Bohumil Štíbr

J. Organomet. Chem. 690 (2005) 2853

New approaches to cluster modification in the 12-vertex metallatricarbollide series

Cluster opening, followed by oxidation and cluster expansion generates new compounds of the 11-, 12- and 13-vertex metallatricarbaborane series that are otherwise unavailable by conventional synthetic methods.

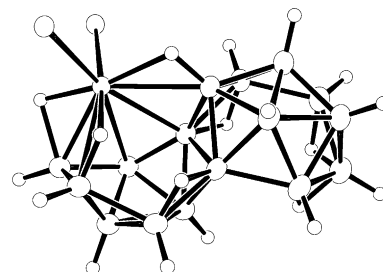


Michael J. Carr, Sarath D. Perera,
Tomáš Jelínek, Colin A. Kilner,
Bohumil Štíbr, John D. Kennedy

J. Organomet. Chem. 690 (2005) 2857

Macropolyhedral boron-containing cluster chemistry. An unusual 'neonido' ten-vertex subcluster configuration in a $[(\text{PPh}_3)_2\text{-RuB}_{16}\text{H}_{20}]$ species

Reaction of $\text{B}_{16}\text{H}_{20}$ with $[\text{RuCl}_2(\text{PPh}_3)_3]$ gives $[(\text{PPh}_3)_2\text{RuB}_{16}\text{H}_{20}]$ in which the cluster configuration consists of a conventional *nido* ten-vertex $\{\text{B}_{10}\}$ unit fused via a common $\{\text{B}_3\}$ face with a ten-vertex $\{\text{RuB}_9\}$ unit of novel 'neonido' ten-vertex shape.



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