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Special Issue: Recent Advances in Boron Chemistry

Editorial 1587

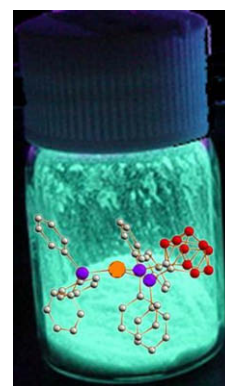
Review

Olga Crespo, M. Concepción Gimeno, Antonio Laguna

J. Organomet. Chem. 694 (2009) 1588

Carboranyl C- σ -bonded and C-functionalized carboranes as ligands in gold and silver chemistry

Gold and silver chemistry with C-functionalized carborane ligands and organometallic complexes with Au-C_{carboranyl} σ bonds are summarized. The use of carborane fragments as building blocks leads to unusual structures, clusters, rod like complexes and to interesting properties like luminescent emissions.



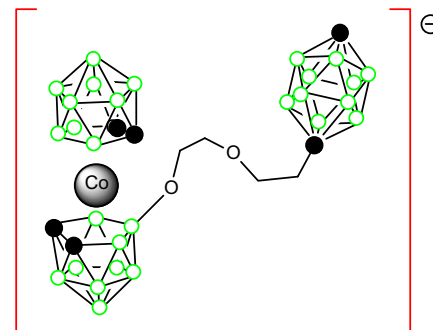
Regular Papers

Václav Šícha, Pau Farràs, Bohumil Štíbr, Francesc Teixidor, Bohumír Grüner, Clara Viñas

J. Organomet. Chem. 694 (2009) 1599

Syntheses of C-substituted icosahedral dicarbaboranes bearing the 8-dioxane-cobalt bisdicarbollide moiety

Double-cluster mono and dianions containing cobaltadiborollide and 12-vertex carborane structures interconnected via 1,4-dioxahexane chain were prepared.

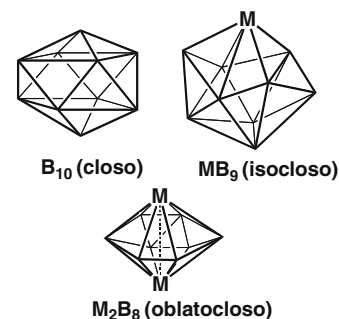


R. Bruce King

J. Organomet. Chem. 694 (2009) 1602

Geometry and chemical bonding in polyhedral boranes, metallaboranes, and dimetallaboranes: From *closo* to *isocloso* to *oblatocloso* polyhedra

The *closo* \rightarrow *isocloso* \rightarrow *oblatocloso* deltahedra for metal-free boranes, metallaboranes, and dimetallaboranes, respectively, all have n formal surface bonds. The *closo* deltahedra supplement their surface bonding with an n -center two-electron core bond, which is absent in the corresponding *isocloso* metallaborane deltahedron. The *oblatocloso* dimetallaboranes contain a formal metal-metal double bond inside the deltahedron in addition to the surface bonding.

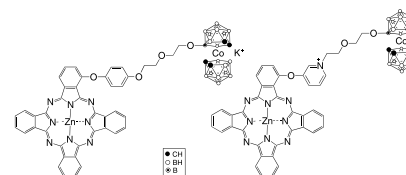


**Hairong Li, Frank R. Fronczek,
M. Graça H. Vicente**

J. Organomet. Chem. 694 (2009) 1607

Cobaltacarborane–phthalocyanine conjugates: Syntheses and photophysical properties

The syntheses of two cobaltacarboranyl-phthalocyanines, one anionic and one zwitterionic, are described. While the anionic phthalocyanine exists mainly as a monomer in polar organic solvents and has fluorescence quantum yields in the region 0.2–0.3, the zwitterionic phthalocyanine aggregates in solution and displays lower quantum yields ~0.1 in organic solvents.

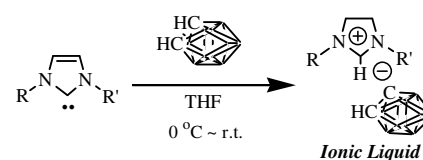


**Noriyoshi Matsumi, Mari Miyamoto,
Keigo Aoi**

J. Organomet. Chem. 694 (2009) 1612

Preparation of ionic liquids bearing *o*-carborane anion via *N,N'*-dialkylimidazol-2-ylidene carbene

Novel ionic liquids including a carborane anion were successfully prepared via reaction of *N,N'*-dialkylimidazol-2-ylidene carbene with *o*-carborane. One of the obtained ionic liquids showed relatively low melting point of 30.4 °C. The ionic conductivity of the 1-ethyl-3-methylimidazolium type ionic liquid was found to be 2.9×10^{-5} S cm⁻¹ at 51 °C.

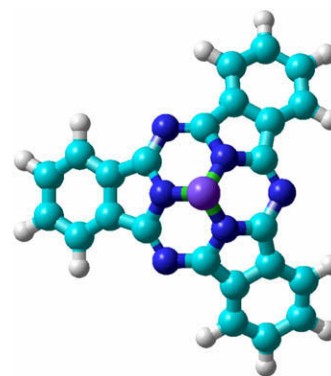


**David González-Rodríguez, Tomás Torres,
Elton L.G. Denardin, Dimitrios Samios,
Valter Stefani, Dione Silva Corrêa**

J. Organomet. Chem. 694 (2009) 1617

Thermal stability of boron subphthalocyanines as a function of the axial and peripheral substitution

We report on the synthesis and thermogravimetric study of 10 different boron subphthalocyanines, in order to compare their thermal stabilities under non-oxidizing conditions as a function of their axial and peripheral substitution.

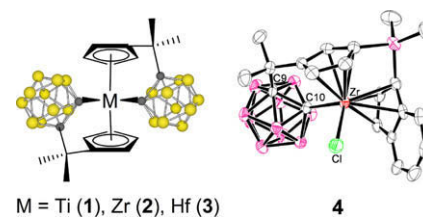


**Chang Hwan Shin, Yonggyu Han,
Min Hyung Lee, Youngkyu Do**

J. Organomet. Chem. 694 (2009) 1623

Group 4 *ansa*-metallocenes derived from *o*-carborane and their luminescent properties

Luminescent properties of group 4 complexes derived from *o*-carborane, $M(\eta^5\text{-}\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$ ($M = \text{Ti}$; **1**, Zr ; **2**, Hf ; **3**) and $\text{Me}_2\text{Si}(\eta^5\text{-Ind})[\eta^5\text{-}\eta^1\text{-Cp-3-(CMe}_2\text{CB}_{10}\text{H}_{10}\text{C})]\text{ZrCl}$ (**4**) are described. Photo-, mechano- and electroluminescent properties of the non-centrosymmetric **1–3** and electron-transporting properties of the centrosymmetric **4** are discussed.

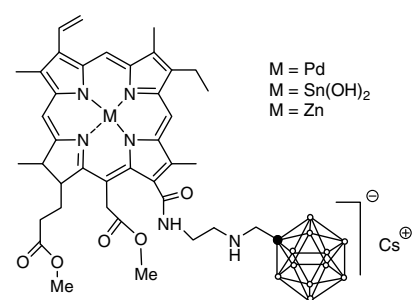


**Valentina A. Ol'shevskaya,
Arina N. Savchenko, Andrei V. Zaitsev,
Elena G. Kononova, Pavel V. Petrovskii,
Alla A. Ramonova, Victor V. Tatarskiy Jr.,
Oleg V. Uvarov, Mihail M. Moisenovich,
Valery N. Kalinin, Alexander A. Shtil**

J. Organomet. Chem. 694 (2009) 1632

Novel metal complexes of boronated chlorin e_6 for photodynamic therapy

Chlorin e_6 metal complexes with anionic boron polyhedra for photodynamic therapy.

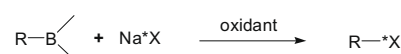


George W. Kabalka, Min-Liang Yao

J. Organomet. Chem. 694 (2009) 1638

No-carrier-added radiohalogenations utilizing organoboranes: The synthesis of iodine-123 labeled curcumin

The use of organoborane intermediates for radiohalogenations is briefly reviewed. The synthesis of an iodine-123 labeled curcumin derivative using a newly developed radio-iodination technique is reported.

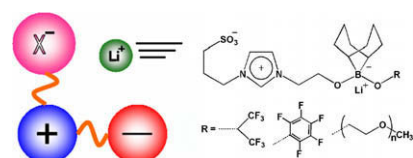


**Wataru Shibayama, Asako Narita,
Noriyoshi Matsumi, Hiroyuki Ohno**

J. Organomet. Chem. 694 (2009) 1642

Design and evaluation of imidazolium cation-based ionic liquids having double-armed anions for selective cation conduction

A series of organoborate type triple ionic molten salts were prepared using lithium 9-borabicyclo[3.3.1]nonane hydride. The ionic conductivity of the organoborate type triple ions was much higher than those for previously reported double sulfonate type triple ions. The lithium transference number observed for a triple ion was found to be 0.73, which was significantly higher in comparison with zwitterionic molten salts reported so far.

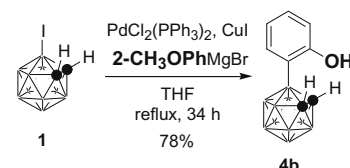


**Kiminori Ohta, Hiroto Yamazaki,
Yasuyuki Endo**

J. Organomet. Chem. 694 (2009) 1646

Magnesium-assisted intramolecular demethylation utilizing carborane C-H geometry

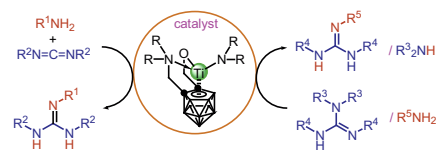
A novel type of demethylation reaction accompanies the Pd-catalyzed coupling reaction of **1** with 2-CH₃OPhMgBr. A mechanism involving intramolecular C-Mg...O interaction is proposed.



Hao Shen, Zuwei Xie*J. Organomet. Chem.* 694 (2009) 1652

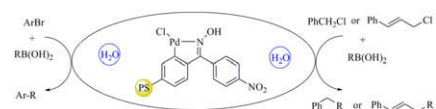
Titanacarborane mediated C–N bond forming/breaking reactions

This brief account summarizes our very recent work on the synthesis, structure, reactivity, and catalysis of half-sandwich constrained-geometry titanacarboranes [$\sigma:\eta^1:\eta^5-(\text{OCH}_2)(\text{R}_2\text{NCH}_2)\text{C}_2\text{B}_9\text{H}_9$] $\text{Ti}(\text{NR}_2)$ (R = Me, Et).

**Emilio Alacid, Carmen Nájera***J. Organomet. Chem.* 694 (2009) 1658

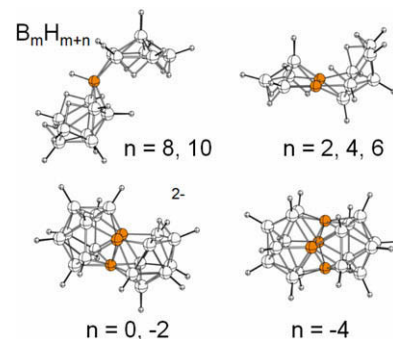
Kaiser oxime resin-derived palladacycle: A recoverable polymeric precatalyst in Suzuki–Miyaura reactions in aqueous media

Representative cross-coupling reactions of aryl bromides with different types of aryl-, alkyl, trivinylboroxine–pyridine complex, and alkenylboronic acids are performed using a polymer-bonded palladacycle derived from Kaiser oxime resin as precatalyst and potassium carbonate as base under water reflux.

**Matthias Hofmann, Farooq Ahmad Kiani***J. Organomet. Chem.* 694 (2009) 1666

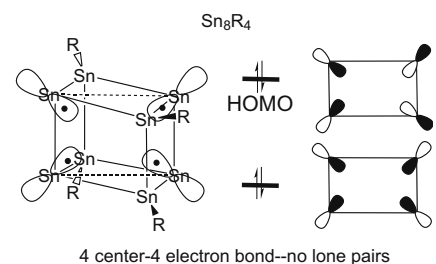
Rules for macropolyhedral boranes

For each class of macropolyhedral B_mH_{m+n} boranes a preferred number (between one and four) shared vertexes is identified. The number of skeletal electron pairs is thereby defined and allows to derive the type of fused cluster fragments. The 12-vertex *closo* and 10-vertex *nido* fragments are found to be favoured.

**Thomas P. Fehlner***J. Organomet. Chem.* 694 (2009) 1671

The relevance of boranes and metallaboranes to the structures of p-block element nanoparticles

The electron counts of metallaboranes of the earlier transition metals can be understood if the usual isolobal requirement of three cluster nonbonding, filled metal orbitals is relaxed. Analogously, the valence counts of partially ligated main group clusters, e.g., Sn_8R_4 , can be predicted if the requirement for localized lone pairs is relaxed.

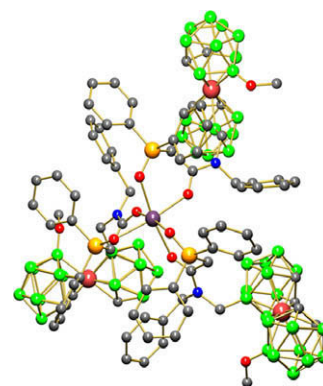


Bohumír Grüner, Magdaléna Kvíčalová, Jaromír Plešek, Václav Šícha, Ivana Čisarová, Mária Lučaníková, Pavel Selucký

J. Organomet. Chem. 694 (2009) 1678

Cobalt bis(dicarbollide) ions functionalized by CMPO-like groups attached to boron by short bonds; efficient extraction agents for separation of trivalent f-block elements from highly acidic nuclear waste

Three new families of CMPO derivatives of the cobalt(III) bis(1,2-dicarbollide)(1-) ion with short covalent bonds between the function group and boron cage were synthesized starting from corresponding ammonium derivatives. The majority of these anionic ligands are of high efficiency for Ln(III)/An(III) group extraction, the highest in low polar solvent being found for compound containing CMPO group attached *via* methylene spacer and an auxiliary CH₃-O-group present on boron atom of the second dicarbollide *sub*-cluster. X-ray structure of calcium complex of this ligand is shown in the picture.

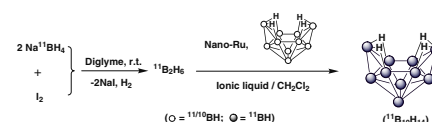


Narayan S. Hosmane, Zhu Yinghuai, John A. Maguire, Wolfgang Kaim, Masao Takagaki

J. Organomet. Chem. 694 (2009) 1690

Nano and dendritic structured carboranes and metallocarboranes: From materials to cancer therapy

Our research has dealt with two important aspects of organometallic chemistry: our continued interest in the structure and properties of the heterocarboranes, and, more recently in the use of metallocarboranes as precursors in the syntheses of nano-metal catalysts. This Account summarizes some of our more important results.

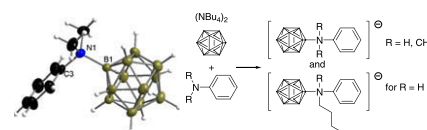


Andrea Vöge, Enno Lork, Behice Şebnem Sesalan, Detlef Gabel

J. Organomet. Chem. 694 (2009) 1698

N-arylammonio- and *N*-pyridinium-substituted derivatives of dodecahydro-closo-dodecaborate(2-)

N-ammonio and arylamino dodecaborates were synthesized by heating of the tetrabutylammonium salt of dodecahydro-closo-dodecaborate(2-) with aryl amines, or nucleophilic attack of [closo-B₁₂H₁₁NH₂]²⁻ on a strongly deactivated aromatic system. With 4-(dimethylamino)pyridine, a pyridinium derivative, [closo-B₁₂H₁₁NC₅H₄N(CH₃)₂]⁻, with a bond between the boron and the pyridinium nitrogen, was obtained.

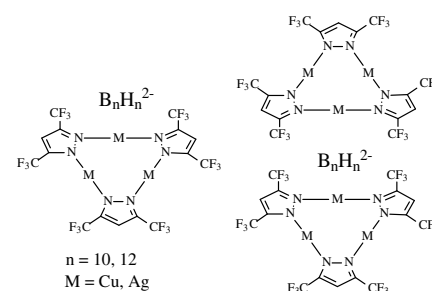


Victoria N. Tsupreva, Oleg A. Filippov, Alexey A. Titov, Antonina I. Krylova, Igor B. Sivaev, Vladimir I. Bregadze, Lina M. Epstein, Elena S. Shubina

J. Organomet. Chem. 694 (2009) 1704

Interaction of polyhedral boron hydride anions [B₁₀H₁₀]²⁻ and [B₁₂H₁₂]²⁻ with cyclic copper and silver 3,5-bis(trifluoromethyl)pyrazolate complexes

The interactions of trinuclear copper(I) and silver(I) metallocycles of 3,5-bis(trifluoromethyl)pyrazolate with polyhedral boron hydrides [B₁₀H₁₀]²⁻ and [B₁₂H₁₂]²⁻ in solution were studied using IR spectroscopy. Two types of complexes were found: {[(3,5-CF₃)₂PzM]₃}[B_{*n*}H_{*n*}]²⁻ and {[(3,5-CF₃)₂PzM]₃]₂[B_{*n*}H_{*n*}]²⁻.

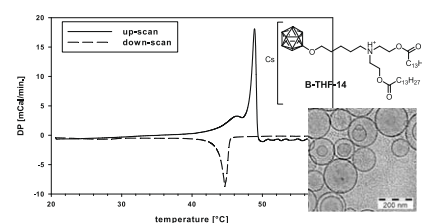


Tanja Schaffran, Franziska Lissel, Brighton Samatanga, Göran Karlsson, Alexander Burghardt, Katarina Edwards, Mathias Winterhalter, Regine Peschka-Süss, Rolf Schubert, Detlef Gabel

J. Organomet. Chem. 694 (2009) 1708

Dodecaborate cluster lipids with variable headgroups for boron neutron capture therapy: Synthesis, physical-chemical properties and toxicity

New boron-containing lipids with potential use in boron neutron capture therapy of tumors have been prepared. They allow the formation of liposomes with and without helper lipids.

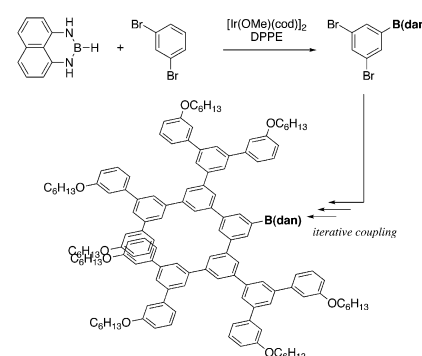


Noriyuki Iwadate, Michinori Suginome

J. Organomet. Chem. 694 (2009) 1713

Synthesis of masked haloareneboronic acids via iridium-catalyzed aromatic C-H borylation with 1,8-naphthalenediaminoborane (danBH)

Masked areneboronic acids were prepared by C-H borylation of arenes with 1,8-naphthalenediaminoborane (danBH) in the presence of $[\text{Ir}(\text{OMe})(\text{cod})]_2$ with DPPE. The C-H borylation products having halogen substituent(s) served as cross-coupling modules for the iterative synthesis of oligoarenes including convergent synthesis of dendrimers.

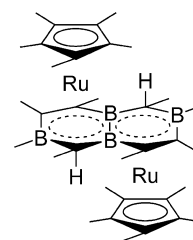


Walter Siebert

J. Organomet. Chem. 694 (2009) 1718

1,3-Diboraheterocycles as ligands in metal complexes involving *endo*-C-H bonds

The involvement of *endo*-C-H bonds in the bonding of transition metal (2,3-dihydro-1,3-diborole) compounds is essential for their stabilization. It occurs predominantly via bridging C-H-B 3c,2e interactions, which activates the C-H bond regarding deprotonation and cleavage. In bis(1,3-diborole)nickel complexes with two *endo*-C-H bonds elimination of dihydrogen is observed at ambient temperature. Axial H-C-M bonding occurs in the slipped triple-decker $[(\text{Cp}^*\text{Ru})_2(\mu\text{-C}_6\text{B}_4\text{H}_2\text{Me}_8)]$.

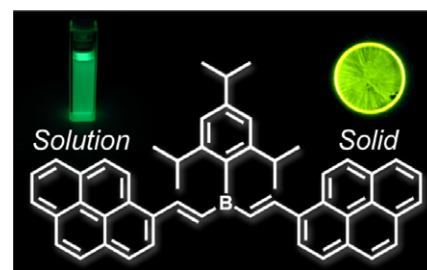


Yuuya Nagata, Yoshiki Chujo

J. Organomet. Chem. 694 (2009) 1723

Synthesis and luminescent properties of pyrenylvinylene-substituted tripylborane

A novel luminescent compound, bis((E)-2-pyren-1-yl-vinyl)-2,4,6-triisopropylphenylborane was synthesized by hydroboration reaction and was fully characterized. The extended structure of the compound obtained tells us their herringbone structures with closely faced pairs of the molecules. The fluorescence emission spectra of this compound reflected the strong π -stacking.

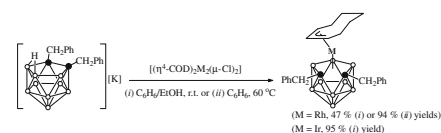


**Leonid S. Alekseev,
Alexander V. Safronov,
Fedor M. Dolgushin,
Alexander A. Korlyukov,
Ivan A. Godovikov, Igor T. Chizhevsky**

J. Organomet. Chem. 694 (2009) 1727

An unexpected cluster opening upon the formation of electronically unsaturated η^3 -(cyclooctenyl)metallacarboranes of rhodium(III) and iridium(III) with sterically reduced $[(\text{PhCH}_2)_2\text{C}_2\text{B}_9\text{H}_9]^{2-}$ ligand

Novel 16-electron *pseudocloso* rhoda- and iridacarboranes with C,C'-dibenzylsubstituted $\{\text{C}_2\text{B}_9\}$ -carborane ligand were synthesized and characterized by a combination of NMR and single-crystal X-ray diffraction data as well as Bader's topological analysis based on solid-state DFT calculations. Possible mechanism of stabilization of 16-electron metal (III) centers in these complexes via donating to metals of electron density released from the polyhedral C-C bond cleavage is discussed.

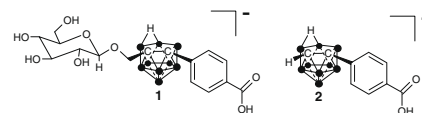


**Andrew E.C. Green, Shannon K. Parker,
John F. Valliant**

J. Organomet. Chem. 694 (2009) 1736

Synthesis and screening of bifunctional radiolabelled carborane-carbohydrate derivatives

Two new bifunctional *nido*-carboranedi-gands were prepared and labelled with ^{125}I . These compounds are platforms for preparing targeted molecular imaging and therapy agents

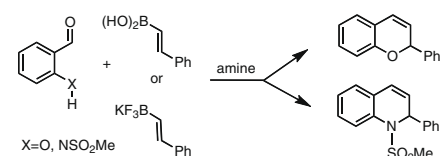


Nicos A. Petasis, Alexey N. Butkevich

J. Organomet. Chem. 694 (2009) 1747

Synthesis of 2*H*-chromenes and 1,2-dihydroquinolines from aryl aldehydes, amines, and alkenylboron compounds

The one-step reaction of salicylaldehydes with amines and alkenylboronic acids or alkenyl trifluoroborates to form 2*H*-chromenes (2*H*-1-benzopyrans) has been investigated in more detail and new suitable conditions have been identified, including the use of tertiary amines and protic solvents including water. This process was applied to a concise synthesis of a tocopherol analog. The analogous condensation reaction between 2-sulfamidobenzaldehydes and alkenyl trifluoroborates provides an efficient synthesis of 1,2-dihydroquinoline derivatives.

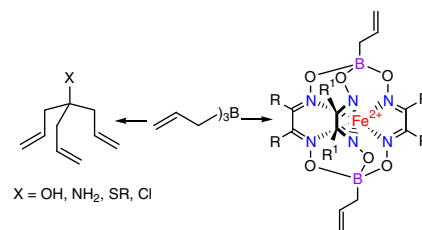


**Yu.N. Bubnov, M.E. Gurskii,
S.Yu. Erdyakov, O.A. Kizas,
G.D. Kolomnikova, N.Yu. Kuznetsov,
T.V. Potapova, O.A. Varzatskii,
Y.Z. Voloshin**

J. Organomet. Chem. 694 (2009) 1754

Allylic boranes are chemist's best friends: Reactivity, applications, new opportunities

Allylboranes reactions proceeding with the rearrangement of allylic moiety or via a direct rupture of the B-C bond (with retention) have been used for the preparation of various unsaturated, cyclic and cage compounds.

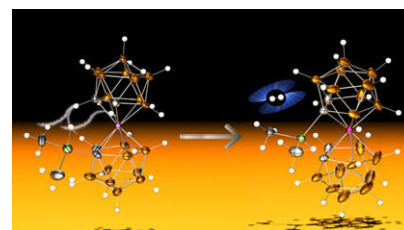


Emilio José Juárez-Pérez, Clara Viñas, Francesc Teixidor, Rosario Núñez

J. Organomet. Chem. 694 (2009) 1764

First example of the formation of a Si–C bond from an intramolecular Si–H···H–C dihydrogen interaction in a metallocarborane: A theoretical study

The Quantum Theory of Atoms in Molecules of Bader (QTAIM) at different levels of theory (B3LYP/6-311(d,p) and BP86/TZ2P(+)) has been used to study the H···H interactions found in the crystal structure of $[1\text{-SiMe}_2\text{H-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$. This has permitted to define the H···H interactions and explain the formation of $[1,1'\text{-}\mu\text{-SiMe}_2\text{-3,3'-Co-(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$. The two Si–H···H–C contacts are interpreted as an asymmetric bifurcated DHB.

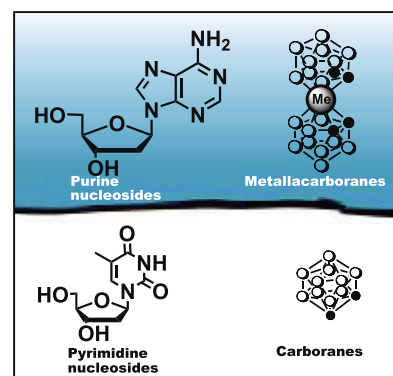


Zbigniew J. Lesnikowski

J. Organomet. Chem. 694 (2009) 1771

Nucleoside–boron cluster conjugates – Beyond pyrimidine nucleosides and carboranes

Proposed methodologies help to bypass limitations in the synthesis of nucleoside–boron cluster conjugates expanding the range of available derivatives and make possible study of broad spectrum of new pyrimidine as well as purine nucleoside conjugates in search for biological activities and technical applications.



Noriyoshi Matsumi, Keita Kawaguchi, Yousuke Hirota, Keigo Aoi

J. Organomet. Chem. 694 (2009) 1776

Preparation of fluoride anion responsive poly(*N*-vinylcarbazole)-borane complexes

A series of novel fluoride anion responsive materials were facily prepared by complex formation of poly(*N*-vinylcarbazole) with organoboron compounds in tetrahydrofuran, in which emission was efficiently quenched by adding fluoride anion.

