

# AUSTRALIAN JOURNAL OF CHEMISTRY

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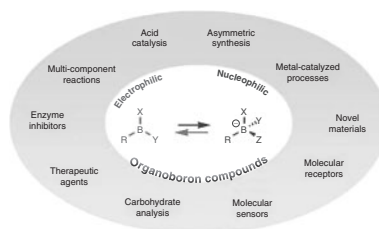
## RESEARCH FRONT: Organoborons

### Foreword

#### Expanding Roles for Organoboron Compounds – Versatile and Valuable Molecules for Synthetic, Biological and Medicinal Chemistry

Nicos A. Petasis

*Aust. J. Chem.* **2007**, *60*, 795–798.



Organoboron compounds retain reactivity both as electrophilic as well as nucleophilic species, and have evolved into vital tools for synthetic and medicinal chemistry, particularly in asymmetric synthesis, metal-catalyzed processes, acid catalysis, and multicomponent reactions. The boronic acid moiety is also being increasingly incorporated into new bioactive molecules and in novel chemosensors for carbohydrates. These features of organoboron compounds are highlighted in this issue's Research Front.

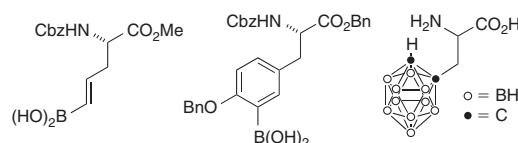
### Reviews

#### Organoboron Reagents in the Preparation of Functionalized $\alpha$ -Amino Acids

Peter F. Kaiser, Quentin I. Churches, Craig A. Hutton

*Aust. J. Chem.* **2007**, *60*, 799–810.

Over the past decade, major advances in the preparation and utilization of organoboron reagents have been applied to virtually all areas of organic synthesis. This review collates recent examples of the use of organoboron reagents in the synthesis of  $\alpha$ -amino acids, and the preparation of amino acid derivatives with organoboron functionality on the side-chain. The use of boron-containing amino acids in the synthesis of cross-linked amino acids and complex cyclic peptide natural products, and in boron neutron capture therapy, is also described.

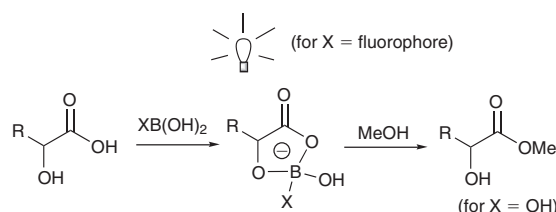


#### Tapping into Boron/ $\alpha$ -Hydroxycarboxylic Acid Interactions in Sensing and Catalysis

Todd A. Houston, Stephan M. Levonis, Milton J. Kiefel

*Aust. J. Chem.* **2007**, *60*, 811–815.

The high affinity of boronic acids for  $\alpha$ -hydroxycarboxylic acids can be manipulated for a variety of uses in analytical and synthetic chemistry. Boron-based sensors and catalysts can selectively target this hydroxyacid functional group and nearly all work in this area has appeared in the past 5 years. This short review provides some historical perspective on related work and highlights challenges for future sensor and catalyst development.

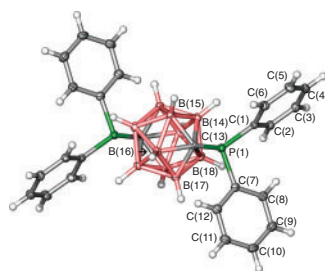


## Rapid Communications

**Mono- and Di-nuclear Gold(I) Complexes Containing 1,12-Dicarba-*closo*-dodecaborane(12)**

Joseph A. Ioppolo, Cameron J. Kepert,  
David J. Price, Louis M. Rendina

*Aust. J. Chem.* **2007**, *60*, 816–820.



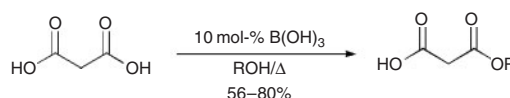
The first examples of gold(I) complexes containing monodentate diphenylphosphine-1,12-carborane and bidentate 1,12-bis(diphenylphosphine)-1,12-carborane ligands are reported.

**Selective Monoesterification of Malonic Acid Catalyzed by Boric Acid**

Stephan M. Levonis,  
Laurent F. Bornaghi, Todd A. Houston

*Aust. J. Chem.* **2007**, *60*, 821–823.

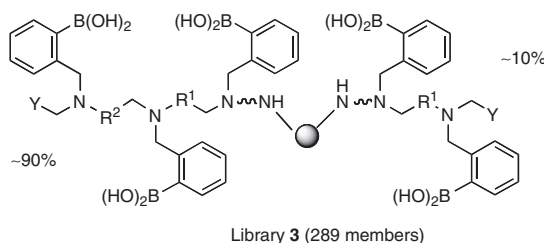
It has previously been shown that boric acid can activate  $\alpha$ -hydroxycarboxylic acids toward esterification by a chelative intermediate. Malonic acid can be selectively monoesterified in the presence of boric acid, presumably through a similar type of chelative activation.

**Synthesis, Decoding, and Preliminary Screening of a Bead-Supported Split-Pool Library of Triboronic Acid Receptors for Complex Oligosaccharides**

Sukhdev Manku, Dennis G. Hall

*Aust. J. Chem.* **2007**, *60*, 824–828.

The discovery of small molecular receptors that can bind tightly and selectively to oligosaccharides in water is a continuing challenge in the area of chemical biology, and the combined use of boronic acids with combinatorial chemistry techniques is a promising approach to address this problem. In this preliminary study, a controlled synthesis of a prototypic bead-supported combinatorial library of 289 triamine-derived triboronic acid receptors for oligosaccharides was achieved using the split-pool strategy with bead encoding using the method of partial termination synthesis. It was found that single beads from the library can be decoded efficiently using HPLC with electrospray mass spectrometric detection.

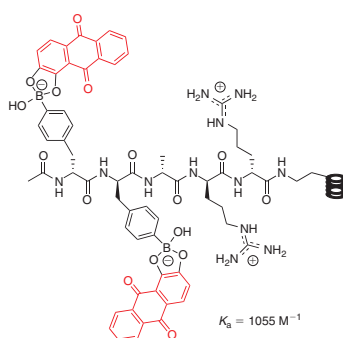


## Full Papers

**The Preparation of Solid-Supported Peptide Boronic Acids Derived from 4-Borono-L-phenylalanine and their Affinity for Alizarin**

Peter J. Duggan, Daniel A. Offermann

*Aust. J. Chem.* **2007**, *60*, 829–834.

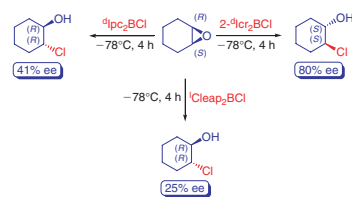


The development of synthetic polyol binders capable of recognizing specific carbohydrates or polysaccharides has a multitude of potential applications. This article describes the development of a new type of hybrid peptide–boronic acid sugar receptor library that combines the covalent interactions provided by boronic acids with the non-covalent interactions delivered by the backbone and side chains of the peptides. The selective binding characteristics of these boronic acid–peptide hybrids suggest their potential use in carbohydrate sensors and cell-specific diagnostics and therapeutics.

### Asymmetric Synthesis using Organoboranes. Relative Effectiveness of the *B*-Halobis (terpenyl)boranes for the Enantioselective Halogenative Cleavage of Representative *meso*-Epoxides

Chandra D. Roy, Herbert C. Brown

*Aust. J. Chem.* **2007**, 60, 835–842.



The synthetic importance of halohydrins is well recognized in halogenated marine natural products and pharmaceuticals. The enantiomerically enriched halohydrins are prepared by the asymmetric ring opening of three representative *meso*-epoxides with chiral Ter2BX. This study should contribute to significant advances in asymmetric synthesis using chiral organoboranes.

### Rapid Communications

#### Biodegradable Ionic Liquids: Selected Synthetic Applications

Sandrine Bouquillon, Thomas Courant, Darrell Dean, Nicholas Gathergood, Saibh Morrissey, Bruce Pegot, Peter J. Scammells, Robert D. Singer

*Aust. J. Chem.* **2007**, 60, 843–847.

3-Methyl-1-(alkyloxycarbonylmethyl)imidazolium octylsulfate ionic liquids (e.g. **1a** and **2a**) have previously been shown to be readily biodegradable in the CO<sub>2</sub> headspace test (ISO 14593). In this study, these ionic liquids were evaluated as reaction media for Diels–Alder and hydrogenation reactions and gave comparable results to other, non-biodegradable, ionic liquids.

#### Use of the Anti-Oxidant Butylated Hydroxytoluene in situ for the Synthesis of Readily Oxidized Compounds: Application to the Synthesis of the Moth Pheromone (*Z,Z,Z*)-3,6,9-Nonadecatriene

Noel W. Davies, Graham Meredith, Peter P. Molesworth, Jason A. Smith

*Aust. J. Chem.* **2007**, 60, 848–849.

The degradation of organic compounds during workup after a synthesis is frustrating and results in reduced yields. We have found that the anti-oxidant BHT can be added to an unstable starting material and be carried through a three-step synthesis without interference, resulting in an increased yield of an unstable triene from 20 to 85%. This small modification to the use of anti-oxidants could have a wider application in synthesis of products and intermediates susceptible to autoxidation.

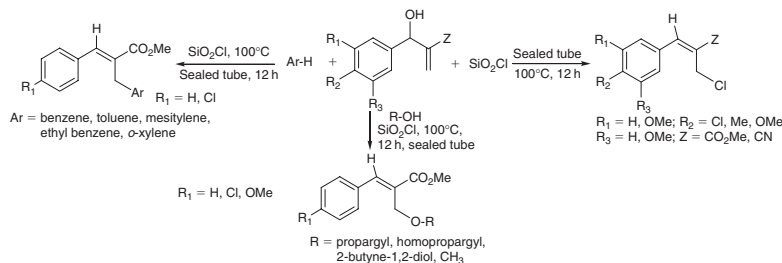
### Full Papers

#### Silica Chloride-Catalyzed One-Pot Isomerization–Chlorination, Arylation, and Etherification of Baylis–Hillman Adducts

Ponnusamy Shanmugam, Baby Viswambharan, Vadivel Vaithiyanathan

*Aust. J. Chem.* **2007**, 60, 850–856.

A convenient and efficient one-pot isomerization–chlorination, arylation, and etherification of a number of Baylis–Hillman adducts with silica chloride, an eco-friendly heterogeneous catalyst, silica chloride–arenes, and silica chloride–saturated and unsaturated alcohols as reagent systems are reported. These reactions furnished highly functionalized isomerized Baylis–Hillman derivatives in good yield.

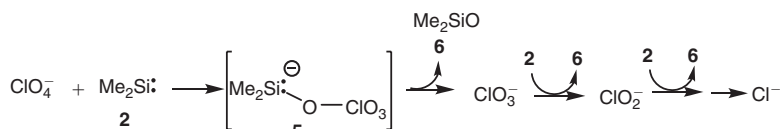


#### Phototransformation of Perchlorate to Chloride in the Presence of Polysilanes

Carmen Lazar, Annamaria Halasz, Chantale Beaulieu, Sonia Thiboutot, Guy Ampleman, Jalal Hawari

*Aust. J. Chem.* **2007**, 60, 857–861.

Health concerns surrounding the presence of perchlorate in several terrestrial and aquatic matrices has led here to its photolytic deoxygenation to the chloride anion in the presence of dodecamethylcyclohexasilane (Me<sub>2</sub>Si)<sub>6</sub> **1** with 100% removal efficiency. Dimethylsilylene, Me<sub>2</sub>Si: **2**, a reactive intermediate produced by the photolysis of **1**, is found to be in part responsible for the deoxygenation of perchlorate.

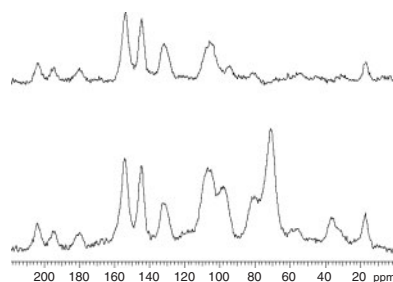


### Characterization of Eucalyptus and Chemically Related Exudates by Nuclear Magnetic Resonance Spectroscopy

Joseph B. Lambert, Yuyang Wu,  
Michael A. Kozminski,  
Jorge A. Santiago-Blay

*Aust. J. Chem.* **2007**, 60, 862–870.

The gummy material exuded by eucalyptus trees has been characterized by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy. The spectroscopic pattern is distinct from that of other types of exudates (resins, gums, gum resins), which are indistinguishable by physical appearance. Similar patterns appear in exudates from other genera (*Corymbia*, *Prosopis*, *Centrolobium*, *Guaiacum*), which permit definition of a general class of materials that we term *kinos*.

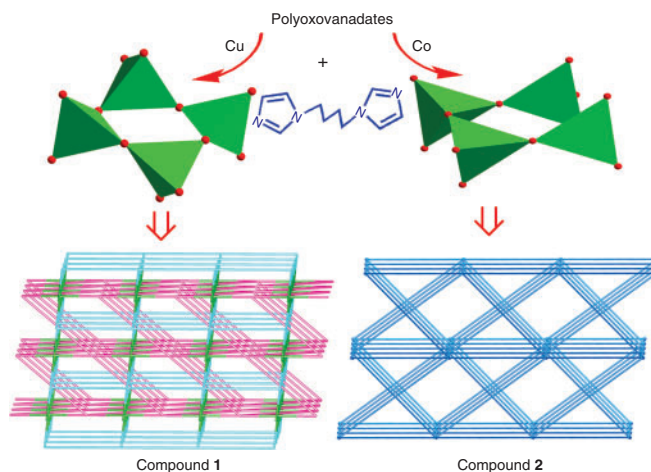


### Two New Three-Dimensional Networks Constructed on Polyoxovanadates

Yan-Fei Qi, Dongrong Xiao, Enbo Wang,  
Zhiming Zhang, Xinlong Wang

*Aust. J. Chem.* **2007**, 60, 871–878.

To investigate the role of polyoxovanadates in the network connectivity, two new organic–inorganic hybrid vanadates with three-dimensional self-catenated frameworks, namely  $[\text{Cu}_2(\text{biim})_3\text{V}_4\text{O}_{12}]$  **1** and  $[\text{Co}_2(\text{biim})_3\text{V}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$  **2**, have been synthesized.



### *N,N'*-Dichlorobis(2,4,6-trichlorophenyl) urea (CC-2): an Efficient Reagent for the Synthesis of Chemical Weapons Convention Related Dialkyl-*N,N*-dialkylphosphoramidates from Dialkylphosphites

Arvind K. Gupta, Deepak Pardasani,  
Hemendra K. Gupta, Devendra K. Dubey

*Aust. J. Chem.* **2007**, 60, 879–882.

A rapid and one-pot synthesis of phosphoramidates is of paramount importance considering their biological activity and close relation to the nerve agent tabun. Conventional means of their synthesis involve two-step reactions using unstable and moisture-sensitive reactants. This newly developed process makes use of a new positive chlorine-releasing reagent in conjunction with dialkylamines to afford the phosphoramidates in high yield in one pot. The stability of the reagent and easy removal of by-products makes it suitable for the synthesis of a variety of phosphoramidates.

### $\text{Bi}(\text{NO}_3)_3\text{-Al}_2\text{O}_3$ -Mediated Efficient Synthesis of 4-Aryl-2,6-dicoumarinylpyridines Under Solventless Conditions

Anil K. Verma, Summon Koul,  
Kamal K. Kapoor, Tej K. Razdan

*Aust. J. Chem.* **2007**, 60, 883–888.

4-Aryl-2,6-dicoumarinylpyridines are an important class of compounds that are expected to play a significant role as photosensitizing agents and may prove useful future candidates for photodynamic pharmacotherapy. An efficient, short, and eco-friendly methodology is given and the solid-phase synthesis involves an interesting mechanism.

