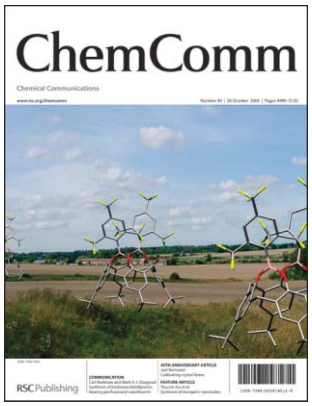
IN THIS ISSUE

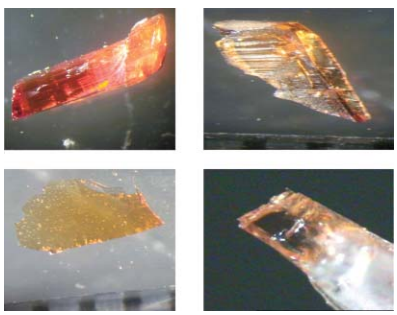
ISSN 1359-7345 CODEN CHCOFS (40) 4989–5120 (2005)



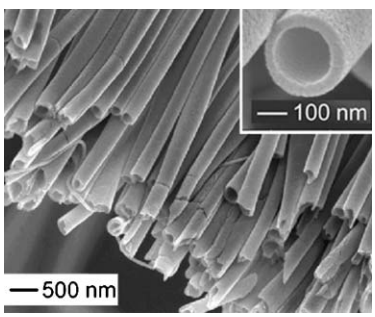
Cover
See Carl Redshaw *et al.*, page 5056.
Calixarene chemistry is flourishing in East Anglia: here perfluoroaryl bis(bora)calix[4]arenes align in pylon-type fashion against a typical Norfolk landscape.
Image reproduced by permission of Carl Redshaw and Mark R. J. Elsegood from *Chem. Commun.*, 2005, 5056–5058.

Inside cover
See Shuxia Liu *et al.*, page 5023.
Hexadecavanadate clusters and a 3D nickel complex have combined to form a unique organic–inorganic hybrid material.
Image reproduced by permission of Shuxia Liu, Linhua Xie, Bo Gao, Chundan Zhang, Chunyan Sun, Dehui Li and Zhongmin Su, from *Chem. Commun.*, 2005, 5023–5025.

40TH ANNIVERSARY ARTICLE



FEATURE ARTICLE



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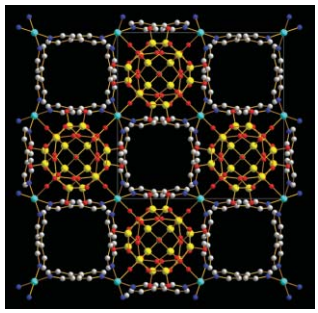

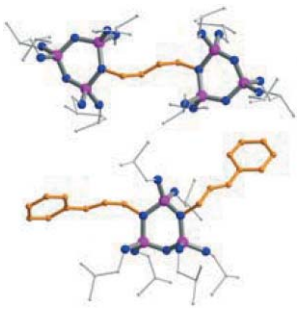

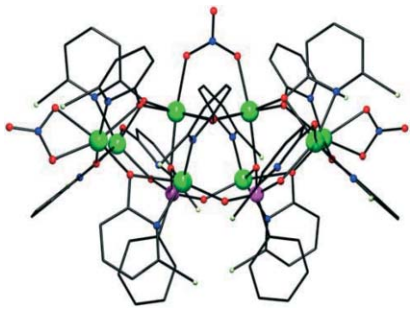

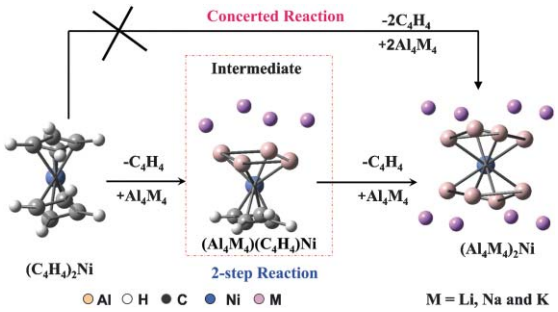

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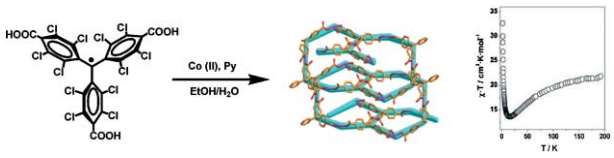
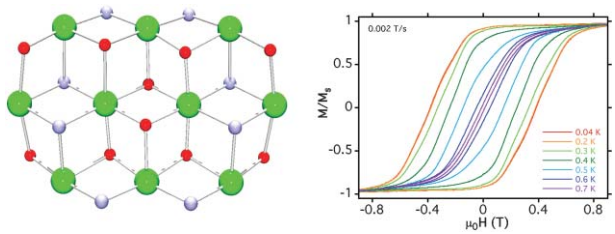


Coexistence of ferro- and antiferromagnetic interactions in a metal–organic radical-based (6,3)-helical network with large channels

Daniel Maspoch, Neus Domingo, Daniel Ruiz-Molina,* Klaus Wurst, Joan-Manel Hernández, Gavin Vaughan, Concepció Rovira, Francesc Lloret, Javier Tejada and Jaume Veciana*

A metal–organic open-framework that exhibits an unusual topology, 1-D nanochannels and mixed ferro- and antiferromagnetic interactions between Co(II) and radical units.

5038

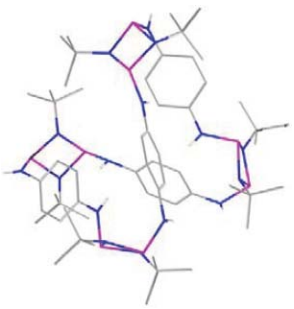


Synthesis, structure and magnetic properties of a decametallic Ni single-molecule magnet

Guillem Aromí, Simon Parsons, Wolfgang Wernsdorfer, Euan K. Brechin* and Eric J. L. McInnes*

Ferromagnetic exchange between the ten Ni^{2+} ions in the complex $[Ni_{10}(tmp)_2(N_3)_8(acac)_6(MeOH)_6]$ leads to a spin ground state of $S = 10$. Single crystal M *vs.* H studies reveal the temperature and sweep rate dependent hysteresis loops expected for a single-molecule magnet.

5041

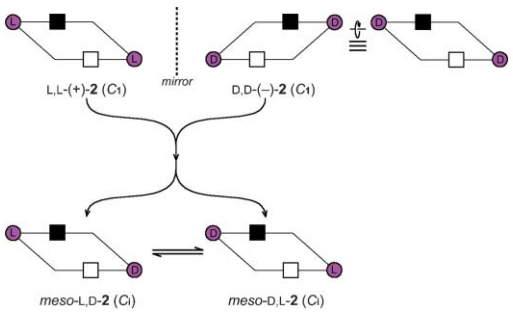


The folded, tetrameric phosph(III)azane macrocycle $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2C_6H_4\}]_4$

Fay Dodds, Felipe García, Richard A. Kowenicki, Mary McPartlin, Lucía Riera, Alexander Steiner and Dominic S. Wright*

The tetrameric macrocycle $[\{P(\mu\text{-}N^tBu)\}_2\{1,4\text{-}(NH)_2C_6H_4\}]_4$ has an unusual folded conformation in the solid state, containing a roughly tetrahedral arrangement of *endo* N–H groups for the potential coordination of anions.

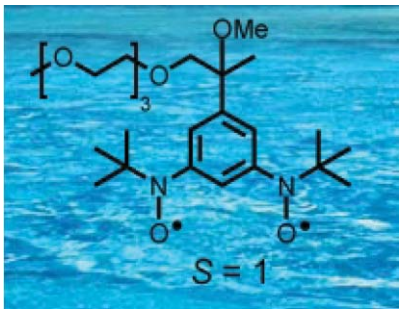
5044

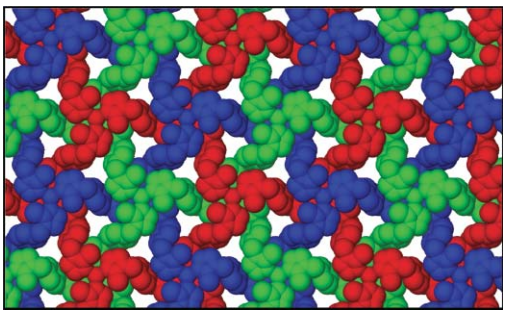


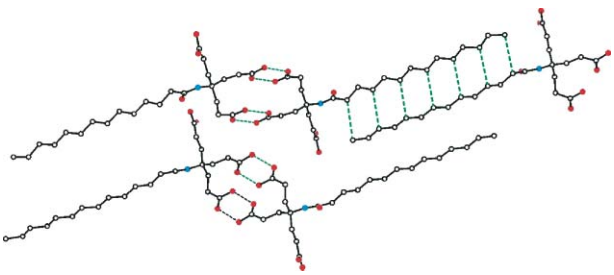
Stereoisomerism in polyoxometalates: structural and spectroscopic studies of bis(malate)-functionalized cluster systems

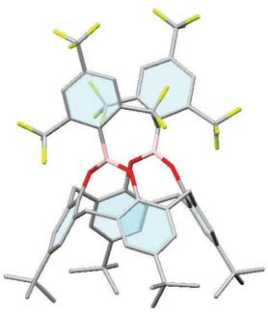
Xikui Fang, Travis M. Anderson, Yu Hou and Craig L. Hill*

Desymmetrization of centrosymmetric polytungstate clusters by introduction of multiple chiral organic ligands allows the isolation of enantiopure isomers; their interconversion to *meso* diastereomers is demonstrated.









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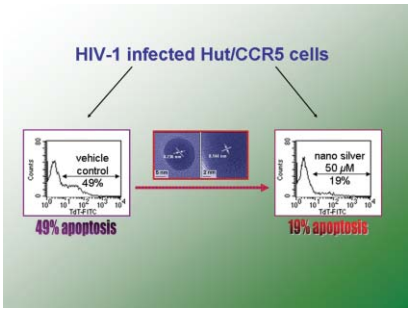
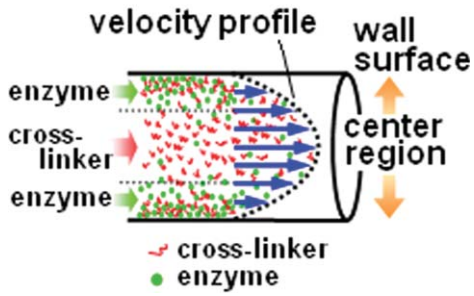


Silver nanoparticles fabricated in Hepes buffer exhibit cytoprotective activities toward HIV-1 infected cells

Raymond Wai-Yin Sun, Rong Chen, Nancy P.-Y. Chung, Chi-Ming Ho, Chen-Lung Steve Lin* and Chi-Ming Che*

Silver nanoparticles fabricated in Hepes buffer exhibit potent cytoprotective and post-infected anti-HIV-1 activities toward Hut/CCR5 cells.

5062

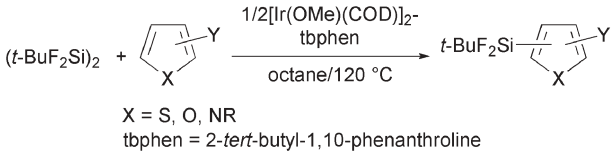


Immobilization of enzymes on a microchannel surface through cross-linking polymerization

Takeshi Honda, Masaya Miyazaki,* Hiroyuki Nakamura and Hideaki Maeda*

We have developed a novel and facile method for the preparation of an enzyme-immobilized microreactor. Enzymes were immobilized as an enzyme-polymer membrane formed on the inner wall of the microchannel by a cross-linking polymerization method.

5065

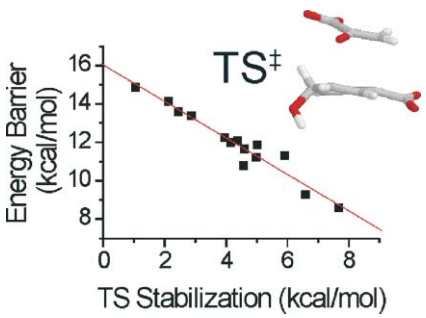


Regioselective aromatic C–H silylation of five-membered heteroarenes with fluorodisilanes catalyzed by iridium(I) complexes

Tatsuo Ishiyama,* Kazuaki Sato, Yukihiro Nishio, Takeaki Saiki and Norio Miyaura*

The aromatic C–H silylation of five-membered heteroarenes with 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane regioselectively proceeded at 120 °C in octane in the presence of a catalytic amount of iridium(I) complexes generated from 1/2[Ir(OMe)(COD)]$_2$ and 2-*tert*-butyl-1,10-phenanthroline.

5068



Multiple high-level QM/MM reaction paths demonstrate transition-state stabilization in chorismate mutase: correlation of barrier height with transition-state stabilization

Frederik Claeyssens, Kara E. Ranaghan, Frederick R. Manby, Jeremy N. Harvey and Adrian J. Mulholland*

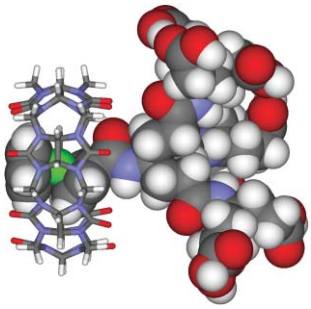
Chorismate mutase is at the centre of current debates on enzyme catalysis. DFT/MM barriers agree with experiment and show significant TS stabilization by the enzyme.

5071

Binding interactions between the host cucurbit[7]uril and dendrimer guests containing a single ferrocenyl residue

David Sobransingh and Angel E. Kaifer*

The thermodynamic stability of the inclusion complexes formed between the host cucurbit[7]uril and dendrimer guests containing a single ferrocenyl residue increases with molecular weight.

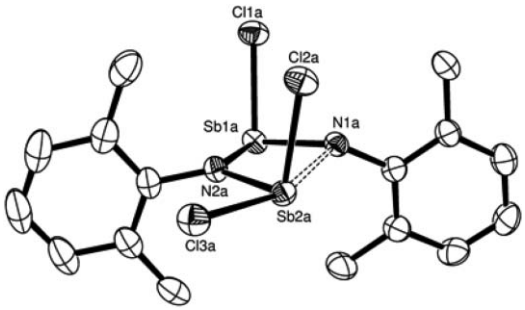


5074

Identification of new N–Sb topologies: understanding the sequential dehydrochloride coupling of primary amines and trichloropnictines

Neil Burford,* Ezra Edelstein, Jeff C. Landry, Michael J. Ferguson and Robert McDonald

The subtle steric strain imposed by substituents on N–Sb frameworks has enabled identification of an amine–stibine adduct, a bisamine–stibine adduct, the first acyclic dipnictadiazane and the first six-membered cyclotristibatriazane.

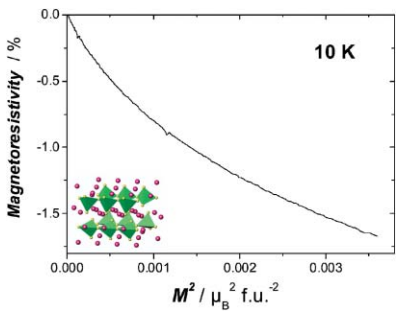


5077

Negative magnetoresistance in Ba_2CoS_3

Thomas Baikie, Vincent Hardy, Antoine Maignan and M Grazia Francesconi*

Ba_2CoS_3 is the first 2-1-3 sulfide to show conducting-like behaviour and a rare example of a one-dimensional sulfide with negative magnetoresistance.

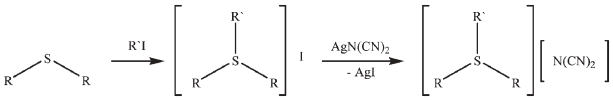


5080

Trialkylsulfonium dicyanamides - a new family of ionic liquids with very low viscosities

Dirk Gerhard, Samim Cenk Alpaslan, Heiner Jakob Gores, Marc Uerdingen and Peter Wasserscheid*

Trialkylsulfonium dicyanamides show surprisingly low viscosities down to −20 °C and are therefore highly interesting liquid materials for separation processes and electrolyte applications at low temperatures.



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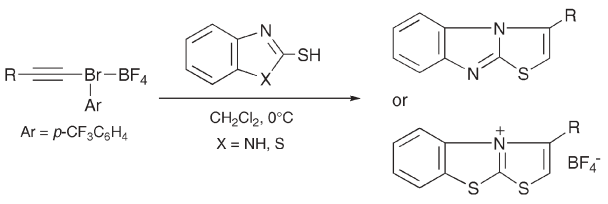
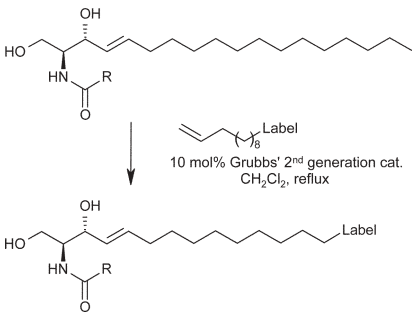


Domino Michael addition-carbene rearrangement-cyclization reaction of 1-alkynyl(aryl)-λ^3-bromanes with 2-mercapto-1,3-benzazoles

Masahito Ochiai* and Norihiro Tada

Exposure of 1-alkynyl[*p*-(trifluoromethyl)phenyl]-(tetrafluoroborato)-λ^3-bromanes to 2-mercaptobenzimidazole or benzothiazole in CH_2Cl_2 at 0 °C under argon resulted in a domino Michael addition–carbene rearrangement–cyclization to give directly tricyclic heterocycles in high yields, whereas the reaction with 2-mercaptobenzoxazole gave 1-alkynyl sulfides.

5086

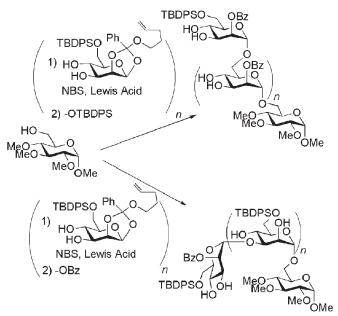


One-step labelling of sphingolipids *via* a scrambling cross-metathesis reaction

Peter Nussbaumer,* Peter Ettmayer, Carsten Peters, Daniela Rosenbeiger and Klemens Högenauer

The alkyl chain in the backbone of sphingosine derivatives can be exchanged with functionalised (labelled) side chains in a single step under cross-metathesis reaction conditions.

5088

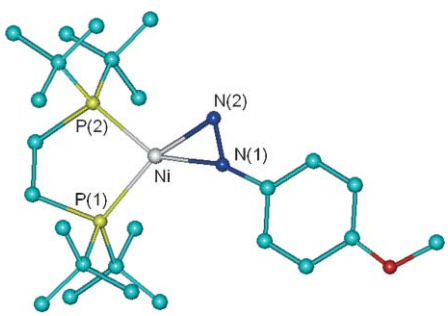


Iterative, orthogonal strategy for oligosaccharide synthesis based on the regioselective glycosylation of polyol acceptors with partially unprotected *n*-pentenyl-orthoesters: further evidence for reciprocal donor acceptor selectivity (RDAS)

J. Cristóbal López,* Attila Agocs, Clara Uriel, Ana M. Gómez and Bert Fraser-Reid

An efficient iterative, orthogonal protocol based on the regioselective glycosyl coupling of D-mannose polyols with, partially unprotected, *n*-pentenyl orthoester donors permits the synthesis of linear and branched oligosaccharides.

5091



Synthesis and characterization of side-bound aryldiazo and end-bound nitrosyl complexes of nickel

Vlad M. Iluc, Alexander J. M. Miller and Gregory L. Hillhouse*

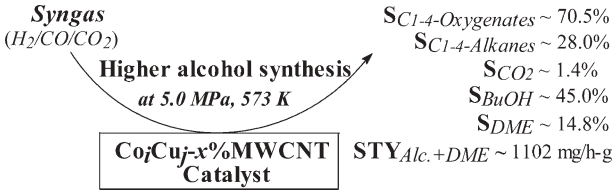
Reaction of an aryldiazonium salt with a Ni(0) phosphine complex gives an unusual side-bound aryldiazo adduct, but nitrosonium adds in an end-on fashion.

5094

Carbon nanotube-promoted Co–Cu catalyst for highly efficient synthesis of higher alcohols from syngas

Hong-Bin Zhang,* Xin Dong, Guo-Dong Lin, Xue-Lian Liang and Hai-Yan Li

A carbon-nanotube-promoted Co_iCu_j catalyst achieves highly selective formation of BuOH and DME from syngas, and demonstrates great potential in commercial use for higher alcohol synthesis.

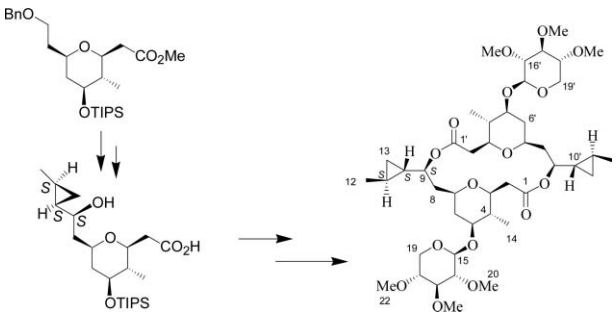


5097

Total synthesis of a diastereomer of the marine natural product clavosolide A

Conor S Barry, Nick Bushby, Jonathan P. H. Charmant, Jon D. Elsworth, John R. Harding and Christine L. Willis*

The total synthesis of the reported structure of the sponge metabolite clavosolide A is described and the target molecule was found to be a diastereomer of the natural product.

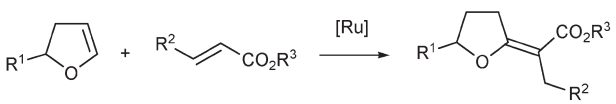


5100

Synthesis of 2-alkylidenetetrahydrofurans by Ru-catalyzed regio- and stereoselective codimerization of dihydrofurans with α,β-unsaturated esters

Hiroshi Tsujita, Yasuyuki Ura, Kenji Wada, Teruyuki Kondo and Take-aki Mitsudo*

2-(1-Alkoxycarbonyl)alkylidenetetrahydrofurans were readily synthesized by the codimerization of 2,3- or 2,5-dihydrofurans with α,β-unsaturated esters using a zerovalent Ru catalyst, Ru(cod)(cot) [cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene], with high regio- and stereoselectivity.

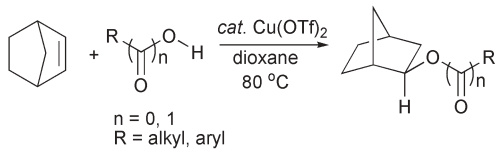


5103

Copper(II)-catalysed addition of O–H bonds to norbornene

Jason G. Taylor, Neil Whittall and King Kuok (Mimi) Hii*

$Cu(OTf)_2$ is an inexpensive, air- and moisture-stable catalyst for the O–H addition of aliphatic and aromatic acids and alcohols to norbornene.



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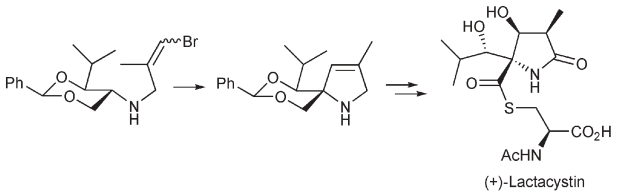
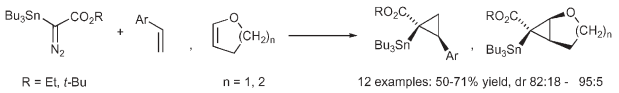


A formal synthesis of (+)-lactacystin

Duncan J. Wardrop* and Edward G. Bowen

A formal synthesis of the proteasome inhibitor, (+)-lactacystin is reported. The key step in this endeavor involves the generation of the C-5 quaternary stereocenter *via* intramolecular C–H insertion of an alkylidenecarbene intermediate.

5109

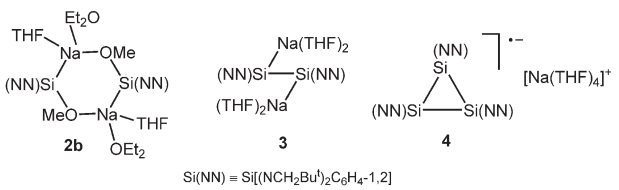


Stannyl cyclopropanes by diastereoselective cyclopropanations with (tributylstannyl)-diazoacetate esters catalyzed by Cu(I) *N*-heterocyclic carbene

Robert E. Gawley* and Sanjay Narayan

Stannyl cyclopropanes having a quaternary tin-bearing carbon atom are made using a NHC copper catalyst in good yields and excellent diastereoselectivity, with no competing dimerization of carbene.

5112

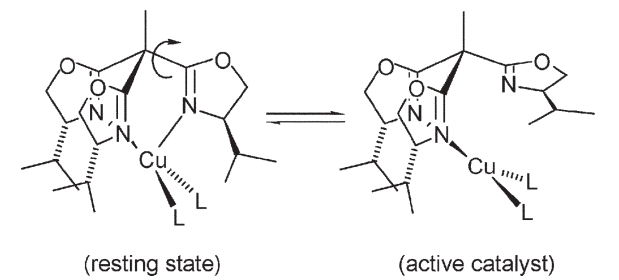


Crystalline Na–Si(NN) derivatives [Si(NN) = Si{$(NCH_2tBu)_2C_6H_4$-1,2}]: the silylenoid $[Si(NN)OMe]^-$, the dianion $[(NN)Si–Si(NN)]^{2-}$, and the radical anion *c*-$[Si(NN)]_3^-$

Floria Antolini, Barbara Gehrhus,* Peter B. Hitchcock and Michael F. Lappert*

Reactions of the silylene Si[$(NCH_2tBu)_2C_6H_4$-1,2] with NaOMe, excess Na or 1/3 Na yield the X-ray-characterised crystalline compounds **2b**, **3** and **4**.

5115



Exploiting C_3-symmetry in the dynamic coordination of a chiral trisoxazoline to copper(II): improved enantioselectivity, and catalyst stability in asymmetric lewis acid catalysis

Carole Foltz, Björn Stecker, Guido Marconi, Stéphane Bellemin-Laponnaz,* Hubert Wadepohl and Lutz H. Gade*

C_3-symmetric trisoxazolines form highly efficient enantioselective Cu^{II} Lewis acid catalysts which are based on the concept of *stereoelectronic hemilability*.

AUTHOR INDEX

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