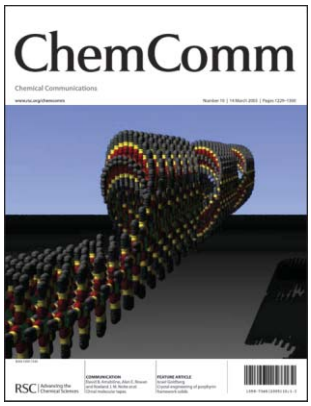
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (10) 1229–1360 (2005)

In this issue...

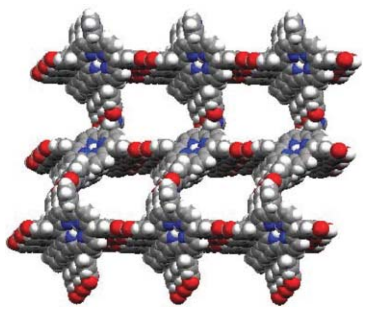
The feature article reviews recent achievements in the area of targeted synthesis of porphyrin-based framework solids by various non-covalent mechanisms of molecular recognition. See Israel Goldberg, pp. 1243–1254.



Cover

Artistic interpretation of the self-association of tetra(thiafulvalene-crown-ether)-substituted phthalocyanine building blocks. See page 1255.
Image reproduced by permission of Professor Roeland J. M. Nolte.

FEATURE ARTICLE



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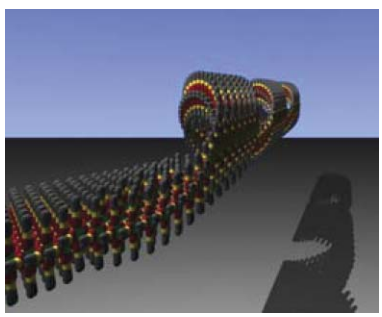

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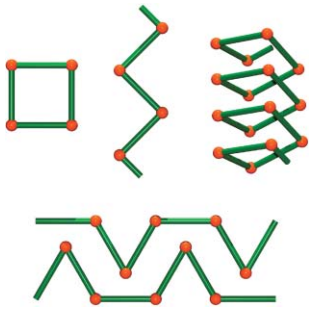

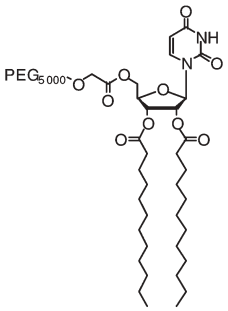

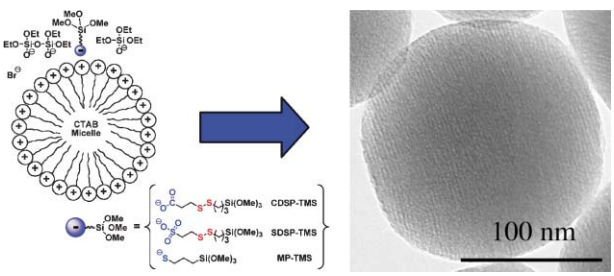

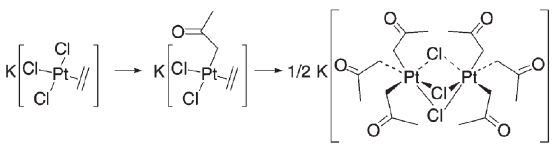

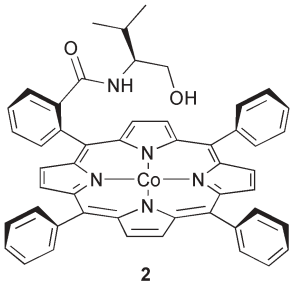

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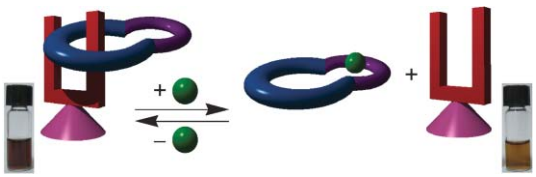

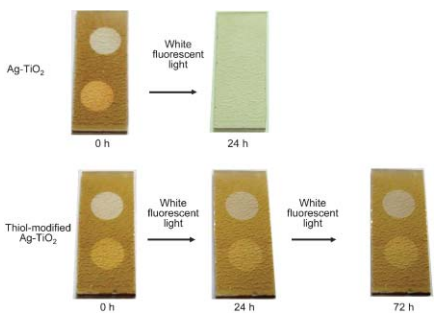

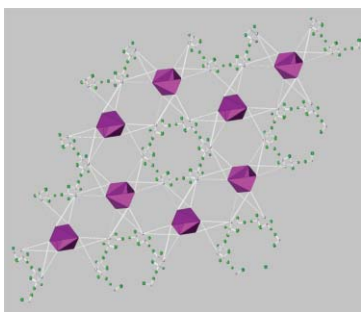

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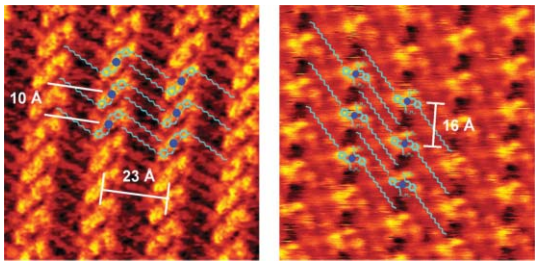
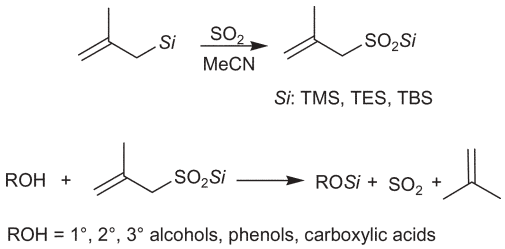


Structure controlled self-assembly of Cu(II) salicylic aldehyde and aldimine derivative complexes

Philipp Zell, Florian Mögele, Ulrich Ziener and Bernhard Rieger*

The orientation of metal complexes in 2D surface structures and hence the relative distances between the individual Cu(II) ions have been controlled by ligand design as a tool for the "fine-tuning" of intermolecular interactions.

1297

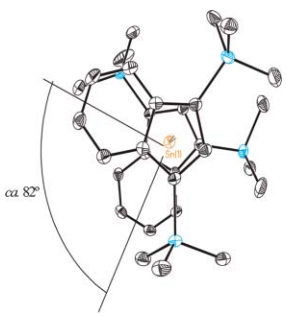


Silyl methallylsulfinates: efficient and powerful agents for the chemoselective silylation of alcohols, polyols, phenols and carboxylic acids

Xiaogen Huang, Cotinica Craita, Loay Awad and Pierre Vogel*

Alcohols, phenols and carboxylic acids are silylated with very good yield in the presence of silyl methallylsulfinates under non-basic conditions and with the formation of volatile co-products.

1300

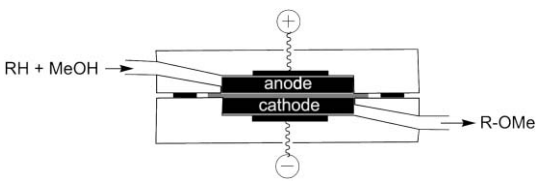


π-Indenyl tin(II) and lead(II) compounds

Jamie N. Jones and Alan H. Cowley

The first π-indenyl tin(II) complexes are reported; the bis(π-indenyl) tin(II) derivative has an essentially parallel arrangement of indenyl rings.

1303



Microflow electroorganic synthesis without supporting electrolyte

Roberto Horcajada, Masayuki Okajima, Seiji Suga and Jun-ichi Yoshida*

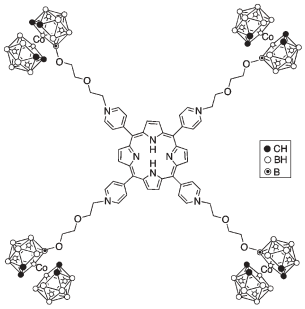
Anodic methoxylation of several organic compounds has been successfully achieved in the absence of intentionally added supporting electrolyte using an electrochemical microflow system.

1306

Expeditious synthesis of porphyrin–cobaltacarborane conjugates

Erhong Hao and M. Graça H. Vicente*

The high yield synthesis of two new porphyrin–cobaltacarborane conjugates is described. These conjugates of high boron content display spectroscopic properties characteristic of porphyrin macrocycles and may have application in the BNCT treatment of tumors.

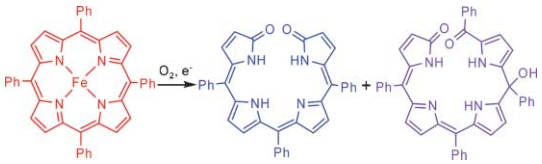


1309

A facile and versatile preparation of bilindiones and biladienones from tetraarylporphyrins

Takae Yamauchi, Tadashi Mizutani,* Kenji Wada, Shoji Horii, Hirotaka Furukawa, Shigeyuki Masaoka, Ho-Chol Chang and Susumu Kitagawa

Coupled oxidation of iron tetraarylporphyrins with dioxygen and ascorbic acid afforded *meso*-arylbilindiones and *meso*-arylbiladienones in 20–63% yield. The crystal structure of *meso*-triphenylbilindione showed that it has larger helix pitch than β-octaethylbilindione.

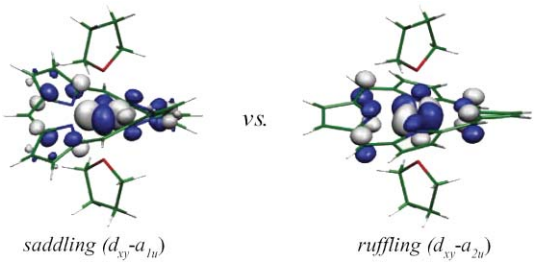


1312

An unexpected bonding interaction between d_{xy} and a_{1u} orbitals mediated by porphyrin deformation

Ru-Jen Cheng,* Yen-Ku Wang, Ping-Yu Chen, Ya-Ping Han and Chih-Ching Chang

The extraordinary bonding interaction between d_{xy} and a_{1u} orbitals in the saddle-shaped $[Fe(OETPP)(THF)_2]^+$ complex offers a novel symmetry-controlled mechanism for the formation of the unusual intermediate-spin electronic structure $(d_{xz}d_{yz})^3(d_{xy})^1(d_z2)^1$ that is consistent with the reported NMR data.

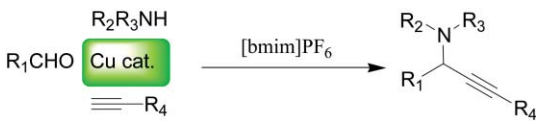


1315

An efficient synthesis of propargylamines *via* C–H activation catalyzed by copper(I) in ionic liquids

Soon Bong Park and Howard Alper*

An efficient three-component coupling of aldehydes with amines and alkynes to form propargylamines has been developed *via* C–H activation catalyzed by a copper(I) compound in an ionic liquid; the catalysts were recycled five times without any significant loss of catalytic activity.



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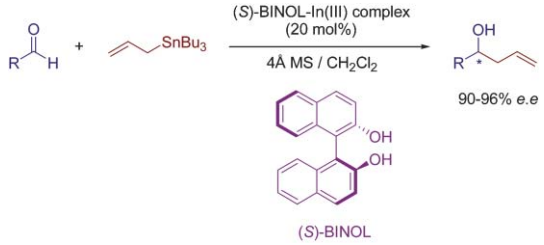
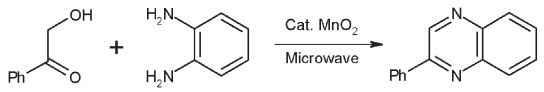


Catalytic asymmetric allylation of aldehydes *via* a chiral indium(III) complex

Yong-Chua Teo, Kui-Thong Tan and Teck-Peng Loh*

A chiral indium complex has been discovered to effect high enantioselectivities in the addition of allyltributyl stannanes to aldehydes. The allylation of a variety of aromatic, α,β-unsaturated and aliphatic aldehydes resulted in good yields and high enantioselectivities (90–96% ee).

1321

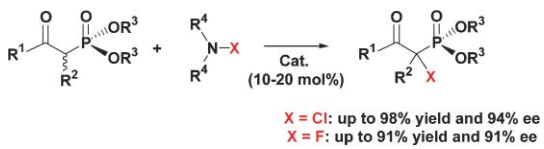


Manganese(IV) dioxide-catalyzed synthesis of quinoxalines under microwave irradiation

So Yeon Kim, Kang Hyun Park and Young Keun Chung*

We synthesize quinoxalines, catalyzed by manganese(IV) dioxide, from a variety of α-hydroxyketones followed by trapping with aromatic or aliphatic 1,2-diamines without using a solvent, within one minute under microwave irradiation.

1324

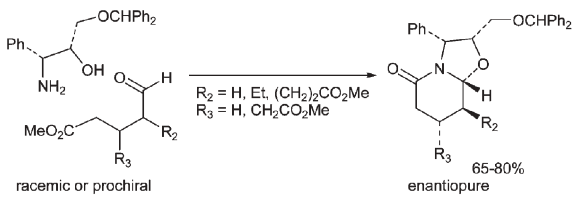


Enantioselective chlorination and fluorination of β-keto phosphonates catalyzed by chiral Lewis acids

Luca Bernardi and Karl Anker Jørgensen*

The direct enantioselective chlorination and fluorination of β-keto phosphonates catalyzed by chiral Lewis acids is presented; both reactions proceed in good yields furnishing the corresponding highly valuable α-halo phosphonate derivatives with high enantioselectivities.

1327



Highly enantioselective dynamic kinetic resolution and desymmetrization processes by cyclocondensation of chiral aminoalcohols with racemic or prochiral δ-oxoacid derivatives

Mercedes Amat,* Oriol Bassas, Miquel A. Pericàs, Mireia Pastó and Joan Bosch*

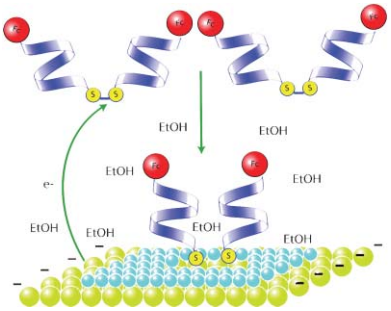
Cyclocondensation reactions of aminoalcohols **7** and **8** with racemic or prochiral δ-oxoacid derivatives provide polysubstituted lactams with high enantioselectivity in a process that involves dynamic kinetic resolution and/or desymmetrization of enantiotopic or diastereotopic ester groups.

1330

Electrodeposition of ferrocenoyl peptide disulfides

Grzegorz A. Orlowski, Somenath Chowdhury, Yi-Tao Long, Todd C. Sutherland and Heinz-Bernhard Kraatz*

Using electrodeposition of cyclic and acyclic Fc–peptide disulfides tightly-packed Fc–peptide monolayers were conveniently formed, which exhibit significant differences in their electron transfer kinetics.

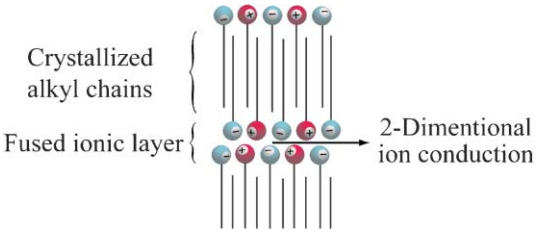


1333

Anisotropic ion conduction in a unique smectic phase of self-assembled amphiphilic ionic liquids

Tomohiro Mukai, Masafumi Yoshio, Takashi Kato, Masahiro Yoshizawa and Hiroyuki Ohno*

Anisotropic ion conduction was observed in a supercooled smectic phase composed of crystallized alkyl chains and fused ionic layer.

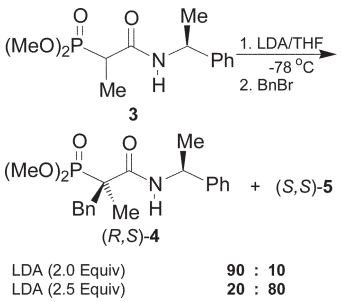


1336

Asymmetric alkylation of dimethoxyphosphoryl-*N*-[1-(*S*)-α-methylbenzyl]acetamide enolates. Synthesis of both stereoisomers from the same source of chirality by changing the equivalents of LDA

Mario Ordóñez,* Eugenio Hernández-Fernández, Janet Xahuentitla and Carlos Cativiela

A new methodology has been developed for the synthesis of both stereoisomers from a single chiral source.

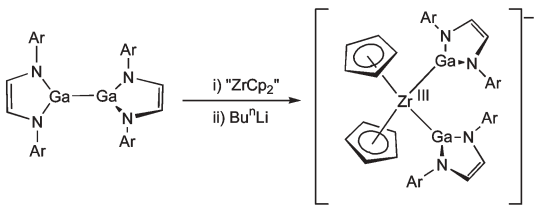


1339

Evidence for the first oxidative insertion of a transition metal into a digallane(4): synthesis, structural characterisation and EPR studies of $[Cp_2Zr^{III}\{Ga[N(Ar)C(H)]_2\}_2][Li(THF)_4]$, Ar = $C_6H_3Pr^i_2$-2,6

Robert J. Baker, Cameron Jones* and Damien M. Murphy

The first gallyl–Group 4 complex has been prepared *via* an unusual reaction involving an unprecedented oxidative insertion of a transition metal centre into a digallane(4).



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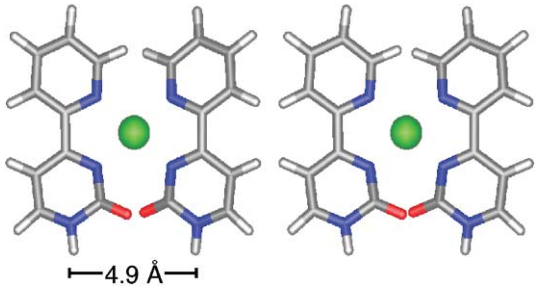
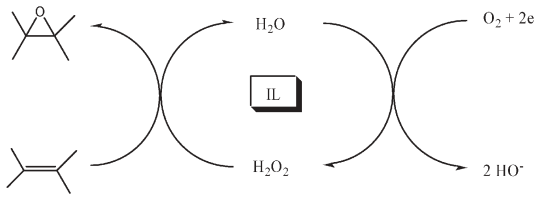


A pyrimidine-like nickel(II) DNA base pair

Christopher Switzer* and Dongwon Shin

We report an improbable naturally inspired DNA self-pair based on a pyrimidine scaffold. The $Pyr^{P}{\cdot}Ni^{2+}{\cdot}Pyr^{P}$ metallo base-pair (Pyr^{P} = 4-(2′-pyridyl)-pyrimidinone) has mismatch discrimination and stability on a par with natural Watson–Crick base-pairs despite assuming a base–base distance predicted to be half the corresponding natural dimension.

1345

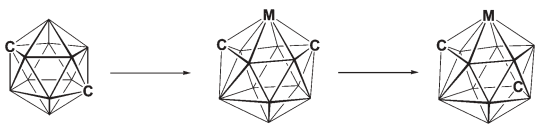


Electrosynthesis of hydrogen peroxide in room temperature ionic liquids and *in situ* epoxidation of alkenes

Michael Chi-Yung Tang, Kwok-Yin Wong and Tak Hang Chan*

Hydrogen peroxide can be electrosynthesized from oxygen in [bmim][BF_4]–water or 0.04M NaOH and used *in situ* for the epoxidation of alkenes.

1348

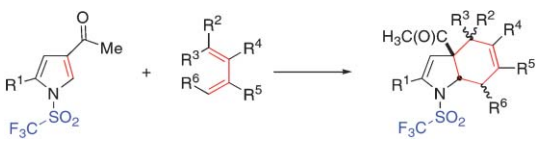


The first 4,1,10-MC_2B_{10} supraicosahedral metallacarboranes and a route to previously inaccessible 4,1,12-ruthenium arene species

David Ellis, Maria Elena Lopez, Ruaraidh McIntosh, Georgina M. Rosair, Alan J. Welch* and Romain Quenardelle

Reduction and subsequent metallation of 1,12-*closo*-$C_2B_{10}H_{12}$ affords the first examples of 4,1,10-MC_2B_{10} supraicosahedral metallacarboranes: these undergo quantitative isomerisation to the corresponding 4,1,12 isomers on heating.

1351



1-Triflylpyrroles as efficient dienophiles in normal electron demand [4+2] cycloaddition reactions under pressure

Antony Chrétien, Isabelle Chataigner and Serge R. Piettre*

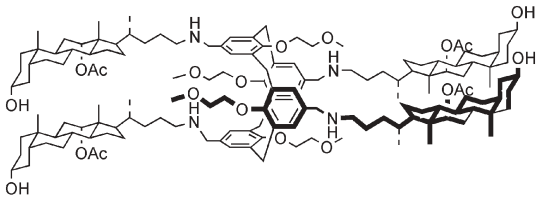
1-Triflylpyrroles bearing acetyl group(s) on position 3, or 2 and 4, are efficient dienophiles in normal electron demand Diels–Alder reactions activated by high pressures and Lewis acids.

1354

Calix[4]arene-cholic acid conjugates: a new class of efficient synthetic ionophores

Nakia Maulucci, Francesco De Riccardis,* Cinzia Barbara Botta, Agostino Casapullo, Elena Cressina, Massimo Fregonese, Paolo Tecilla* and Irene Izzo*

The synthesis of a new class of amphiphilic calix[4]arene-based ionophores, relying on direct reductive amination as a key step, and the evaluation of their H^+ and Na^+ transporting properties is described.



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