



**Cover** Juxtaposition of triple-decker cations and triplanes (pp. 2369–2375).

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November 2004/Volume 1/Issue 11 www.rsc.org/chemicalscience Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.



#### FEATURE ARTICLE

From group 13–group 13 donor–acceptor bonds to triple-decker cations

Alan H. Cowley

Boranediyls (RB) and heavier congeneric univalent group 13 molecules possess a lone pair of electrons and are therefore able to form group 13–group 13 donor–acceptor bonds when treated with appropriate Lewis acids.

#### COMMUNICATIONS

Active site structure and redox processes of cytochrome c oxidase immobilised in a novel biomimetic lipid membrane on an electrode

Marcel G. Friedrich, Frank Gieβ, Renate Naumann, Wolfgang Knoll, Kenichi Ataka, Joachim Heberle, Jana Hrabakova, Daniel H. Murgida and Peter Hildebrandt\*

Surface enhanced resonance Raman spectroscopy of cytochrome c oxidase, embedded in a lipid bilayer and immobilised on an electrode, reveals preservation of the active site structures and electron exchange with the electrode.



Chemical Science

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	COMMUNICATIONS
	<ul> <li>Preparation of aqueous gel beads coated by lipid bilayers</li> <li>Andrew Campbell, Pietro Taylor, Olivier J. Cayre and Vesselin N. Paunov*</li> <li>Novel giant liposome microcapsules have been fabricated based on aqueous gel cores encapsulated with a lipid bilayer. The method involves templating of lipid-stabilised water-in-oil emulsions after gelling the aqueous phase.</li> </ul>
	Metallaborane reaction chemistry. A facile and reversible dioxygen capture by a B-frame-supported bimetallic: structure of [(PMe2Ph)4(O2)Pt2B10H10]Jonathan Bould, Yvonne M. McInnes, Michael J. Carr and John D. Kennedy*The {Pt2} unit of [(PMe2Ph)4Pt2B10H10] 1 reversibly takes up atmospheric dioxygen to give the dioxygen-dimetallaborane complex [(PMe2Ph)4(O2)Pt2B10H10] 2; the resulting {Pt2}-{O2} binding mode is fluxional.
DRIFTS Reactor Mass spectrometer FTIR	<ul> <li>Synchronous, time resolved, diffuse reflectance FT-IR, energy dispersive EXAFS (EDE) and mass spectrometric investigation of the behaviour of Rh catalysts during NO reduction by CO</li> <li>Mark A. Newton*, Bhrat Jyoti, Andrew J. Dent, Steven G. Fiddy and John Evans*</li> <li>Synchronous, time resolved, infra-red, XAFS, and mass spectroscopies are simultaneously applied <i>in situ</i> to the investigation of the dynamic behaviour of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts during NO reduction by CO; NO conversion, and its kinetic character are closely correlated to the conversion of Rh(1) (predominantly Rh<sup>1</sup>(CO)<sub>2</sub>) to Rh(0).</li> </ul>
	Non-interpenetrating honeycomb-like 2D [6,3] network built by a novel trigonal metalloligand Kyoung-Tae Youm, Seong Huh, Young Jun Park, Sangwoo Park, Moon-Gun Choi and Moo-Jin Jun* Novel silver trigonal metalloligands are interlinked through linear linkers to result in a large non-interpenetrating honeycomb-like 2D [6,3] network lattice.
$\begin{array}{c} 2386 \\ \hline \\ $	Photochemical regulation of the activity of an endonuclease BamHI using an azobenzene moiety incorporated site-selectively into the dimer interface Koji Nakayama, Masayuki Endo and Tetsuro Majima* An endonuclease BamHI possessing phenylazophenylalanine (azoAla) was designed and synthesized. When azoAla was incorporated site- selectively into the dimer interface at the 132 position, the <i>trans</i> -form of azoAla suppressed the activity. After photoirradiation for generation of the <i>cis</i> -isomer, the azoAla-BamHI recovered the activity whose level was purposely controlled by the photoirradiation time.



2390

239

D' L

HH

quinone

pool

reaction

center

D' D' D

#### COMMUNICATIONS

# Synthesis of long Poly(dG) Poly(dC) DNA using enzymatic reaction

Shin-ichi Tanaka, Masateru Taniguchi, Susumu Uchiyama, Kiichi Fukui and Tomoji Kawai\*

Non-defect Poly(dG)·Poly(dC) of 500 bp (170 nm) has been synthesized by using enzymatic reactions and was characterized by its UV spectrum, showing that conjugated  $\pi$ -electrons between base pairs are spread over the DNA molecule suggesting the absence of structural defects.

## Octahedral metal clusters as building units in a neutral layered honeycomb network, [Zn(en)]<sub>2</sub>[Nb<sub>6</sub>Cl<sub>12</sub>(CN)<sub>6</sub>]

Bangbo Yan, Cynthia S. Day and Abdessadek Lachgar\*

A novel organic–inorganic cluster compound with a double-layered honeycomb structure was successfully synthesized through the self-assembly of cyano-chloride octahedral niobium clusters and Zn(en) coordination complexes.

# A simulation of key aspects of a primary process in natural photosynthesis by a Langmuir-Blodgett film assembly

Masaru Sakomura\*, Kazuyoshi Ueda and Masamichi Fujihira

An advanced biomimetic model designed to replicate key aspects (antenna, reaction center, and quinone pool) of a primary process in natural photosynthesis is reported.

#### Cobalt-mediated cyclotrimerisation of bis-alkynes and cyanamides

Llorente V. R. Boñaga, Han-Cheng Zhang and Bruce E. Maryanoff\*

CpCo(CO)<sub>2</sub>-mediated cyclotrimerisation of bis-alkynes and cyanamides is effective for the synthesis of multisubstituted 2-aminopyridines, including macrocyclic products.



#### Novel Mg<sub>2</sub>SiO<sub>4</sub> structures

R. L. D. Whitby\*, K. S. Brigatti, I. A. Kinloch, D. P. Randall and T. Maekawa

The formation of novel Forsterite ( $Mg_2SiO_4$ ) structures shows that they are comprised of a myriad of tightly packed leaf-like layers, each exhibiting a high aspect ratio from the nanometer to the micrometer scale.

i v

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D

antenna

pigmen

1,4-dioxane, reflux ~ 20 h R = H, alkyl, aryl



Potential, V(SHE)

Potential, V(SHE)



 $Rh_{2}(II) = (M)-Rh_{2}(O_{2}CCF_{3})_{2}[(p-Me_{3}Si-C_{6}H_{3})P(p-Me_{3}Si-C_{6}H_{4})_{2}]_{2}$ 

COMMUNICATION

Enantio- and diastereocontrol in intermolecular cyclopropanation reaction of styrene catalyzed by dirhodium(II) complexes with bulky *ortho*-metalated aryl phosphines

Francisco Estevan, Pascual Lahuerta\*, Julio Lloret, Mercedes Sanaú, M. Angeles Ubeda\* and Jaume Vila

Steric factors greatly improve the diastereoselectivity of dirhodium(II) compounds with *ortho*-metalated phosphines in the cyclopropanation reaction of styrene.





state isomerisation

Self-organisation in P-substituted guanidines leading to solution-

Joanna Grundy, Martyn P. Coles\*, Anthony G. Avent and Peter B. Hitchcock

The amidine unit within *P*,*P*-diphenyl-*N*,*N*'-dialkylchalcogenophosphinylformamidines, Ph<sub>2</sub>P(E)C{NR'}{NHR'} [E = S, Se; R' = <sup>i</sup>Pr, Cy], self-organises through N*H*···E interactions which promote formation of the  $Z_{syn}$  isomer in solution.

#### Intein-mediated purification of a recombinantly expressed peptide

John A. Pezza, Karen N. Allen and Dean R. Tolan\*

A 26 amino acid peptide has successfully been purified *via* recombinant expression as an intein fusion protein accompanied by cleavage without the need for any exogenous proteases or cofactors, thus offering a practical, inexpensive approach to produce isotopically labelled peptides.

# Facile fabrication and characterization of hierarchically porous calcium carbonate microspheres

Jiaguo Yu, Jimmy C. Yu\*, Lizhi Zhang, Xinchen Wang and Ling Wu

Higher-order porous calcite microspheres exhibiting high specific surface areas, unusual morphologies and textures were produced by a simple precipitation reaction of  $CaCO_3$  in the presence of a crystal modifier.

#### Development of highly active and selective novel Pd based acetoxylation catalysts and prevention of catalyst deactivation by Bi modification

A. Benhmid, K. V. Narayana, A. Martin\*, B. Lücke and M.-M. Pohl

Remarkably high selectivity of benzyl acetate (*ca.* 95%) at higher conversion of toluene (*ca.* 70%) was achieved for the first time through vapour phase acetoxylation of toluene over Pd–Sb–Bi/TiO<sub>2</sub> novel catalysts and the method successfully overcomes the problem of catalyst deactivation.











Bond energy, aromatic stabilization energy and strain in IPR fullerenes

Michał K. Cyrański\*, Siân T. Howard and Michał L. Chodkiewicz

The cyclic  $\pi$  electron delocalisation does not stabilize the fullerene C<sub>60</sub> formation and 5-6 and 6-6 types of CC bonds have near identical bond stretch potentials.

#### Thin Pd membrane prepared on macroporous stainless steel tube filter by an in-situ multi-dimensional plating mechanism

Jianhua Tong\* and Yasuyuki Matsumura

Thin dense Pd membrane was directly prepared on a macroporous stainless steel tube filter by a multi-dimensional plating mechanism shown in route (a).



# 2464





reflux 17 hours



Kristof T. J. Loones, Bert U. W. Maes\*, Roger A. Dommisse and Guy L. F. Lemière

A new strategy for the synthesis of the title compounds via a regioand chemoselective one-pot inter- and intramolecular Buchwald-Hartwig amination of 2-chloro-3-iodopyridine with aminoazines and -diazines is reported.



Soumendra Rana, Bijoy Kundu and Susheel Durani\*

A canonical planar  $\beta$ -hairpin peptide stereochemically reengineered to a semicircular bracelet type motif by L-to-D stereochemical inversion in two pairs of its cross-strand neighbor residues displays protein-like ordering including two-state behavior in H<sub>2</sub>O, which is unusual for a small peptide of this size.

#### Synthesis and properties of rhenium tricarbonyl complex bearing N-fused tetraphenylporphyrin ligand

Motoki Toganoh, Tomoya Ishizuka and Hiroyuki Furuta\*

An N-fused porphyrin rhenium complex was synthesized by the thermal reaction of an N-confused porphyrin with  $Re_2(CO)_{10}$  and its structure was determined by X-ray crystallographic analysis.



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3a

2 mol% of catalyst 3

Et<sub>2</sub>Zn -



Aziridine sulfides and disulfides as catalysts for the enantioselective addition of diethylzinc to aldehydes

Antonio L. Braga\*, Priscila Milani, Marcio W. Paixão, Gilson Zeni, Oscar E. D. Rodrigues and Elenilson F. Alves

Chiral aziridine sulfides and disulfides were synthesized from readily available and inexpensive *R*-cysteine by a Mitsunobu reaction; their application in the addition of diethylzinc to aldehydes provides secondary alcohols with up to 99% *ee* and *S*-configuration.





#### Enhanced photoluminescence from poly(phenylene vinylene) : dendrimer polyelectrolyte assemblies in solution

Gabriel A. Montaño, Andrew M. Dattelbaum, Hsing-Lin Wang and Andrew P. Shreve\*

Poly(2,5-methoxy-propyloxy sulfonate phenylene vinylene) (MPS-PPV) and DAB-Am-16, a generation 3.0 polypropylenimine hexadecamine dendrimer (DAB), are shown to form a tunable photoresponsive polyelectrolyte assembly in aqueous solution with an enhanced emission signal of up to 18-times that of MPS-PPV alone.

#### Chiral discrimination within disordered adlayers on metal surfaces

Andrew Mulligan, Ian Lane, Gilles B. D. Rousseau, Lutz Hecht, Shona M. Johnston, David Lennon and Malcolm Kadodwala\*

Using a novel non-linear optical technique enantiomeric excess within a translationally disordered overlayer on a metal surface has been monitored for the first time.





#### Enantioselective synthesis of allenyl carbinols by the CBS reduction in nitroethane: dramatic solvent effect for reactivity and enantioselectivity

Chan-Mo Yu\*, Chunsan Kim and Jae-Hong Kweon

Enantioselective synthesis of allenyl carbinols 2 and 4 from the corresponding allenyl ketones 1 and 3, or  $\alpha,\beta$ -ynones 6 by the CBS reduction in nitroethane has been accomplished in high levels of enantioselectivity.

## Mesostructured SBA-3 silica containing Reichardt's dye as an optical ammonia sensor

Barbara Onida, Luisa Borello, Sonia Fiorilli, Barbara Bonelli, C. Otero Areán and Edoardo Garrone

An optical sensing system reversibly responding to gaseous ammonia has been prepared incorporating Reichardt's dye in mesostructured silica/CTABr composite. The response time is a few seconds, the intensity is proportional to ammonia partial pressure and the sensitivity can be tailored by changing the dye content in the mesophase.





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