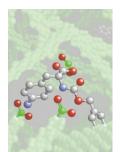
# Chem Comm

CHEMICAL COMMUNICATIONS • www.rsc.org/chemcomm



## Cover

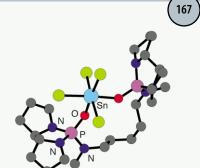
By the imprinting of a molecular memory in synthetic polymers, these can be tailored to bind selectively to defined molecular targets, which makes these materials useful as artificial antibodies and receptors.



Chemical biology articles published in this journal also appear in the Chemical Biology Virtual Journal: www.rsc.org/chembiol

# contents

## **FOCUS ARTICLE**



## Catalytic enantioselective allylation with chiral Lewis bases

Scott E. Denmark\* and Jiping Fu

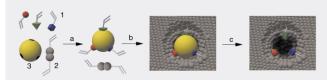
The advent of chiral Lewis base-promoted allylation of aldehydes has opened a new direction in the catalytic enantioselective construction of homoallylic alcohols. This short review outlines the conceptual framework for the creation of this new process and the interplay of mechanistic investigations and synthetic studies that have conspired to produce a useful new reaction. The current state-of-the-art in catalyst design and application of the reaction in synthesis are briefly illustrated.

## FEATURE ARTICLE



## Imprinted polymers—Tailor-made mimics of antibodies and receptors

Karsten Haupt



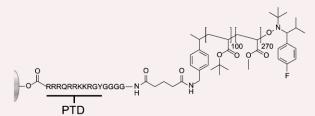
The technique of molecular imprinting allows the formation of specific recognition sites in synthetic polymers through the use of molecular templates.

## COMMUNICATIONS

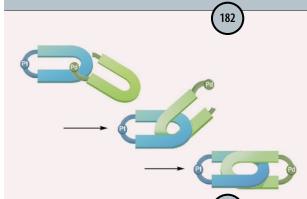


Peptide-polymer bioconjugates: hybrid block copolymers generated *via* living radical polymerizations from resin-supported peptides

Matthew L. Becker, Jianquan Liu and Karen L. Wooley\*



A novel strategy for the preparation of peptidic-synthetic bioconjugate block copolymers is based upon sequential condensation and living radical addition polymerizations, each performed upon a solid support.



## Selective cross-catenation of Pd(II) and Pt(II) coordination rings

Akiko Hori, Hisashi Kataoka, Takashi Okano, Shigeru Sakamoto, Kentaro Yamaguchi and Makoto Fujita\*

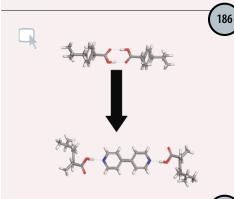
Preformed  $Pd(\Pi)$ - and  $Pt(\Pi)$ -linked rings undergo rapid and highly selective cross-catenation. The trick of the cross-catenation lies behind the labile nature of the Pd–N bond that dissociates rapidly while the Pt–N bond, being inert, does not.

## (1)

# A methylene-bis-triazolium ligand precursor in an unusual rearrangement of norbornadiene to nortricyclyl

Jose A. Mata, Eduardo Peris, Christopher Incarvito and Robert H. Crabtree\*

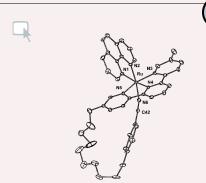
Reaction of [(nbd)RhCl]<sub>2</sub> with a chelating methylene-bis-[1,2,4]-triazolium salt gives a nortricyclyl Rh complex with three fac C-bound ligands.



## Crystal engineering of the composition of pharmaceutical phases

R. D. Bailey Walsh, M. W. Bradner, S. Fleischman, L. A. Morales, B. Moulton, N. Rodríguez-Hornedo and M. J. Zaworotko\*

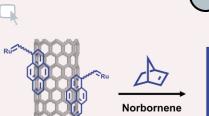
The carboxylic acid-pyridine supramolecular heterosynthon can be exploited to predictably generate binary crystalline phases involving *rac*-ibuprofen, *rac*-flurbiprofen or aspirin.



# Photochemical and thermal ligand exchange in a ruthenium ( ${\rm II}$ ) complex based on a scorpionate terpyridine ligand

Emma R. Schofield, Jean-Paul Collin,\* Nathalie Gruber and Jean-Pierre Sauvage\*

A ruthenium(II) complex containing a 1,10-phenanthroline unit and a terpyridine fragment covalently linked to a benzonitrile group has been synthesised. Coordination and decoordination of the benzonitrile group can be induced thermally and photochemically respectively, in an acetone—water mixture.



Pyrene-anchored ROMP initiator on SWNT



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Poly(norbornene)coated SWNT

Ring opening metathesis polymerization on non-covalently functionalized single-walled carbon nanotubes

Fernando J. Gómez, Robert J. Chen, Dunwei Wang, Robert M. Waymouth\* and Hongjie Dai\*

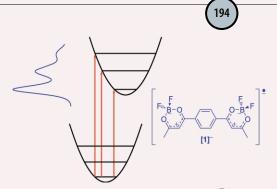
Ring opening metathesis polymerization (ROMP) of norhornene

Ring opening metathesis polymerization (ROMP) of norbornene directly off the surface of single-walled carbon nanotubes has been enabled through the use of a pyrene-linked Ru initiator. The pyrenyl group serves as a non-covalent anchor that binds selectively to the nanotube surface.

# Polymer-supported formamides as reusable organocatalysts for allylation of aldehydes with allyltrichlorosilane

Chikako Ogawa, Masaharu Sugiura and Shū Kobayashi\*

New types of polymer-supported formamides have been synthesized from chloromethylated resins and formamides. They work well as organocatalysts in the allylation of aldehydes with allyltrichlorosilane to afford homoallylic alcohols in high yields.



## An anionic organic mixed-valence system with a remarkably wellresolved vibrational structure in its intervalence band

Chad Risko, Stephen Barlow,\* Veaceslav Coropceanu, Marcus Halik, Jean-Luc Brédas\* and Seth R. Marder\*

A bis(dioxaborine) radical anion is one of the most strongly delocalised examples of organic mixed-valence anions; details of the vibrations coupled to the intervalence electron transfer were obtained directly from the intervalence band.

# Studies towards the total synthesis of an epoxy isoprostane phospholipid, a potent activator of endothelial cells

Michael E. Jung,\* Annika Kers, Ganesamoorthy Subbanagounder and Judith A. Berliner

Studies toward the total synthesis of an epoxy isoprostane, namely the preparation of compound **9** which is an analogue of the elimination product **7** of the naturally occurring epoxy isoprostane **4**, are reported.

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## Further reactions of phenyldimethylsilyllithium with N,N-dimethylamides

Ian Fleming\* and Matthew G. Russell

Phenyldimethylsilylithium reacts with *N*,*N*-dimethylamides to give a tetrahedral intermediate, which breaks down to a carbene or carbenoid susceptible to nucleophilic attack, and giving a variety of outcomes, depending upon the nature of the nucleophile and the structure of the substrate.

# 200

## Reactions of phenyldimethylsilyllithium with $\beta$ -N,N-dimethylaminoenones

Ian Fleming,\* Elena Marangon, Chiara Roni, Matthew G. Russell and Sandra Taliansky Chamudis

Phenyldimethylsilyllithium reacts with ethyl  $\beta$ -N,N-dimethylaminoacrylate by conjugate addition. Treatment with methyl iodide before the aqueous quench anomalously causes elimination of the dimethylamino group to give ethyl  $\beta$ -dimethyl(phenyl)-silylacrylate rather than the expected product of enolate methylation.



## The reaction of phenyldimethylsilyllithium with N-phenylpyrrolidone

Marina Buswell and Ian Fleming\*

Phenyldimethylsilyllithium reacts with *N*-phenylpyrrolidone to give the known tetracyclic amines **6** and **7**, but the mechanism of this reaction is not likely to be the same as that suggested for earlier syntheses, since various by-products indicate that it follows a path involving a carbene or carbenoid being attacked by the enolate of the lactam.



## A practical access to acyl radicals from acyl hydrazides

Sophie Bath, Nieves M. Laso, Heraclio Lopez-Ruiz, Béatrice Quiclet-Sire and Samir Z. Zard\*

$$\begin{array}{c|cccc} O & CPh_3 & PhSeO_2H & O \\ \hline NH & PhSeSePh & \\ \hline Toluene & \\ \Delta & & \\ \end{array}$$

Various acyl radicals can be generated from the corresponding acyl triphenylmethyldiazo derivatives, produced by *in situ* oxidation of hydrazide precursors with phenylseleninic acid.

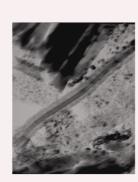




## Electrochemical synthesis of novel polypyrrole microstructures

Liangti Qu and Gaoquan Shi\*

Polypyrrole microstructures with unusual morphologies have been synthesized by direct electrochemical oxidation of pyrrole in  $\beta$ -naphthalenesulfonic acid aqueous solution.



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## A novel nanostructure of nickel nanotubes encapsulated in carbon nanotubes

Jianchun Bao, Keyu Wang, Zheng Xu,\* Hong Zhang and Zuhong Lu

A novel nanostructure of Ni nanotubes encapsulated in carbon nanotubes has been obtained via the pyrolysis of  $C_2H_2$  on an array of Ni nanotubes in an alumina membrane support and a possible mechanism has been proposed.





# A new thioether functionalized organic–inorganic mesoporous composite as a highly selective and capacious $Hg^{2+}$ adsorbent

Lingxia Zhang, Wenhua Zhang, Jianlin Shi,\* Zile Hua, Yongsheng Li and Jina Yan

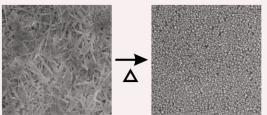
A new thioether functionalized ordered mesoporous adsorbent with high  ${\rm Hg}^{2^+}$  selectivity and capacity (up to 2700 mg Hg  ${\rm g}^{-1}$ ; Hg/S > 2) was synthesized for the first time by a one-step co-condensation method.



Development of silver film *via* thermal decomposition of layered silver alkanecarboxylates for surface-enhanced Raman spectroscopy

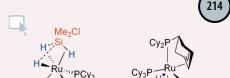
Seung Joon Lee and Kwan Kim\*

Optically tunable SERS-active Ag films can be reproducibly fabricated on glass by the thermal decomposition of layered silver alkanecarboxylates.



CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOAg

**SERS-Active Ag Film** 



# Mechanistic studies on ethylene silylation with chlorosilanes catalysed by ruthenium complexes

Sébastien Lachaize, Sylviane Sabo-Etienne,\* Bruno Donnadieu and Bruno Chaudret

σ-Chlorosilane and chlorosilyl complexes are involved in the efficient catalytic formation of chlorovinylsilanes, using the bis(dihydrogen) complex  $RuH_2(\eta^2 - H_2)_2(PCy_3)_2$  as catalyst precursor.

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# Cationic arylation through photo(sensitised) decomposition of diazonium salts. Chemoselectivity of triplet phenyl cations

Silvia Milanesi, Maurizio Fagnoni\* and Angelo Albini\*

Photosensitised decomposition of diazonium salts gives triplet aryl cations which add to  $\pi$  nucleophiles such as benzene or allyltrimethylsilane and yield the corresponding arylated derivatives.



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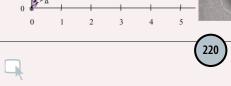
Product Yield (%)

# Equilibrium conversion — 100

# Knoevenagel condensation reaction in a membrane microreactor

Sau Man Lai, Rosa Martin-Aranda and King Lun Yeung\*

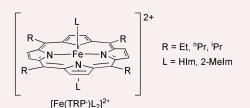
Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was conducted in a microreactor using Cs-exchanged NaX faujasite zeolite as catalyst. Supra-equilibrium conversion, higher product purity and better catalyst performance were achieved when a membrane microreactor was used.

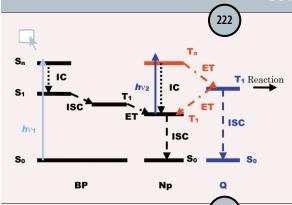


# Effects of a nonplanar porphyrin rings on the spin-spin interactions in low-spin ferric porphyrin radical cations

Takahisa Ikeue, Yoshiki Ohgo and Mikio Nakamura\*

Low-spin ferric porphyrin radical cations with  $S_4$  ruffled porphyrin rings show antiferromagnetic coupling which is interpreted in terms of the interaction between porphyrin  $a_{2u}$  and iron  $d_{xy}$  orbitals.





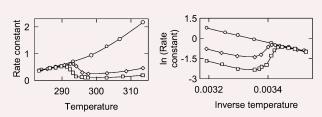
## Naphthalene in the higher triplet excited state

Xichen Cai, Michihiro Hara, Kiyohiko Kawai, Sachiko Tojo and Tetsuro Majima\*

Naphthalene in the higher triplet excited state  $Np(T_n)$  was generated using two-colour two-laser photolysis and the lifetime of  $Np(T_n)$  was estimated to be 4.5 ps from the triplet energy quenching.

## **Heat inhibited reactions**

D. Martin Davies\* and Estelle L. Stringer



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The reaction of aqueous hydrogen peroxide and a hydrophobic ester (circles) in the presence of millimolar amounts of a poly(ethylene oxide)—poly(propylene oxide)—poly(ethylene oxide) triblock copolymer (diamonds and squares) shows a very unusual temperature dependence.

# Ph N 2n N Ph

# Synthesis and photophysics of a linear non-covalently linked porphyrin-fullerene dyad

Stephen R. Wilson,\* Shaun MacMahon, Fatma T. Tat, Peter D. Jarowski and David I. Schuster\*

The synthesis and characterization of a new pyridinofullerene ligand **1** capable of forming axially symmetric complexes with ZnTPP is reported. Molecular modelling studies, <sup>1</sup>H NMR, UV–Vis spectroscopy and fluorescence quenching data support formation of a strong complex between the new ligand and ZnTPP.

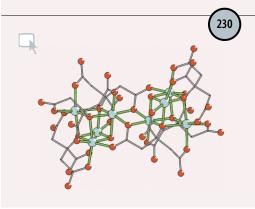


# The synthesis of a single enantiomer of a major $\alpha$ -mycolic acid of *Mycobacterium tuberculosis*

Juma'a R. Al Dulayymi, Mark S. Baird\* and Evan Roberts

$$CH_3(CH_2)_{19}^{\text{OAc}} \overset{OAc}{\underset{(CH_2)_{14}}{}} COOMe$$

We report a synthesis of a single enantiomer of a dicyclopropane containing mycolic acid from *Mycobacterium tuberculosis*; this method can be simply varied to modify the chain lengths or the absolute stereochemistry of either cyclopropane.



# Increasing the crystallisation temperature to access new spin clusters: conversion of $[Ni_8(cit)_6(OH)_2(H_2O)_2]^{10-}$ to $[Ni_8(cit)_6(OH)_2]^{10-}$

Mark Murrie,\* Daniel Biner, Helen Stœckli-Evans and Hans U. Güdel

A new synthetic route to nickel(II) spin clusters has been developed. We show how the temperature of crystallisation can be used to produce changes in both structure and magnetic properties. The double-cubane  $[Ni_8(cit)_6(OH)_2]^{10-}$  (H<sub>4</sub>cit = citric acid) isolated at 50 °C, possesses an S=4 spin ground state.

3.0 equivalents for n = 2

Effect of pressure and temperature upon tin alkoxide-promoted ringopening polymerisation of ε-caprolactone in supercritical carbon dioxide

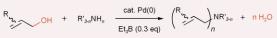
Fabrice Stassin\* and Robert Jérôme

Ring-opening polymerisation of ε-caprolactone in supercritical carbon dioxide is slowed down by carbonation of tin alkoxide initiator.



## Pd·Et<sub>3</sub>B-catalyzed alkylation of amines with allylic alcohols

Masanari Kimura,\* Makoto Futamata, Kazufumi Shibata and Yoshinao Tamaru\*



1.2 equivalents for n = 1

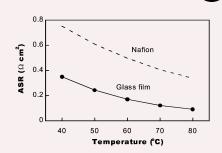
A combination of catalytic amounts of Pd(0) and Et<sub>3</sub>B (0.3 eq.) promotes allylic alkylation of primary and secondary aromatic and aliphatic amines by the direct use of allylic alcohols, providing tertiary amines in excellent yields under mild conditions.



## Ordered mesoporous phosphosilicate glass electrolyte film with low area specific resistivity

Haibin Li and Masayuki Nogami\*

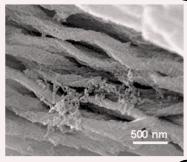
Ordered mesoporous phosphosilicate glass electrolyte film exhibiting low area specific resistivity (ASR) compared with those of Nafion has been synthesized using non-ionic surfactant as the structure-directing agent.



## Controlled formation of biosilica structures in vitro

Rajesh R. Naik, Patrick W. Whitlock, Francisco Rodriguez, Lawrence L. Brott, Diana D. Glawe, Stephen J. Clarson and Morley O. Stone\*

Herein we describe the controlled formation of biosilica structures by manipulation of the physical reaction environment; a variety of silica structures were obtained by controlling the biosilification reaction environment.

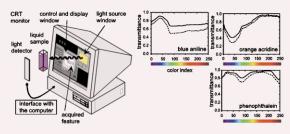


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## Computer screen as a programmable light source for visible absorption characterization of (bio)chemical assays

Daniel Filippini,\* Samuel P. S. Svensson and Ingemar Lundström

Visible absorption features suitable for colour recognition and micro-plate reading of a standard bioassay are performed by the combination of a computer screen used as a programmable light source and a web camera as detector.





# Preparation of a mesoporous silicon boron nitride *via* a non-aqueous sol-gel route

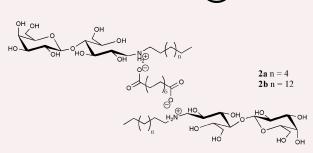
Fei Cheng, Berangere Toury, Frédéric Lefebvre and John S. Bradley\*

A mesoporous silicon boron nitride with high surface area and narrow pore size distribution is obtained by pyrolysis of a silicon boron imide based gel prepared from catalytic ammonolysis of tris[tris(dimethylamino)silylamino]boron.

$$B([NHSi(NMe_2)]_3 \xrightarrow{CF_3SO_3H} \\ NH_3, 50 °C \\ Si_3B(NH)_x(NH_2)_y(NMe_2)_z \text{ gel} \xrightarrow{Pyrolysis} \\ NH_3, flow, 1000 °C$$

Mesorporous Si<sub>3</sub>N<sub>4</sub> / BN





# Correlation between structure, aggregation behaviour and cellular toxicity of anti-HIV catanionic analogues of galactosylceramide

Muriel Blanzat,\* Emile Perez, Isabelle Rico-Lattes, Armand Lattes and Annette Gulik

The self-association process of catanionic analogues of galactosylceramide and in particular the arrangement of their hydrophobic part seems to play a key role in their cellular toxicity.

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# Sulfonic acid-functionalized silica through quantitative oxidation of thiol groups

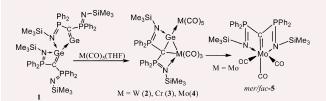
E. Cano-Serrano, J. M. Campos-Martin and J. L. G. Fierro\*

We have developed a simple and effective procedure to incorporate sulfonic groups on silica *via* monolayer thiol group functionalization which quantitatively renders  $-SO_3H$  groups.



# A novel synthesis of metallogermacyclopropane and molybdenum bis(iminophosphorano)carbene complexes from bisgermavinylidene

Wing-Por Leung,\* Cheuk-Wai So, Jin-Zhi Wang and Thomas C. W. Mak



Bisgermavinylidene  $[(Me_3SiN=PPh_2)_2C=Ge\longrightarrow Ge=C(PPh_2=NSiMe_3)_2]$  (1) reacted with  $M(CO)_5(THF)$  (M=Cr, W, Mo) affording metallagermacyclopropane  $[(Me_3SiN=PPh_2)_2CGeM(CO)_3\{M(CO)_5\}]$  [M=W (2), Cr (3), Mo (4)]; compound 4 further transformed to the 'pincer' carbene complex  $[(CO)_3Mo\{C(Ph_2P=NSiMe_3)_2\}]$  (5).



## ${\it In~situ}~{\it co-crystallisation~as~a~tool~for~low-temperature~crystal~engineering}$

Andrew D. Bond



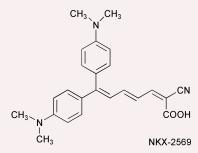
Synthesis and single-crystal X-ray diffraction of a series of low-melting co-crystals of pyrazine and *n*-alkyl carboxylic acids demonstrates *in situ* co-crystallisation as a versatile tool for low-temperature crystal engineering.

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## Novel polyene dyes for highly efficient dye-sensitized solar cells

Kohjiro Hara, Mitsuhiko Kurashige, Shunichiro Ito, Akira Shinpo, Sadaharu Suga, Kazuhiro Sayama and Hironori Arakawa\*

Successful molecular design of novel polyene-dye photosensitizers and their high performance in dye-sensitized nanocrystalline TiO<sub>2</sub> solar cell are reported.



# 254 ON THE STATE OF THE STATE

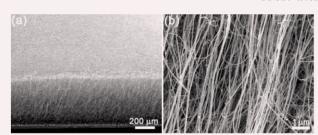
# Novel thymidine-based organogelators and their gelation behaviours

Young Ji Yun, Sun Min Park and Byeang Hyean Kim\*

Novel nucleoside-based organogelators were designed and synthesized. They showed different gelation types in relation to structure and solvent. Their gelation behaviours were studied by SEM, FT-IR, and DSC.

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# Direct synthesis of aligned silicon carbide nanowires from the silicon substrates



Hwa Young Kim, Jeunghee Park\* and Hyunik Yang

Aligned silicon carbide nanowires were synthesized directly from the silicon substrates via a novel catalytic reaction with a methane–hydrogen mixture at 1100 °C, with a mean diameter of 40 nm and length of 500  $\mu$ m.

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## Gas phase transport of gold with gold(III) oxide and carbon monoxide

Elizabeth A. Willneff, Catharina Klanner and Sven L. M. Schroeder\*

The reaction between commercially available gold(III) oxide and carbon monoxide leads to the volatilisation of some gold through an unknown short-lived gas phase intermediate.

5000 Au(111) Au(200)

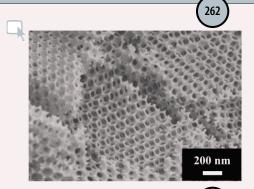
The property of the prop

# A novel stereoselective one-pot conversion of alcohols into alkyl halides mediated by N,N'-diisopropylcarbodiimide

ROH 
$$\frac{\text{Cu(OTf)}_2}{\text{THF}}$$
  $\frac{\text{HN}}{\mu\omega,100^{\circ}}$  RX  $\frac{\text{CH}_3\text{COX}}{5\text{ min}}$  R= primary or secondary X= CI, Br

Stefano Crosignani, Brice Nadal, Zhengning Li and Bruno Linclau\*

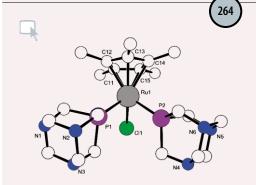
A novel, high yielding, stereoselective conversion of alcohols into alkyl halides has been achieved using very short reaction times through a one-pot, phosphine-free procedure under microwave irradiation.



# In situ cyclodextrin-based homogeneous incorporation of metal (M = Pd, Pt, Ru) nanoparticles into silica with bimodal pore structure

Yong Zhou,\* Shu-Hong Yu, Arne Thomas and Bao-Hang Han

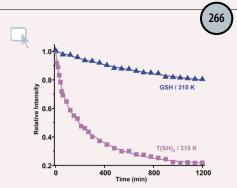
*In situ* cyclodextrin (CD)-based homogeneous incorporation of metal (M = Pd, Pt, Ru) nanoparticles into silica with bimodal pore structure has been realized by utilizing the self-assembly aggregation and inclusion capability of the CDs.



# Synthesis, catalytic properties and biological activity of new water soluble ruthenium cyclopentadienyl PTA complexes $[(C_5R_5)RuCl(PTA)_2]$ (R = H, Me; PTA = 1,3,5-triaza-7-phosphaadamantane)

Dina N. Akbayeva, Luca Gonsalvi, Werner Oberhauser, Maurizio Peruzzini,\* Francesco Vizza,\* Peter Brüggeller, Antonio Romerosa, Gianni Sava and Alberta Bergamo

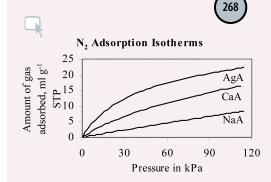
These new water soluble ruthenium complexes were applied to regioselective catalytic hydrogenation of unsaturated ketones in aqueous biphasic conditions and in studies of cytotoxic activity towards adenocarcinoma cells.



# Rapid reduction of pentavalent antimony by trypanothione: potential relevance to antimonial activation

Siucheong Yan, Iris L. K. Wong, Larry M. C. Chow and Hongzhe Sun\*

The dithiol trypanothione can reduce an antiparasitic pentavalent antimony agent to trivalent rapidly. This reduction process is both pH and temperature dependent and trypanothione may therefore play an important role in the activation of the drug.



# Anomalous adsorption of nitrogen and argon in silver exchanged zeolite $\boldsymbol{A}$

Jince Sebastian and Raksh V. Jasra\*

A new adsorbent, zeolite AgA, having  $N_2$  adsorption capacity of 22.3 cc  $g^{-1}$  at 101.3 kPa and  $N_2/O_2$  selectivity of 5 to 14.6 at 303 K is reported. The adsorbent also shows Ar selectivity over  $O_2$ .



# Fast peroxyoxalate chemiluminescence for minimized analytical separation systems

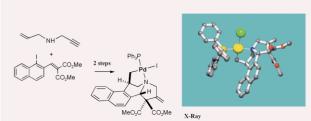
Ji Hoon Lee,\* Jongtae Je, Mark A. Schlautman and Elizabeth R. Carraway

An advanced minimized analytical separation system with OD4MI-CL detection is developed to determine low-level concentrations of luminophores.

(

Unexpected isolation, and structural characterization, of a  $\beta$ -hydrogen-containing  $\sigma$ -alkylpalladium halide complex in the course of an

intramolecular Heck reaction. Synthesis of polycyclic isoquinoline derivatives



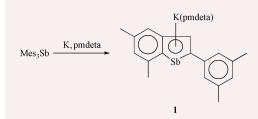
Blandine Clique, Charles-Henry Fabritius, Cédric Couturier, Nuno Monteiro\* and Geneviève Balme\*

The isolation of a stable  $\beta$ -hydrogen-containing R-PdL<sub>n</sub>-X complex (R = alkyl; X = halide) issued from a Heck reaction is reported together with some aspects of its reactivity.

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Synthesis of a stibindolyl anion from trimesitylantimony and potassium

Hans Joachim Breunig,\* Mihaiela Emilia Ghesner and Enno Lork

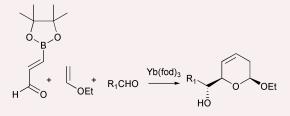


 $2\text{-}(3',5'\text{-Dimethylphenyl})\text{-}5,7\text{-}dimethylstibindolyl potassium-pmdeta}$  (1) (pmdeta = pentamethyldiethylenetriamine) is obtained from trimesitylantimony, potassium and the amine ligand in tetrahydrofuran. Crystals of 1 consist of stacks of (pmdeta)K $^{\scriptscriptstyle +}$  ions and stibindolyl anions with alternating Sb–K and  $\eta^5\text{-SbC}_4\text{-K}$  interactions.

A novel diastereoselective route to  $\alpha$ -hydroxyalkyl dihydropyrans using a hetero Diels-Alder/allylboration sequence

Michael Deligny, François Carreaux,\* Bertrand Carboni, Loïc Toupet and Gilles Dujardin

The development of a new strategy for the synthesis of  $\alpha$ -hydroxyalkyl dihydropyrans is reported. This approach is based on a tandem hetero[4+2]/allylboration reaction.

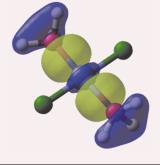


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Factors controlling the relative stabilities of  $\it cis-$  and  $\it trans-[PtX_2L_2]$  isomers: Chatt and Wilkins—50 years on

Jeremy N. Harvey,\* Katie M. Heslop, A. Guy Orpen and Paul G. Pringle

What determines the position of *cis-trans* equilibria in d<sup>8</sup> [MX<sub>2</sub>L<sub>2</sub>] and related compounds? DFT computations are used to explore bonding in these complexes.



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The sixth-generation dendrimer

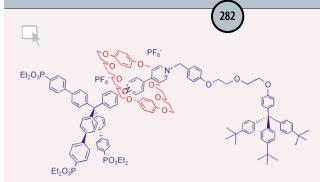
 $C_{6279}H_{10278}P_{378}Pt_{189}Si_{192}$ FW = 139750

 $\bullet = Pt(PEt_3)_2$ 

A divergent approach to the precise synthesis of giant organometallic dendrimers using platinum-acetylides as building blocks

Kiyotaka Onitsuka, Atsushi Shimizu and Shigetoshi Takahashi\*

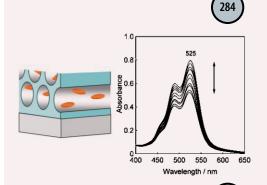
Giant platinum-acetylides dendrimers were precisely synthesized by a divergent method; the sixth generation dendrimer, the diameter of which is larger than 10 nm, has 189 Pt atoms per molecule, and its molecular weight is as high as 139750.



## Synthesis of tripodal [2]rotaxanes: high concentration principle

Kirill Nikitin, Brenda Long and Donald Fitzmaurice\*

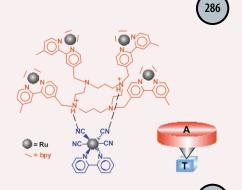
Tripodal[2]rotaxane which can be adsorbed normal to the surface of a metal oxide nanoparticle have been synthesised in high yield under ambient conditions and offer the prospect of the bottom-up assembly in solution of function nanoscale devices.



# Alignment control of a cyanine dye using a mesoporous silica film with uniaxially aligned mesochannels

Ayumu Fukuoka, Hirokatsu Miyata\* and Kazuyuki Kuroda\*

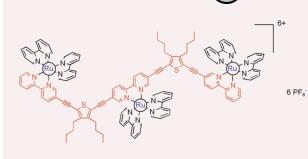
Alignment control of a cyanine dye using a mesoporous silica film with uniaxially aligned mesochannels led to the formation of an optically anisotropic nanocomposite film.



An artificial antenna complex containing four  $Ru(bpy)_3^{2+}$ -type chromophores as light-harvesting components and a  $Ru(bpy)(CN)_4^{2-}$  subunit as the energy trap. A structural motif which resembles the natural photosynthetic systems

Frédérique Loiseau, Giovanni Marzanni, Silvio Quici, Maria Teresa Indelli and Sebastiano Campagna

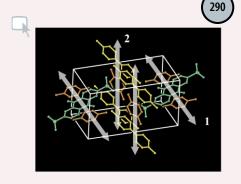
A cyclam scaffold with appended  $\operatorname{Ru}(\operatorname{bpy})_3^{2+}$ -type chromophores and  $\operatorname{Ru}(\operatorname{bpy}(\operatorname{CN})_4^{2-}$  (energy trap) are connected *via* H bonding. There is efficient energy transfer from the cyclam-appended chromophores to the energy trap.



One-pot synthesis of 2,5-diethynyl-3,4-dibutylthiophene substituted multitopic bipyridine ligands: redox and photophysical properties of their ruthenium(II) complexes

Antoinette De Nicola, Yao Liu, Kirk S. Schanze\* and Raymond Ziessel\*

Novel mono-, di, and trinuclear  $Ru(\Pi)$  complexes have been synthesized from the corresponding multitopic ligands. These compounds exhibit well-defined redox and photophysical properties with long excited state lifetimes.



# Unique crystal structures of donor-acceptor complexes: crossed arrangement of two charge-transfer columns

Masatoshi Kidowaki and Nobuyuki Tamaoki\*

A novel donor–acceptor (DA) crossed arrangement of two DA columns (hydroquinone–anthraquinone disulfonate (1) and hydroquinone–methyl viologen (2)) is observed in one of the single crystals.

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