**Cover (far left)**

The first automated oligosaccharide synthesizer based on an ABI Peptide Synthesizer. Depicted against a backdrop of the custom-designed reaction vessel where the assembly of the oligosaccharide occurs at low temperature, are the cartridges containing the building blocks used in the assembly process and the needle used to deliver dissolved building blocks to the instrument (pp. 1115–1121).

**Inside cover (left)**

Formation of new amorphous silica structures, uniquely synthesized by a bioinspired synthetic system (pp. 1122–1123).

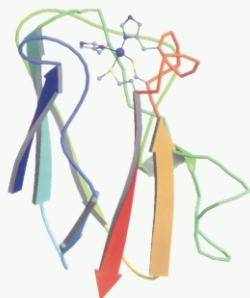
# contents

## FOCUS ARTICLE

1109

### Metallo-enzyme catalysis

R. J. P. Williams



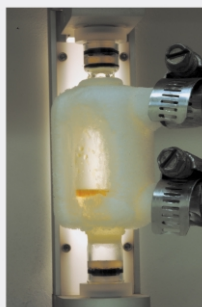
With illustrative examples from copper, iron and zinc proteins, the author shows how the metal ion sites in metallo-enzymes are 'designed' for selective uptake and catalytic activity.

## FEATURE ARTICLE

1115

### Automated carbohydrate synthesis to drive chemical glycomics

Peter H. Seeberger\*



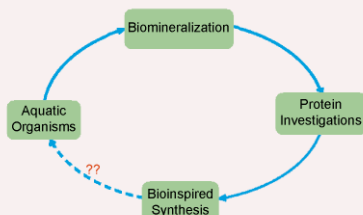
The development of the first automated oligosaccharide synthesizer has already begun to influence biochemistry, biology and medicine as evidenced by the development of a new malaria vaccine candidate.

## COMMUNICATIONS

1122

### Bioinspired synthesis of new silica structures

Siddharth V. Patwardhan, Niloy Mukherjee, Miriam Steinitz-Kannan and Stephen J. Clarson\*



The formation of new amorphous silica structures that were uniquely synthesized by a bioinspired synthetic system is reported.

Chemical Communications  
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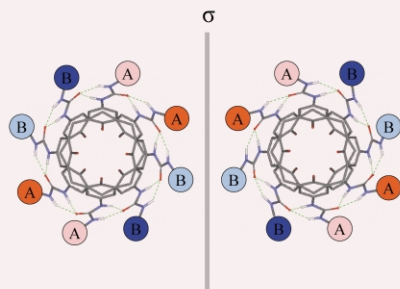
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1124

**Self-assembled dimers with supramolecular chirality**

Anca Pop, Myroslav O. Vysotsky, Mohamed Saadioui and Volker Böhmer\*

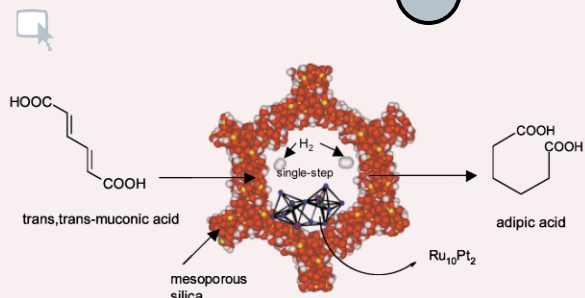


Calix[4]arenes composed of two different phenolic urea units are synthesized; the **supramolecular chirality** of their dimeric capsules is analyzed and demonstrated.

1126

**Bimetallic nanocatalysts for the conversion of muconic acid to adipic acid**

John Meurig Thomas,\* Robert Raja,\* Brian F. G. Johnson,\* Timothy J. O'Connell, Gopinathan Sankar and Tetyana Khimyak

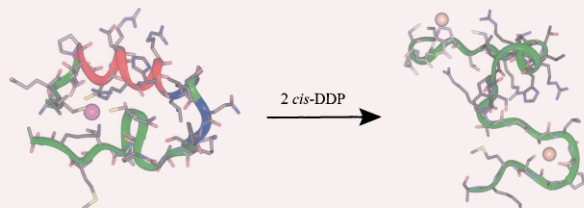


Industrially desirable chemical products such as adipic acid may be produced in good yields and selectivities from plant-crop sources, using highly active bimetallic nanocatalysts anchored onto mesoporous silica.

1128

**Unwinding of DNA polymerases by the antitumor drug, *cis*-diamminedichloroplatinum(II)**

Erika Volckova, Ferenc Evanics, Wei W. Yang and Rathindra N. Bose\*

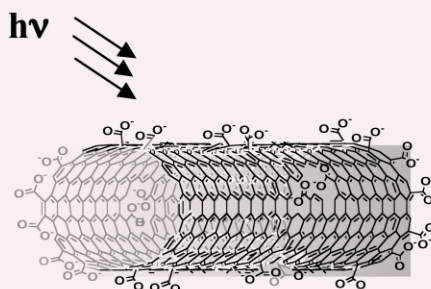


The helix-turn-helix motifs of the DNA binding domains of human polymerase- $\alpha$  and polymerase- $\kappa$  are dramatically perturbed upon binding to cisplatin with concomitant release of zinc.

1130

**First comparative emission assay of single-wall carbon nanotubes—solutions and dispersions**

Dirk M. Guldi,\* Michael Holzinger, Andreas Hirsch,\* Vasilios Georgakilas and Maurizio Prato\*

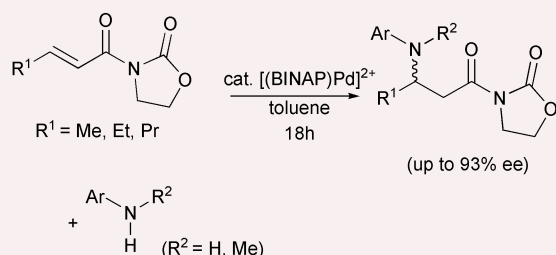


A variety of single-wall carbon nanotube samples were tested in steady-state and time-resolved emission experiments, where it was found that chemical functionalization and different degrees of oxidation affect the emission behavior.

1132

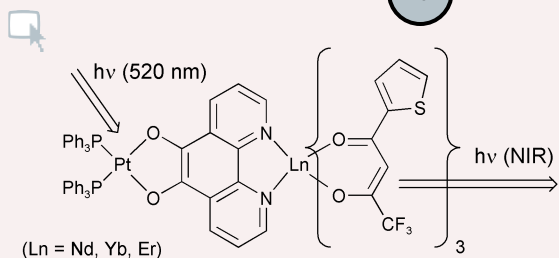
**Dicationic [(BINAP)Pd(solvent)<sub>2</sub>]<sup>2+</sup>[TfO<sup>-</sup>]<sub>2</sub>: enantioselective hydroamination catalyst for alkenoyl-*N*-oxazolidinones**

Kelin Li and King Kuok (Mimi) Hii\*



Addition of primary aromatic amines to  $\alpha$ ,  $\beta$ -unsaturated oxazolidinones has been achieved in high yields and ee's (up to 93%) for the first time.

1134



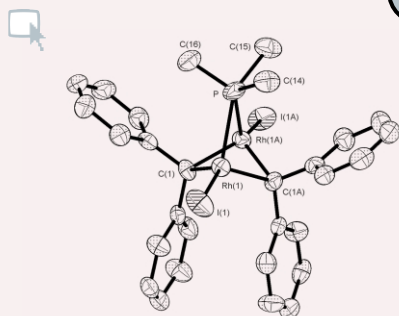
Energy-transfer from a Pt(II) chromophore results in sensitised near-IR emission from covalently-attached Yb, Nd or Er centres.

### Sensitised near-infrared emission from lanthanides using a covalently-attached Pt(II) fragment as an antenna group

Nail M. Shavaleev, Lucy P. Moorcraft, Simon J. A. Pope, Zöe R. Bell, Stephen Faulkner\* and Michael D. Ward\*

In a series of heterodinuclear complexes in which a Pt(PPh<sub>3</sub>)<sub>2</sub>(catecholate) chromophore is covalently linked to a lanthanide tris(diketonate) unit, sensitised near-IR emission from Yb(III), Nd(III) and Er(III) occurs on excitation of the Pt(II) chromophore at 520 nm.

1136

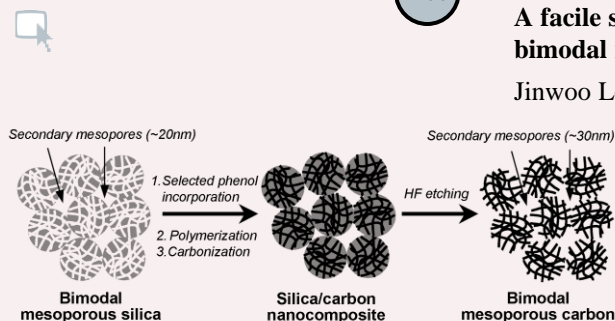


### The truly symmetrical doubly-bridging mode of trimethylphosphine in a dinuclear rhodium complex

Thomas Pechmann, Carsten D. Brandt and Helmut Werner\*

The dinuclear complex [Rh<sub>2</sub>I<sub>2</sub>(μ-CPh<sub>2</sub>)<sub>2</sub>(μ-PMe<sub>3</sub>)] was prepared from the Rh<sub>2</sub>(acac)<sub>2</sub> counterpart and Me<sub>3</sub>SiI and shown crystallographically to contain the PMe<sub>3</sub> ligand in a truly symmetrical bridging position; a new synthetic route to migrate more bulky phosphines such as PPh<sub>3</sub> and P<sup>t</sup>Pr<sub>3</sub> from a terminal into a doubly-bridging site is also described.

1138

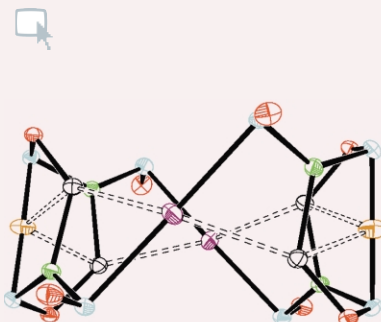


### A facile synthesis of bimodal mesoporous silica and its replication for bimodal mesoporous carbon

Jinwoo Lee, Jaeyun Kim and Taeghwan Hyeon\*

Bimodal mesoporous silica material composed of 30 nm sized nanoparticles with 3.5 nm sized mesopores was synthesized. Using the bimodal mesoporous silica as a template, bimodal mesoporous carbon was synthesized.

1140



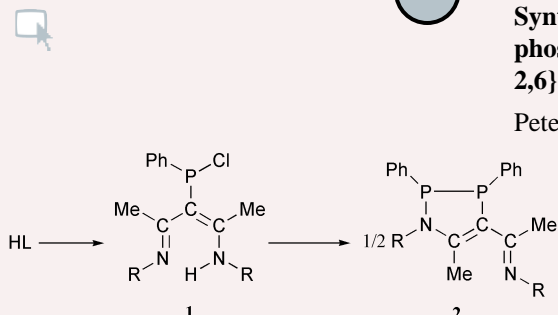
### Synthesis of the mixed lithium-potassium-(bis)magnesium N-metallated/N, C-dimetallated amide [Li<sub>2</sub>K<sub>2</sub>Mg<sub>4</sub>{Bu<sup>t</sup>(Me<sub>3</sub>Si)N}<sub>4</sub>{Bu<sup>t</sup>[Me<sub>2</sub>(H<sub>2</sub>C)Si]N<sub>4</sub>]: an inverse crown molecule with an atomless cavity

- Carbon
- Silicon
- Nitrogen
- Lithium
- Magnesium
- Potassium

Glenn C. Forbes, Fiona R. Kenley, Alan R. Kennedy, Robert E. Mulvey,\* Charles T. O'Hara and John A. Parkinson

Introducing a third metal variable into a synergic amide mixture results in a novel new structural arrangement.

1142

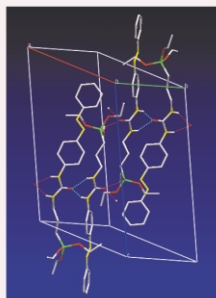


### Synthesis, structure and reductive dechlorination of the C-centred phosphorus(III) β-diketimate PCl(Ph)L [L = C{C(Me)NC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6}{C(Me)NHC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup>-2,6}]

Peter B. Hitchcock, Michael F. Lappert\* and Jacek E. Nycz

Treatment of the β-diketimine HL with successively LiBu<sup>n</sup> and PCl<sub>2</sub>Ph gave the first C-centred monodentate β-diketimate PCl(Ph)L; with C<sub>8</sub>K it underwent reductive dechlorination yielding a novel N-P<sup>III</sup>-P<sup>III</sup>-C=C heterocycle.

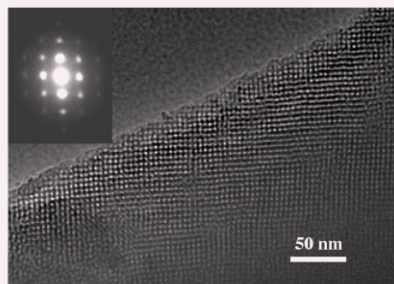
1144

**Synthesis and crystallographic structure of a novel photoresponsive azobenzene-containing organosilane**

Nanguo Liu, Darren R. Dunphy, Mark A. Rodriguez, Sarany Singer and Jeffrey Brinker\*

A novel photoresponsive azobenzene-containing organosilane (4-(3-triethoxysilylpropyl-ureido)azobenzene) was synthesized *via* an isocyanato-amino coupling reaction and its crystal structure was determined by X-ray crystallography.

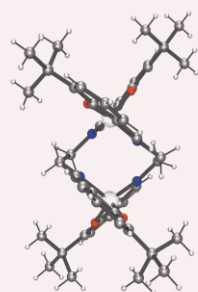
1146

**Synthesis and characterization of highly ordered functional mesoporous silica thin films with positively chargeable –NH<sub>2</sub> groups**

Nanguo Liu, Roger A. Assink, Bernd Smarsly and C. Jeffrey Brinker\*

Highly ordered mesoporous hybrid silica thin films with covalently bonded, positively chargeable –NH<sub>2</sub> terminal groups, useful for mimicking biological ion channels, were synthesized by evaporation induced self-assembly.

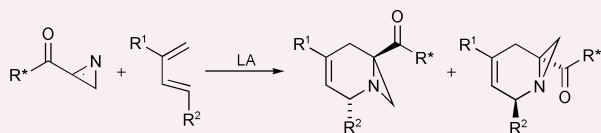
1148

**First helical zinc(II) complex with a salen ligand**

Shin Mizukami,\* Hirohiko Houjou, Yoshinobu Nagawa and Masatoshi Kanesato\*

The structure of a tetra-coordinated zinc(II) complex with a salen ligand was determined for the first time; unexpectedly, the complex was an interesting 2:2 metal-to-ligand complex.

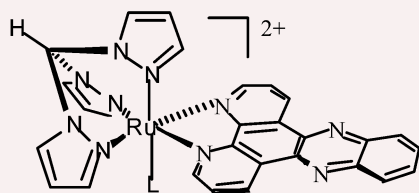
1150

**Stereoselective aza-Diels–Alder reactions with 2*H*-azirines as dienophiles furnishing highly functionalized tetrahydropyridines**

Åsa Sjöholm Timén, Andreas Fischer and Peter Somfai\*

Stereoselective Diels–Alder reactions of various dienes and 2*H*-azirines with a chiral auxiliary gave in the presence of Lewis acids products with up to 97 % de.

1152



L = pyridine, MeCN

**A ruthenium dipyridophenazine complex that binds preferentially to GC sequences**

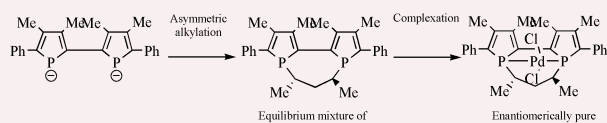
Clive Metcalfe, Harry Adams, Ihtshamul Haq\* and Jim A. Thomas\*

The synthesis of achiral complexes incorporating the [Ru<sup>II</sup>(dppz)] moiety is outlined. Luminescence and calorimetry studies indicate that they bind to DNA with high affinity. Uniquely for any dppz complexes, one of the new complexes shows almost an order of magnitude binding preference for GC rich sequences.

1154

**Chirality control in 2,2'-biphosphole ligand leading to enantiopure Pd complex**

Carmen Ortega, Maryse Gouygou\* and Jean-Claude Daran\*

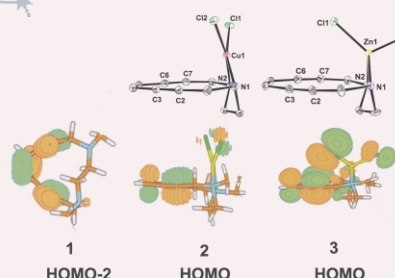


A new enantiomerically pure 2,2'-biphosphole complex has been synthesized *via* a process involving chirality control of the 2,2'-biphosphole ligand.

1156

**Isolation of electronic from geometric contributions to Bergman cyclization of metallocenediynes**

Sibaprasad Bhattacharyya, Aurora E. Clark, Maren Pink and Jeffrey M. Zaleski

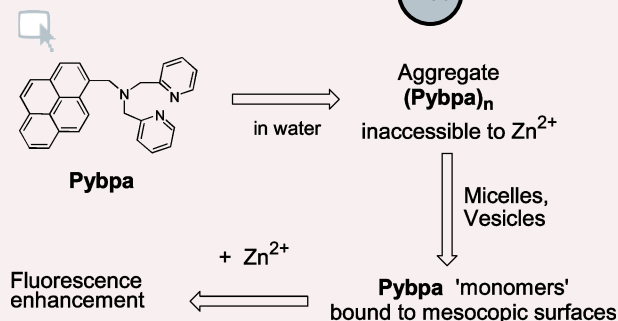


Conformationally constrained ethylene-diamine metallocenediynes exhibit alkyne termini separations that are constant and independent of metal center geometry, ancillary chloride ligand electron donation into the Bergman cyclization reaction coordinate, however, dramatically influences the observed temperatures.

1158

**First report of Zn<sup>2+</sup> sensing exclusively at mesoscopic interfaces**

Santanu Bhattacharya\* and Akash Gulyani

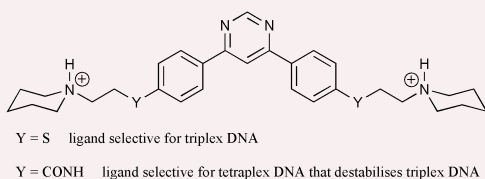


1-Pyrenyl-methyl-bis(2-picolyl) amine (**Pybpa**) forms a certain type of aggregate in water and is inaccessible to metal ions in such a state. Micellar or vesicular assemblies solubilize **Pybpa** and when bound to such mesoscopic aggregates, the probe can sense interfacial Zn<sup>2+</sup> ions.

1160

**Biarylpyrimidines: a new class of ligand for high-order DNA recognition**

Peter M. Murphy, Victoria A. Phillips, Sharon A. Jennings, Nichola C. Garbett, Jonathan B. Chaires, Terence C. Jenkins and Richard T. Wheelhouse\*

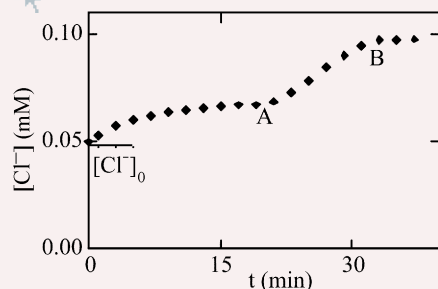


Biarylpyrimidines have been designed as ligands for high-order DNA structures: changing the functional group for sidechain attachment from thioether to amide switches the structural binding preference from triplex to tetraplex DNA.

1162

**Photoaccelerated oxidation of chlorinated phenols**

Gábor Lente and James H. Espenson\*

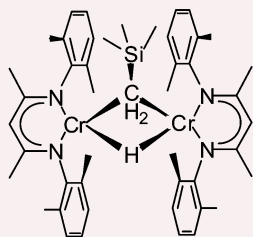


Illumination by visible light (between points A and B in the graph) accelerates the release of chloride ions during the catalyzed destructive oxidation of chlorophenols (the oxidation of 2,6-dichlorophenol by H<sub>2</sub>O<sub>2</sub> catalyzed by Fe(TPPS)<sup>+</sup> is shown here).

1164

**A stable alkyl hydride of a first row transition metal**

Leonard A. MacAdams, Gerald P. Buffone, Christopher D. Incarvito, James A. Golen, Arnold L. Rheingold and Klaus H. Theopold\*

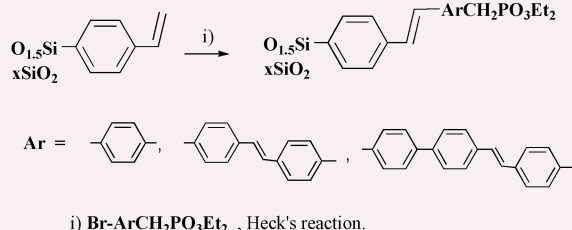


Hydrogenolysis of a Cr(III) dialkyl precursor produced a binuclear chromium complex with a bridging hydride and a bridging alkyl; this structurally characterized organometallic compound is thermally very stable and does not undergo the expected reductive elimination of alkane.

1166

**Studies of the functionalisation of organic–inorganic hybrid materials by using the Heck reaction**

Céline Carbonneau,\* Jean-Olivier Durand, Michel Granier and Gérard F. Lanneau

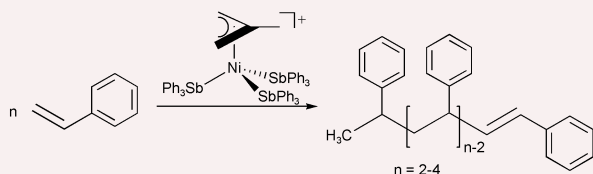


Cogelation of 4-styryltrimethoxysilane was performed using  $\text{NH}_4\text{F}$  as catalyst. The functionalisation of the styryl group was then studied by using Heck's reaction with ethyl 4-bromobenzyl or 4-bromoarylvinylbenzyl phosphonates. The efficiency of the solid-phase reaction was highly dependent on the texture of the solids.

1168

 **$[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{SbPh}_3)_3][\text{BAR}'_4]$ : an extremely active cationic allyl nickel–stibine catalyst for the oligomerization of styrene**

Manuel Jiménez-Tenorio, M. Carmen Puerta, Isabel Salcedo, Pedro Valerga,\* Sandra I. Costa, Pedro T. Gomes and Kurt Mereiter

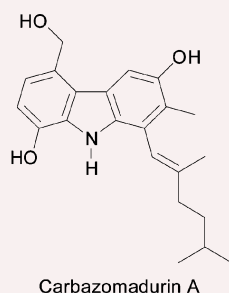


Despite its coordinatively saturated character, the novel pseudotetrahedral complex  $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{SbPh}_3)_3][\text{BAR}'_4]$  ( $\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$ ) is an extremely efficient catalyst for the regioregular oligomerization of styrene

1170

**First total synthesis of the neuronal cell protecting carbazole alkaloid carbazomadurin A by sequential transition metal-catalyzed reactions**

Hans-Joachim Knölker\* and Jan Knöll

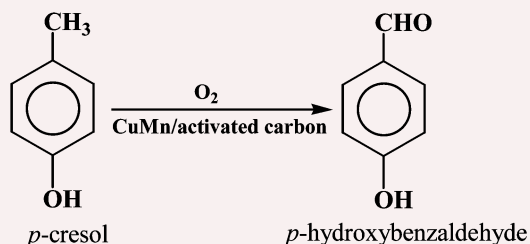


The highly oxygenated neuronal cell protecting carbazole alkaloid carbazomadurin A was synthesized in nine steps and 11% overall yield from isovanillic acid.

1172

**Copper and manganese: two concordant partners in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde**

Feng Wang, Guan-yu Yang, Wei Zhang, Wen-hai Wu and Jie Xu\*



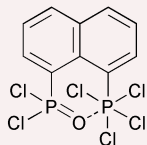
Copper and manganese are found to be two concordant partners in the catalytic oxidation of *p*-cresol to *p*-hydroxybenzaldehyde. Under mild conditions, this research realised 95.6% selectivity for *p*-hydroxybenzaldehyde at 98.5% conversion of *p*-cresol.

1174

**New mode of sterically imposed phosphorus hypercoordination**

Petr Kilian, Alexandra M. Z. Slawin and J. Derek Woollins\*

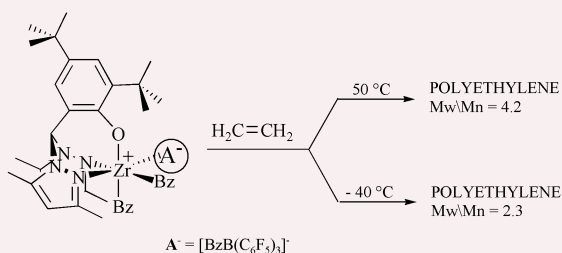
Secondary P=O...P bonding interaction in 1,8-diphosphanaphthalene derivative reported here provide example of an early stage in the interaction of an electrophile with a nucleophile.



1176

**Cationic benzyl zirconium heteroscorpionates: synthesis and characterization of a novel ethylene polymerisation catalyst showing an unusual temperature dependent polymerisation mechanism**

Stefano Milione, Cosimo Montefusco, Tomas Cuenca and Alfonso Grassi\*

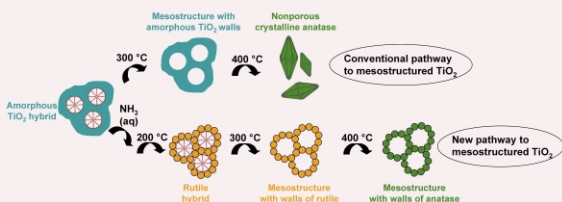


The ion pair  $[(\text{bpzmp})\text{Zr}(\text{CH}_2\text{Ph})_2]^+[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]^-$  is an active ethylene polymerisation catalyst that produces polyethylene samples with polydispersity values depending on temperature.

1178

**A new strategy towards ultra stable mesoporous titania with nanosized anatase walls**

K. Cassiers,\* T. Linssen, V. Meynen, P. Van Der Voort, P. Cool and E. F. Vansant



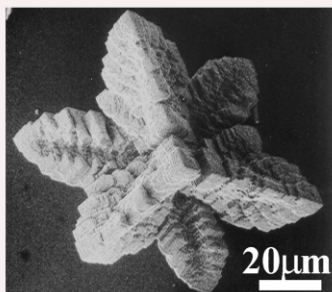
A strategy has been developed to synthesise thermally stable micelle-templated mesoporous titanias built up of nanosized anatase walls by the intermediate formation of titania hybrids with nanosized rutile walls.

1180

**Well-defined star-shaped calcite crystals formed in agarose gels**

Dong Yang, Limin Qi\* and Jiming Ma

Unique star-like calcite crystals with eight trident-like arms extending radially from initial rhombohedral calcite nuclei were produced by controlled crystallization of  $\text{CaCO}_3$  in agarose gels.

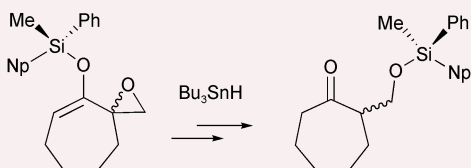


1182

**Homolytic 1,5-transfer of chiral organosilicon groups from an enoxy oxygen to an alkoxy oxygen—implications for mechanism**

Sonia M. Horvat, Sunggak Kim and Carl H. Schiesser\*

1,5-Homolytic transfers of chiral organosilicon groups from enoxy oxygen to alkoxy oxygen proceed with retention of configuration.



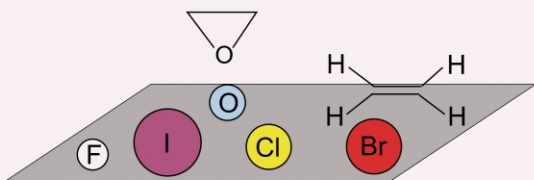


1184

### Halogen-induced selectivity in heterogeneous epoxidation is an electronic effect—fluorine, chlorine, bromine and iodine in the Ag-catalysed selective oxidation of ethene

Richard M. Lambert,\* Rachael L. Cropley, Alifiya Husain and Mintcho S. Tikhov

Selectivity promotion in the Ag-catalysed heterogeneous epoxidation of ethene correlates with halogen electron affinity showing that it is an electronic phenomenon rather than a steric or geometrical effect.

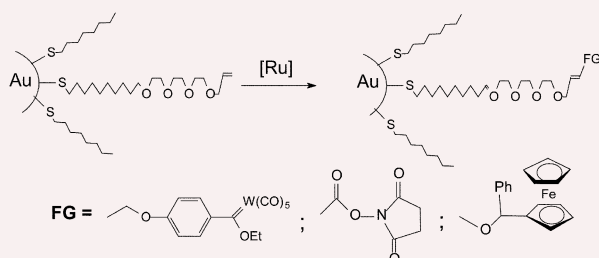


1186

### Towards “designer” surfaces: functionalisation of self-assembled monolayer (SAM) on colloidal gold by alkene metathesis

Debasis Samanta, Nicolas Faure, Francis Rondelez and Amitabha Sarkar\*

Using ruthenium-catalyzed cross-metathesis reaction as a mild and convenient strategy, organic and organometallic functional groups have been grafted on monolayer-protected gold clusters.

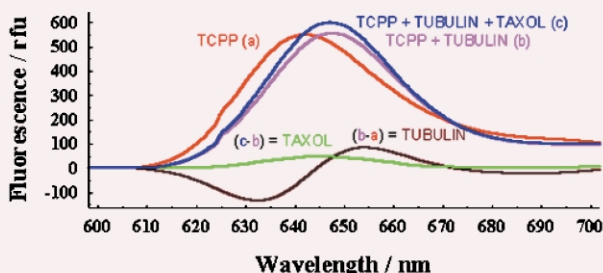


1188

### A novel bioassay for screening and quantification of taxanes

Sergi Morais, P. C. Pandey, Wilfred Chen and Ashok Mulchandani\*

The bioassay is a novel method for the detection of antimitotic agents such as Taxol® through changes in the fluorescence spectrum of metal free tetrakis(4-carboxyphenyl)porphyrin (TCPP) using the receptor tubulin.

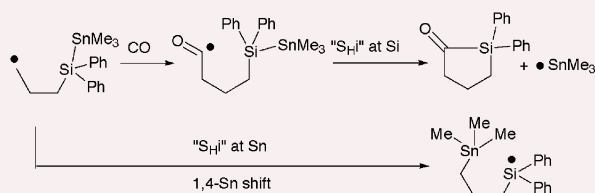


1190

### Two types of intramolecular homolytic substitution reactions at group XIV atoms: unusual radical 1,4-Sn shifts from Si to C and carbonylative S<sub>H</sub>i reaction at Si

Armido Studer,\* Stephan Amrein, Hiroshi Matsubara, Carl H. Schiesser,\* Takashi Doi, Tomonori Kawamura, Takahide Fukuyama and Ilhyong Ryu\*

Two types of intramolecular homolytic substitution reactions: (i) an S<sub>H</sub>i-type reaction of acyl radical at Si and (ii) a 1,4-Sn shift from Si to C atom, are described.

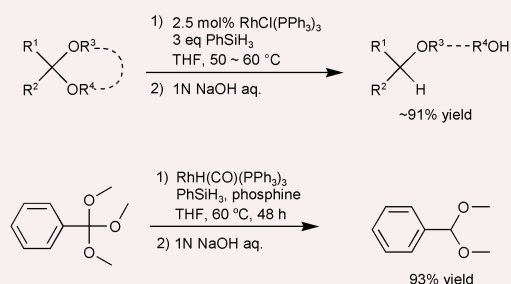


1192

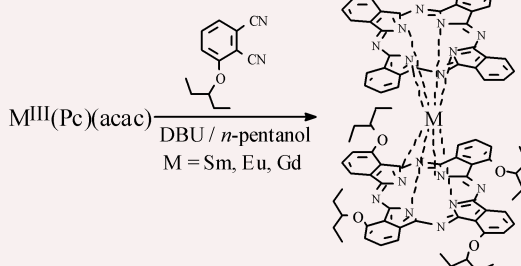
### Reductive cleavage of the C–O bond of acetals and orthoesters: reduction by silane in the presence of a Rh–PPh<sub>3</sub> complex

Tetsuo Ohta,\* Tsugumi Michibata, Kazuyuki Yamada, Ryohei Omori and Isao Furukawa

Acetals are smoothly reduced to ethers by hydrosilane using rhodium catalyst, and orthoester is selectively reduced to acetal by hydrosilane using rhodium catalyst in the presence of additional phosphine.



1194

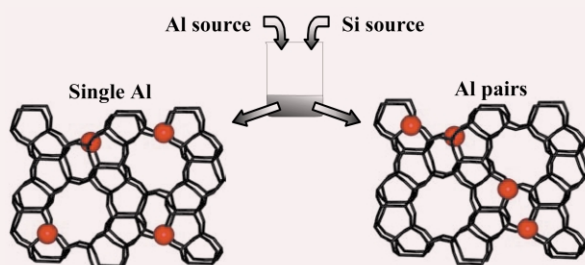


### Synthesis, spectroscopic characterisation and structure of the first chiral heteroleptic bis(phthalocyaninato) rare earth complexes

Yongzhong Bian, Rongming Wang, Jianzhuang Jiang,\* Chi-Hang Lee, Jinzhi Wang and Dennis K. P. Ng\*

A series of chiral heteroleptic bis(phthalocyaninato) lanthanide(III) complexes  $M^{III}(Pc)[Pc(OC_5H_{11})_4]$  (M = Sm, Eu, Gd) have been synthesised. The Sm and Eu analogues represent the first mixed phthalocyaninato complexes which have been structurally characterised.

1196

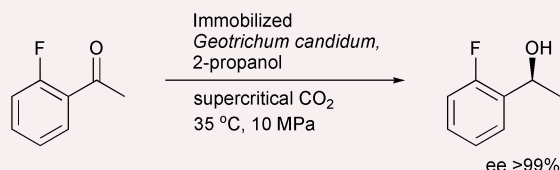


### Control of Al distribution in ZSM-5 by conditions of zeolite synthesis

Vendula Gábová, Jiří Dědeček and Jiří Čejka

Al Distribution (concentration of Al “pairs” and “single” Al atoms) in ZSM-5 can be controlled by the variation of Al and Si sources used for zeolite synthesis.

1198

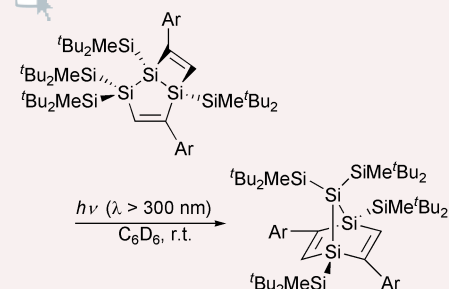


### Biocatalytic reduction of ketones by a semi-continuous flow process using supercritical carbon dioxide

Tomoko Matsuda,\* Kazunori Watanabe, Takashi Kamitanaka, Tadao Harada and Kaoru Nakamura

The immobilized resting-cell of *Geotrichum candidum* was used as a catalyst for the reduction of a ketone in a semi-continuous flow process using supercritical carbon dioxide for the first time; it was also applied for the asymmetric reduction of a ketone and resulted in excellent enantioselectivity (ee >99%) and space-time yield.

1200

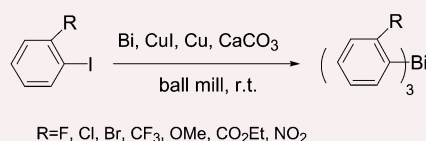


### Photochemical isomerization of 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene to 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene

Tadahiro Matsuno, Masaaki Ichinohe and Akira Sekiguchi\*

The 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene derivative photochemically isomerizes to 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene *via* skeletal rearrangement.

1202



### A novel dry route to *ortho*-functionalized triarylbismuthanes that are difficult to access by conventional wet routes

Mika Urano, Shinobu Wada and Hitomi Suzuki\*

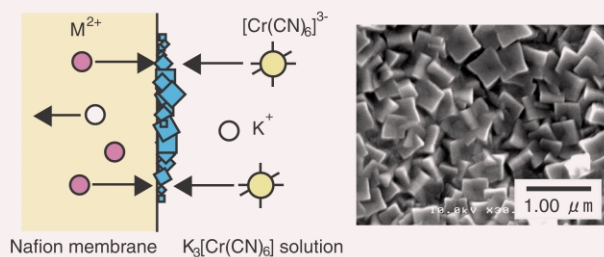
When aryl iodides bearing an electron-withdrawing group at the *ortho* position were milled together with Bi shots and calcite in the presence of Cu powder and CuI, the *ortho*-functionalized triarylbismuthanes were obtained in moderate to good yield.

1204

**Ion-exchange synthesis and magneto-optical spectra of colored magnetic thin films composed of metal(II) hexacyanochromate(III)**

Masanori Tozawa, Shin-ichi Ohkoshi,\* Norimichi Kojima and Kazuhito Hashimoto\*

Magnetic thin films composed of hexacyanochromate-based magnets were prepared on Nafion membrane by an ion-exchange process and their Faraday spectra were observed in the visible region.

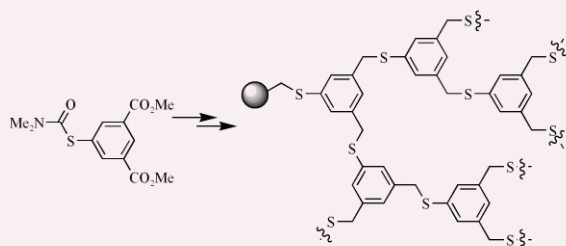


1206

**Preparation of novel polythioether dendrons on a solid support**

Adi Dahan, Avi Weissberg and Moshe Portnoy\*

Novel solid-phase synthesis of unprecedented polythioether dendrons, based on a new mercaptoisophthalate furcated unit, has been demonstrated. The dendronized resins have been applied in Heck reaction catalysis.



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