

Cover

A tRNA/aminoacyl-tRNA synthetase complex and several unnatural amino acids, against a backdrop of an expanded genetic codon table with the addition of one unnatural base X.

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contents

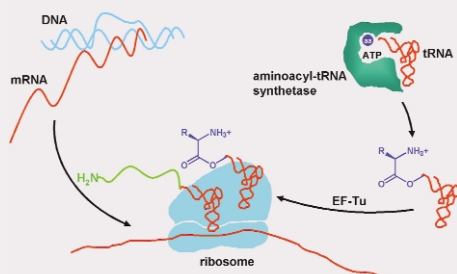
FEATURE ARTICLE

1

Expanding the genetic code

Lei Wang and Peter G. Schultz

A general method has been developed that allows for the site-specific incorporation of unnatural amino acids into proteins *in vivo*, effectively expanding the genetic code of *Escherichia coli*.



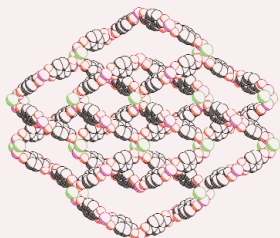
COMMUNICATIONS

12

A novel ribbon-candy-like supramolecular architecture of cadmium(II)-terephthalate polymer with giant rhombic channels: twofold interpenetration of the 3D 8²10-a net

Jing-Cao Dai, Xin-Tao Wu, Zhi-Yong Fu, Sheng-Min Hu, Wen-Xing Du, Chuan-Peng Cui, Li-Ming Wu, Han-Hui Zhang and Rui-Qing Sun

A novel ribbon-candy-like supramolecular architecture of polymer $\{[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{Cd}(\text{tp})\cdot\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$ containing large rhombic channels has been synthesised under hydrothermal conditions based on the templating effects of large bulky cation $[\text{Ph}_3\text{PCH}_2\text{Ph}]^+$.

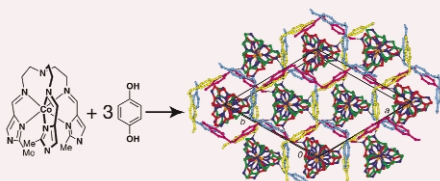


14

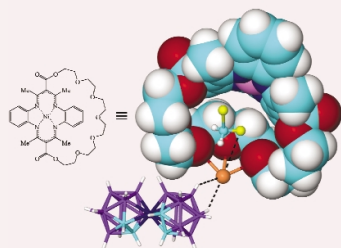
Hydrogen-bonded extended structure of the 1:3 adduct of a C₃ symmetric cobalt(III) complex with a tripod-ligand involving three imidazolate groups and hydroquinone or resorcinol

Shigeyuki Nagasato, Yukinari Sunatsuki, Susumu Ohsato, Takafumi Kido, Naohide Matsumoto, and Masaaki Kojima

A chiral C₃ symmetric cobalt(III) complex reacts with hydroquinone to give a hydrogen-bonded 3D extended structure derived from the template effect of the complex.



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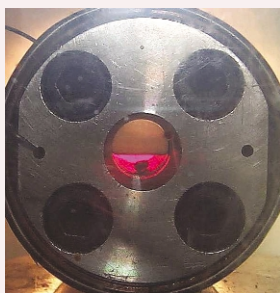


Ni(II) N₄-macrocycle grafted crown ether: caesium cobalt(III) bis(dicarbollide) coordination polymer

Nino Malic, Peter J. Nichols and Colin L. Raston

A Ni (TMTAA) grafted crown ether forms a 2D coordination polymer with the caesium salt of the globular like anion, cobalt(III) bis(dicarbollide), through O...Cs⁺ interactions, with the soft anion involved in B-H...Cs⁺ interactions.

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Super acid catalysis in supercritical fluid reaction media for the formation of linear alkyl benzenes

Mark A. Harmer and Keith W. Hutchenson

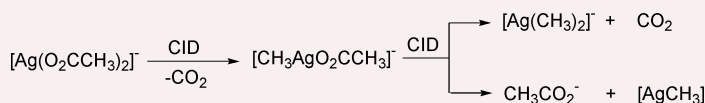
High catalytic activity is demonstrated for the formation of linear alkylbenzenes using a perfluorosulfonic acid catalyst in supercritical fluid reaction media: enhanced alkylation activity is observed in fluoroform (CHF₃) compared to carbon dioxide.

20

Dimethylargenate is a stable species in the gas phase

Richard A. J. O'Hair

The formation of dimethylargenate from silver diacetate has been explored using multistage mass spectrometry experiments in a quadrupole ion trap and DFT theory.

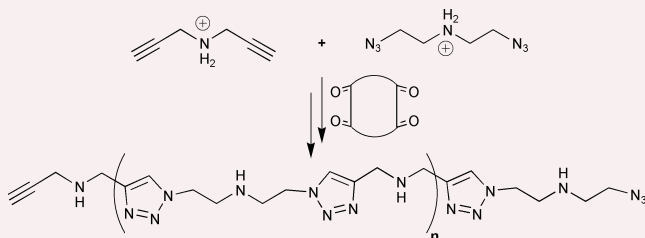


22

Formation of oligotriazoles catalysed by cucurbituril

Theodora C. Krasia and Joachim H. G. Steinke

The catalytic activity of cucurbituril in 1,3-dipolar cycloadditions has been applied to the synthesis of oligotriazoles.

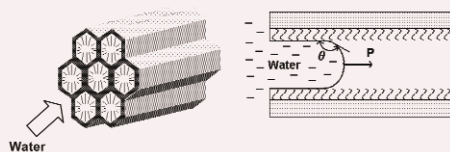


24

Dissipative water intrusion in hydrophobic MCM-41 type materials

T. Martin, B. Lefevre, D. Brunel, A. Galarnau, F. Di Renzo, F. Fajula, P. F. Gobin, J. F. Quinson and G. Vigier

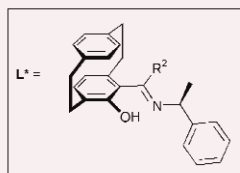
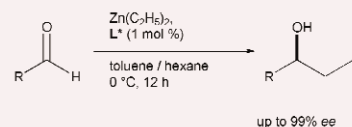
Texture-related features of water intrusion in hydrophobised MCM-41 silicas render these materials especially suitable for energy dissipation in mechanical dampers.



26

Planar and central chiral [2.2]paracyclophane-based *N,O*-ligands as highly active catalysts in the diethylzinc addition to aldehydes

Stefan Dahmen and Stefan Bräse

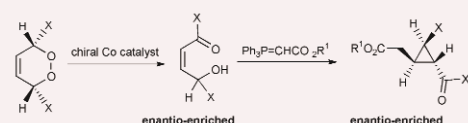


Planar and central chiral [2.2]paracyclophane-based *N,O*-ligand catalysts in asymmetric diethylzinc additions to reveal an unusual substrate spectrum and remarkably high activity.

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First examples of the catalytic asymmetric ring-opening of *meso* 1,2-dioxines utilising cobalt(II) complexes with optically active tetradentate Schiff base ligands: formation of enantio-enriched cyclopropanes

Thomas D. Avery, Natalie F. Jenkins, Marc C. Kimber, David W. Lupton and Dennis K. Taylor

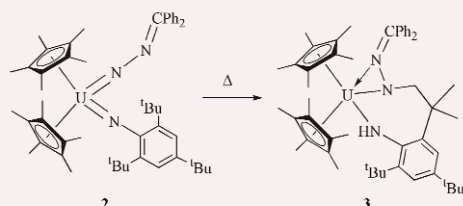


The combination of chiral cobalt β -ketoiminato or cobalt salen complexes and *meso* 1,2-dioxines leads to catalytic asymmetric ring-opening affording enantio-enriched *cis* γ -hydroxy enones; subsequent capture by an ylide affords enantio-enriched cyclopropanes.

30

Enhancing the reactivity of uranium(VI) organoimido complexes with diazoalkanes

Jaqueline L. Kiplinger, David E. Morris, Brian L. Scott and Carol J. Burns

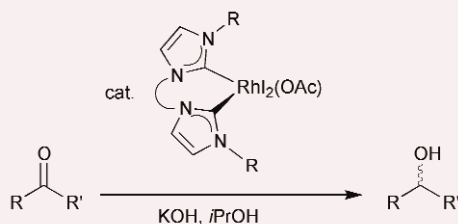


Oxidation of $(\text{C}_5\text{Me}_5)_2\text{U}(\text{=N}-2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)$ (1) using diphenyldiazomethane gives the uranium(VI) mixed bis(imido) complex 2 which undergoes cyclometallation upon thermolysis to afford the uranium(IV) bis(amide) complex 3.

32

Chelating bis-carbene rhodium(III) complexes in transfer hydrogenation of ketones and imines

Martin Albrecht, Robert H. Crabtree, Jose Mata and Eduardo Peris

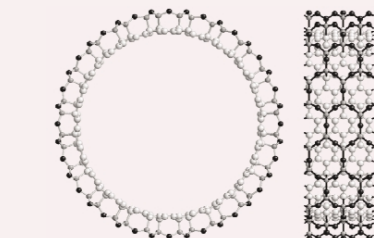


Chelating rhodium(III) carbene complexes are accessible *via* a simple synthesis and are catalytically active for hydrogen transfer from alcohols to ketones and imines.

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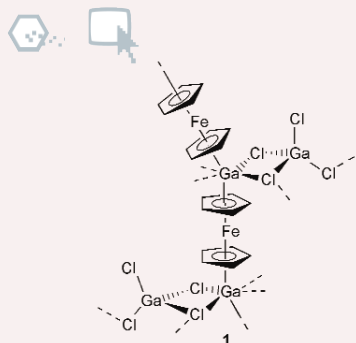
Nanotube composites: novel SiO_2 coated carbon nanotubes

T. Seeger, Th. Köhler, Th. Frauenheim, N. Grobert, M. Rühle, M. Terrones and G. Seifert



A novel nanocomposite consisting of multi-walled carbon nanotubes (MWNTs) embedded in amorphous SiO_x has been produced in bulk. The material is oxidation resistant and theoretical calculations indicate novel properties for these SiO_x coated MWNTs.

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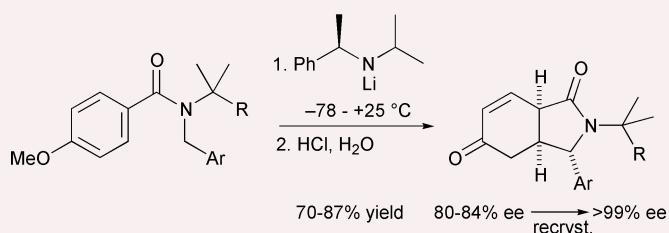


A novel multidecker sandwich complex from the reaction of ferrocene with GaCl₃

Stefan Scholz, Jennifer C. Green, Hans-Wolfram Lerner, Michael Bolte and Matthias Wagner

A redox reaction takes place between GaCl₃ and an excess of ferrocene, leading to the multidecker sandwich complex **1**, [–Ga(C₅H₅)Fe(C₅H₅)Ga(C₅H₅)Fe(C₅H₅)–]_n–[GaCl₄]_{2n}, which features an array of alternating Ga(I) and Fe(II) ions bridged by cyclopentadienyl moieties.

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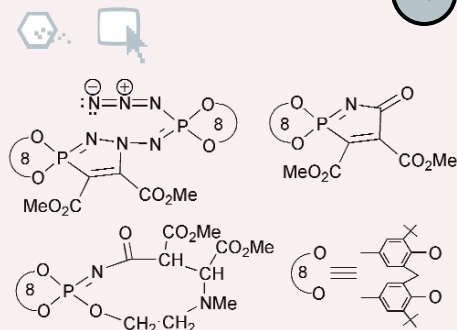


Asymmetric deprotonation and dearomatizing cyclisation of *N*-benzyl benzamides using chiral lithium amides: formal synthesis of (–)-kainic acid

Jonathan Clayden, Christel J. Menet and Darren J. Mansfield

Chiral lithium amides deprotonate *N*-benzyl benzamides enantioselectively, initiating an asymmetric dearomatizing cyclisation to enantiomerically enriched isoindolinones.

40

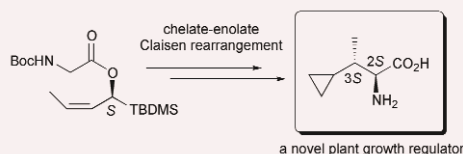


Novel reactions of phosphorus(III) azides and isocyanates: unusual modes of cycloaddition with dipolarophiles and an unexpected case of ring expansion

Sudha Kumaraswamy, Praveen Kommana, N. Satish Kumar and K. C. Kumara Swamy

Treatment of [CH₂(6-*t*-Bu-4-Me-C₆H₂O)₂]P–X (X = N₃ and NCO) with the dipolarophile MeO₂CC≡CCO₂Me leads to new modes of 1,3-dipolar cycloaddition, and to an unprecedented ring expansion to a spirocycle.

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Total synthesis and determination of the stereochemistry of 2-amino-3-cyclopropylbutanoic acid, a novel plant growth regulator isolated from the mushroom *Amanita castanopsidis* Hongo

Yoshiki Morimoto, Mamoru Takaishi, Takamasa Kinoshita, Kazuhiko Sakaguchi and Kozo Shibata

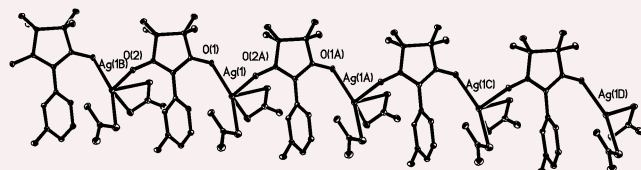
The unknown stereostructure of 2-amino-3-cyclopropylbutanoic acid **1**, a novel plant growth regulator isolated from the mushroom *Amanita castanopsidis* Hongo, was determined to be (2*S*,3*S*)-**2** through its racemic and enantioselective syntheses employing the chelate–enolate Claisen rearrangement as a key step.

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1D silver(I) complex of nitronyl nitroxide with strong spin–spin interaction through silver(I) ion

Deqing Zhang, Liang Ding, Wei Xu, Huaiming Hu, Daoben Zhu, Yuanhe Huang and Decai Fang

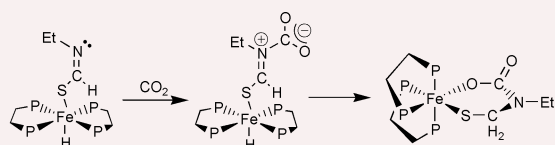


A 1D silver(I) complex derived from *m*-*N*-methylpyridinium nitronyl nitroxide iodide and AgNO₃ shows a strong interaction of nitronyl nitroxides through silver(I) ions ($J/k_B = -84$ K)

46

Functionalisation of carbon dioxide by an iron(II) complex

Leslie D. Field, Warren J. Shaw and Peter Turner

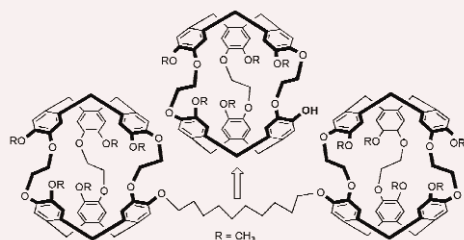


Addition of carbon dioxide to *trans*-Fe(dmpe)₂(SCHN(Et)H) **2** affords the iminium carboxylate *trans*-Fe(dmpe)₂(SCHN⁺(Et)CO₂⁻)H **4**, which rearranges to the ferracycle *cis*-Fe(dmpe)₂(SCH₂N(Et)C(O)O- κ ,S,O) **5**.

48

Cryptophanols, new versatile compounds for the synthesis of functionalized cryptophanes and polycryptophanes

Magali Darzac, Thierry Brotin, Denis Bouchu and Jean-Pierre Dutasta

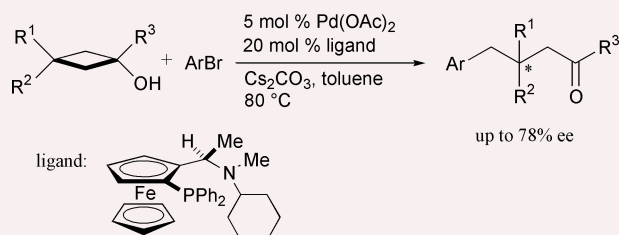


After deprotection with a palladium catalyst, mono-allylated cryptophane-A (**1**, **2**) and cryptophane-E (**3**) gave the new cryptophanols **4**, **5** and **6**, respectively, which are important key compounds for the preparation of mono-functionalized cryptophanes as well as for the design of large supramolecular hosts such as the bis-cryptophanes **7** and **8**.

50

Palladium-catalysed asymmetric arylation of *tert*-cyclobutanols via enantioselective C–C bond cleavage

Takahiro Nishimura, Satoshi Matsumura, Yasunari Maeda and Sakae Uemura

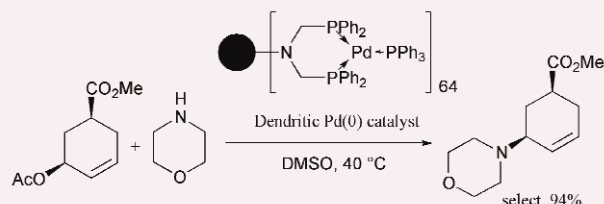


Palladium-catalysed arylation of *tert*-cyclobutanols with aryl bromide involving enantioselective C–C bond cleavage affords chiral ketones with moderate to good enantioselectivity.

52

Novel catalysis of dendrimer-bound Pd(0) complexes: sterically steered allylic amination and the first application for a thermomorphic system

Tomoo Mizugaki, Makoto Murata, Masahiko Ooe, Kohki Ebitani and Kiyotomi Kaneda

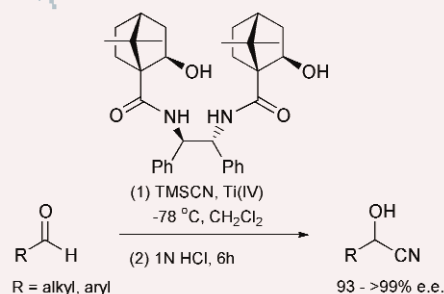


Phosphinated dendrimer-bound Pd(0) complex catalysts show high stereoselectivity for allylic amination due to the surface congestion of dendrimers and can be easily recycled without loss of activity under thermomorphic conditions.

54

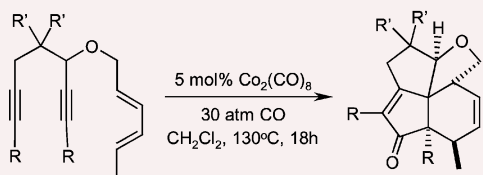
1,2-Diphenylethylenediamine linked chiral Ti(IV) complex—a new entry to the highly enantioselective silylcyanation of aliphatic and aromatic aldehydes

Chun-Wei Chang, Chun-Tzu Yang, Chyuan-Der Hwang and Biing-Jiun Uang



Highly enantioselective silylcyanation of aliphatic and aromatic aldehydes was achieved by using a 1,2-diphenylethylenediamine linked chiral Ti(IV) complex as the catalyst.

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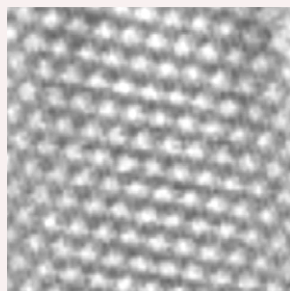


Catalytic one-pot synthesis of [5.5.5.6]fenestrane systems *via* a dicobalt octacarbonyl-catalyzed tandem cycloaddition of dienediynes

Do Han Kim, Seung Uk Son, Young Keun Chung and Sueg-Geun Lee

Catalytic one-pot synthesis of fenestrane derivatives from dienediynes was developed. Fenestranes were synthesized in high yields by a dicobalt octacarbonyl-catalyzed tandem cycloaddition of dienediynes.

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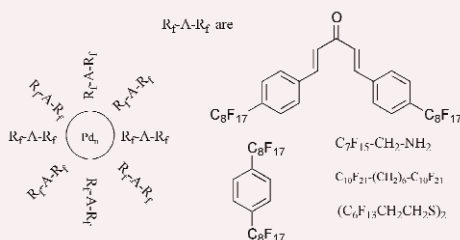


In situ STM imaging of surface dissolution and rearrangement of a Pt–Fe alloy electrocatalyst in electrolyte solution

Li-Jun Wan, Takahiko Moriyama, Megumi Ito, Hiroyuki Uchida and Masahiro Watanabe

Surface dissolution and rearrangement of a Pt–Fe alloy with a high CO tolerance and O₂ reduction activities for fuel cell applications is observed in an electrolyte solution by STM for the first time, indicating formation of a Pt skin layer and a Pt(111)-(1 × 1) structure as shown.

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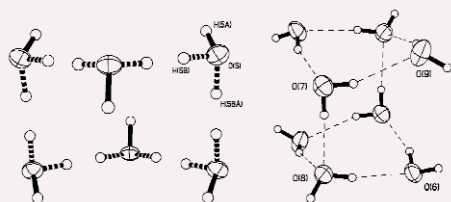


Palladium nanoparticles stabilised by polyfluorinated chains

Marcial Moreno-Mañas, Roser Pleixats and Silvia Villarroya

Palladium nanoparticles can be prepared by reduction of palladium(II) chloride in the presence of different compounds featuring long perfluorinated carbon chains.

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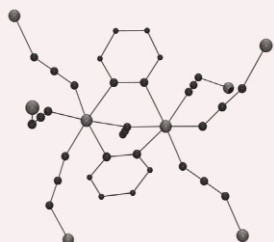


Novel water clusters in the crystalline state: structures of a symmetrical, cyclic hexamer and an 'opened-cube' octamer

Robert J. Doedens, Elizabeth Yohannes and M. Ishaque Khan

Six- and eight-membered hydrogen-bonded water clusters of novel structure types have been found in crystalline hydrates.

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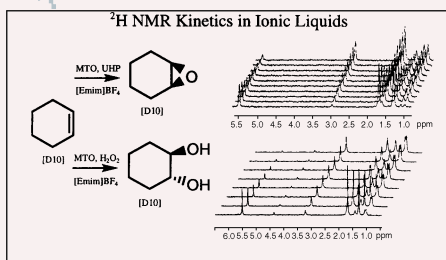


[M(N₃)₂(L)]_n: building 3-D M^{II}-azido networks with new topologies

Albert Escuer, Ramon Vicente, Franz A. Mautner, Mohamed A. S. Goher and Morsy A. M. Abu-Youssef

The different coordination possibilities of the azido ligand combined with those of 1,2- or 1,3-diazines proves to be an efficient way to generate new topologies and varied magnetic properties of new 3-D M^{II} networks.

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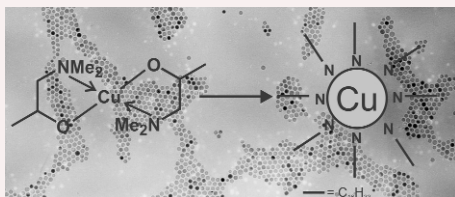


Deuterium NMR spectroscopy is a versatile and economical tool for monitoring reaction kinetics in ionic liquids

Armando Durazo and Mahdi M. Abu-Omar

Time-resolved ^2H NMR spectroscopy is used to monitor the progress of and gain kinetic information for a variety of reactions in different ionic media.

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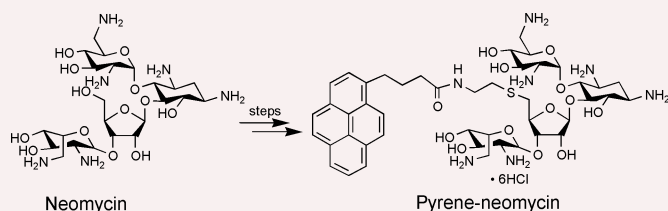


A non-aqueous organometallic route to highly monodispersed copper nanoparticles using $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$

Julia Hambrock, Ralf Becker, Alexander Birkner, Jurij Weiß and Roland A. Fischer

Good quality, highly monodispersed capped copper metal nanoparticles have been synthesised in a non-hydrolytic approach using thermal decomposition of the Cu(II) precursor $[\text{Cu}(\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2)_2]$ in a hot coordinating solvent without further reducing agents.

70

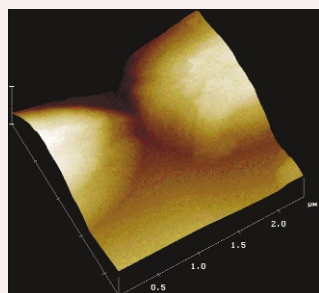


Pyrene–neomycin conjugate: dual recognition of a DNA triple helix

Liang Xue, I. Charles and Dev P. Arya

The synthesis of pyrene–neomycin conjugate and its ability to stabilize DNA/RNA triple helices is described.

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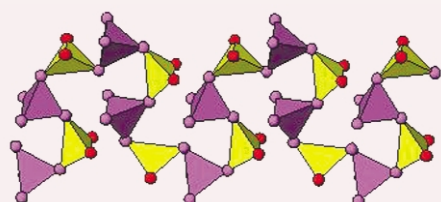


Fabrication of a nano-scale gap by selective chemical deposition

Lan Huang, Lina Xu, Haiqin Zhang and Ning Gu

An electrode nanogap of 45 nm has been prepared by a new method in which the initial gap of 1–2 μm obtained by conventional lithography was shortened by selective chemical deposition of copper onto the electrodes.

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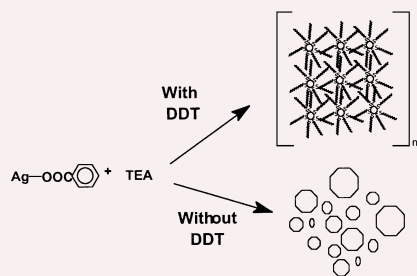


$[\text{Cu}(\text{pyrazine-2-carboxylate})_2]_2\text{Cd}_4\text{I}_8$: unprecedented 1-D serpentine inorganic chains and regular 2-D metal–organic square grids in a 3-D framework

Delia M. Ciurtin, Mark D. Smith and Hans-Conrad zur Loye

A rare example of a coordination polymer containing two chemically and structurally different non-interpenetrating structural motifs is described. In this new mixed metal polymer, copper containing square grid sheets alternate with cadmium containing serpentine chains.

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Single phase preparation of monodispersed silver nanoclusters using a unique electron transfer and cluster stabilising agent, triethylamine

Nirmalya K. Chaki, Surendra G. Sudrik, Harikrishan R. Sonawane and K. Vijayamohan

A simple and reproducible single phase preparation of 2.5 nm silver nanoclusters is described using silver benzoate along with triethylamine (TEA) and dodecanethiol (DDT); these spontaneously self-assemble to a two-dimensional array whereas in the absence of thiol only polydispersed nanoclusters are obtained.

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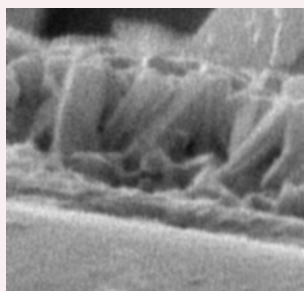


Labile coordination dendrimers

Xingling Xu, Elizabeth J. MacLean, Simon J. Teat, Mark Nieuwenhuyzen, Mark Chambers and Stuart L. James

Addition of anionic benzylsulfate dendrons to dynamic mixtures of Ag^+ and triphosphine ligands results in the assembly of loosely-bonded cage-core dendrimers.

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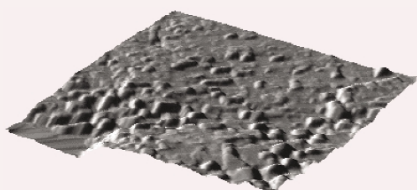


Novel low temperature solution deposition of perpendicularly orientated rods of ZnO: substrate effects and evidence of the importance of counterions in the control of crystallite growth

David S. Boyle, Kuveshni Govender and Paul O'Brien

Perpendicularly orientated ZnO rods have been grown on thin ZnO templates, from aqueous solutions of zinc acetate and hexamethylenetetraamine (HMT); growth along the *c*-axis of the ZnO crystallites is promoted by the presence of acetate in the bath.

82

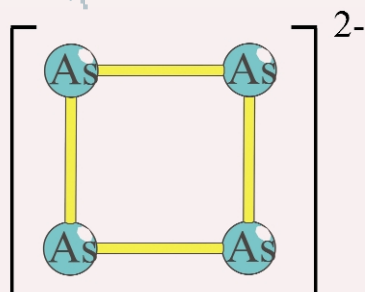


Atomic force microscopy studies of the KF (100) surface: formation of water-rich surface phases in moist *N,N*-dimethylformamide

Gavin Macfie, Shelley J. Wilkins and Richard G. Compton

A water rich surface phase is observed in the system KF-DMF- H_2O by atomic force microscopy; the effects on surface morphology and likely implications for halogen exchange reactions using KF are discussed.

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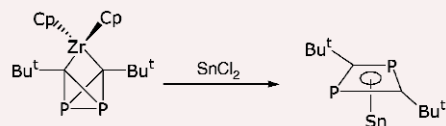


An isolated *cyclo*-tetraarsendiide: low temperature synthesis and crystal structure of bis-pentaamminesodium tetraarsendiide-ammonia (1/3) $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$

Nikolaus Korber and Markus Reil

As_4^{2-} has been a 'lost' species of the Zintl anion group for a long time. It has now been found as an isolated anion in the reduction product of an excess of arsenic with sodium in liquid ammonia.

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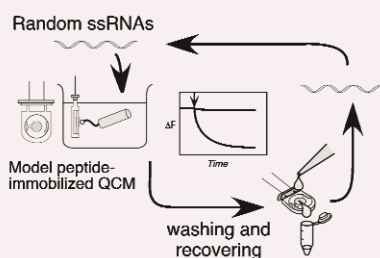


Synthesis, crystal and molecular structure of [Sn(η^4 -P₂C₂Bu^t)]: the first non transition metal 1,3-diphosphacyclobutadienyl compound

Matthew D. Francis and Peter B. Hitchcock

Treatment of [Zr(η^5 -C₅H₅)₂(PCBu^t)₂] with SnCl₂ led to the novel monomeric (1,3-diphosphacyclobutadienyl)tin(II) half sandwich complex [Sn(η^4 -P₂C₂Bu^t)] which has been characterised by multinuclear NMR spectroscopy and in the solid state by a single crystal X-ray diffraction study.

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In vitro selection and evaluation of RNA aptamers that recognize arginine-rich-motif model peptide on a quartz-crystal microbalance

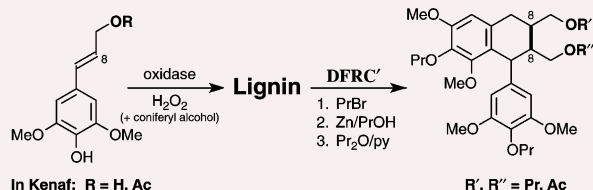
Shinobu Fukusho, Hiroyuki Furusawa and Yoshio Okahata

To study RNA–peptide interactions, we performed an *in vitro* selection of RNA on a simple α -helical peptide-immobilized quartz-crystal microbalance (QCM) and evaluated the association constants (10^7 M⁻¹) of the selected RNA to the model peptide on the same QCM plate.

90

Preliminary evidence for sinapyl acetate as a lignin monomer in kenaf

Fachuang Lu and John Ralph



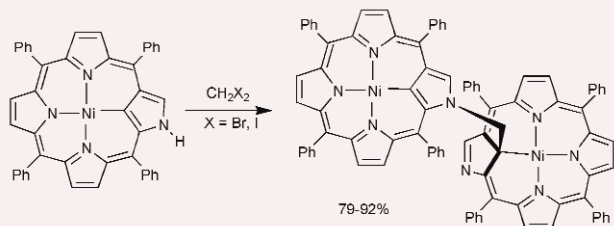
9-Acetylated syringyl 8–8-linked dehydromers are degradation products released from kenaf lignins, implicating sinapyl acetate as a lignin precursor.

92



First example of a covalently bound dimeric inverted porphyrin

Izabela Schmidt and Piotr J. Chmielewski

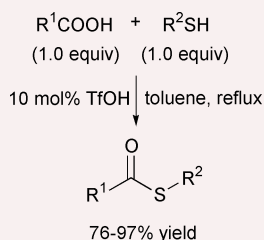


An asymmetric methylene-linked bis-carbaporphyrinoid containing two different coordination cores is formed very efficiently in a reaction of nickel(II) complex of inverted porphyrin with dihalomethanes.

94

Direct thioesterification from carboxylic acids and thiols catalyzed by a Brønsted acid

Shinya Imura, Kei Manabe and Shū Kobayashi



In the presence of a catalytic amount of trifluoromethanesulfonic acid, free carboxylic acids reacted with free thiols directly to afford the corresponding thioesters in high yields.

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Supplementary crystallographic data are available: see article for further information.



Electronic supplementary information is available on <http://www.rsc.org/esi>: see article for further information.

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