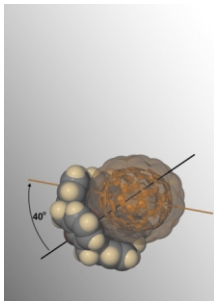
ISSN 1359-7345 • CHCOFS (18)2257-2387 (2003)

ChemComm

CHEMICAL COMMUNICATIONS • www.rsc.org/chemcomm



Cover (far left)
Nepali villagers drifting crossing the Rapti river on a canoe ferry. The same principle is used on the molecular level to promote the transport of ions and phospholipids across bilayer membranes. Background photo by Arie van der Velden, © 2002, Front Range Publishing (pp. 2261–2268).

Inside cover (left)
The asymmetric unit of calix[5]arene : C_{70} (pp. 2270–2271).

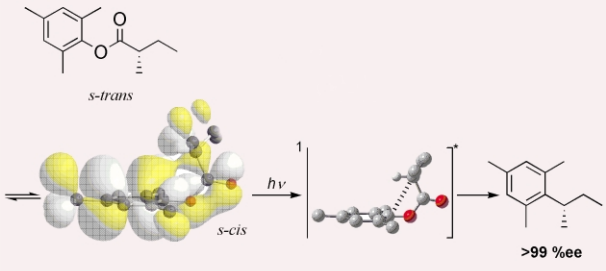
contents

Chemical Communications
http://www.rsc.org/chemcomm

Chemical Communications (print: ISSN 1359-7345; electronic: ISSN 1364-548X) is published 24 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. All orders accompanied by payment should be sent directly to Turpin Distribution Services Ltd, Blackhorse Road, Letchworth, Herts, UK SG6 1HN. 2003 Annual (print + electronic) subscription price: £878; US$1450. 2003 Annual (electronic) subscription price: £790; US$1305. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT. If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA. US Postmaster: send address changes to *Chemical Communications*, c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight.
PRINTED IN THE UK.

Advertisement sales: Tel +44 (0)1223 432243; Fax +44 (0)1223 426017; E-mail advertising@rsc.org

2302

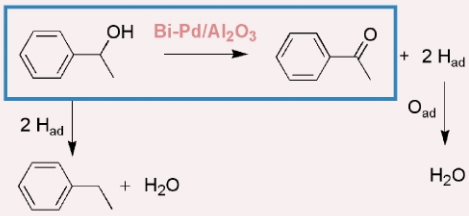


Complete memory of chirality upon photodecarboxylation of mesityl alkanoate to mesitylalkane: theoretical and experimental evidence for cheletropic decarboxylation *via* a spiro-lactonic transition state

Tadashi Mori,* Hideaki Saito and Yoshihisa Inoue*

The photodecarboxylation of chiral mesityl alkanoate proceeds to give the alkylmesitylene in >99% ee under a variety of conditions, indicating the concerted cheletropic extrusion of CO_2 from the energetically less favored *s-cis* conformation.

2304

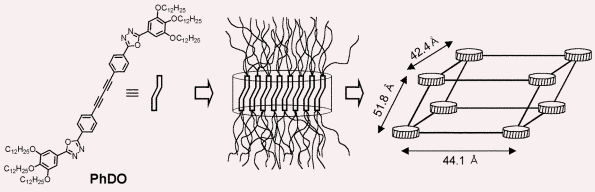


Liquid phase oxidation of alcohols with oxygen: *in situ* monitoring of the oxidation state of Bi-promoted Pd/Al_2O_3

Csilla Keresszegi, Jan-Dierk Grunwaldt, Tamas Mallat and Alfons Baiker*

In situ, time-resolved XAS studies on a $Bi–Pd/Al_2O_3$ catalyst indicate that Pd, and Bi located on the Pd surface, are in a reduced, metallic state during the oxidation of 1-phenylethanol with molecular oxygen.

2306

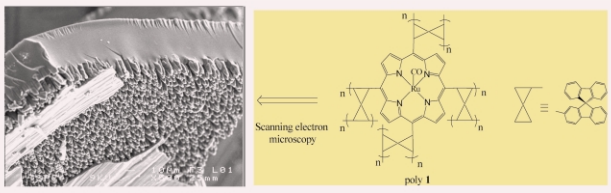


Supramolecular assembly of fluorescent phasmidic diacetylene and its photopolymerization

Bong Gi Kim, Sehoon Kim, Jangwon Seo, Nam-Keun Oh, Wang-Cheol Zin and Soo Young Park*

The closed micellar triclinic structure of a fluorescent phasmidic diacetylene (PhDO) has been fixed by topochemical photopolymerization which induced fluorescence quenching to offer a novel method of image photopatterning.

2308

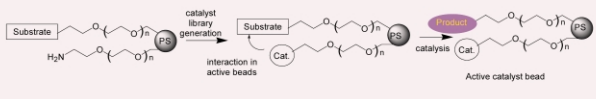


Poly(ruthenium carbonyl spirobifluorenylporphyrin): a new polymer used as a catalytic device for carbene transfer

Cyril Poriel, Yann Ferrand, Paul le Maux, Christine Paul, Joëlle Rault-Berthelot* and Gerard Simonneaux*

Poly(tetraspirobifluorenylporphyrin ruthenium(II) carbonyl) materials are able to catalyze heterogeneous cyclopropanation and 2,3 sigmatropic rearrangement with ethyl diazoacetate.

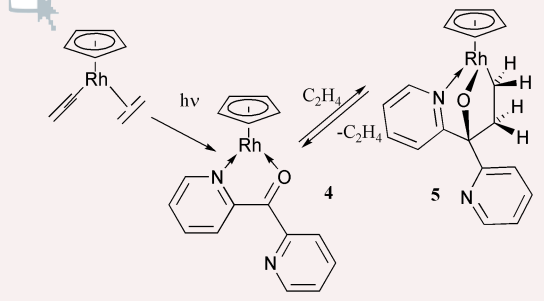
2310



Dyad beads and the combinatorial discovery of catalysts

Iain Lingard, Gurdip Bhalay and Mark Bradley*

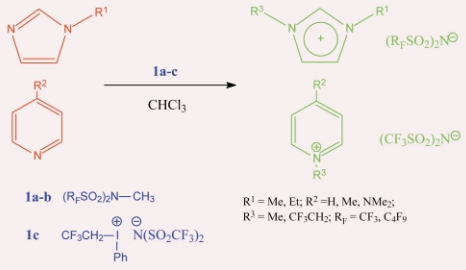
The discovery of catalysts from combinatorial libraries using site to site substrate–catalyst interaction has been developed and could be a valuable new method in the combinatorial discovery and development of catalysts. The technique can readily be adapted to any catalytic bond forming reaction, as long as one substrate can be immobilised onto a solid support and the other labelled with a dye.



Dipyridylketone binding and subsequent C–C bond insertion reactions at cyclopentadienylrhodium

Cyril Godard, Simon B. Duckett,* Simon Parsons and Robin N. Perutz

The κ^2-N,O binding mode of UV irradiation of 2,2′-dipyridylketone is established unequivocally in its (η^5-C_5H_5)Rh complex **4**; the latter undergoes an unusual insertion reaction to form a bicyclic oxametallacyclopentane **5**.



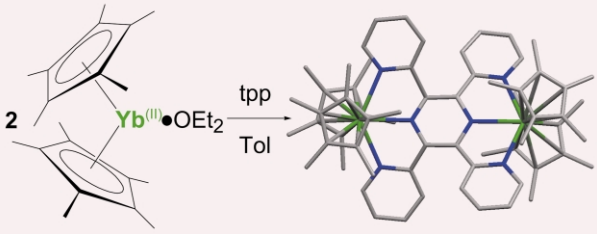
Direct methylation and trifluoroethylation of imidazole and pyridine derivatives

Jie Zhang, George Robert Martin and Darryl D. DesMarteau*

Direct methylation or trifluoroethylation of imidazole and pyridine derivatives using *N*-methyl bis((perfluoroalkyl)sulfonyl)imides or trifluoroethyl phenyliodonium bis((trifluoromethyl)sulfonyl)imide affords high yields of the corresponding salts. This methodology provides a simple route to a variety of room temperature ionic liquids (RTILs).

Toward new paradigms in mixed-valency: ytterbocene–terpyridine charge-transfer complexes

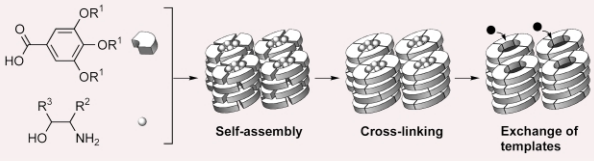
Christopher J. Kuehl, Ryan E. Da Re, Brian L. Scott, David E. Morris* and Kevin D. John*



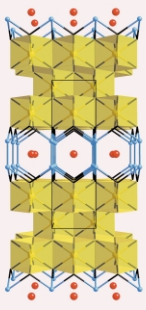
$(C_5Me_5)_2Yb{\cdot}OEt_2$ reacts with terpyridine and tetrapyridinylpyrazine to afford new mixed-valent systems.

Template polymerization of columnar architectures based on the salts of a carboxylic acid and 2-amino alcohols: application to the molecular recognition of 2-amino alcohols

Yasuhiro Ishida, Sayaka Amano and Kazuhiko Saigo*



We found that the salts of trialkoxybenzoic acids and 2-amino alcohols generally show a columnar liquid crystalline phase. When a polymerizable acid unit is used, the resultant columnar structure can be fixed by an *in situ* cross-linking reaction, where the ordered structure is essentially maintained.



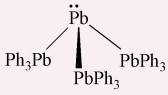
$REAu_4Al_8Si$: the end member of a new homologous series of intermetallics featuring thick $AuAl_2$ layers

Susan E. Latturner and Mercouri G. Kanatzidis*

$REAu_4Al_8Si$ (RE = Ce-Gd, and Yb) is a new intermetallic structure grown from aluminium flux; this new structure contains thick antifluorite $AuAl_2$ slabs and the ytterbium analog exhibits mixed-valent behavior.

Tris(triphenylplumbyl)plumbate: an anion with three stretched lead–lead bonds

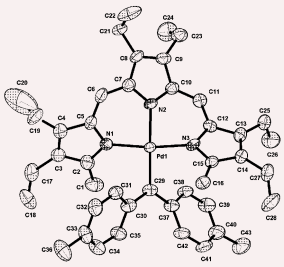
Frank Stabenow, Wolfang Saak and Manfred Weidenbruch*



Treatment of lead(II) bromide with phenylmagnesium bromide at low temperature furnished yellow crystals of an ionic compound whose anion contains three stretched Pb–Pb bonds and Pb–Pb–Pb angles of about 93°.

The first Pd^{II} complex of a non-heteroatom stabilised carbene ligand

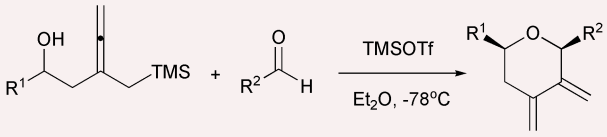
Martin Bröring,* Carsten D. Brandt and Sascha Stellwag



The reaction of the cationic tripyrrinato palladium species TrpyPd BAr^F with di(*p*-tolyl)diazomethane yields the first Pd^{II} carbene complex with a non-heteroatom stabilised carbene ligand.

Synthesis of novel 2,6-disubstituted-3,4-dimethylidene tetrahydropyrans *via* Prins-type cyclization

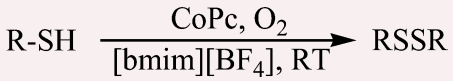
Yong Seo Cho,* Kaliyan Karupaiyan, Hyun Jung Kang, Ae Nim Pae,* Joo Hwan Cha, Hun Yeong Koh and Moon Ho Chang



Synthesis of novel substituted tetrahydropyrans with adjacent *exo*-methylene groups the at C3 and C4 positions *via* Prins-type cyclization has been described.

Oxidation of thiols with molecular oxygen catalyzed by cobalt(II) phthalocyanines in ionic liquid

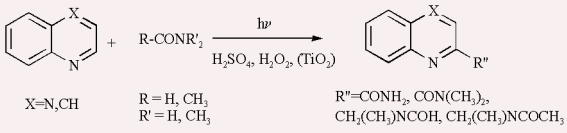
S. M. S. Chauhan,* Anil Kumar and K. A. Srinivas



An efficient procedure for catalyst solubility, recycling and easy product isolation in oxidation of thiols to disulfides with molecular oxygen catalyzed by cobalt(II) phthalocyanines immobilized in ionic liquid at room temperature is reported.

Sunlight induced functionalisation of some heterocyclic bases in the presence of polycrystalline TiO_2

T. Caronna,* C. Gambarotti, L. Palmisano, C. Punta and F. Recupero

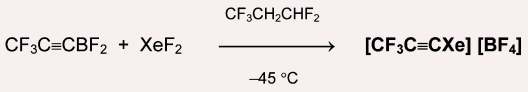


Sunlight induced functionalisation of some heterocyclic bases in the absence or presence of polycrystalline TiO_2 is reported as a new method of less environmental impact.

2352

Trifluoropropynylxenon(II) tetrafluoroborate [$CF_3C{\equiv}CXe$] [BF_4] – isolation of an alkynylxenon(II) compound for the first time

Hermann-Josef Frohn* and Vadim V. Bardin

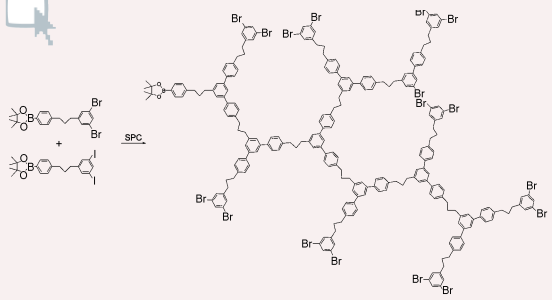


The reaction of the hitherto unknown borane $CF_3C{\equiv}CBF_2$ with XeF_2 yielded the first isolated alkynylxenon(II) salt [$CF_3C{\equiv}CXe$] [BF_4], a compound of relatively high thermal stability in the solid state as well as in anhydrous HF solution.

2354

"AB_2 + AC_2" approach to hyperbranched polymers with a high degree of branching

Zhishan Bo* and A. D. Schlüter

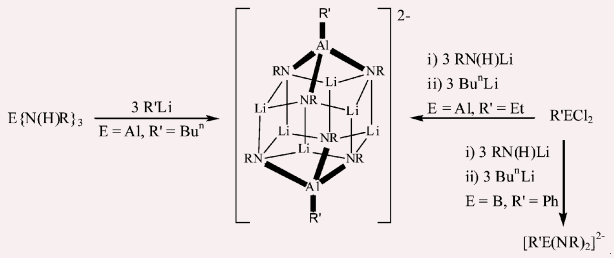


A novel one-pot "AB_2 + AC_2" approach based on palladium catalyzed Suzuki polycondensation was developed to prepare hyperbranched aryl/alkyl polymers with a high degree of branching.

2356

Heterobimetallic lithium alkyltriimido aluminate cages containing the $[R'Al(NR)_3]^{4-}$ tetraanion (R′ = Bu^n, Et; R = 2-$OMeC_6H_4$)

May C. Copsey, John C. Jeffery, Christopher A. Russell,* John M. Slattery and Jennifer A. Straughan

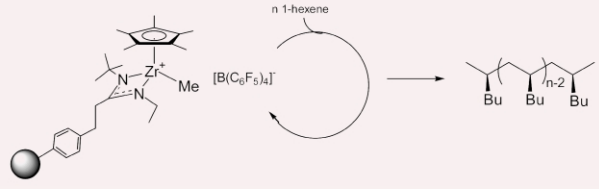


Attempted metallation of a triamidoaluminane gives a complex containing the $[R'Al(NR)_3]^{4-}$ anion whose formal tetranegative charge is the highest charge observed crystallographically for a simple mononuclear imido main group anion system.

2358

Solid-supported stereospecific living Ziegler–Natta polymerization of α-olefins

Yonghui Zhang and Lawrence R. Sita*

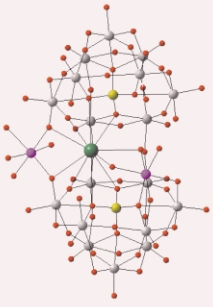


A successful strategy has been developed for the synthesis of a cationic pentamethylcyclopentadienyl zirconium amidinate initiator on a lightly crosslinked polystyrene-divinylbenzene support that can be used to polymerize α-olefins in a living and stereospecific fashion.

2360

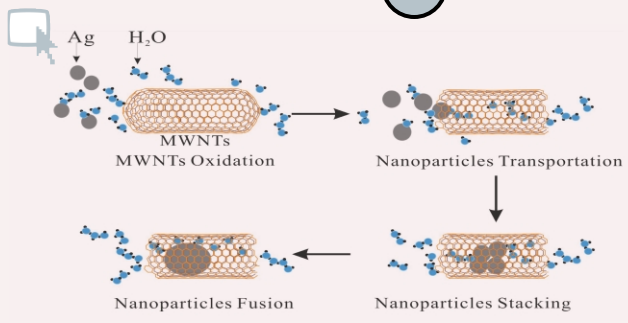
Synthesis, molecular structure and chemical properties of a new tungstosilicate with an open Wells–Dawson structure, α-$[Si_2W_{18}O_{66}]^{16-}$

Nathalie Laronze,* Jérôme Marrot and Gilbert Hervé



A new tungstosilicate α-$[Si_2W_{18}O_{66}]^{16-}$ has been synthesized and its structure determined. It is an intermediate in the formation of the hypothetical α-$[Si_2W_{18}O_{62}]^{8-}$ Wells–Dawson anion. Its open structure allows the fixation of three potassium and transition metal cations.

2362



Transportation of silver nanopaticles in nanochannels of carbon nanotubes with supercritical water

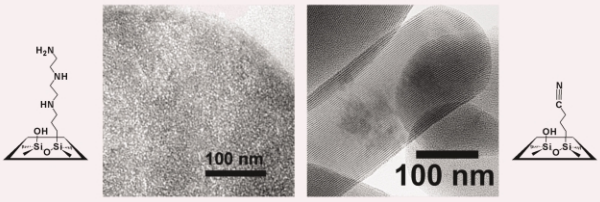
Jia-Yaw Chang, Fu-Der Mai, Bertrand Lo, Jia-Jiu Chang, Shin-Hwa Tzing, Anil Ghule and Yong-Chien Ling*

The destructive nature of supercritical water (SCW) was utilized to open multiwall carbon nanotubes (MWNTs) and to break silver aggregates into nanoparticles (diameter 2–20 nm), which transported in nanochannels of MWNTs by capillary suction and fluidity of SCW, stacked and fused to form nanorods.

2364

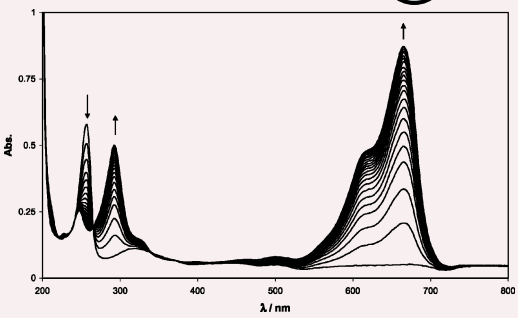
Tuning of particle morphology and pore properties in mesoporous silicas with multiple organic functional groups

Seong Huh, Jerzy W. Wiench, Brian G. Trewyn, Seahn Song, Marek Pruski and Victor S.-Y. Lin*



A synthetic method that can control both multi-functionalization and morphology of mesoporous organic–inorganic hybrid materials has been developed by introducing different molar ratios of organoalkoxysilanes to a co-condensation of silicate.

2366

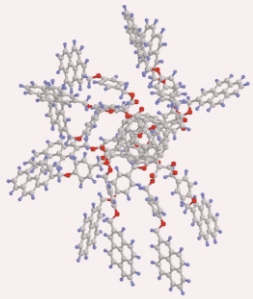


Novel photochemistry of *leuco*-Methylene Blue

Soo-Keun Lee and Andrew Mills*

leuco-Methylene Blue undergoes photo-oxidative quenching with dissolved oxygen to generate Methylene Blue.

2368



Interesting fluorescence properties of C_{60}-centered dendritic adduct with twelve symmetrically attached pyrenes

Robert B. Martin, Kefu Fu, Huaping Li, Daniel Cole and Ya-Ping Sun*

A C_{60}-centered dendritic adduct with 12 symmetrically attached pyrene species was synthesized and found to have relatively simple fluorescence emission kinetics, in particular, the mono-exponential decay of the significant pyrene excimer emission.

2370

$$E_a = \frac{Fd^2}{8}$$

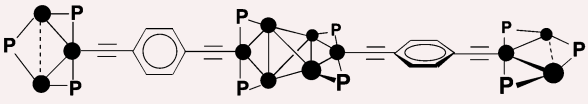
Relationship between rate and distance

Fredric M. Menger,* Ashley L. Galloway and Djamaladdin G. Musaev*

The activation energies for four Smiles reactions vary with the distance squared between the nucleophilic and electrophilic atoms (consistent with theoretical considerations and pertinent to organic and enzymatic catalyses).

Trinuclear and hexanuclear platinum clusters as building blocks for organometallic one-dimensional structures

Piero Leoni,* Fabio Marchetti, Lorella Marchetti and Marco Pasquali



7

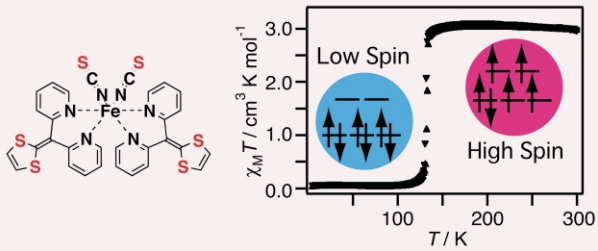
P = PBu^t_2

CO omitted for clarity

The reaction between the new hexa- and trinuclear clusters $Pt_6(CO)_4(\mu\text{-}PtBu_2)_4(CC\text{–}C_6H_4\text{–}CCH)_2$ (**4**) and $Pt_3(\mu\text{-}PtBu_2)_3(CO)_2Cl$(**6**) in CuI/Amine gives the thermally and air stable molecular wire **7**, where the cluster units are separated by conjugated 1,4-diethynylphenyl groups.

An abrupt spin transition based on short S···S contacts in a novel Fe(II) complex whose ligand contains a 1,3-dithiole ring

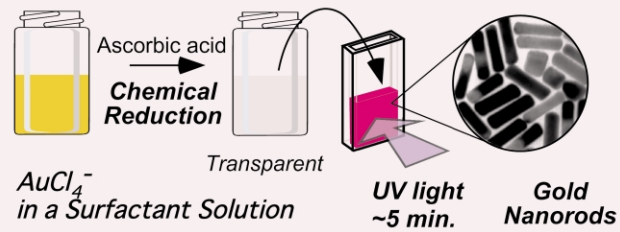
Kazuyuki Takahashi, Tomoko Kawakami, Zhong-ze Gu, Yasuaki Einaga, Akira Fujishima and Osamu Sato*



The first preparation of an Fe(II) spin-crossover complex including a 1,3-dithiole ligand is reported. Crystal analyses of both the low- and the high-temperature phases reveal that short S···S contacts play a key role in an abrupt spin transition.

Rapid synthesis of gold nanorods by the combination of chemical reduction and photoirradiation processes; morphological changes depending on the growing processes

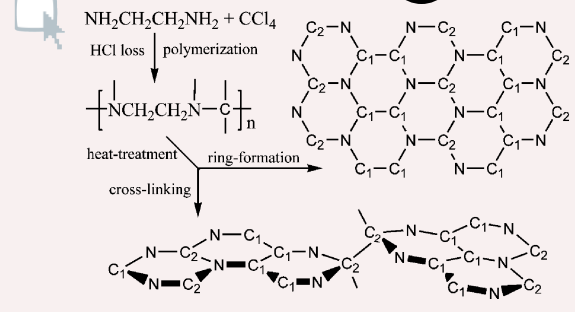
Yasuro Niidome,* Koji Nishioka, Hideya Kawasaki and Sunao Yamada*



Combination of chemical reduction of tetrachloroaurate by ascorbic acid and subsequent ultraviolet photoirradiation resulted in the quick generation of gold nanorods.

Chemical synthesis of turbostratic carbon nitride, containing C–N crystallites, at atmospheric pressure

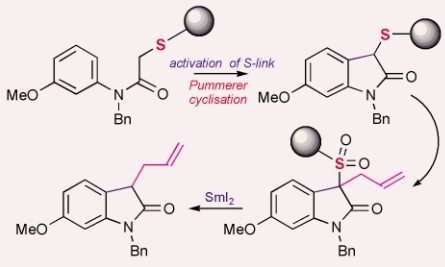
Yu Qiu and Lian Gao*



Turbostratic carbon nitride (*t*-CN_x) is chemically synthesized at atmospheric pressure, containing small C–N crystallites in the α-C_3N_4 structure. This *t*-CN_x material is a very promising precursor for superhard carbon nitride synthesis at atmospheric pressure.

The first Pummerer cyclisations on solid phase. Convenient construction of oxindoles enabled by a sulfur-link to resin

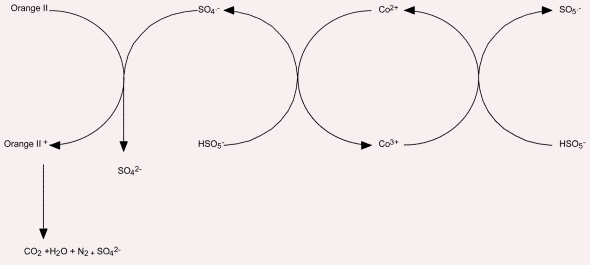
Laura A. McAllister, Stephen Brand, Rémy de Gentile and David J. Procter*



α-Sulfanyl *N*-aryl acetamides attached to resin *via* sulfur undergo efficient Pummerer cyclisation to give oxindoles upon activation of the sulfur link. The sulfur link enables the cyclisation chemistry but remains intact. Heterocyclic products are cleaved from resin using SmI_2.

2382

Photobleaching of Orange II within seconds using the oxone/Co^{2+} reagent through Fenton-like chemistry



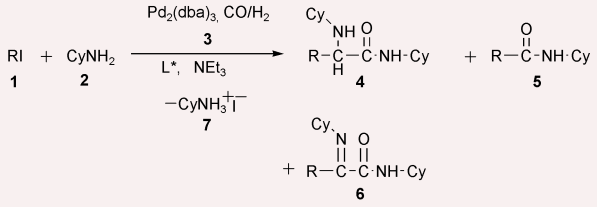
Javier Fernandez, Victor Nadtochenko and John Kiwi*

The oxidation of organic compounds by peroxomonosulfate under visible light in the presence of Co^{2+} produces highly oxidizing sulfate radicals able to photobleach azo-dyes within seconds in Fenton-like processes.

2384

Asymmetric synthesis of α-aminoamides by Pd-catalyzed double carbohydroamination

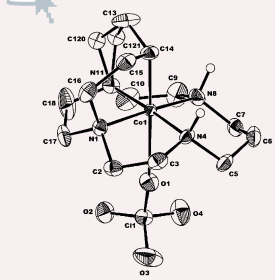
Perli Nanayakkara and Howard Alper*

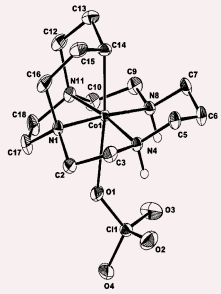


Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] catalyzed asymmetric double carbohydroamination of iodoarenes in the presence of a chiral ligand is an excellent method for the chiral synthesis of α-aminoamides (**4**) in up to 99% ee.

2386

The first structurally characterised perchlorato-cobalt(III) complexes, involving the C-bonded macrobicyclic ligand 1,4,8,11-tetraazabicyclo[9.5.2]octadecane





Xiangting Zhou, Anthony I. Day, Anthony C. Willis and W. Gregory Jackson*

Two isomeric C-bonded complexes, *sym-anti*-$[Co(L\text{-}C)(OH_2)]^{2+}$ and *sym-syn*-$[Co(L\text{-}C)(OH_2)]^{2+}$ (L = 1,4,8,11-tetraazabicyclo[9.5.2]octadecane) when crystallised from aqueous $NaClO_4$ remarkably yielded the corresponding perchlorato complexes.

COPIES OF CITED ARTICLES

The Library and Information Centre (LIC) of the RSC offers a first class Document Delivery Service for items in Chemistry and related subjects. Contact the LIC, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, UK.

This service is only available from the LIC in London and not the RSC in Cambridge.

ADVANCE CONTENTS LISTS

Contents lists in advance of publication are available on the web via www.rsc.org/chemcomm – or take advantage of our free e-mail alerting service (www.rsc.org/ej_alert) to receive notification each time a new list becomes available.

ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See www.rsc.org/ejs for more information.

* Indicates the author for correspondence: see article for contact details.

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

NOTE: An asterisk in the heading of each paper indicates the author who is to receive any correspondence.