

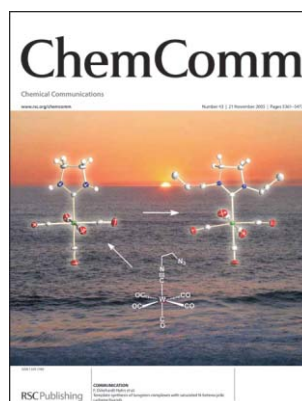
IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (43) 5361-5472 (2005)



Cover

See Christoph Weder, page 5378. The introduction of π -conjugated cross-links between conjugated macromolecules leads to network polymers with interesting electronic characteristics. Image reproduced by permission of Christoph Weder from *Chem. Commun.*, 2005, 5378.



Inside cover

See F. Ekkehardt Hahn *et al.*, page 5390. A new route leading to complexes with imidazolin-2-ylidene ligands by template controlled cyclization of 2-azidoethyl isocyanide is presented. Image reproduced by permission of F. Ekkehardt Hahn, Volker Langenhahn and Tania Pape from *Chem. Commun.*, 2005, 5390.

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T41

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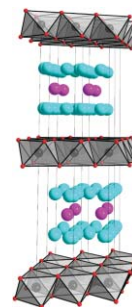
40TH ANNIVERSARY ARTICLE

5373

Contemporary superconducting materials

R. J. Cava

Recently discovered superconductors are described from a chemical perspective and put in context.



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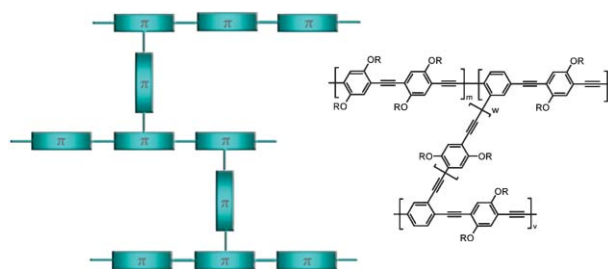
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5378

Synthesis, processing and properties of conjugated polymer networks

Christoph Weder*

The introduction of π -conjugated cross-links between conjugated macromolecules leads to network polymers that may offer interesting electronic characteristics, in particular improved charge transport. In this review, the synthesis, processing and electronic properties of such materials are discussed on the basis of selected examples.



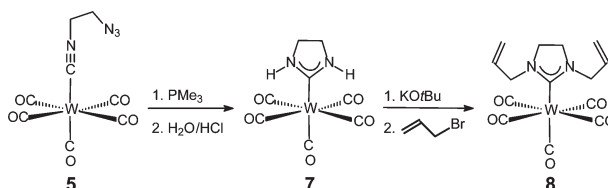
COMMUNICATIONS

5390

Template synthesis of tungsten complexes with saturated N-heterocyclic carbene ligands

F. Ekkehardt Hahn,* Volker Langenhahn and Tania Pape

A tungsten complex with an imidazolidin-2-ylidene ligand, **8**, was obtained from the isocyanide complex **5** by activation of the azido group in a Staudinger reaction followed by hydrolysis and cyclization to complex **7** and subsequent double *N*-alkylation.

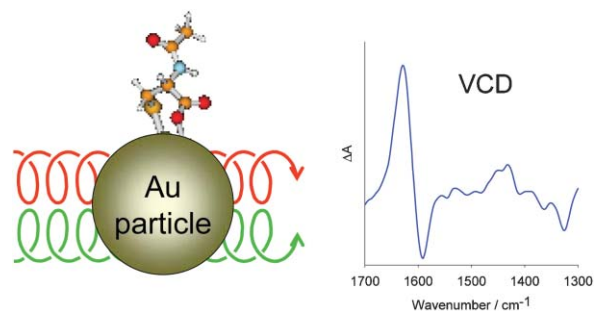


5393

Vibrational circular dichroism of *N*-acetyl-L-cysteine protected gold nanoparticles

Cyrille Gautier and Thomas Bürgi*

Vibrational circular dichroism reveals the conformation of a chiral thiol, *N*-acetyl-L-cysteine, adsorbed on gold nanoparticles by a comparison between experimental and calculated spectra.

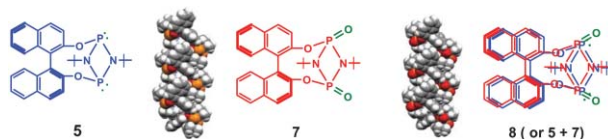


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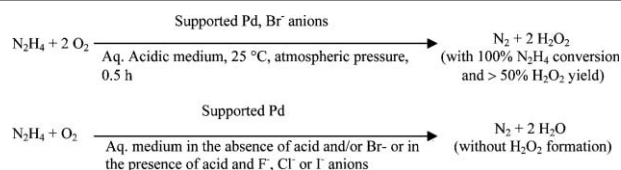
Non-stoichiometry induced by differential oxygen/lone pair occupation in chiral bicyclic 1,1'-binaphthoxy cyclodiphosphazanes

Manab Chakravarty, Praveen Kommana and K. C. Kumara Swamy*

A set of chiral binaphthol based phosphorus compounds in which there is interchangeability of oxygen and lone pair positions that allows them to crystallize in an isostructural manner, and further to non-stoichiometry, is highlighted.



5399

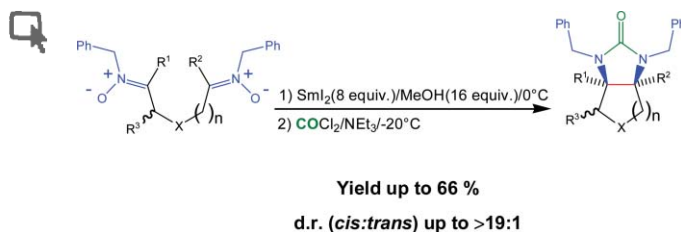


A novel route for *in-situ* H₂O₂ generation from selective reduction of O₂ by hydrazine using heterogeneous Pd catalyst in an aqueous medium

Vasant R. Choudhary,* Chanchal Samanta and Prabhas Jana

Selective reduction of dioxygen by hydrazine using supported Pd catalyst in aqueous medium provides a novel route for *in-situ* H₂O₂ generation in high yields at ambient conditions with formation of nitrogen and water as by-products.

5402

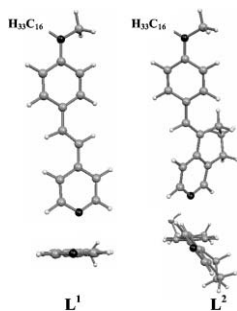


Samarium diiodide-induced intramolecular pinacol coupling of dinitrones: synthesis of cyclic *cis*-vicinal diamines

Jean-Philippe Ebran, Rita G. Hazell and Troels Skrydstrup*

Pinacol coupling of alkyl dinitrones mediated by SmI₂ was achieved in the presence of a proton source allowing the synthesis of cyclic vicinal diamines with good *cis*-selectivity.

5405

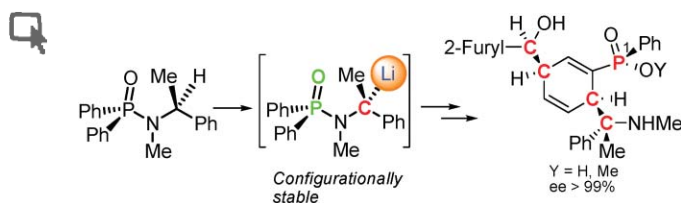


The unexpected similar second-order NLO response for nearly planar and largely twisted push–pull stilbazole chromophores: EFISH and theoretical TD-DFT evidence

Danika Locatelli, Silvio Quici, Dominique Roberto* and Filippo De Angelis*

The quadratic hyperpolarizability (β) of planar (*E*)-4-[2-(4-(*N*-methyl-*N*-hexadecylamino)phenyl)ethenyl]pyridine (L¹) and [Ir(CO)₂CIL¹] is similar to that of related but twisted ligand (L²) and [Ir(CO)₂CIL²], respectively, showing that a planar structure is *not compulsory* to reach high β .

5408



Unprecedented asymmetric induction through configurationally stable lithium *N*-(α -methylbenzyl)-phosphinamides. A new entry to enantiomerically pure γ -aminophosphinic acids and esters

Ignacio Fernández, Gloria Ruiz Gómez, Ignacio Alfonso, María J. Iglesias and Fernando López Ortiz*

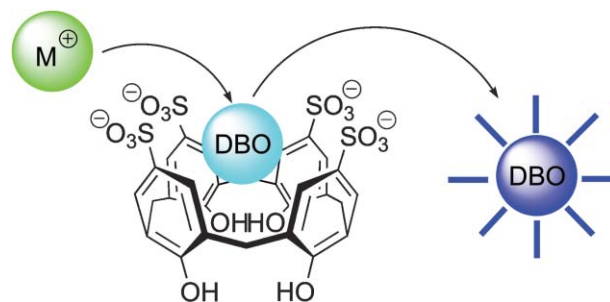
The first examples of configurationally stable *N*-benzyl-*N*-phosphinoyl carbanions and their applications to the synthesis of homochiral γ -aminophosphinic acids and esters *via* highly enantioselective dearomatizing reactions are described.

5411

Binding of inorganic cations by *p*-sulfonatocalix[4]arene monitored through competitive fluorophore displacement in aqueous solution

Hüseyin Bakirci, Apurba L. Koner and Werner M. Nau*

Binding of monovalent cations (alkali and ammonium) to the water-soluble *p*-sulfonatocalix[4]arene, which has previously evaded detection, can be sensitively monitored by competitive displacement of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), a fluorescent azoalkane.

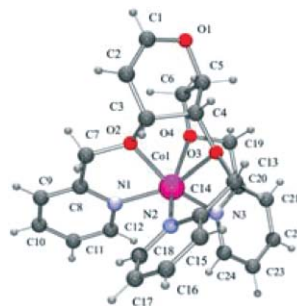


5414

Superoxide dismutase-like activity of cobalt(II) complexes based on a sugar platform

François Bellot, Renaud Hardré, Giorgio Pelosi, Michel Thérísod and Clotilde Policar*

In the strategy introduced here, sugars are used as a distribution frame that organizes Lewis bases in space to generate a chelation site for metal cation. Two crystallized Co(II) complexes with SOD-like activity are presented.

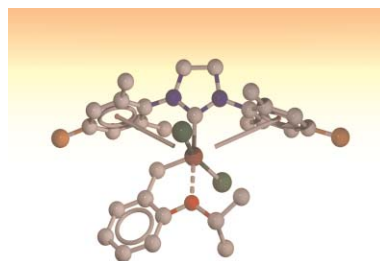


5417

π -Face donor properties of N-heterocyclic carbenes

Marcus Süßner and Herbert Plenio*

In order to fully account for the donor properties of N-heterocyclic carbenes, interactions of the π -face of the aryl substituents with the metal center have to be considered.

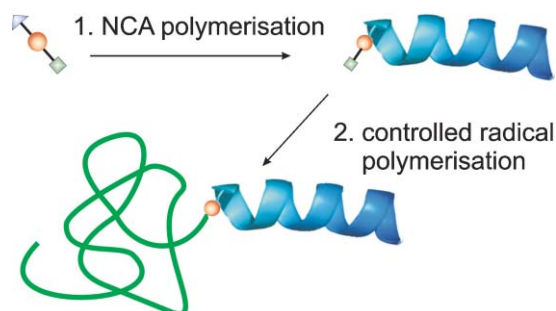


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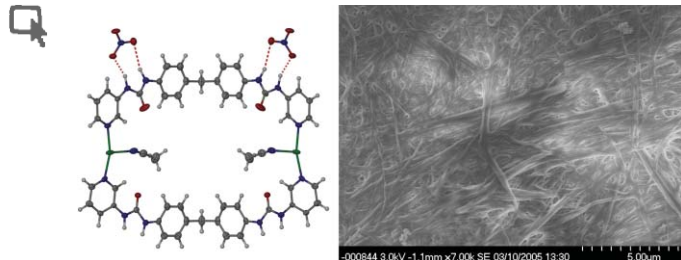
Synthesis of polypeptide based rod-coil block copolymers

Simone Steig, Frauke Cornelius, Peter Witte, Bastiaan B. P. Staal, Cor E. Koning, Andreas Heise and Henning Menzel*

Synthesis of polypeptide based rod-coil block copolymers was accomplished employing a bifunctional initiator in a sequence of a nickel initiated polymerization of γ -benzyl-L-glutamate-*N*-carboxy anhydride and atom transfer radical polymerization of methyl methacrylate.



5423

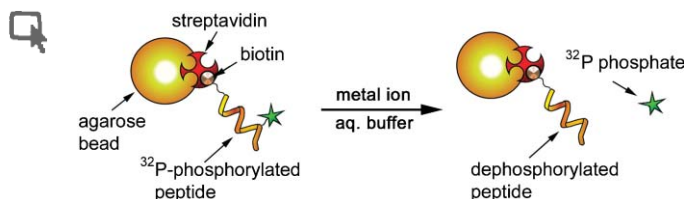


Modular nanometer-scale structuring of gel fibres by sequential self-organization

Lucas Applegarth, Nigel Clark, A. Christine Richardson, Andrew D. M. Parker, Ivana Radosavljevic-Evans, Andres E. Goeta, Judith A. K. Howard and Jonathan W. Steed*

Metal complexes of rigid bis(urea) ligands form metallogels with properties dependent on the identity of the added metal salt.

5426

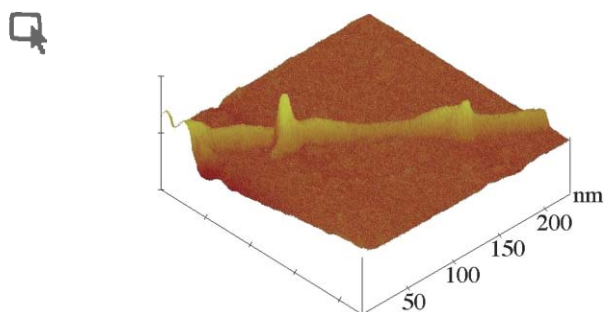


Lanthanide-mediated phosphoester hydrolysis and phosphate elimination from phosphopeptides

Nathan W. Luedtke and Alanna Schepartz*

Lanthanide ions can mediate both phosphomonoester hydrolysis and β -elimination of inorganic phosphate from polypeptide substrates under near-physiological conditions of pH, temperature, and salt.

5429

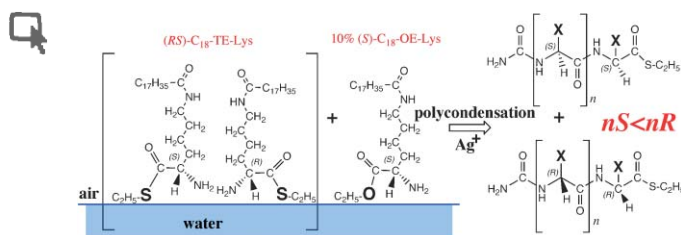


AFM and STM characterization of thiol and thiophene functionalized SWNTs: pitfalls in the use of chemical markers to determine the extent of sidewall functionalization in SWNTs

Lei Zhang, Jun Zhang, Nicolaus Schmandt, Justin Cratty, Valery N. Khabashesku, Kevin F. Kelly* and Andrew R. Barron*

STM measurements show that the use of Au nanoparticles as chemical markers for AFM imaging can lead to misleading results for substituent distribution.

5432



Homochiral oligopeptides generated via an asymmetric induction in racemic 2D crystallites at the air-water interface; the system ethyl/thio-ethyl esters of long-chain amphiphilic α -amino acids

Irina Rubinstein, Kristian Kjaer, Isabelle Weissbuch* and Meir Lahav*

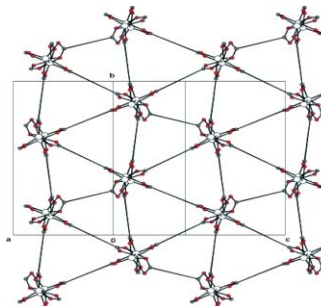
N^{ϵ} -stearoyl-lysine-ethyl-ester is an efficient desymmetrizing agent for the generation of homochiral oligopeptides via a reaction catalyzed by Ag^+ in 2D quasi-racemic crystallites of the corresponding thio-ester self-assembled at the air-water interface.

5435

A unique example of a 3^6 tessellated 2-D net based on a tri-nuclear zinc(II)-1,4-benzenedicarboxylate framework

Colleen A. Williams, Alexander J. Blake, Peter Hubberstey* and Martin Schröder*

An unprecedented 3^6 tessellated 2-D sheet architecture in which tri-nuclear zinc(II)-containing building blocks are linked by bridging 1,4-benzenedicarboxylate (1,4-BDC) anions is adopted by $\{[\text{Zn}_3(1,4\text{-BDC})_3(\text{DEF})_2]\cdot\text{DEF}\}_\infty$ (DEF = diethylformamide).

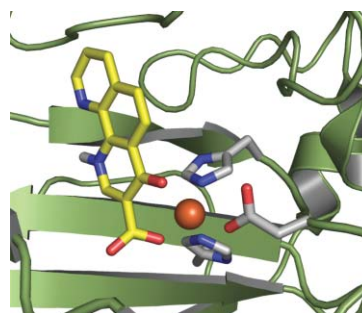


5438

The inhibition of factor inhibiting hypoxia-inducible factor (FIH) by β -oxocarboxylic acids

Biswadip Banerji, Ana Conejo-Garcia, Luke A. McNeill, Michael A. McDonough, Matthew R. G. Buck, Kirsty S. Hewitson, Neil J. Oldham and Christopher J. Schofield*

Cyclic β -oxocarboxylic acids inhibit factor inhibiting hypoxia-inducible factor *via* ligation to the active site iron.

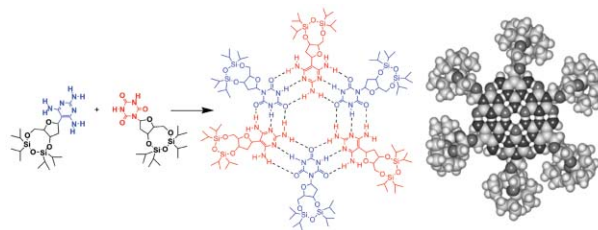


5441

Hydrogen-bond self-assembly of DNA-analogues into hexameric rosettes

Felaniaina Rakotonradany, Alison Palmer, Violeta Toader, Bingzhi Chen, M. A. Whitehead and Hanadi F. Sleiman*

Triaminopyrimidine and cyanuric acid-based nucleosides undergo self-assembly into a DNA-analogue hexameric rosette, which subsequently aggregates into rod-like morphologies.

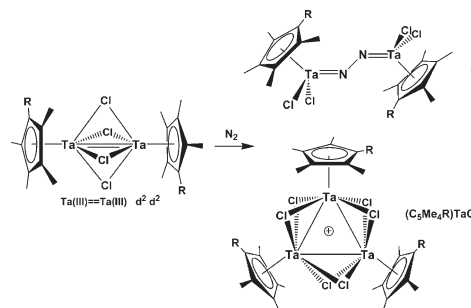


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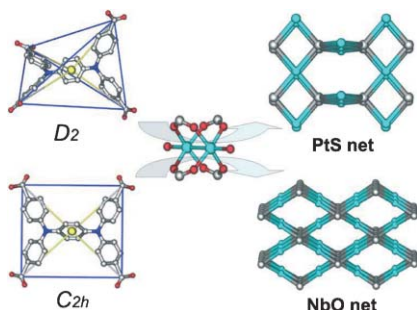
Four-electron reduction of dinitrogen during solution disproportionation of the organodimetallic $(\eta\text{-C}_5\text{Me}_4\text{R})_2\text{Ta}_2(\mu\text{-Cl})_4$ ($\text{R} = \text{Me}, \text{Et}$) to a new $\mu\text{-}\eta^1, \eta^1\text{-N}_2$ complex and odd-electron organotrimetallic cluster

Ting-Yu Lee, Alfred J. Wooten, Jeffrey J. Luci, Dale C. Swenson and Louis Messerle*

The $d^2\text{-}d^2$ organodimetallic $(\text{C}_5\text{Me}_4\text{R})_2\text{Ta}_2(\mu\text{-Cl})_4$ disproportionates in toluene under N_2 to the new organodimetallic N_2 complex $[(\text{C}_5\text{Me}_4\text{R})\text{TaCl}_2]_2(\mu\text{-N}_2)$ and novel organotrimetallic cluster $[(\text{C}_5\text{Me}_4\text{R})_3\text{Ta}_3(\mu\text{-Cl})_6][(\text{C}_5\text{Me}_4\text{R})\text{TaCl}_4]$.



5447

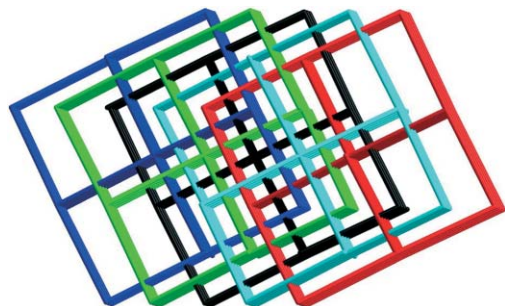


Temperature-dependent supramolecular stereoisomerism in porous copper coordination networks based on a designed carboxylate ligand

Daofeng Sun, Yanxiong Ke, Tracy M. Mattox, Betty A. Ooro and Hong-Cai Zhou*

Two temperature-determined, supramolecular stereoisomers of porous copper coordination networks possessing PtS and NbO net topologies, based on a new tetra-carboxylate ligand, have been synthesized and characterized.

5450

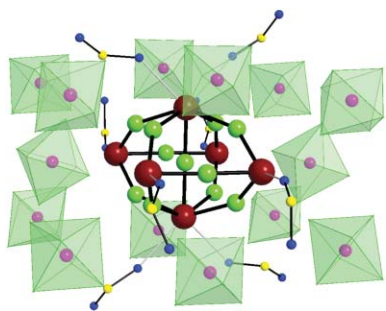


An unprecedented fivefold interpenetrated 1vt network containing the exceptional racemic motifs originated from nine interwoven helices

Xin-Long Wang, Chao Qin, En-Bo Wang,* Yang-Guang Li and Zhong-Min Su*

An unprecedented fivefold interpenetrated 1vt network, containing the rare racemic motifs originated from nine interwoven helices, is reported, representing the highest degree of interpenetration presently known for 3D nets containing only planar four-coordinate nodes.

5453

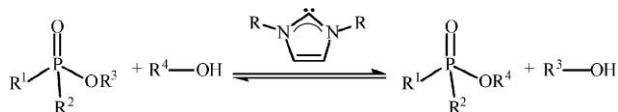


[Bi₆F₁₁]⁷⁺—an unusual, highly charged bismuth fluoro complex in (Se₄)[Bi₆F₁₁][AsF₆]₉·10 SO₂

Johannes Beck* and Folker Steden

The oxidation of Bi₂Se₃ by AsF₅ in liquid SO₂ achieves (Se₄)[Bi₆F₁₁][AsF₆]₉·10 SO₂ as yellow crystals in high yield. Besides square-planar Se₄²⁺ ions the structure contains a unique, highly charged cationic bismuth fluoro cluster [Bi₆F₁₁]⁷⁺ which is surrounded by [AsF₆]⁻ ions and coordinated SO₂ molecules.

5456



Synthesis of phosphorus esters by transesterification mediated by *N*-heterocyclic carbenes (NHCs)

Rohit Singh and Steven P. Nolan*

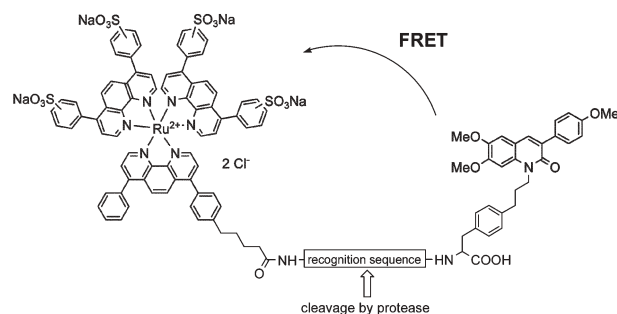
The nucleophilic organic catalysts *N*-heterocyclic carbenes (NHCs) have been shown to effectively mediate the transesterification of phosphorus esters under mild conditions. The effect of various parameters on the efficiency of the protocol has been studied. User-friendly imidazolium salts can also be employed as pre-catalysts.

5459

Synthesis of a new pair of fluorescence resonance energy transfer donor and acceptor dyes and its use in a protease assay

Eva Katharina Kainmüller, Eulàlia Pinyol Ollé and Willi Bannwarth*

A new, efficient and very robust fluorescence resonance energy transfer (FRET) system, which can be measured in a normal as well as in a time-resolved mode, was developed and its feasibility demonstrated in a protease assay format.

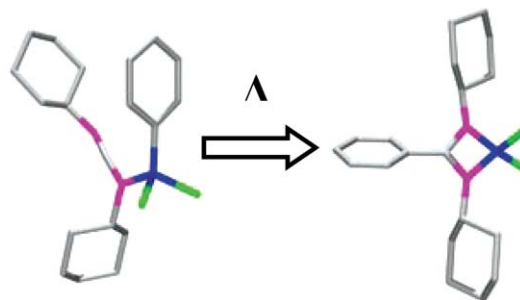


5462

Isolation of an intermediate in the insertion of a carbodiimide into a boron-aryl bond

Nicholas J. Hill, Jennifer A. Moore, Michael Findlater and Alan H. Cowley*

A 1 : 1 Lewis acid–base complex between $\text{CyN}=\text{C}=\text{NCy}$ and PhBCl_2 has been isolated and structurally characterized, heating of which in refluxing toluene results in the amidinate, $[\text{PhC}\{\text{NCy}\}_2\text{BCl}_2]$; the overall reaction has been modeled by DFT calculations.

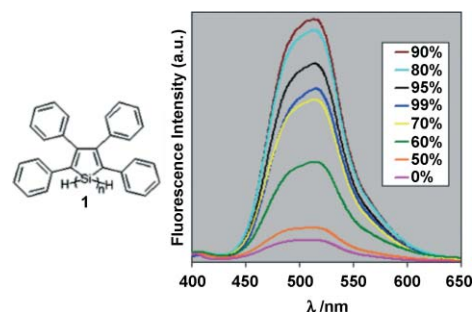


5465

Luminescent oligo(tetraphenyl)silole nanoparticles as chemical sensors for aqueous TNT

Sarah J. Toal, Douglas Magde* and William C. Troglor*

Colloidal oligo(tetraphenyl)silole nanoparticles in THF/ H_2O suspensions show increased luminescence and offer a method to detect TNT as low as 20 ppb in an aqueous environment.

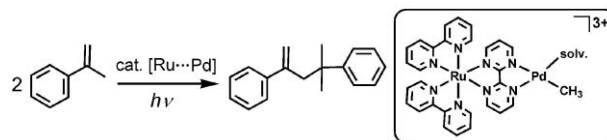


5468

Highly selective photo-catalytic dimerization of α -methylstyrene by a novel palladium complex with photosensitizing ruthenium(II) polypyridyl moiety

Akiko Inagaki,* Shinichi Edure, Shinichi Yatsuda and Munetaka Akita*

A novel dinuclear $\text{Ru}\cdots\text{Pd}$ complex containing a photo-sensitizing unit and the Pd center was effective toward selective dimerization of α -methylstyrene to give 2,4-diphenyl-4-methyl-1-pentene under visible-light irradiated conditions.




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