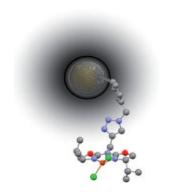
# CONTENTS

# REVIEWS

High surface area, excellent accessibility, and the ability to readily disperse in common solvents facilitate the use

of nanoparticles as semi-heterogeneous supports. Reversible agglomeration through solvent changes and magnetic separation provide technically attractive alternatives to classical catalyst filtration.



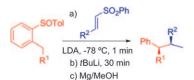
#### Nanocatalysis

A. Schätz, O. Reiser, W. J. Stark\*......8950 – 8967

Nanoparticles as Semi-Heterogeneous **Catalyst Supports** 

# COMMUNICATIONS

One-pot benzylation of (E)-vinylsulfones with optically pure 2-p-tolylsulfinylbenzyl carbanions and desulfinylation with tBuLi, followed by desulfonylation of the resulting 1-sulfonylpropanes, provided acyclic hydrocarbons containing two connected chiral centers in very smooth conditions and almost complete control of the stereoselectivity (see scheme).

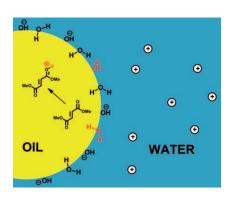


# **Asymmetric Synthesis**

J. L. García Ruano,\* C. Schöpping, C. Alvarado, J. Alemán\*... 8968-8971

Synthesis of Unfunctionalized Carbonated Fragments Containing Two Vicinal Chiral Centers: Stereocontrolled Benzylation of Vinylsulfones Mediated by a Remote Sulfinyl Group

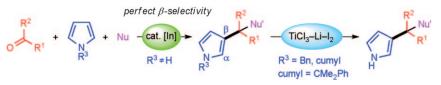
Acid catalysis by interfacial water: A new mechanism is proposed for onwater catalysis, the acceleration of organic reactions when conducted in aqueous emulsions. It involves the protonation of a substrate by water, driven by the strong adsorption of hydroxide ions at aqueous interfaces with oils. This accounts for the specific role of water, and a deuterium isotope effect, at the interface, on reactions known to be acid-catalysed.



# **Biphasic Catalysis**

J. K. Beattie, \* C. S. P. McErlean, \* C. B. W. Phippen ...... 8972 – 8974

The Mechanism of On-Water Catalysis .....



No longer difficult: Just mixing readily available carbonyl compounds, pyrroles, and nucleophiles with an indium catalyst was found to give β-alkylpyrroles in a regiospecific manner.

Removal of benzyl (Bn) and cumyl groups from the nitrogen atoms of the products enables access to nitrogenunsubstituted β-alkylpyrroles (see scheme).

#### **Indium Catalysis**

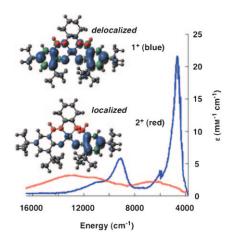
T. Tsuchimoto,\* M. Igarashi, K. Aoki ...... 8975 – 8979

under Indium Catalysis: Carbonyl Compounds as Sources of Alkyl Groups

#### **Nickel Intervalence Complexes**

T. Storr, P. Verma, Y. Shimazaki,\* E. C. Wasinger,

Ligand Radical Localization in a
Nonsymmetric One-Electron Oxidized
Ni<sup>II</sup> Bis-phenoxide Complex



Catching the radical: Characterization of an oxidized nonsymmetric Ni<sup>II</sup>–Salalen complex 2<sup>+</sup> has demonstrated that the ligand radical is localized on the more electron-rich aminophenolate, and can be described as a Class II intervalence complex. This is in contrast to the oxidized symmetric salen analogue 1<sup>+</sup>, in which the radical is fully delocalized across the ligand framework, a Class III species.

#### Allylation

C. M. R. Volla, D. Marković, S. Laclef, P. Vogel\*......8984-8988

☐ The Catalyzed Desulfinylative Allylation of Carbonyl Compounds with Alk-2-enesulfonyl Chlorides and Silyl Alk-2-enesulfinates

$$R^{3} \xrightarrow{R^{1}} R^{1} \xrightarrow{+SO_{2}} R^{3} \xrightarrow{R^{2}} R^{1}$$

$$X = CI \text{ or } Me_{3}Si$$

Coupling up with sulfonyl chlorides:

An ene reaction of alkenes with  $SO_2 \cdot BCl_3$  permits the one-pot conversion of simple alkenes into  $\beta, \gamma$ -unsaturated sulfonyl chlorides or sulfinic silyl esters. These compounds can then be used as nucleophilic allylating agents

with aldehydes and ketones to generate the corresponding homoallylic alcohols (see scheme) with good chemo- and diastereoselectivity in the presence of a suitable catalyst and reducing agent.

#### **Asymmetric Synthesis**

*J. Karthikeyan, M. Jeganmohan, C.-H. Cheng*\*......8989 – 8992

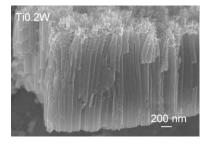
Cobalt-Catalyzed Addition Reaction of Organoboronic Acids with Aldehydes: Highly Enantioselective Synthesis of Diarylmethanols

**Predicted outcomes**: The addition reaction of organoboronic acids with aldehydes in the presence of  $K_2CO_3$  catalyzed by  $CoI_2/(R,R)$ -BDPP gives chiral secondary alcohols in excellent yields with 90–99% enantiomeric excess (see scheme; (R,R)-BDPP = (2R,4R)-(+)-2,4-bis(diphenylphosphino)pentane). This method provides an alternative to prepare an R and S enantiomeric pair by using the same chiral ligand and allows the stereochemical outcome of the reaction to be predicted.

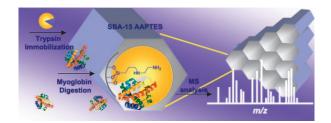
#### Nanostructures

I. Paramasivam, Y.-C. Nah, C. Das, N. K. Shrestha,

**■ WO**√TiO₂ Nanotubes with Strongly Enhanced Photocatalytic Activity



Mixed oxide photocatalysts:  $WO_3$ -containing  $TiO_2$  nanotubes were prepared by self-organizing electrochemical anodization of TiW alloys (Ti0.2W) see figure, and Ti9W). It is shown that a content of only 0.2 at %  $WO_3$  with respect to the titania nanotubes leads to a very significant increase of the photocatalytic reaction rate compared not only to pure anatase  $TiO_2$  nanotubes, but also in comparison with any other modified  $TiO_2$  nanotube system reported up to now.



Efficient mesoporous proteolytic networks: N-(2-Aminoethyl)-3-aminopropyl-derivatized mesoporous silica particles, with a 4.4 nm pore diameter, efficiently promote a comfortable entrapment of trypsin into mesoporous networks, thus providing very fast and

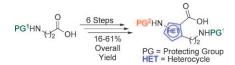
effective proteolytic activity. The rapid digestion and highly confident protein identification (100% sequence coverage in just 1 min) offers a practical and convenient alternative to conventional in-solution digestion.

#### **Proteolytic devices**

F. Casadonte, L. Pasqua, R. Savino, R. Terracciano\*......8998-9001

Smart Trypsin Adsorption into N-(2-Aminoethyl)-3-aminopropyl-Modified Mesoporous Silica for Ultra Fast **Protein Digestion** 

An efficient strategy has been developed for the synthesis of heteroaromatic amino acids (HAAs). These methods generate mono- or orthogonally protected diamino acids from βamino acids (see scheme). Their synthetic reliability and biological potential was demonstrated through the synthesis of an anthranilate synthase (AS) and isochorismate synthase (IS) inhibitor with improved potency.



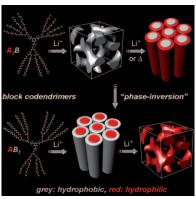
## **Diversity-Oriented Methods**

J. D. Butler, K. C. Coffman, K. T. Ziebart, M. D. Toney, M. J. Kurth\*.....9002-9005

**Orthogonally Protected Thiazole and** Isoxazole Diamino Acids: An Efficient Synthetic Route

Self-Assembly -

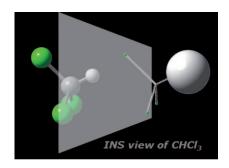
Discotic block codendrimers, consisting of two different nonmesogenic aliphatic polyether dendrons and a discotic linker, exhibited induced hexagonal columnar and bicontinuous cubic (unprecedented in dendrimers) liquidcrystalline (LC) phases by the addition of lithium salt (see figure). The interior and exterior of these morphologies can be altered by changing the majority dendritic block.



J.-W. Choi, M.-H. Ryu, E. Lee, B.-K. Cho\*......9006-9009

**Ion-Induced Bicontinuous Cubic and** Columnar Liquid-Crystalline Assemblies of Discotic Block Codendrimers

Weak interactions revealed: C-H...O hydrogen bonds were studied in the chloroform -- acetone system (see picture) by using inelastic neutron scattering (INS) spectroscopy to search for the vH···O anti-translational mode associated with the interaction itself. C-H--O systems behave as an entity independent from the separate donor and acceptor, and thus these interactions play a key role in supramolecular chemistry.



# **FULL PAPERS**

## **Hydrogen Bonds**

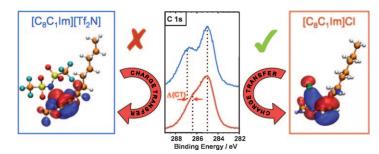
P. D. Vaz,\* M. M. Nolasco, F. P. S. C. Gil, P. J. A. Ribeiro-Claro,\* *J. Tomkinson* ...... 9010 – 9017

Hydrogen-Bond Dynamics of C-H...O 🔲 Interactions: The Chloroform...Acetone Case

#### **Ionic Liquids**

T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, R. Wölfel, P. S. Schulz, P. Wasserscheid, H. Weber, J. Thar, B. Kirchner, F. Maier,\* H.-P. Steinrück ...... 9018 – 9033

☐ Towards a Molecular Understanding of Cation-Anion Interactions-**Probing the Electronic Structure of Imidazolium Ionic Liquids by NMR** Spectroscopy, X-ray Photoelectron **Spectroscopy and Theoretical Calculations** 



Charges in charged systems: Anion and cation interactions in ionic liquids strongly modify the charges on the ions as proven by XPS, NMR spectroscopy and DFT calculations. The smaller, more basic and, thus, more strongly coordinating the anion, the

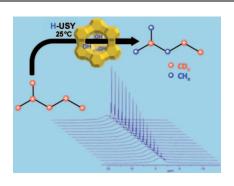
more pronounced the charge transfer to the cation (see graphic). Hydrogenbonding-type interactions between anion and cation do not significantly influence the amount of charge transferred.

#### **Kinetics**

M. Haouas,\* G. Fink, F. Taulelle,\* *J. Sommer* ...... 9034 – 9039



Low-Temperature Alkane C-H Bond Activation by Zeolites: An In Situ Solid-State NMR H/D Exchange **Study for a Carbenium Concerto** 



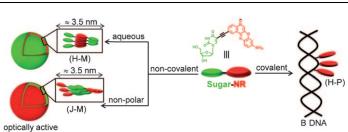
**C-H bond activation**: The in situ MASNMR H/D exchange study between 2-[D<sub>14</sub>]methylpentane and H-USY zeolite proves that even at room temperature, carbenium ions are bona fide reaction intermediates on this catalyst (see figure).

#### **Dye Aggregates**

R. Varghese,

H.-A. Wagenknecht\*......9040-9046

■ Non-covalent Versus Covalent Control of Self-Assembly and Chirality of Nile Red-modified Nucleoside and DNA



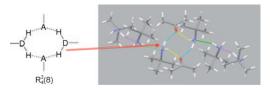
Twisted chemistry! Non-covalent assembly of Nile-red-modified 2'-deoxyuridine results in the formation of optically active vesicles (see scheme) in non-polar media through lefthanded helically twisted J-type (J-M) packing of the dye, whereas helically

twisted H-type (H-M) packing of the same chirality is favoured in aqueous media. The subsequent covalent incorporation of the nucleoside into DNA reveals an inversion of the induced chirality of the H-aggregates (H-P).

#### **Crystal Engineering**

J. Bernstein,\* J. J. Novoa, R. Boese, S. A. Cirkel ...... 9047 – 9055

**Design and Preparation of Co-crystals** Utilizing the R<sub>4</sub><sup>2</sup>(8) Hydrogen-Bonding Motif

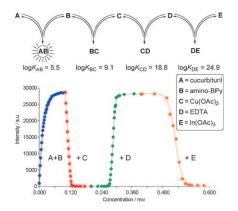


#### A 4-center supramolecular synthon:

The energetics of co-crystal formation based on the hydrogen-bond motif  $R_4^2(8)$  have been computationally

investigated and experimentally verified (see figure; A = acceptor, D = donor).

Join the cascade: Remarkably large fluorescence enhancement occurs upon formation of inclusion complexes between 4-aminobipyridine derivatives and cucurbit[6]uril (see figure), and is used as a switchable beacon to monitor cascades of binding networks. These beacons were used for chemical sensing of transition metals and other ligands, direct measurement of binding constants, and quantitative monitoring of biocatalytic reactions and determination of their kinetic parameters.



#### **Host–Guest Chemistry**

M. K. Sinha, O. Reany, G. Parvari, A. Karmakar, E. Keinan\*..9056-9067

Switchable Cucurbituril-Bipyridine Beacons



**Multitasking**: A class of multitask-specific phosphonium ionic liquids (ILs) containing a functionality that is capable of further organic transformations is reported. Multitask-specific ILs are

accessible by reaction of maleimide with a Michael donor capable of serving some function. A ferrocenyl thiol is used to illustrate this concept (see scheme).

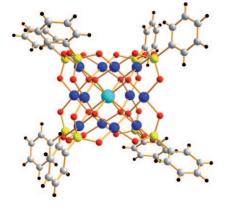
#### **Ionic Liquids**

J. J. Tindale, K. D. Hartlen, A. Alizadeh, M. S. Workentin,\* P. J. Ragogna\*......9068–9075

Maleimide-Modified Phosphonium Ionic Liquids: A Template Towards (Multi)Task-Specific Ionic Liquids

#### **Core-shell on the molecular level:**

Twelve different lanthanide(III) ions, as well as yttrium(III), have been encapsulated in a molecular palladium-oxo shell. In the heteropolypalladate family  $[X^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}$  (X=Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) the central guest X (light blue in the figure) exhibits a cubic coordination geometry, and this  $\{XO_8\}$  unit is further surrounded by a cubic  $\{Pd_{12}O_{24}\}$  shell, which is capped on its corners by phenylarsonate groups.

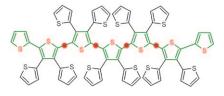


# Polyoxometalates -

M. Barsukova, N. V. Izarova, R. N. Biboum, B. Keita, L. Nadjo, V. Ramachandran, N. S. Dalal, N. S. Antonova, J. J. Carbó, J. M. Poblet, U. Kortz\*.....9076–9085

Polyoxopalladates Encapsulating Yttrium and Lanthanide Ions,  $[X^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{5-}(X=Y,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu)$ 

Branching out: A series of multi-thiophene systems comprising 5, 8, 11, 14, and 17 thiophene units (an example of which is depicted), their longest  $\alpha$ -conjugated chain consisting of tri-, tetra-, penta-, hexa-, and heptathiophene moieties, respectively, has been synthesized and fully characterized from the structural, spectroscopic, and electrochemical point of view.



#### **Dendrimers**

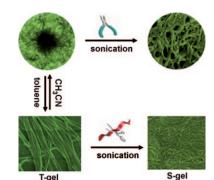
- T. Benincori, V. Bonometti,
- F. De Angelis, L. Falciola, M. Muccini,
- P. R. Mussini, T. Pilati, G. Rampinini,
- S. Rizzo, S. Toffanin,
- F. Sannicolò\* ...... 9086 9098

Towards Molecular Design Rationalization in Branched Multi-Thiophene Semiconductors: The 2-Thienyl-Persubstituted α-Oligothiophenes

#### **Responsive Gels**

X. Yu, Q. Liu, J. Wu, M. Zhang, X. Cao, S. Zhang, Q. Wang, L. Chen, 





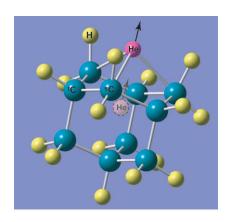
Ultrasound switch: A highly thermostable organogel with a unique coreshell structure was obtained at high temperature and pressure. Ultrasound could break these core-shell microspheres into nanoballs, which could be fractured and cross-linked with each other to form entangled fibers under mild conditions (see images).

## **Chemical Concepts** -

S.-G. Wang, Y.-X. Qiu, W. H. E. Schwarz\*.......... 9107 – 9116



MP Antibond Breaking—The Formation and Decomposition of He@Adamantane: Descriptions, Explanations, and **Meaning of Concepts** 



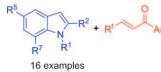
**Diversity training**: The inherent diversity of chemistry requires a diversity of physically based tools. The exothermic decay path of He@adamantane (see figure) over a barrier is described by energy partition and by electron-density analyses. Details are qualitatively predictable by exploiting traditional chemical concepts, such as ring tension and nonbonding interactions.

#### Asymmetric Synthesis

G. Blay, I. Fernández, M. C. Muñoz, J. R. Pedro, \* C. Vila ...... 9117 – 9122



Synthesis of Functionalized Indoles with a Trifluoromethyl-Substituted **Stereogenic Tertiary Carbon Atom** Through an Enantioselective Friedel-Crafts Alkylation with β-Trifluoromethyl-α,β-enones



with indoles



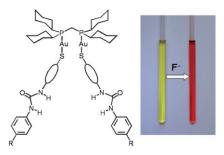
yield up to 96% ee up to 99%

**Enantioselective Friedel-Crafts reac**tion: Chiral complexes of BINOLbased ligands with zirconium tert-butoxide catalyze the Friedel-Crafts alkylation reaction of indoles with β-trifluoromethyl-α,β-unsaturated ketones to give functionalized indoles with an asymmetric tertiary carbon center attached to a trifluoromethyl group with ees of up to 99% (see scheme).

#### **Anion Sensing**

X. He, F. Herranz, E. C.-C. Cheng, R. Vilar,\* V. W.-W. Yam\*... 9123 – 9131

Design, Synthesis, Photophysics, and Anion-Binding Studies of Bis(dicyclohexylphosphino)methane-Containing **Dinuclear Gold(I) Thiolate Complexes** with Urea Receptors



Anion-sensing Au complexes: Three different dinuclear gold(I) thiolate complexes incorporating a bis(dicyclohexylphosphino)methane ligand and urea receptor units have been synthesized. Differences between the luminescence properties seen in solution and the solid state are indicative of Au...Au interactions. By introducing electron-withdrawing NO2 groups to the system, a highly selective colorimetric probe, which shows a distinct color change from vellow to red in the presence of F- ions, was obtained (see graphic).

Synergistic merger: A new strategy within the context of asymmetric dual activation catalysis that combines the concepts of Lewis acid and aprotic organic ion pair catalysis in a single catalyst has been developed (see

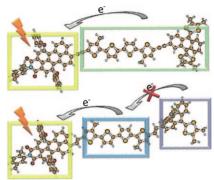
scheme). This allowed the *trans*-selective catalytic asymmetric [2+2] cyclocondensation of acyl bromides with aliphatic and aromatic aldehydes to give 3,4-disubstituted  $\beta$ -lactones as masked *anti*-aldol products.

#### Cooperative Catalysis

*T. Kull, J. Cabrera, R. Peters*\*...............................9132–9139

Catalytic Asymmetric Synthesis of trans-Configured β-Lactones: Cooperation of Lewis Acid and Ion Pair Catalysis

Hole-transfer triads that include a perylene monoimide chromophore and quaterthiophene and extended tetrathiofulvalene donor units undergo fast photoinduced electron transfer, but relatively inefficient hole shift and long-range charge separation (see figure). DFT calculations are insightful showing that hole shift is much less exergonic than predicted by electrochemistry and that when the connectors are alkynyl groups, the two donor units would be better considered as a single delocalized molecular component.



#### **Photoinduced Charge Separation** -

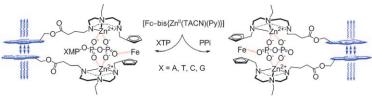
J. Boixel, E. Blart, Y. Pellegrin, F. Odobel,\* N. Perin, C. Chiorboli, S. Fracasso, M. Ravaglia, F. Scandola\*...................9140-9153

Hole-Transfer Dyads and Triads Based on Perylene Monoimide, Quaterthio-

phene, and Extended Tetrathia-

fulvalene

better considered as a ed molecular compo-



**Recognition receptor**: A new receptor, [Fc-bis{Zn<sup>II</sup>(TACN)(Py)}], comprising two Zn<sup>II</sup>(TACN) (TACN = 1,4,7-triazacyclononane) ligands that have fluorescent pyrene (Py) chromophores linked by an electrochemically active ferro-

cene (Fc) molecule, has been synthesised. It achieves fluorescent and electrochemical recognition of a variety of polyphosphate anionic guests with high selectivity by forming a 1:1 macrochelate complex (see scheme).

# Bioinorganic Chemistry

Z. Zeng, A. A. J. Torriero, A. M. Bond,\* L. Spiccia\*. . 9154–9163

Fluorescent and Electrochemical Sensing of Polyphosphate Nucleotides by Ferrocene Functionalised with Two Zn<sup>II</sup>(TACN)(pyrene) Complexes

Carbenoid-chain reactions: An alkylative carbocyclization reaction of  $\omega$ -iodoalkynyl tosylates with alkynyllithiums to give products with incorporated iodine atoms is reported. The reaction is proposed to proceed through a car-

benoid-chain process involving the *exo* cyclization of lithium acetylides and the vinylic substitution of the resulting carbenoids by 1-alkynyllithiums (see scheme).

#### **Cyclization Reactions -**

Alkylative Carbocyclization of ω-Iodoalkynyl Tosylates with Alkynyllithium Compounds Through a Carbenoid-Chain Process Leading to (1-Iodoprop-2-ynylidene)tetrahydrofurans and -cyclopropanes

## **Antitumor Agents**

E. I. Montero, J. Zhang, J. J. Moniodis, S. J. Berners-Price,\*

N. P. Farrell\* ...... 9175 – 9185

The trans Influence in the Modulation of Platinum Anticancer Agent Biology: The Effect of Nitrite Leaving Group on Aquation, Reactions with S-Nucleophiles and DNA Binding of Dinuclear and Trinuclear Compounds

$$\begin{array}{c} \text{CI} \\ \text{NH}_3 \\ \text{H}_3 \\ \text{N} \\ \text{1} \\ \text{1} \\ \text{1} \\ \text{2} \\ \end{array} \begin{array}{c} \text{GS} \\ \text{NH}_3 \\ \text{NH}_4 \\ \text{NH}_5 \\ \text{$$

trans-Influence is biological: Use of nitrite as a leaving group modifies the reactions of dinuclear platinum compounds with glutathione (GS), result-

ing in different possible pathways of metabolism in comparison to the parent chlorides (see scheme).

#### Steric Effects

The Torsional Barriers of 2-Hydroxyand 2-Fluorobiphenyl: Small but Measurable

$$(M)$$
 $AG^{\dagger}$ 
 $(P)$ 
 $(F_3)$ 
 $(X = F, OH)$ 

Unmatched performance as a diastereotopicity probe is shown by the  $\alpha$ -hydroxyhexafluoroisopropyl group. Using this probe as a detector made it possible to determine experimentally, by dynamic NMR spectroscopy measurements, the very small barriers to aryl–aryl torsion of 2-fluorobiphenyl and 2-hydroxybiphenyl (see picture) and to elucidate other important features of the stereomutation as well.

## **Carbonylative Cycloaddition**

The Nickel-Catalyzed Carbonylative Cycloaddition of Allyl Halides and Acetylenes: An Efficient Tool for Cyclopentane Annelation

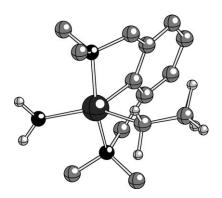
**Cyclopentane synthesis:** We present the study of the intermolecular [2+2+1] carbonylative cycloaddition reaction between alkynes and allyl halides and its evolution from the previ-

ous stoichiometric process to a nickelcatalyzed methodology (see scheme) based on experimental mechanistic observations.

COOCH<sub>2</sub>

#### **Homogeneous Catalysis -**

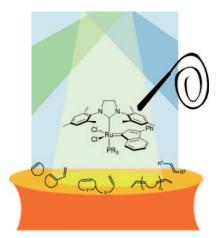
A Computational Study of Rhodium Pincer Complexes with Classical and Nonclassical Hydride Centres as Catalysts for the Hydroamination of Ethylene with Ammonia



Without precursor: A variety of rhodium and iridium hydride complexes with pincer ligand backbones were investigated in the hydroamination of ethylene and ammonia by means of DFT calculations. An amido alkyl rhodium complex (see picture) interestingly turned out to be able to catalyse the hydroamination directly without activation.

# CONTENTS

**Ringmaster**: A simple synthetic route leads to a series of  $[RuCl_2(NHC)(P(p-RC_6H_4)_3)(Ind)]$  (Ind=indenylidene) complexes that has been evaluated in a number of olefin metathesis reactions. The optimised catalysts have been identified for ring-closing metathesis, ring-rearrangement metathesis, ring-opening metathesis polymerisation and cross-metathesis reactions.



#### Metathesis -

The Influence of Phosphane Ligands on the Versatility of Ruthenium-Indenylidene Complexes in Metathesis

A clear-cut switch: A series of Ru<sup>II</sup>– and Os<sup>II</sup>–polypyridine modules linked to a pre-organised truxene platform have been synthesised and fully characterised. Very fast and efficient photoinduced energy-transfer processes from the truxene bridging ligand to the terminal-metal chromophores and subsequently from Ru- to Os-based levels have been scrutinised.



#### **Energy Transfer -**

S. Diring, R. Ziessel,\* F. Barigelletti, A. Barbieri,\* B. Ventura .... 9226 – 9236

A Pre-organised Truxene Platform for Phosphorescent [Ru(bpy)<sub>2</sub>] and [Os-(bpy)<sub>2</sub>] Metal Centres: A Clear-Cut Switch from Förster- to Dexter-Type Energy-Transfer Mechanism



**Supramolecular catalysis:** Anchoring a PPh<sub>2</sub> group at the upper rim of conical calix[4] arenes provides robust monophosphanes suitable for fast Suzuki cross-coupling reactions (see scheme). The observed high reaction rates, which are unusual for triarylphos-

phanes, possibly reflect the supramolecular receptor properties of these ligands that are able to form self-inclusion complexes with metal-arene units, thereby promoting the formation of monoligand Pd intermediates.

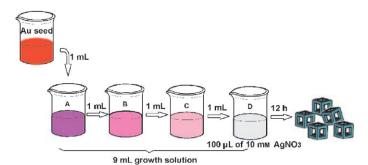
#### Calixarenes -

Cavity-Shaped Ligands: Calix[4]arene-Based Monophosphanes for Fast Suzuki-Miyaura Cross-Coupling

#### **Hollow Nanostructures**

Y. Zhang, F. Xu, Y. Sun, C. Guo, K. Cui, Y. Shi, Z. Wen, Z. Li\*......9248–9256

Seed-Mediated Synthesis of Au Nanocages and Their Electrocatalytic Activity towards Glucose Oxidation



**Au nanocages:** For the first time, uniform Au nanocages with an outer-edge length of  $(54.6\pm13.3)$  nm were synthesized by a modified seed-mediated growth approach without the use of

solid templates (see figure). The functions of the reagents were investigated in detail, and a possible mechanism for the growth of the nanocages was proposed.

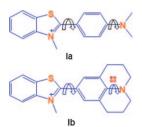
#### **Sensors**

A. Srivastava, P. K. Singh,

M. Kumbhakar, T. Mukherjee,

S. Chattopadyay, H. Pal,

Identifying the Bond Responsible for the Fluorescence Modulation in an Amyloid Fibril Sensor



Let's twist again: The synthesis of two thioflavin T derivatives has been carried out to identify which of the two possible bonds is responsible for its sensing activity (see scheme). Detailed photophysical studies along with ultrafast time-resolved fluorescence studies identified the derivative with a rigid C-N bond to be a better viscosity sensor than the one with the free C-N bond.

#### **Synthetic Methods**

T. Y. Xu, Q. Yang, D. P. Li, J. H. Dong, Z. K. Yu, \* Y. X. Li\*........ 9264-9272

Iron(III)-Catalyzed Cyclization of Alkynyl Aldehyde Acetals: Experimental and Computational Studies

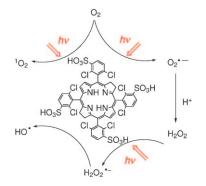
Cat. 
$$FeCl_3 \cdot 6H_2O$$
 or  $FeBr_3$  OEt  $n = 1$  OET  $n$ 

Iron-catalyzed Prins reaction (cyclization/halogenation) of alkynyl aldehyde acetals has been realized with acetyl halides as the halogen sources to afford 2-(1-halobenzylidene or alkylidene)-substituted five-membered carbo- and heterocycles, and thus provide an alternative route for vinylic C-

Cl and C-Br bond formation. An efficient protocol for the synthesis of five-to eight-membered cyclic enones has been developed on the basis of FeCl<sub>3</sub>·6 H<sub>2</sub>O-catalyzed intramolecular cyclization of alkynyl aldehyde acetals under mild conditions (see scheme).

Improving cancer photodynamic ther-

apy: The mechanism of singlet-oxygen sensitization with bacteriochlorins (see figure) indicates that the efficacy of the photodynamic therapy (PDT) of cancer may be improved by delivering a light dose over a more extended period of time. Charge-transfer interactions and superoxide-ion generation additionally suggest that using ferrous ions as adjuvants may increase the yield of reactive oxygen species.



#### Photosensitizers -

Mechanisms of Singlet-Oxygen and Superoxide-Ion Generation by Porphyrins and Bacteriochlorins and their Implications in Photodynamic Therapy



Golden reactions: Propargylamines can be obtained from amines and terminal alkynes in chlorinated solvents by catalysis with gold compounds and nanoparticles under mild reaction conditions (see scheme). The use of dichloromethane allows for the activation of two C—Cl bonds and a clean transfer of the methylene fragment to the final product.

# **Multicomponent Reactions**

D. Aguilar, M. Contel,\* E. P. Urriolabeitia\*....... 9287 – 9296

Mechanistic Insights into the One-Pot Synthesis of Propargylamines from Terminal Alkynes and Amines in Chlorinated Solvents Catalyzed by Gold Compounds and Nanoparticles



Full Papers labeled with this symbol have been judged by two referees as being "very important papers".



A video clip is available as Supporting Information on the WWW (see article for access details).

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# **CORRIGENDUM**

R. Grisorio, G. P. Suranna, P. Mastrorilli\*......8054–8061

Chain-Growth Versus Step-Growth Mechanisms for the Suzuki-Heck Polymerisation of Fluorenyldibromides with Potassium Vinyl Trifluoroborate

Chem. Eur. J., 2010, 16

DOI: 10.1002/chem.201000110

In their Full Paper, the authors have found errors in references [11] and [19]. The correct references are given below. The Editorial Office apologizes for this oversight.

- [11] a) Nomura, Miyamoto, Morimoto, Geerts, J. Polym. Sci. Part A: Polym. Chem. 2005, 43, 6166-6177; b) Nomura, Morimoto, Imanishi, Ramhani, Geerts, J. Polym. Sci. Part A: Polym. Chem. 2001, 39, 2463-2470.
- [19] a) Grisorio, Mastrorilli, Nobile, Romanazzi, Suranna, Gigli, Piliego, Ciccarella, Cosma, Acierno, Amendola, *Macromolecules* 2007, 40, 4865–4873;
  b) Grisorio, Piliego, Fini, Cosma, Mastrorilli, Gigli, Suranna, Nobile, *J. Polym. Sci. Part A: Polym. Chem.* 2008, 46, 6051–6063;
  c) Grisorio, Piliego, Striccoli, Cosma, Fini, Gigli, Mastrorilli, Suranna, Nobile, *J. Phys. Chem. C* 2008, 112, 20076–20087;
  d) Grisorio, Piliego, Cosma, Fini, Mastrorilli, Gigli, Suranna, Nobile, *J. Polym. Sci. Part A: Polym. Chem.* 2009, 47, 2093–2104;
  e) Grisorio, Suranna, Mastrorilli, Nobile, *Org. Lett.* 2007, 9, 3149–3152;
  f) Grisorio, Mastrorilli, Nobile, Romanazzi, Suranna, *Tetrahedron Lett.* 2005, 46, 2555–2558.

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