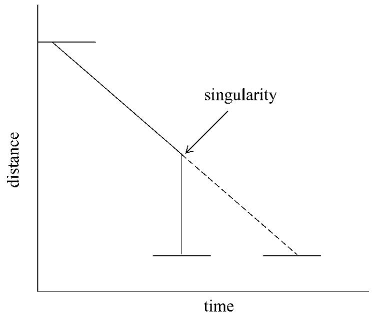
CONCEPTS

Singularity Model

*F. M. Menger,**
R. Karaman .... 1420 – 1427

A Singularity Model for Chemical Reactivity



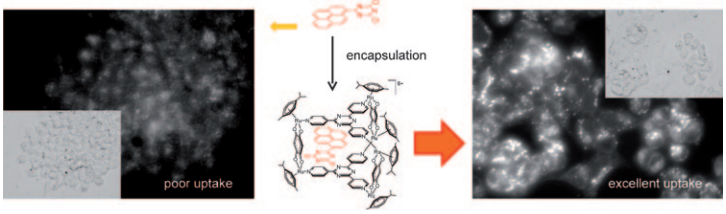
An absolute catastrophe! A singularity (or catastrophe) is defined classically as an abrupt change resulting from a smooth increase or decrease in external conditions. This article proposes a model for chemical reactivity that involves singularities in the timing of bond-making and bond-breaking events. Experimental observations are provided to support the singularity effect.

COMMUNICATIONS

Drug Delivery

*O. Zava, J. Mattsson, B. Therrien,**
*P. J. Dyson** .... 1428 – 1431

Evidence for Drug Release from a Metalla-Cage Delivery Vector Following Cellular Internalisation

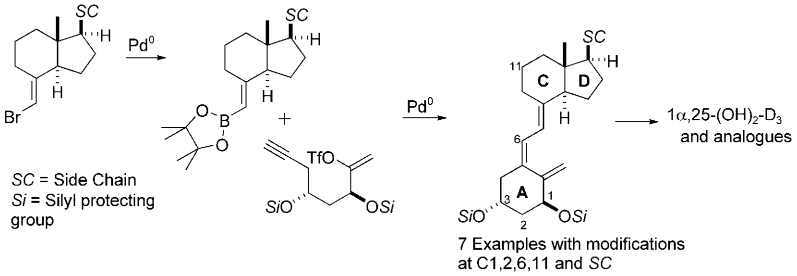


A new journey in the Trojan horse odyssey: Encapsulation of a fluorescent guest in the hydrophobic cavity of a cationic metalla-prismatic cage shows that the guest is released following cellular uptake, which illustrates the potential of this kind of water-soluble metalla-cage to act as drug carrier.

Synthesis Design

P. Gogoi, R. Sigüeiro, S. Eduardo,
*A. Mouriño** .... 1432 – 1435

An Expeditious Route to 1α,25-Dihydroxyvitamin D$_3$ and Its Analogues by an Aqueous Tandem Palladium-Catalyzed A-Ring Closure and Suzuki Coupling to the C/D Unit

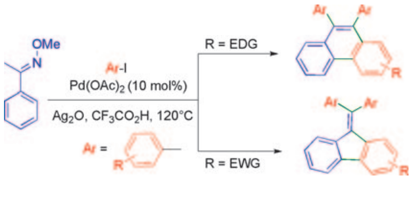


Daily vitamins: A mild, general, and highly stereoselective Pd^0-catalyzed cascade to the triene system of the hormone 1α,25-dihydroxyvitamin D$_3$ and six representative analogues is reported. The intramolecular cyclization of an enol–triflate (lower fragment) followed in situ by Suzuki–Miyaura coupling with an alkenyl boronic ester (upper fragment, also efficiently prepared by Pd^0-catalyzed coupling) in equimolar amounts under protic conditions is ideal for the preparation of small amounts of new vitamin D analogues for biological testing (see scheme).

C−H Activation

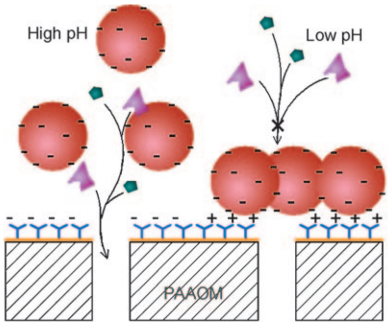
V. S. Thirunavukkarasu,
K. Parthasarathy,
*C.-H. Cheng** .... 1436 – 1440

One-Pot Synthesis of Diarylmethylidenefluorenes and Phenanthrenes by Palladium-Catalyzed Multiple C−H Bond Functionalization



A palladium-catalyzed rapid synthesis of diarylmethylidenefluorenes and phenanthrenes by multiple C−H bond activation, C−C bond formation, and Heck-type cyclization is described (see scheme).

Open for business! A novel pH-responsive gate has been constructed of nanochannels, nanoparticles, and amphoteric compounds to form a complete gate (see figure; PAAOM = porous anodic aluminum oxide membrane). The advantage of this system is that more readily available and tunable compounds than smart polymers have been used.

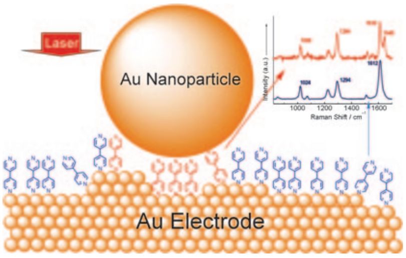


Porous Membranes

Five and six: 3,4-Cyclopentyl- and cyclohexyl-fused 2-arylchromans could be readily prepared from the intramolecular hetero-Diels–Alder reactions of the corresponding *ortho*-quinone methide (*o*-QM) precursors tethered to the styrenes under mild reaction conditions. The products were obtained with good to excellent diastereoselectivity (up to > 99:1 dr; see scheme; MOM = methoxymethyl).

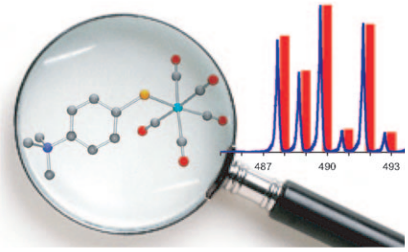
Stereoselective Reactions

Up the junction! Au/molecule/Au junctions were obtained by spreading Au NPs over an Au substrate pre-adsorbed with molecules with a bifunctional group. Molecules binding to the surface with the heterocyclic aromatic molecules show signature a band after the formation of molecular junctions, as revealed by SERS and quantum chemical calculations.



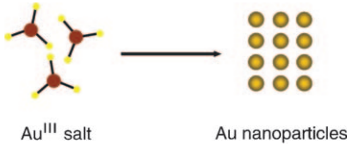
Molecular Junctions

Trapped! Transient electrophilic phosphinidenes [R–P=W(CO)$_5$] have emerged as versatile intermediates that are highly valuable in the synthesis of a plethora of organophosphorus compounds, nevertheless their existence has never been unequivocally established. By employing electrospray ionisation tandem mass spectrometry (ESI-MS/MS), this low-valent species has now been detected and its gas-phase reactivity perfectly matches the well-established solution-phase data.



Phosphinidene Complexes

Cluster control: Highly stable, monodisperse, water-soluble gold nanoparticles with high X-ray attenuation have been prepared by controlling the reaction kinetics for the formation and growth of the gold nuclei by a green single-phase method (see figure). The process developed can produce high-quality gold nanoparticles in controlled sizes without going through a laborious size-sorting procedure.



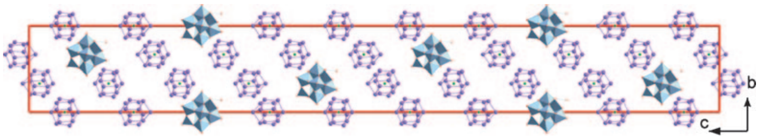
Nanoparticles

FULL PAPERS

Cluster Compounds

*F. Gruber, M. Schulz-Dobrick,
M. Jansen** .... 1464 – 1469

Structure-Directing Forces in Intercluster Compounds of Cationic [Ag_{14}-($C\equiv CtBu)_{12}Cl]^+$ Building Blocks and Polyoxometalates: Long-Range versus Short-Range Bonding Interactions

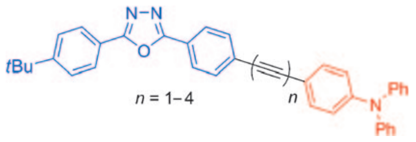


Power of the force: Opposite to the expectation that structures of intercluster compounds, consisting of charged, nanometer-sized building blocks, were primarily determined by long-range Coulomb interactions (an example is shown here), the topologies found experimentally are rather indicative for various types of short-range bonding to dominate, even allowing direct contact among equally charged nanounits.

Oligoynes

L.-O. Pålsson, C. Wang,
A. S. Batsanov, S. M. King, A. Beeby,
A. P. Monkman,
M. R. Bryce** .... 1470 – 1479

Efficient Intramolecular Charge Transfer in Oligoyne-Linked Donor–π–Acceptor Molecules

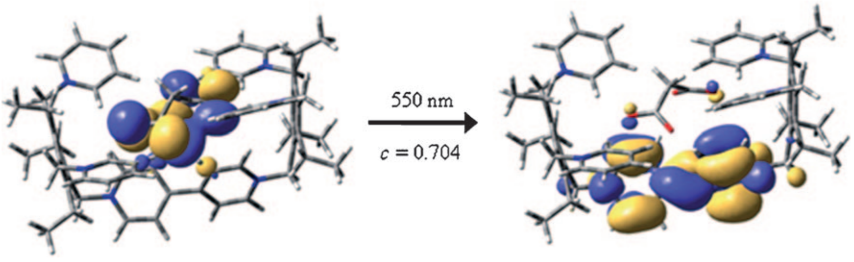


Conjugation makes the difference: The synthesis of a series of triphenylamine–$(C\equiv C)_n$–2,5-diphenyl-1,3,4-oxadiazole dyad molecules (see picture) and a related triphenylamine–C_6H_4–$(C\equiv C)_3$–oxadiazole dyad is reported. Cyclic voltammetric and photophysical studies of these compounds reveal new insights into conjugative effects in oligoyne molecular wires.

Anion Sensing

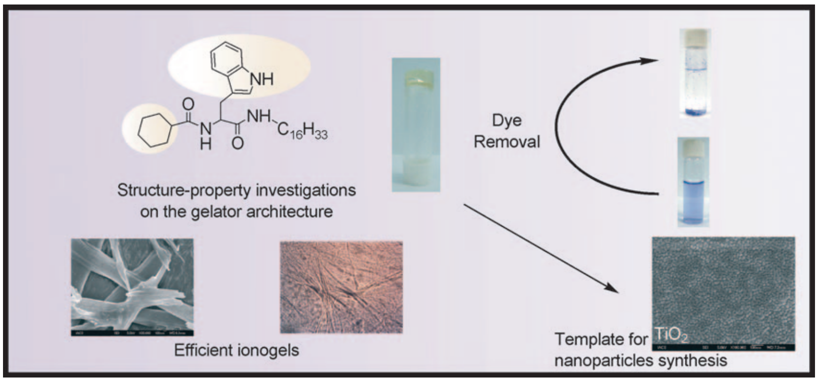
*A. N. Swinburne, M. J. Paterson,
K. H. Fischer, S. J. Dickson,
E. V. B. Wallace, W. J. Belcher,
A. Beeby,* J. W. Steed** ..... 1480 – 1492

Colourimetric Carboxylate Anion Sensors Derived from Viologen-Based Receptors



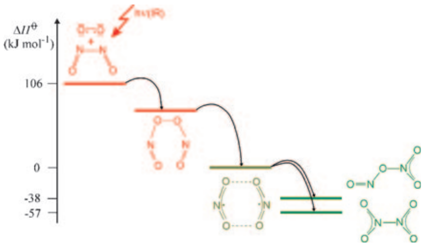
Purple patch! Tri- and tetrapodal viologen-based anion receptors showing a colourimetric response to carboxylates, such as acetate, have been synthesised. Alteration of the anion binding sites allows for binding-site competition within a receptor, resulting in a delayed colourimetric response that is dependent on the binding arms. DFT calculations and experimental measurements allow the colour change to be assigned to an anion–receptor charge-transfer process (see scheme).

Ionic Liquids



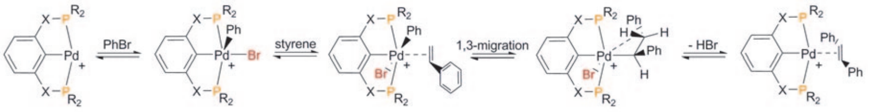
Such a versatile medium: Ionic liquids are immobilized with amino acid based low-molecular-weight gelators. A logical structure–property correlation is shown between the probable factors of ionogelation by using various spectroscopic and microscopic studies. The self-assembled supramolecular ionogels are used as a template for the synthesis of small-sized TiO_2 nanoparticles (see picture). A representative ionogel was also used for water purification because these gels show efficient dye-adsorption abilities.

Reactive Intermediates



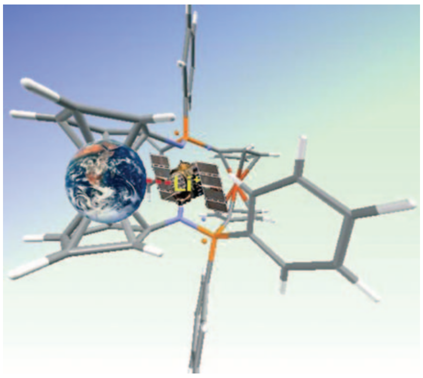
Triple change: IR irradiation is shown to induce a rearrangement of the *cis*-$N_2O_2{\cdot}O_2$ complex isolated in a Ne matrix to form a weakly bound $(NO_2)_2$ radical pair, which further isomerises to *trans*-$ONONO_2$ and *sym*-N_2O_4 (D_{2h}) (see figure).

Reaction Mechanisms



Controversial Pd^{II}/Pd^{IV} cycles often have been proposed in Heck reactions promoted by pincer complexes as alternatives to the formation of palladium nanoparticles. Computational studies on experimentally used aminophosphine-, phosphine-, and phosphite-based pincer-type Heck catalysts demonstrate that Pd^{II}/Pd^{IV} mechanisms (see scheme) are indeed thermally accessible and hence are a true alternative to palladium nanoparticle formation. Consequently, pincer-type Pd^{IV} complexes should be considered as intermediates in polar, nonprotic solvents in reactions with aryl halides performed at elevated temperatures.

Metal-Ion Recognition

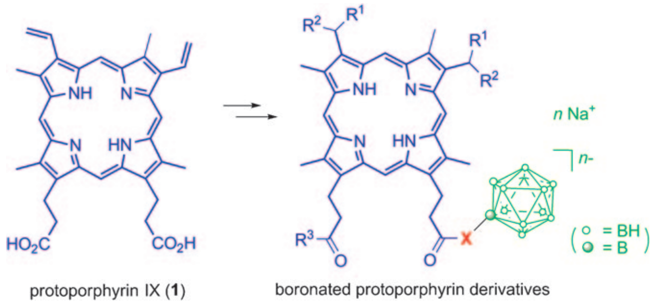


Selective metal-ion recognition: In the same way as a geostationary satellite is fixed in a planetary orbit, a Li^+ ion is selectively trapped in the planetary orbit of a ferrocene with the help of the attractive field of the two nitrogen atoms of the iminophosphorane bridges of a structurally rigid [2.2]ferrocenophane (see figure). The rigid architecture of multinuclear [2.2]ferrocenophane also permits, in another receptor, the selective binding of Zn^{2+} in the presence of Cd^{2+}.

Boronated Protoporphyrins

M. E. El-Zaria, H. S. Ban,
*H. Nakamura** .... 1543 – 1552

Boron-Containing Protoporphyrin IX Derivatives and Their Modification for Boron Neutron Capture Therapy: Synthesis, Characterization, and Comparative In Vitro Toxicity Evaluation

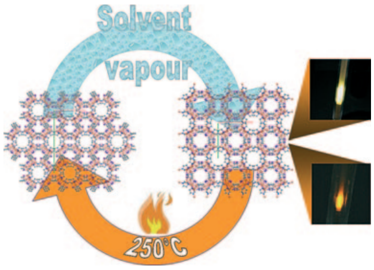


Prodrugs: A new series of natural boronated protoporphyrins with systematically varied properties was prepared. The differences in the natures of the covalent bonds between the porphyrin and the borate anion components, as well as in the lengths of the alkoxy chain linkages to the former vinyl groups of protoporphyrin IX resulted in molecules that exhibited a wide spectrum of water solubility.

Metal–Organic Frameworks

D. Braga, L. Maini, P. P. Mazzeo,*
*B. Ventura** .... 1553 – 1559

Reversible Interconversion between Luminescent Isomeric Metal–Organic Frameworks of $[Cu_4I_4(DABCO)_2]$ (DABCO = 1,4-Diazabicyclo[2.2.2]octane)

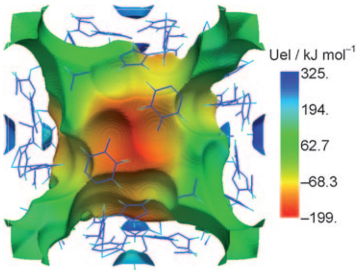


Switch your MOF: Metal–organic frameworks (MOF) of cluster $[Cu_4I_4(DABCO)_2]$ have been prepared and characterized as two different crystalline forms, **I** and **II**. MOF **I** converts into **II** on exposure to acetonitrile or methanol vapour, whereas **II** reverts to **I** when heated in a closed pan at 250 °C (see figure). Both isomers exhibit luminescence properties in the solid state and these have been characterized at room temperature and at 77 K.

Zeolite Analogues

J. Pérez-Pellitero, H. Amrouche,
F. R. Siperstein, G. Pirngruber,
C. Nieto-Draghi, G. Chaplais,*
A. Simon-Masseron, D. Bazer-Bachi,
D. Peralta, N. Bats .... 1560 – 1571

Adsorption of CO_2, CH_4, and N_2 on Zeolitic Imidazolate Frameworks: Experiments and Simulations

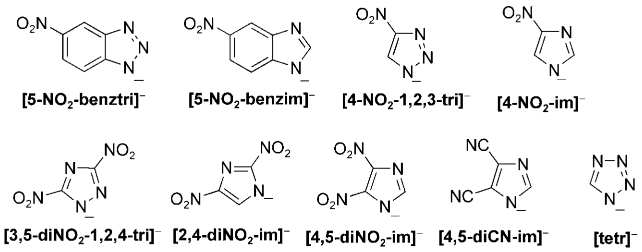


Successful simulation: A newly developed intermolecular force field can accurately reproduce the measured gas-adsorption isotherms on two zeolitic imidazolate frameworks. The simulation results can be used to identify preferential adsorption sites, which can be correlated with various parameters by topological mapping of electrostatic potential-energy surfaces (see figure).

Ionic Liquids

M. Smiglak, C. C. Hines, T. B. Wilson,
S. Singh, A. S. Vincek, K. Kirichenko,
A. R. Katritzky,
*R. D. Rogers** .... 1572 – 1584

VIP Ionic Liquids Based on Azolate Anions

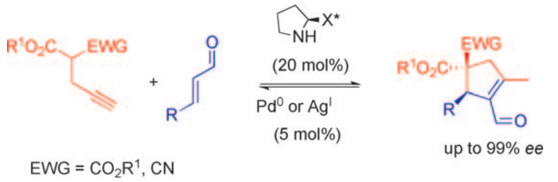


Energetic ionic liquids: We present work the on synthesis and characterization of new energetic organic salts with an emphasis on organic azolate anions. Thirty one salts were synthesized (such as depicted) by pairing diverse cations with azolate energetically substituted anions. The azolates in general are surprisingly stable in the systems explored and ionic liquid behavior was observed with all combinations of the 1-butyl-3-methylimidazolium cation and the heterocyclic azolate anions studied.

Organocatalysis

*G.-L. Zhao, F. Ullah, L. Deiana, S. Lin, Q. Zhang, J. Sun, I. Ibrahem, P. Dziedzic, A. Córdova** . . 1585–1591

Dynamic Kinetic Asymmetric Transformation (DYKAT) by Combined Amine- and Transition-Metal-Catalyzed Enantioselective Cycloisomerization

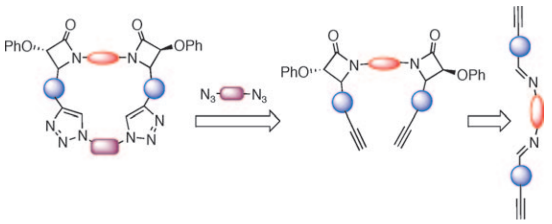


Dual catalysis: A one-pot combination of asymmetric amine organocatalysis and transition-metal catalysis allowed dynamic kinetic asymmetric transformations (DYKATs) with α,β-unsaturated aldehydes and propargylated carbon acids, affording functionalized cyclopentenes with up to 99 % *ee* (see graphic). This system also proved useful for the generation of all-carbon quaternary stereocenters.

Cycloaddition

D. Pellico, M. Gómez-Gallego, P. Ramírez-López, M. J. Mancheño, M. A. Sierra,* M. R. Torres* 1592–1600

The Sequential Building of Chiral Macrocyclic Bis-β-Lactams by Double Staudinger–Cu-Catalyzed Azide–Alkyne Cycloadditions

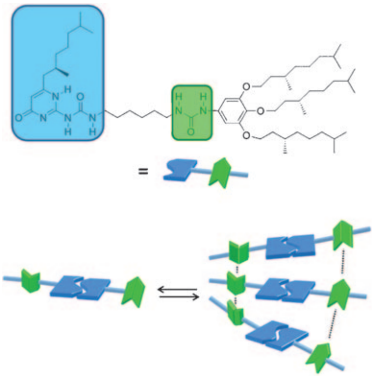


Copper-catalyzed cycloaddition: A novel approach for the synthesis of macrocyclic bis-β-lactams based on the Cu-catalyzed alkyne–azide cycloaddition (CuAAC) is reported (see graphic). The procedure is general and allows access to a full range of diastereomerically or enantiomerically pure macrocyclic cavities in good yields.

Supramolecular Chemistry

M. M. L. Nieuwenhuizen, T. F. A. de Greef, R. L. J. van der Bruggen, J. M. J. Paulusse, W. P. J. Appel, M. M. J. Smulders, R. P. Sijbesma, E. W. Meijer** 1601–1612

Self-Assembly of Ureido-Pyrimidinone Dimers into One-Dimensional Stacks by Lateral Hydrogen Bonding

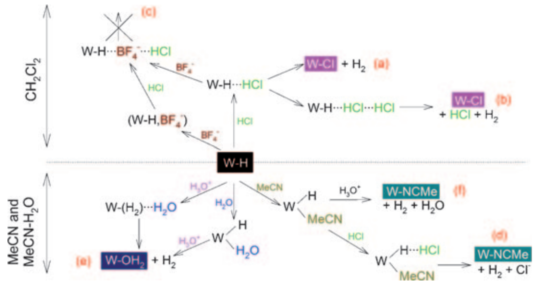


An isodesmic pathway is followed in the self-assembly of ureido-pyrimidinone (UPy) dimers substituted with an additional urea functionality into one-dimensional stacks through lateral non-covalent interactions (see scheme) in various solvents. In $CDCl_3$, NMR studies show the formation of short stacks, whereas temperature-dependent CD studies on chiral UPy dimers in heptane show the formation of larger helical stacks.

Cluster Compounds

A. G. Algarra, M. G. Basallote, M. Feliz, M. J. Fernández-Trujillo, R. Llusar,* V. S. Safont** 1613–1623

The Role of Solvent on the Mechanism of Proton Transfer to Hydride Complexes: The Case of the $[W_3PdS_4H_3(dmpe)_3(CO)]^+$ Cubane Cluster

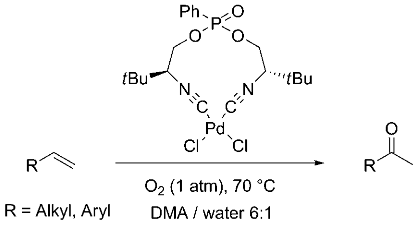


It's down to the solvent! Proton transfer from acids to the coordinated hydride in the $[W_3PdS_4H_3(dmpe)_3(CO)]^+$ cluster can go through a variety of reaction pathways that depend on the nature of the solvent. In noncoordinating solvents such as dichloromethane, the reaction goes through dihydrogen-bonded adducts with one and two acid molecules.

Oxidation of Alkenes

*A. Naik, L. Meina, M. Zabel, O. Reiser** . . . . 1624 – 1628

Efficient Aerobic Wacker Oxidation of Styrenes Using Palladium Bis(isonitrile) Catalysts

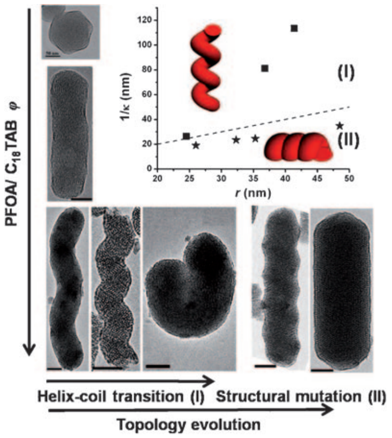


No cocatalysts needed! Bidentate isonitrile ligands were synthesized from readily available oxazolines. Their palladium complexes proved to be effective in the oxidation of alkenes to give the corresponding ketones in high yield and selectivity (see scheme). Molecular oxygen at ambient pressure could be employed as the oxidant without the need of additional cocatalysts.

Porous Materials

P. Yuan, L. Zhao, N. Liu, G. Wei, Y. Wang, G. J. Auchterlonie, J. Drennan, G. Q. Lu, J. Zou, C. Yu** . . . . 1629 – 1637

Evolution of Helical Mesostructures

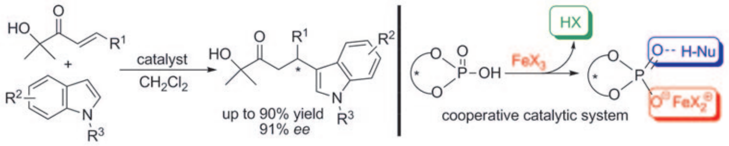


A simple transition: An evolution from a straight internal helical to hierarchical helical (HH) mesostructure with both internal and external helices or screwlike and concentric circular (CC) mesostructures is successfully observed. The HH structures with both internal and external helices are formed during the helix–coil transition process (region I; see picture). Structural mutation occurs in the restricted region (II), thus resulting in the complicated screwlike and CC mesostructures.

Asymmetric Catalysis

L. Yang, Q. Zhu, S. Guo, B. Qian, C. Xia, H. Huang** . . . . 1638 – 1645

Chiral Brønsted Acid Directed Iron-Catalyzed Enantioselective Friedel–Crafts Alkylation of Indoles with β-Aryl α′-Hydroxy Enones

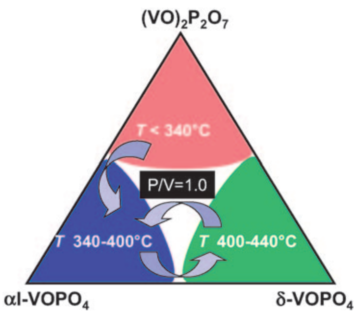


A tiny proton makes a big difference: A cooperative catalytic system established by the combination of an iron salt and a chiral Brønsted acid has proven to be effective in the asymmetric Friedel–Crafts alkylation of indoles with β-aryl α′-hydroxy enones. The reaction exhibits high catalytic activity and enantioselectivity (see scheme).

Raman Spectroscopy

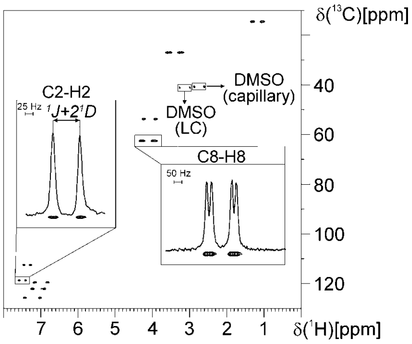
F. Cavani, S. Luciani, E. D. Esposti, C. Cortelli, R. Leanza* . . . . . . 1646 – 1655

Surface Dynamics of A Vanadyl Pyrophosphate Catalyst for *n*-Butane Oxidation to Maleic Anhydride: An In Situ Raman and Reactivity Study of the Effect of the P/V Atomic Ratio



Phased out: The nature of the active layer in vanadyl pyrophosphate, a catalyst for *n*-butane oxidation to maleic anhydride, is a function of the atomic phosphorus/vanadium ratio in catalysts and of the temperature of reaction (see figure).

Get tuned! The orienting properties of poly(γ-benzyl-L-glutamate) (PBLG) can be tuned by the use of additives. CCl_4 allows for increased enantiodiscrimination, whereas DMSO makes the orientation of a salt, which is insoluble in chloroform (see figure), possible.



Enantiodifferentiation

*A. Marx, B. Böttcher, C. M. Thiele** .... 1656 – 1663

Enhancing the Orienting Properties of Poly(γ-benzyl-L-glutamate) by means of Additives

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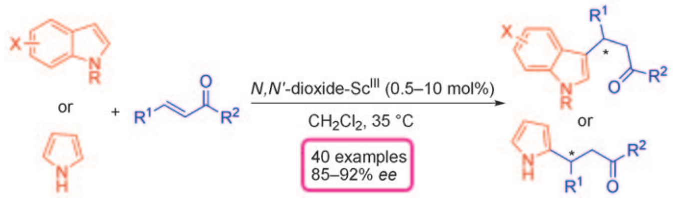

Scimply the best: A highly enantioselective Friedel–Crafts alkylation of indoles and pyrrole with chalcone derivatives catalyzed by a chiral *N,N′*-dioxide–Sc^{III} complex has been developed (see scheme). The reaction tolerates a wide range of substrates and proceeds in moderate to excellent yields and high enantioselectivities (85–92 % *ee*).

Asymmetric Catalysis

*W. Wang, X. Liu, W. Cao, J. Wang, L. Lin, X. Feng** .... 1664 – 1669

Highly Enantioselective Synthesis of β-Heteroaryl-Substituted Dihydrochalcones Through Friedel–Crafts Alkylation of Indoles and Pyrrole

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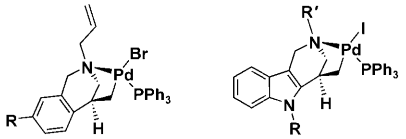
Heck intermediates: A series of novel bridged five-membered palladacycles (see picture) arising from intramolecular Heck cyclizations of *N*-allyl-2-halobenzylamines were isolated and purified. These σ-alkylpalladium complexes showed high stability to air, moisture, and heating. Moreover, they were proven to be effective precatalysts in Heck, Suzuki, and Stille reactions.



Bridged Palladacycles

*E. M. Beccalli, E. Borsini, S. Brenna, S. Galli, M. Rigamonti, G. Broggini** .... 1670 – 1678

σ-Alkylpalladium Intermediates in Intramolecular Heck Reactions: Isolation and Catalytic Activity

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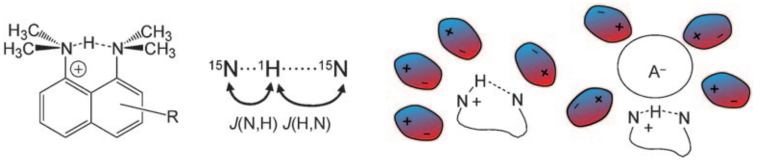


Chilled sponges: By using low-temperature NMR spectroscopy, the properties of the intramolecular hydrogen bonds of doubly ^{15}N-labeled protonated sponges of the 1,8-bis(dimethylamino)naphthalene type (see image) have been studied as a function of the solvent, counteranion, and temperature.

Hydrogen Bonds

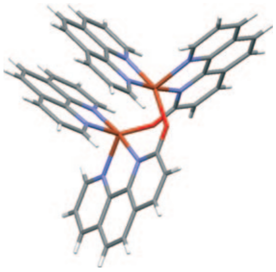
*M. Pietrzak, J. P. Wehling, S. Kong, P. M. Tolstoy, I. G. Shenderovich, C. López, R. M. Claramunt, J. Elguero, G. S. Denisov, H.-H. Limbach** .... 1679 – 1690

Symmetrization of Cationic Hydrogen Bridges of Protonated Sponges Induced by Solvent and Counteranion Interactions as Revealed by NMR Spectroscopy

Covalent Hydrates

*K. B. Szpakolski, K. Latham,**
C. J. Rix, J. M. White, B. Moubaraki,
K. S. Murray .... 1691 – 1696

Synthetic and Structural Studies on Copper 1*H*-[1,10]-Phenanthrolin-2-one Coordination Complexes: Isolation of a Novel Intermediate During 1,10-Phenanthroline Hydroxylation

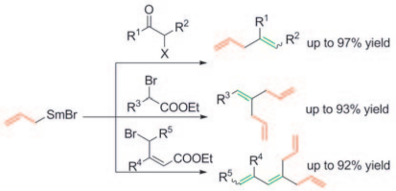


Covalent hydrates code cracked? Here's Hophen: The synthesis and crystal structure elucidation of a novel intermediate dinuclear heteroleptic copper(II) complex (see figure), has led to the suggestion of an alternative mechanism in the formation of covalent hydrates.

Diene Synthesis

*Y. Hu, T. Zhao, S. Zhang**. 1697 – 1705

Applications of Allylsamarium Bromide as a Grignard Reagent and a Single-Electron Transfer Reagent in the One-Pot Synthesis of Dienes and Trienes



Two in one! A general, efficient, and experimentally simple one-pot method for the preparation of 1,4-dienes and trienes is described. The utility of allylsamarium bromide simultaneously acting as a nucleophilic reagent and a single-electron transfer (SET) reagent is reported for the first time.

* Author to whom correspondence should be addressed

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

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F. Nahra, F. Liron, G. Prestat,
C. Mealli, A. Messaoudi,
*G. Poli** 11078–11082

Striking AcOH Acceleration in Direct Intramolecular Allylic Amination Reactions

Chem. Eur. J., **2009**, *15*

DOI: 10.1002/chem.200901946

After submission of the paper describing the use of AcOH as a solvent to accelerate Pd/bis-sulfoxide catalyzed allylic C−H amination processes to form oxazolidinones and oxazinanones, a paper appeared by M. C. White et al. on the use of *N*-nosyl carbamate nucleophiles to accelerate analogous transformations.[1] The authors would like to bring this to the reader's attention.

[1] G. T. Rice, M. C. White, *J. Am. Chem. Soc.* **2009**, *131*, 11 707 – 11 711.